

Kinetics and Thermodynamics of the Diels-Alder Addition to Fullerenes

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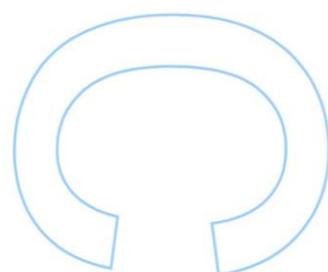
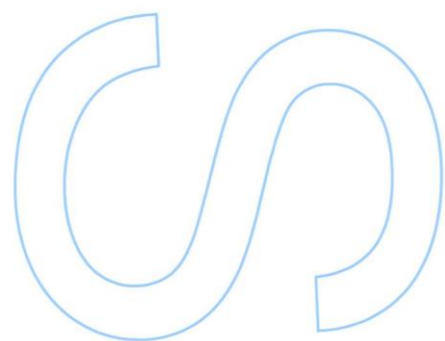
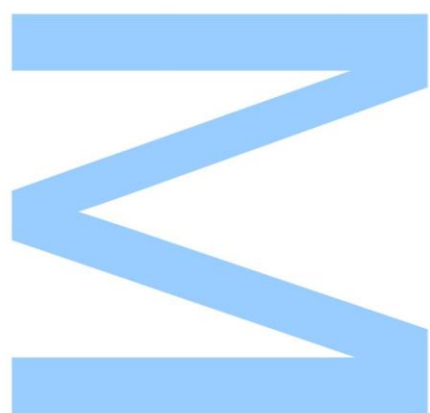
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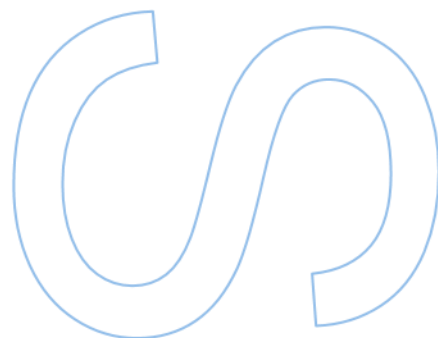
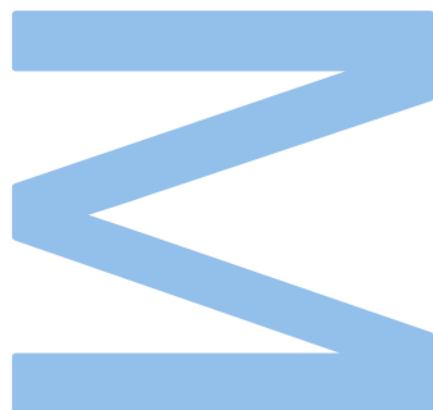
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Diogo José Lopes Rodrigues

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Abstract

Fullerenes are highly symmetric molecules with a wide variety of applications and potential uses. Fullerenes can be functionalized via chemical reactions to obtain derivatives with enhanced physical and chemical properties in order to tune their functionality and applicability. In this work, we study the reactivity of fullerenes C_{60} , C_{70} and ICMA (indene- C_{60} monoadduct) towards Diels-Alder addition with two conjugated dienes: anthracene and 9,10-dimethylantracene. We evaluate the impact of symmetry, isomerism, nature of the addend, aromaticity, dispersive interactions and solvation in the reactivity of fullerenes.

In this thesis the reaction of C_{60} and C_{70} with anthracene in *m*-xylene is studied kinetic and thermodynamically, using UV-Vis spectroscopy. A thermodynamic study of the reactions of C_{60} , C_{70} and ICMA with 9,10-dimethylantracene (in *m*-xylene) is also performed using UV-Vis spectroscopy. The reactions of the three fullerenes with anthracene were further studied using density functional theory, mainly at the M06-2X/6-31+G(d) level of theory, and using the Solvent Model based on Density (SMD) to simulate the solvent. Additionally, the retro Diels-Alder reaction is evaluated in solid ICMA and ICBA (indene- C_{60} bisadduct) using differential scanning calorimetry and thermogravimetric analysis.

The computational study predicts no significant differences in thermodynamic reactivity of the three fullerenes (when excluding contributions of symmetry and isomerism). Experimentally, it was found that C_{60} is more reactive towards Diels-Alder cycloaddition with both anthracene and 9,10-dimethylantracene than both C_{70} and ICMA. This is due to entropic effects which support the manifestation of symmetry in the entropy of reactions in solution. This increases the thermodynamical reactivity of the first addition to C_{60} when compared to subsequent additions. C_{70} was found, also experimentally for both conjugated dienes, to have a more exothermic reaction.

In the kinetic experiments it was found that C_{70} has a higher forward and reverse enthalpy of activation than C_{60} . It also has a less negative direct and reverse entropy of activation. The results suggest that symmetry breaking of the fullerenes occurs in the transition state $\rightarrow$ products step, increasing the entropy change of this step.

This combined computational and experimental approach showed that differences in reactivity of fullerenes is ruled by symmetry and isomerism effects, as well as solvation interactions. To evaluate the effects of isomerism, a mathematical formula to evaluate

this contribution to the entropy of these reactions was derived. This contribution appears in the van 't Hoff equation for the studied systems.

In the retro Diels-Alder studies of crystalline ICMA and ICBA, the reaction was found to occur at a significantly lower temperature in ICBA, partially explained by the less efficient crystal packing in ICBA. In ICBA we found that the reaction occurs in two consecutive steps – the first loss of indene, with a faster reaction rate; and the second loss with a slower reaction rate. Crystal packing interactions also determine that the activation energies of the processes follow the order: ICMA > ICBA step 2 > ICBA step 1. The first step of the retro Diels-Alder in ICBA shows a greater pre-exponential factor (A) which can be explained by the two equivalent indene-fullerene bonds which can be broken. This translates to a difference of $R \cdot \ln(2)$ in the activation entropy between the two ICBA steps.

Keywords: fullerenes, Diels-Alder, cycloaddition, reactivity, kinetics, thermodynamics, symmetry, isomerism, solvation, aromaticity, monoadducts, bisadducts, UV-Vis spectroscopy, DFT, thermal analysis

Resumo

Fulerenos são moléculas altamente simétricas, com um alargado espetro de aplicabilidade. Os fulerenos podem ser funcionalizados por via de reações químicas para obter derivados com propriedades físico-químicas melhoradas, para melhor aplicabilidade. Neste trabalho estudou-se a reatividade dos fulerenos C_{60} , C_{70} e ICMA (indene- C_{60} monoadduct) perante a reação Diels-Alder, com dois dienos conjugados: antraceno e 9,10-dimetilantraceno. Avaliou-se o impacto da simetria, isomerismo, natureza do adendo, aromaticidade, interações dispersivas e solvatação na reactividade de fulerenos.

Neste trabalho a reação do C_{60} e C_{70} com antraceno, em *m*-xileno, foi estudada cinética e termodinamicamente, usando espectroscopia UV-Vis. Foi feito também um estudo termodinâmico das reações do C_{60} , C_{70} e ICMA com 9,10-dimetilantraceno (também em *m*-xileno) usando espectroscopia UV-Vis. As reações destes fulerenos com antraceno foram também estudadas computacionalmente usando teoria do funcional da densidade, ao nível de teoria M06-2X/6-31+G(d); e usando o “*Solvent Model based on Density*” (SMD) para simulação do solvente. Adicionalmente, avaliou-se a reação Diels-Alder reversa para ICMA e ICBA (indene- C_{60} bisadduct) na fase sólida, usando calorimetria diferencial de varrimento e análise termogravimétrica.

O estudo computacional não prevê diferenças significativas na reatividade termodinâmica dos três fulerenos (quando excluídas contribuições de simetria e isomerismo). Experimentalmente, encontrou-se que o C_{60} é mais reativo perante Diels-Alder para ambos os dienos conjugados, quando comparado com C_{70} e ICMA. Esta diferença de reatividade deve-se a efeitos entrópicos, que suportam a presença do efeito da simetria na entropia de reações em solução. Isto faz com que a primeira adição de C_{60} seja favorecida perante adições subsequentes. Os resultados experimentais preveem que o C_{70} tem uma reação mais exotérmica, com ambos os dienos.

Cineticamente, encontrou-se no C_{70} uma maior entalpia de ativação na reação direta e reversa, quando comparado com C_{60} . O C_{70} também demonstra uma entropia de ativação menos negativa para ambos os processos direto e reverso. Os resultados sugerem que a quebra de simetria ocorra na transformação estado de transição $\rightarrow$ produtos, aumentando a variação de entropia associada a este passo.

Os resultados computacionais e experimentais combinados demonstram que as diferenças na reatividade de fulerenos se deve maioritariamente a efeitos de simetria, isomerismo e solvatação. Para avaliar os efeitos do isomerismo, foi feita uma derivação

rigorosa da fórmula matemática que permite avaliar a contribuição do isomerismo para estas reações, e que se manifesta na equação de van 't Hoff para os sistemas estudados.

No estudo da reação Diels-Alder reversa na fase sólida, encontrou-se uma reação no ICBA que ocorre a uma temperatura significativamente mais baixa que no ICMA. Isto é parcialmente explicado pelo “*packing*” cristalino menos eficiente no ICBA. Também se encontrou uma reação que no ICBA ocorre em dois passos – uma primeira perda de indeno mais rápida, e uma subsequente perda de indeno mais lenta. Interações na fase cristalina também causam com que a energia de ativação dos processos varie segundo a seguinte ordem: ICMA > ICBA passo 2 > ICBA passo 1. O primeiro passo da reação no ICBA demonstra um fator pré-exponencial maior, que pode ser explicado pela presença de dois ligações indeno-fulereno equivalentes. Isto traduz-se numa diferença de $R \cdot \ln(2)$ na entropia de ativação do processo.

Palavras-chave: fullerenos, Diels-Alder, cicloadição, reatividade, cinética, termodinâmica, simetria, isomerismo, solvatação, aromaticidade, monoadutos, bisadutos, espectroscopia UV-Vis, DFT, análise térmica

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List of Abbreviations

Abs – Absorbance

AICBA – Adduct of anthracene with ICMA (anthracene,indene- C_{60} bisadduct)

ACMA – Adduct of anthracene with C_{60} (anthracene- C_{60} monoadduct)

AC₇₀MA - Adduct of anthracene with C_{70} (anthracene- C_{70} monoadduct)

Ant – Anthracene

BSSE – Basis set superposition error

DA – Diels-Alder

DCMA – Adduct of 9,10-dimethylantracene with C_{60} (9,10-dimethylantracene- C_{60} monoadduct)

DSC – Differential Scanning Calorimetry

HF – Hartree-Fock

HOMA – Harmonic Oscillator Model of Aromaticity

HPLC – High-performance liquid chromatography

ICMA - Adduct of indene with C_{60} (anthracene- C_{60} monoadduct)

ICBA - Bisadduct of indene with C_{60} (anthracene- C_{60} bisadduct)

Ind – Indene

RDA – Retro Diels-Alder

NMR – Nuclear Magnetic Resonance

SMD – Solvent model based on density

TG - Thermogravimetry

TGA – Thermogravimetric analysis

THN – 1,2,3,4-tetrahydronaphtalene

TS – Transition state

TST – Transition state theory

Chapter 1:

Motivation and State of the Art

1.1. Fullerenes

Fullerenes are allotropes of carbon, consisting of sp^2 hybridized carbon atoms connected by single and double bonds forming closed or partially closed surface(s) composed of five- and six- membered rings.¹⁻³ The most famous fullerene (and easier to produce in bulk quantities) is C_{60} (Fig. 1). C_{60} is a molecule consisting of 60 carbon atoms - making up 12 pentagons and 20 hexagons - arranged in a football-like shape (Fig. 1) of 7.1 Å of mean diameter.^{1, 2, 4} It is a truncated icosahedron, and therefore has icosahedral symmetry (I_h) – the highest symmetry possible in a molecule (with a symmetry number of 120 – meaning there are 120 symmetry operations that leave C_{60} unchanged). Of these, 60 are rotations, and thus its rotational symmetry number, σ_{sym} , of the molecule is 60. This symmetry allows for a very interesting chemistry.^{1, 5}

C_{60} has two distinct types of bonds – [5,6] bonds and [6,6] bonds. [5,6] bonds (1.449 Å) are at the junction of a pentagon and a hexagon, and [6,6] (1.391 Å) bonds at the junction of two hexagons.^{4,7} The latter have higher double bond character, and are represented as double bonds in Fig. 1. C_{60} has low electron delocalization and is not fully aromatic. Shorter bonds on the pentagons would increase the strain in the molecule, and, therefore, the predominant resonant structure is the one with double bonds on the [6,6] bonds (on the hexagons), as illustrated in Fig. 1.^{2, 3, 6} Nevertheless, some authors claim that the hexagons have a slight aromatic character.^{7,8} C_{60} also has a high electron affinity. It thus behaves as a strained, electron-deficient polyene.² The ^{13}C NMR spectrum of C_{60} (in benzene) shows a single line at 142.7 ppm, showing that all carbons are identical, thus supporting the icosahedral structure.⁹

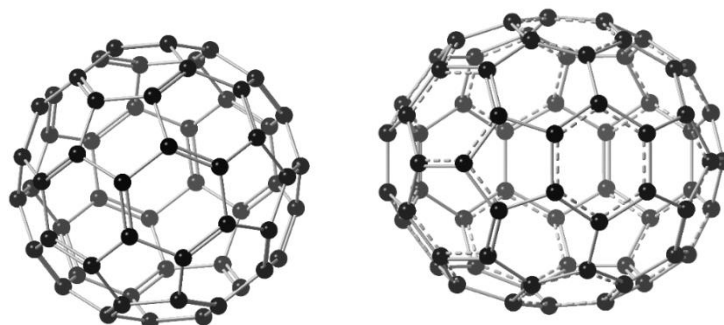


Fig. 1: Structure of the C_{60} fullerene (left), and structure of C_{70} (right). Pictures made using the *GaussView* software.

The second most stable fullerene, after C_{60} , is C_{70} , another important fullerene. It possesses a structure similar to the C_{60} fullerene but with 70 carbon atoms, 25 hexagons and 12 pentagons. When compared to C_{60} , it has an extra 5 hexagons inserted at the equator. This difference results in a significant difference in chemical properties.^{10, 11} The NMR spectrum of C_{70} shows five lines (150.7, 148.1, 147.4, 145.4, and 130.9 ppm in 1:2:1:2:1 ratio, respectively)⁹, meaning there are five distinguishable carbons in C_{70} , two of the five which exist in double the amount of the other three. This is characteristic of a D_{5h} symmetrical “egg-shaped” structure (Fig. 1). C_{70} thus has D_{5h} symmetry, with a symmetry number of 10.⁹ In C_{70} the aromaticity at the edges (where both fullerenes are locally similar) is similar to C_{60} – there being a dominant resonance structure with stronger bonds at the hexagons.^{11, 12} At the equatorial belt the structure is more planar, and has local aromatic character.^{13, 14}

Fullerenes with more than 60 carbon atoms are designated “higher fullerenes”.¹⁰ Beyond C_{70} , there exist other stable fullerenes, like C_{76} , C_{78} , C_{80} , among others; but C_{60} and C_{70} are the most stable and thus easier to produce – as a general rule of thumb, the bigger the fullerenes the less quantity of them can be produced by the usual synthetic methods.¹⁵ Another reason is that higher fullerenes start to exist in different isomers of the same number of carbons, and it is difficult to isolate such isomers.^{1, 10} Euler’s theorem predicts that a closed surface composed of only pentagons and hexagons must contain 12 pentagons.¹⁶ C_{60} has 20 hexagons and C_{70} 25 hexagons. Every other fullerene must also have 12 pentagons, but a different number of hexagons.^{10, 11} The smallest reported stable fullerene is C_{28} , with only two hexagons.¹⁷⁻¹⁹

C_{60} fullerene was first discovered in 1985, by Kroto *et al.*⁴. This discovery led to the award of the 1996 Nobel Prize in Chemistry to Robert F. Curl, Harold W. Kroto, and Richard E. Smalling. The team discovered the molecule when studying the formation of carbon clusters from vaporization of carbon atoms from graphite. They proposed the truncated icosahedral structure due to the high stability of the molecule found, which was later confirmed by experiments like mass spectroscopy and ^{13}C NMR - with the help of Roger Taylor’s chromatography expertise, which allowed the team to isolate samples of C_{60} for the first time.²⁰ They named the molecule buckminsterfullerene, in honor of the geodesic dome of architect R. Buckminster Fuller, which resembles the structure of C_{60} . C_{70} was also discovered in the same process, and the presence of other higher fullerenes was also ascertained.⁴ A simple way to produce macroscopic amounts of C_{60} (and C_{70}) was later reported in 1990, by Krätschmer *et al.*²¹. This opened the necessary doors to, from then onward, vast research be done on fullerenes and their derivatives. Fullerenes

have since become very important in diverse fields of chemistry and science in general.

1

Fullerenes and their derivatives have found applications in a wide range of different areas, ranging from materials science/engineering to medicine.²² Fullerenes can be used as highly efficient lubricants or superconductors.²³ They have been applied in chemical sensors, in hydrogen conversion electrochemical cells, and in photovoltaic cells.²²⁻²⁷ In fact, very high efficiency heterojunction solar cells were obtained by using a mixture of fullerene/polymer – the fullerene acting as a type *n* semiconductor, due to their electrophilic character and ability to transport charge.²⁶⁻²⁸ Fullerenes can encapsulate smaller molecules, which can be useful as a form of drug delivery system.²⁹ C₆₀ can be used as a very small transistor – a potential building block for nanoelectronics.²⁵ The conjugated system of an electronically reduced C₆₀ can act as a great source of electrons and reducing agent. It has been found to be of use in reducing nitrogen to ammonia, in a simpler process when compared to the Haber-Bosch process – the process currently used to produce ammonia, which requires temperatures of 300 °C, high pressures, and expensive catalysts.²⁵ Fullerene derivatives have found applications as electron transport materials for organic semiconductor devices, in particular in organic photovoltaics.³⁰⁻³⁴ Some important examples include ICMA (Indene-C₆₀ MonoAdduct) and ICBA (Indene-C₆₀ BisAdduct)^{31, 32} (Fig. 2, both of which were studied in this work), and the analogous C₇₀ adducts: IC₇₀MA and IC₇₀BA^{32, 34}. Fullerene bisadducts have diverse applications due to their versatile three-dimensional structures, with a wide variety of possible addend groups. Some applications occur in biology and advanced materials.¹

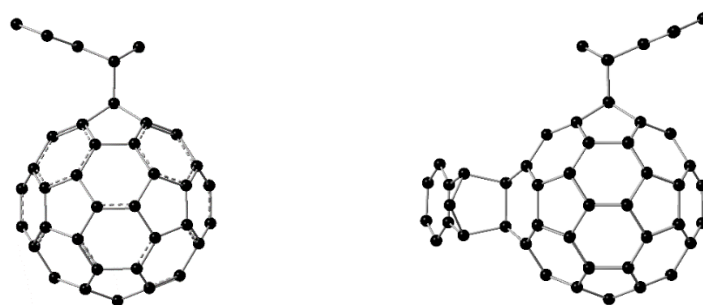


Fig. 2: ICMA (indene-C₆₀ monoadduct) and ICBA (indene-C₆₀ bisadduct). Pictures made using the Gaussview software.

1.2. Fullerene reactivity

Functionalization of fullerenes is the process of adding different functional groups to the fullerene structure via chemical reactions. Fullerene functionalization is important because it allows one to tune the physical and chemical properties of the fullerenes to better suit the desired applications. Fullerenes can be made lipophilic, hydrophilic - and even amphiphilic -, increasing their solubility in certain desired solvents; their optical and electronic properties can be adjusted; etc....^{1, 28} One example of this is fullerene solubility: fullerenes are in themselves slightly soluble only in a limited amount of organic solvents - like xylene and toluene, for example -, but there are ways to make fullerenes soluble in aqueous solutions, by adding hydroxyl groups to its structure, forming fullerenols or polyhydroxylated fullerenes (Fig. 3). This can be done for various types of solvents.³⁵

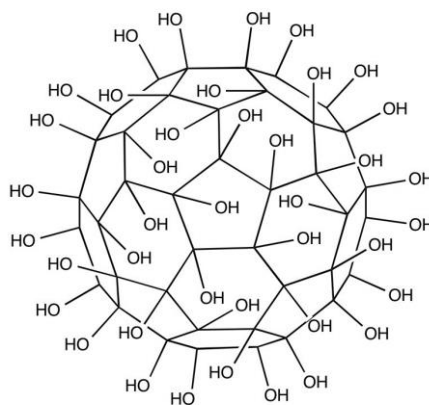


Fig. 3: An example of a polyhydroxylated fullerene.

Another example is the use of ICBA in polymer solar cells – a more soluble fullerene derivative that is attractive when compared to other fullerenes because of its LUMO energy, which allows one to obtain a higher voltage on the solar cells.^{31, 32}

Fullerenes, and their derivatives have the chemistry of electron deficient alkenes. They have conjugated π systems, that, unlike planar aromatic molecules, contain no hydrogens. Thus, their reactivity is very different from classic aromatic molecules.^{1, 3, 6} Fullerenes can undergo redox reactions; they can participate in addition reactions; they can act as dienophiles, and therefore react via Diels-Alder cycloaddition with conjugated dienes (like indene, tetracene and anthracene).^{1, 3, 5, 6, 36} In these reactions the diene binds to the [6,6] carbons of the fullerene (the bonds between two carbon atoms which are both vertices of two adjacent hexagons), which are excellent dienophiles, being the bonds with highest double bond character.^{1, 5, 6, 37} Fullerenes are highly strained

molecules, and thus the principal “driving force” in addition reactions to fullerenes is the strain relief when the carbons go from sp^2 hybridization to sp^3 . These reactions are usually exergonic and exothermic. The limiting problem on studies of fullerene reactivity is their low solubility on most solvents.^{1, 5, 6}

After the first addition, subsequent additions can occur on the fullerene structure. In this scenario, the [6,6] bonds that used to be identical now have different reactivities, and thus a number of different possible isomers arise.^{1, 38, 39} In C_{60} , in theory, eight different bisadduct isomers can be formed (Fig. 4), with a further splitting in different isomers for each if the addends are not symmetrical along the respective [6,6] bond axis.^{1, 39, 40} This is explored in Sections 2.2 and 3.1 of this thesis for bisadducts of C_{60} with one of each indene and anthracene. Fullerene bisadducts have diverse applications due to their particular three-dimensional structures with a wide variety of possible addend groups. Some applications occur in biology and advanced materials.¹

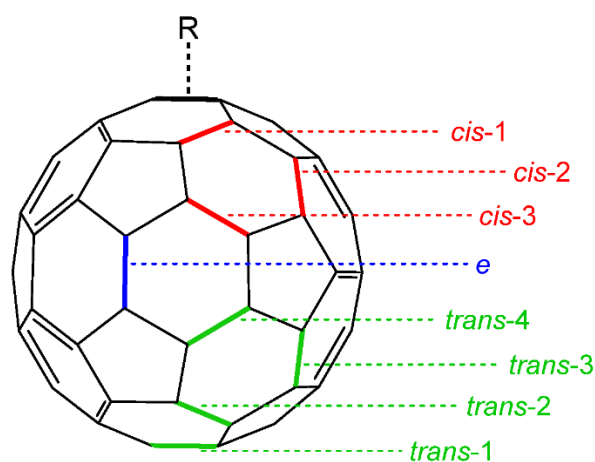


Fig. 4: Possible isomers for C_{60} bisadducts depending on relative positions of the two groups, with respective nomenclature as suggested by Hirsch *et al.*³⁸. **R** represents one addend, and the dashed arrows point to where the second group would bond. Adapted from De La Puente *et al.*¹

In C_{70} there are four different types of [6,6] bonds, as opposed to only one in C_{60} , which results in multiple isomers in the monoadduct resultant of the Diels-Alder reaction.^{1, 10, 11} The different bonds are illustrated in Fig. 5. If we look at a Schlegel diagram for C_{70} , centered on the pentagons on the edge of C_{70} (Fig. 6); the [6,6] bonds can be seen to be between carbon 1 and 2 (C(1)-C(2)), C(5)-C(6), C(7)-C(21) and C(20)-C(21). In terms of reactivity, the C(1)-C(2) bond is the most reactive, followed by the C(5)-C(6) bond, and the less reactive bonds are the C(7)-C(21) and C(20)-C(21) bonds (see Section 4.1.1. for images of the possible isomers, optimized by quantum chemistry

calculations).^{1, 10} The stability of the different possible isomers can be evaluated based on the local curvature of the bonds to which the addend connects. Curvature depends on the fullerene size, and on the distribution of hexagon and pentagons on the surface.^{10, 11} In C_{60} every bond is of the α type (Fig. 4), but in C_{70} only the C(1)-C(2) is of this type. The α type bond is the most curved and thus the most reactive bond type, followed by the β type (C(5)-C(6) bond in C_{70}). With the incorporation of pentagons into a network of hexagons, the [6,6] bonds become more reactive. With the increase of the number of five membered rings close to the bond, and with the reduction of the distance of the bond to those five members rings, the reactivity of the [6,6] bond increases.¹¹ This explains why the α bonds are more reactive than the β bonds, since β bond is surrounded by one less pentagon, making it less curved. The α and β [6,6] bonds are the two most curved bonds in fullerenes, and thus the most reactive.^{10, 11} The other two [6,6] bonds in C_{70} (the ones on the equatorial belt of hexagons) are lowly curved, with few pentagons surrounding them, and are part of a local aromatic character zone - being far less reactive.^{10, 11} In this thesis we will adopt the following nomenclature for C_{70} adduct isomers: isomer **a** when the addend binds to the C(1)-C(2) bonds; isomer **b** when the addend binds to the C(5)-C(6); isomer **c** when it binds to the C(7)-C(21) bond; and isomer **d** when it binds to the C(20)-C(21) bonds (the ordering goes in terms of which bonds are closer to the edge, and thus are more similar to C_{60}).

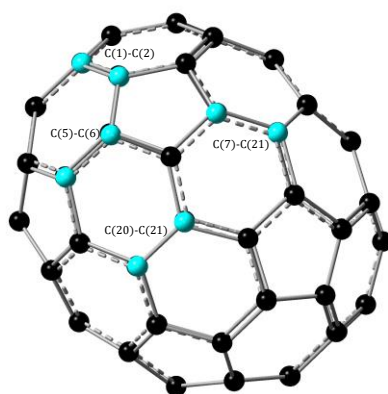


Fig. 5: Different [6,6] bonds in C_{70} , where the addend can bind, originating different isomers of the C_{70} adduct. Picture made using the *Gaussview* software.

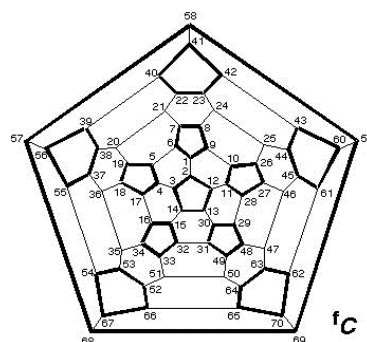


Fig. 6: Schlegel diagram for C_{70} .

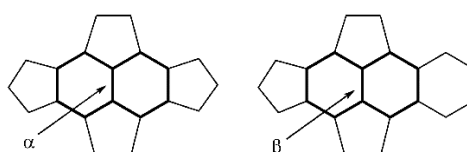


Fig. 7: The two most curved and reactive [6,6] bonds in fullerenes. Adapted from Thilgen *et al.* ¹¹.

The functionalization of fullerenes by Diels-Alder reactions is a common procedure. ⁴¹ Characterization of the kinetics and thermodynamics of these reactions is thus very important, and not a lot of data is available in the literature. Sarova *et al.* studied the kinetics of Diels-Alder addition between C_{60} and anthracene and tetracene in the temperature ranges 22-62 °C, using UV-Vis spectroscopy ⁴¹. For the concentrations used, they found only the presence of a monoadduct with both acenes. Wang *et al.* studied the addition of 9,10-dimethylantracene to endohedral fullerenes $^3\text{He}@C_{60}$ and $^3\text{He}@C_{70}$ via ^3He NRM spectroscopy, in the temperature range of 22-52 °C ⁴². They found the presence of a monoadduct and a bisadduct with 6 isomers in C_{60} ; and a monoadduct with a single relevant isomer and a bisadduct with 3 isomers in C_{70} . They found a more negative enthalpy of reaction ΔH_r^0 and ΔS_r^0 for C_{60} , when compared to C_{70} . They also found that the first addition is more favorable (having a more negative ΔG_r^0 of reaction) than the addition of a second adduct on the fullerene, for both fullerenes studied. The same group found similar ΔH_r^0 and ΔS_r^0 values for $^{129}\text{Xe}@C_{60}$ ⁴³. There is some evidence that endohedral fullerenes might have their symmetry broken ⁴⁴, which might alter the symmetry effects on the reaction when using this methodology. In the work of Murata *et al.*, a difference between the ΔG_r^0 for $\text{H}_2@C_{70}$ and $(\text{H}_2)_2@C_{70}$ was determined ⁴⁵, showing that the presence of this molecules inside the cage of the fullerene might slightly alter their thermodynamic reactivity.

Table 1 presents a compilation of the experimentally data available in the literature for Diels-Alder reactions involving fullerenes. Comparing the values obtained for the same or similar dienes we can see that there is some discrepancy between the values. Thus, there still isn't a definite characterization of these reactions (in particular for anthracene and dimethylantracene, which show high discrepancy between results).

Table 1: Compilation of literature results for reactions involving fullerenes. Enthalpy values in $\text{kJ}\cdot\text{mol}^{-1}$, entropy values in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$.

Fullerene	Diene	Direct				Reverse		$\langle T \rangle / \text{K}^a$	Experimental technique	Solvent	Note, reference
		ΔH_r°	ΔS_r°	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta H^\ddagger$	$\Delta S^\ddagger$				
C_{60}	Anthracene	- 81	- 19	57	-123	138	71	316	UV-Vis	Toluene	⁴¹
C_{60}	Tetracene	-	-	47	- 111	-	-	315	UV-Vis	Toluene	Irreversible reaction, ⁴¹
C_{60}	9,10-Dimethylantracene	- 96	- 256	-	-	-	-	310	NMR	1-methylnaphthalene	³ He@ C_{60} , ⁴²
C_{60}	Cyclopentadiene	- 82	- 149	26	162	109	12	298/ 356	HPLC/ NMR	Toluene/ o-dichlorobenzene- d2	^{46, 47}
C_{60}	9,10-Dimethylantracene	- 95	- 254	-	-	-	-	326	NMR	o-dichlorobenzene	¹²⁹ Xe@ C_{60} , ⁴³
C_{70}	9,10-Dimethylantracene	- 88	- 245	-	-	-	-	310	NMR	1-methylnaphthalene	³ He@ C_{70} , ⁴²
C_{70}	9,10-Dimethylantracene	- 58	- 141	-	-	-	-	313	NMR	o-dichlorobenzene- d4	H_2 @ C_{70} , ⁴⁵
C_{70}	9,10-Dimethylantracene	- 56	- 138	-	-	-	-	313	NMR	o-dichlorobenzene- d4	$(\text{H}_2)_2$ @ C_{70} , ⁴⁵
C_{70}	Cyclopentadiene	-	-	64	- 45	-	-	320	HPLC	Toluene	⁴⁶

^a average temperature for the experiments.

Fullerene reactivity as dienophiles in Diels-Alder cycloadditions have also been studied theoretically. The pioneering computational work of Fujimoto and co-workers suggested that the double addition of butadiene to C_{60} is not highly regioselective.⁴⁸ Solà *et al.* compared the reactivity of C_{60} and C_{70} with butadiene.⁴⁹ The authors found that in gas phase C_{70} seems slightly more reactive, but in toluene solvent effects reverse this order by significantly decreasing the energy barrier in the butadiene addition to C_{60} . As indicated in the comprehensive work of Li and co-workers on the separation of IC₆₀BA regioisomers, the conventional synthesis of ICBA yields no *cis*- isomers owing to steric hindrance.⁵⁰ The *trans*-2, *trans*-3, *trans*-4, and *e*- isomers of NCBA (dihydronaphthyl-based [60]fullerene bisadduct) were isolated and used as acceptors for P3HT based

polymer solar cells (PSCs).⁵¹ The calculated relative stabilities of C₆₀ and C₇₀ bisadducts with anthracene suggest that the thermodynamic stability of the regioisomers decrease in the following order: *trans*-3 $\geq$ *e*- > *trans*-2 > *trans*-4 $\geq$ *trans*-1 > *cis*-3 > *cis*-2.⁴⁰

1.3. Aim, motivation and strategy

Following the importance of fullerenes and of the reactions to functionalize them, and their lack of thermodynamic and kinetic characterization present in the literature; in this thesis we propose to study the Diels-Alder reaction (one of the most used reactions in fullerene functionalization) for different fullerenes (C₆₀, C₇₀, ICMA and ICBA). In particular, we want to evaluate the effect of symmetry and isomerism in these reactions. C₆₀ has the highest symmetry ($\sigma_{sym} = 60$), and its monoadduct has no distinguishable isomers. C₇₀ has a lower symmetry ($\sigma_{sym} = 10$), and different isomers are possible. ICMA has no rotational symmetry ($\sigma_{sym} = 1$) but, upon addition, various different isomers can be formed. Thus, we chose to study and characterize the reactions between these fullerenes and anthracene/9,10-dimethylantracene (Fig. 8 for anthracene, the reaction is the same and the adduct is similar for the reaction with DMA) (for information regarding the choice of these dienes, see Section 3.1.3). The reaction with anthracene will be studied kinetically and thermodynamically, and the reaction with 9,10-dimethylantracene thermodynamically, both in solution (with *m*-xylene as the solvent), using UV-Vis spectroscopy. No distinction between the possible isomers for the adducts formed in these reactions can be made using the experimental techniques we chose in this work, and as such we proposed to study these reactions combining both an experimental and theoretical approach. In this thesis the reactions are theoretically studied in vacuum and in solution. In this way we can evaluate the stability of the different fullerene adduct isomers and have a computational background to anchor the experimental findings.

For analyzing the results obtained using UV-Vis spectroscopy, one needs to know not only the spectra of the reactants, but also the spectra of the adducts. For that, we use the spectra analysis and deconvolution program *HypSpec*⁵², which determines an optimized spectrum of the adduct from equilibrium spectra of solutions containing the fullerene and the diene, and also gives an optimized value of the equilibrium constant for the studied reaction.

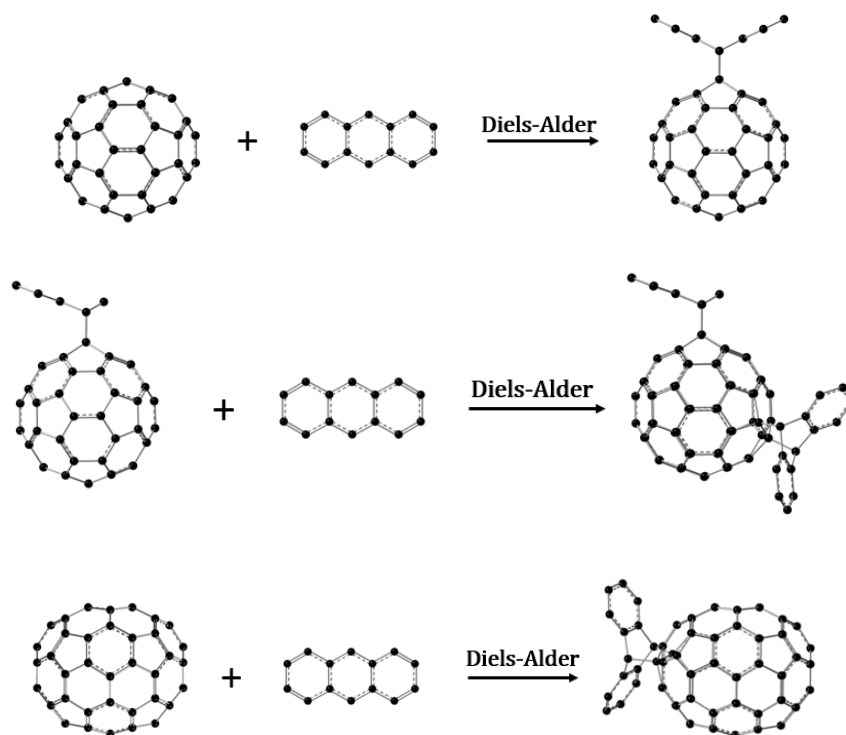


Fig. 8: Diels-Alder reaction between anthracene and C₆₀ (top), ICMA (middle) and C₇₀ (bottom). Products are one specific isomer when there are multiple as is the case with ICMA-anthracene and C₇₀-anthracene adducts (C₇₀-anthracene is present as isomer **a** and ICMA-anthracene is present as the *trans*-4 **b** isomer (nomenclature introduced in Section 3.2.).

We also decided to study the retro Diels-Alder reaction: in this case the adducts we decided to study were ICMA and ICBA. Indene is a very strong diene in Diels-Alder cycloaddition, and thus to remove it from C₆₀ we need to raise the temperature. Thus, we choose to characterize these retro reactions (Fig. 9) on the crystalline phase of ICMA and ICBA, using thermal analysis. Differential Scanning Calorimetry (DSC, which allows us to measure the heat transfer associated with the process) and Thermogravimetric Analysis (TGA, which allows us to obtain kinetic parameters for the retro Diels-Alder reaction) were the techniques chosen. Obviously, since we are characterizing the solid phase, the results will not be directly comparable to the results obtained in solution, but can still us information and insight onto the solid phase of these fullerenes and the fullerene-addend bond.

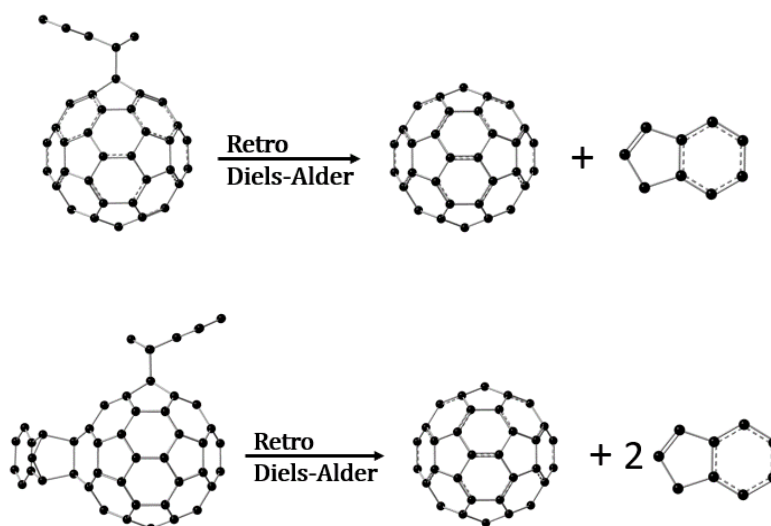


Fig. 9: Retro Diels-Alder reaction for ICMA (top) and ICBA (bottom). ICBA is present as one e-face isomer.

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Chapter 2:

Concepts and Methodologies

2.1. The Diels-Alder reaction

The Diels-Alder (DA) reaction was first described by Otto Diels and his student Kurt Alder in 1928.¹ It is a cycloaddition reaction between a conjugated diene and a dienophile – usually an alkene. It is a [4+2] cycloaddition, where two π electrons from the dienophile and four π electrons from the diene are involving in breaking two π bonds in the reactants forming two σ bonds in the products.²⁻⁴ An example of a Diels-Alder cycloaddition is in Fig. 10.

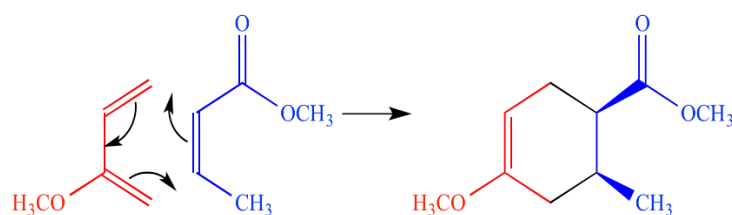


Fig. 10: Scheme of a Diels-Alder cycloaddition. The conjugated diene is represented in red, and the dienophile in blue.

The Diels-Alder reaction is a type of pericyclic reaction – a subset of organic reactions that are characterized by having a single transition state species with cyclic array of interacting orbitals. In these reactions there are no positive or negative charges or intermediates associated – electrons simply reorganize, and the reaction happens in a concerted mechanism – all bond breaking and bond formation is done via one single step.²⁻⁵ Although evidence strongly suggests that the Diels-Alder reaction is an elementary reaction and occurs in a single step, some authors have found possible evidence of multi-step mechanism for specific cases of the reaction.⁶⁻¹⁰

Due to its versatility and simplicity, the Diels-Alder reaction is a very important synthetic method for making six membered rings, and one of the most important organic reactions. It is widely used in organic synthesis to obtain organic compounds of added value.^{1, 4}

The transition state in a Diels-Alder reaction is akin to the structure in Fig. 11. It has aromatic character with six delocalized π electrons, giving it extra stability, which is one of the driving-forces for the Diels-Alder reaction, helping it occur at a significant rate.²⁻⁴ Another driving force of the reaction is the formation of two σ bonds from two π bonds, the former being energetically more favorable.²⁻⁴

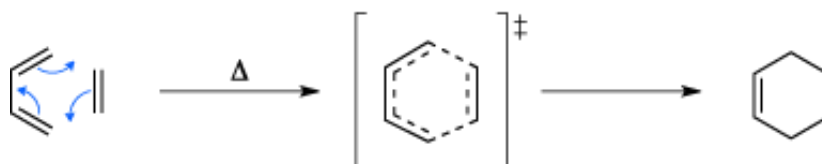


Fig. 11: Scheme of a Diels-Alder reaction between 1,3-butadiene and ethylene, showing the aromatic transition state.

In the Diels-Alder reaction the HOMO (Highest Occupied Molecular Orbital) of the diene and LUMO (Lowest Unoccupied Molecular Orbital) of the dienophile interact to form two new molecular orbitals (Fig. 12). Thus, they need to be of similar energy so overlap can occur. It can be imagined as electrons going from the HOMO of the diene to the LUMO of the dienophile (Fig. 13). The HOMO of conjugated dienes has the correct symmetry for bonding overlap to occur, while for example the HOMO of alkenes does not have the correct symmetry and no reaction occurs due to antibonding overlap of orbitals.^{2, 3, 5} Substituents in the diene or dienophile do not alter the bond breaking/formation of the Diels-Alder reaction, but they do alter the rate of the reaction (altering the energy of the transition state). The reaction is kinetically favored by electron-withdrawing groups on the dienophile, since this will lower the energy of the LUMO. The rate also increases due to the presence of electron-donor groups in the diene, which raise the energy of the HOMO.^{3, 5, 7}

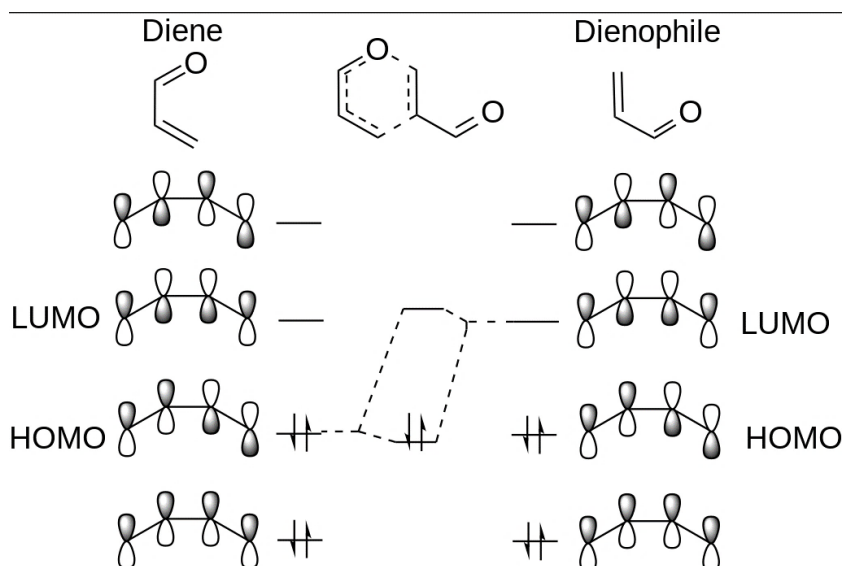


Fig. 12: Frontier orbital description of the Diels-Alder reaction – the HOMO of the diene and LUMO of the dienophile interact to form a new pair of molecular orbitals.

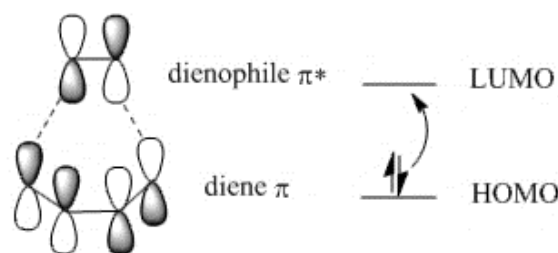


Fig. 13: Frontier orbital overlap in the Diels-Alder reaction. The electrons from the HOMO of the diene “flow” to the LUMO of the dienophile, which has the correct symmetry for the overlap and bond formation to occur.

The diene in the Diels-Alder reaction can be cyclic or not, but it must be on the *s-cis* conformation (Fig. 14). This conformation can be achieved by internal rotation from a *s-trans* conformation, and the reaction will occur if the rotation is sufficiently fast. However, in a cyclic diene only bonds in the *s-cis* conformation will react via cycloaddition. To be readily reactive, the dienophile must have electron-deficient character. Strong electron withdrawing group near the reactive double bonds of the dienophile, or the presence of conjugation, can increase the extension of a Diels-Alder cycloaddition.^{2, 3, 5}

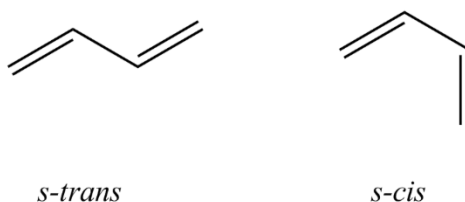


Fig. 14: Illustration of the *s-trans* and *s-cis* conformations for 1,3-butadiene.

Dienes usually have high energy HOMOs and low energy LUMOs, and thus they can react with themselves via Diels-Alder, with one molecule acting as the dienophile. This is called the dimerization of dienes.^{2, 5}

2.2. The van ‘t Hoff equation

The equilibrium constant (K) of a reaction (in solution – as it is the case of the studies in this thesis), assuming unitary activity coefficients (although the proof and equation holds just the same when using activities^{11, 12}); is given by:

$$K \equiv \frac{\prod_j \left(\frac{c_j}{c^0}\right)^{n_j}}{\prod_i \left(\frac{c_i}{c^0}\right)^{n_i}} \quad 1$$

where, the product on the numerator goes over all the products of the reaction, with equilibrium concentrations c_j and reaction coefficients n_j , and likewise in the denominator for the reactants; and c^0 is the standard state concentration. We now define the absolute Gibbs energy (G) of a system (in this case, a species in equilibrium) as $G \equiv H - TS$, where H and S are the absolute enthalpy and entropy of the species, respectively. All of this thermodynamic quantities depend on the temperature, but for simplicity their temperature dependence is omitted. The Gibbs energy is the natural energy of a system in isobaric and isothermal conditions – meaning it is the potential that is minimized in these conditions. This equilibrium constant for a reaction in solution can be expressed as a function of the molar Gibbs energy of the reaction (ΔG_r^0) (for a constant pressure and constant temperature system) as ^{11, 12}:

$$K = e^{-\frac{\Delta G_r^0}{RT}} \quad 2$$

with:

$$\Delta G_r^0 = \sum_j n_j G_j^0 - \sum_i n_i G_i^0 \quad 3$$

G_i^0 being the standard molar absolute Gibbs energy of the reactants and likewise G_j^0 is the standard molar absolute Gibbs energy of the products; T is the temperature and R is the perfect gas constant (in this work we will often refer to standard molar Gibbs energy, standard molar enthalpy and standard molar entropy by dropping the molar and standard prefix – simply calling them Gibbs energy, enthalpy and entropy. From Equation 2, taking the natural logarithm, we get:

$$\ln K = -\frac{\Delta G_r^0}{RT} \quad 4$$

Using the definition of G , we get:

$$\ln K = -\frac{\Delta H_r^0}{RT} + \frac{\Delta S_r^0}{R} \quad 5$$

with ΔH_r^0 and ΔS_r^0 (standard molar enthalpy change and standard molar entropy change of the reaction respectively) defined the same way as ΔG_r^0 in Equation 3. All the thermodynamic quantities used in this equation are at temperature T . This is known as the van 't Hoff equation – in homage to Jacobus Henricus van 't Hoff, who developed it.^{11, 12} The van 't Hoff equation tells us how the equilibrium constant varies with temperature. If we take the partial derivative of $\ln K$ with respect to T while keeping the pressure (P) fixed:

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{\Delta H_r^0}{RT^2} \quad 6$$

(the partial derivative of $\ln K$ with respect to T while keeping the pressure (P) fixed). To reach this result we ignore the variations of the enthalpy and entropy of reaction with temperature, as they are small. We can also reach this result by taking the derivative of $\ln K$ using Equation 4:

$$\begin{aligned} \left(\frac{\partial \ln K}{\partial T}\right)_P &= -\left(\frac{\partial(\Delta G_r^0/RT)}{\partial T}\right)_P = \frac{\Delta G_r^0}{RT^2} - \left(\frac{\partial(\Delta G_r^0)}{\partial T}\right)_P / RT = \frac{\Delta G_r^0}{RT^2} + \frac{\Delta S_r^0}{RT} \\ &= \frac{\Delta H_r^0}{RT^2} \end{aligned} \quad 7$$

The last two equalities arise from the use of the definition $G \equiv H - TS$. Integrating Equation 6 between two different temperatures, T_1 and T_2 , we get:

$$\ln \frac{K_2}{K_1} = \frac{\Delta H_r^0}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad 8$$

where K_1 and K_2 are the equilibrium constant of the system at two different temperatures, T_1 and T_2 , respectively. This equation relates the equilibrium constant of the system at two different temperatures. Again, we ignore the variation of ΔH_r^0 with temperature. This

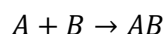
is legitimate if the difference between the temperatures isn't too large, and/or if the variation of the enthalpy of reaction with temperature (which depends on the difference of heat capacities of the products and reactants) is small.

Using the van 't Hoff equation, one can see that a plot of $\ln K$ as a function of $\frac{1}{T}$ - assuming a constant enthalpy and entropy change over the range of temperatures - gives a linear plot with slope $-\frac{\Delta H_r^0(<T>)}{R}$ and intercept $\frac{\Delta S_r^0(<T>)}{R}$, where the enthalpy and entropy of reaction are at temperature $<T>$, where $<T>$ is the central temperature ("average temperature", as usually called - it is an average of the temperature interval, but not necessarily the average of the temperature data points used) of the van 't Hoff plot ($<T> = \frac{T_2 + T_1}{2}$, T_1 and T_2 being the minimum and maximum temperatures of the plot, respectively). This plot is known as a van 't Hoff plot. ^{11, 12}

Equation 2 only holds with K expressed as in Equation 1 for reactions in solution. For species in the gas phase K would have to be written in terms of partial pressures or fugacities, and the standard state would be the ideal gas at 1 bar. ^{11, 12}

2.3. The van 't Hoff equation in the presence of isomers

In a system in equilibrium where one or more of the species can exist as different isomers, the van 't Hoff equation takes on a different form. Imagine the reaction (in solution) of the formation of an adduct described by:



Let's assume AB can exist in the form of n different isomers, which can't be distinguished by the experimental technique used. Assuming we are dealing with an ideal system where the activity coefficients for all species are unity (which is not a necessity for this proof to hold), we can write a global equilibrium constant as:

$$K = \frac{[AB]}{[A][B]} \quad 9$$

where $[AB]$ is the total concentration of the product in equilibrium (the sum of the concentration of all the possible isomers), $[A]$ and $[B]$ the concentration of A and B In equilibrium, respectively (we take $c^0 = 1$ a.u. (arbitrary units – the same units the concentrations are expressed in), for simplicity). This global equilibrium constant can also be expressed in terms of the individual isomers:

$$K = \frac{[AB]}{[A][B]} = \sum_{i=0}^n \frac{[AB]_i}{[A][B]} = \sum_{i=0}^n K_i \quad 10$$

where the index i represents each of the n possible isomers of AB , and K_i is the the equilibrium constant for each of the isomers (as one would write them if one had no issues distinguishing them experimentally). Using the relation described by Equation 10, we can then write the global equilibrium constant as:

$$K = \sum_{i=0}^n e^{-\Delta G_{r,i}^0/RT} \quad 11$$

where $\Delta G_{r,i}^0$ is the Gibbs energy of reaction with the isomer i as the product at a temperature T (again, the temperature dependence is omitted). We want to express the previous equation as a van 't Hoff type equation. A way to accomplish this is to define the average Gibbs energy for the reaction:

$$\langle \Delta G_r^0 \rangle \equiv \sum_{i=0}^n p_i \Delta G_{r,i}^0 \quad 12$$

where:

$$p_i \equiv \frac{e^{-\Delta G_{r,i}^0/RT}}{\sum_{i=0}^n e^{-\Delta G_{r,i}^0/RT}} \equiv \frac{e^{-\Delta G_{r,i}^0/RT}}{Z} = \frac{K_i}{\sum_{i=0}^n K_i} = \frac{[AB]_i}{[AB]} \quad 13$$

is the fraction of isomer i present in equilibrium (or probability of AB being found in the form of isomer i , in a statistical view). We define Z ($= K$) as the system's *pseudo*-partition function. Using this definition, and taking the natural logarithm of Equation 11, we get:

$$\ln K = \ln \left[e^{-\langle \Delta G_r^0 \rangle / RT} \sum_{i=0}^n e^{(\langle \Delta G_r^0 \rangle - \Delta G_{r,i}^0) / RT} \right] \quad 14$$

where we simply multiplied and divided the inside of the natural log on the right side by $e^{-\langle \Delta G_r^0 \rangle / RT}$. Applying the properties of exponentials while using Equation 13:

$$\ln K = -\frac{\langle \Delta G_r^0 \rangle}{RT} + \ln \left[\sum_{i=0}^n p_i Z \prod_{j=0}^n (p_j Z)^{-p_j} \right] \quad 15$$

Applying properties of the logarithm then gives us:

$$\ln K = -\frac{\langle \Delta G_r^0 \rangle}{RT} + \ln \sum_{i=0}^n p_i + \ln Z - \sum_{j=0}^n p_j \ln p_j - \sum_{k=0}^n p_k \ln Z \quad 16$$

the last sum just gives $-\ln Z$, which cancels with the $\ln Z$ from the other term. Also the second term is just $\ln(1)$, which gives zero. Thus, we get:

$$\ln K = -\frac{\langle \Delta G_r^0 \rangle}{RT} - \sum_{i=0}^n p_i \ln p_i \quad 17$$

This is an equivalent expression to Equation 11, but in terms of the average Gibbs energy of the reaction. If we are working at constant pressure and not very low temperatures (in Kelvin), we can expand Equation 17 in a Taylor series, keeping only the terms linear in $1/T$:

$$\ln K \approx \ln K|_{T=\langle T \rangle} + \left(\frac{\partial \ln K}{\partial 1/T} \right)_p |_{T=\langle T \rangle} (1/T - 1/\langle T \rangle) \quad 18$$

where $\langle T \rangle$ is the central temperature (“average temperature”) of the van ‘t Hoff plot

($\langle T \rangle = \frac{T_2 - T_1}{2}$, T_1 and T_2 being the minimum and maximum temperatures of the plot, respectively). Using $\langle \Delta G_r^0 \rangle = \langle \Delta H_r^0 \rangle - T \langle \Delta S_r^0 \rangle$, with the average entropy of reaction and average enthalpy of reaction defined the same way as the average Gibbs energy of reaction in Equation 12; and using Equation 13, we have (neglecting the dependency of enthalpies and entropies of reaction with temperature):

$$\begin{aligned} \left(\frac{\partial \frac{\langle \Delta G_r^0 \rangle}{RT}}{\partial 1/T} \right)_p &= \frac{\langle \Delta H_r^0 \rangle}{R} + \frac{\langle \Delta H_r^0 \rangle^2 - \langle \Delta H_r^0 \rangle^2}{R^2 T} + \frac{\langle \Delta H_r^0 \Delta S_r^0 \rangle - \langle \Delta H_r^0 \rangle \langle \Delta S_r^0 \rangle}{R^2} \\ &= \frac{\langle \Delta H_r^0 \rangle}{R} - \frac{\text{var}(\Delta H_r^0)}{R^2 T} + \frac{\text{cov}(\Delta H_r^0, \Delta S_r^0)}{R^2} \end{aligned} \quad 19$$

where $\langle \Delta H_r^0 \rangle^2 = \sum_{i=0}^n p_i \Delta H_{r,i}^0{}^2$, $\langle \Delta H_r^0 \Delta S_r^0 \rangle = \sum_{i=0}^n p_i \Delta H_{r,i}^0 \Delta S_{r,i}^0$,

$\text{var}(\Delta H_r^0) = \langle \Delta H_r^0 \rangle^2 - \langle \Delta H_r^0 \rangle^2$ is the variance of the ΔH_r^0 evaluated using the distribution given by Equation 13, and $\text{cov}(\Delta H_r^0, \Delta S_r^0) = \langle \Delta H_r^0 \Delta S_r^0 \rangle - \langle \Delta H_r^0 \rangle \langle \Delta S_r^0 \rangle$ is the covariance of ΔH_r^0 and ΔS_r^0 evaluated according to the same distribution. We also have:

$$\left(\frac{\partial \sum_{i=0}^n p_i \ln p_i}{\partial 1/T} \right)_p = \frac{\text{var}(\Delta H_r^0)}{R^2 T} - \frac{\text{cov}(\Delta H_r^0, \Delta S_r^0)}{R^2} \quad 20$$

Using Equation 19 and Equation 20 we can evaluate the derivative in Equation 18 (via Equation 17) as:

$$\left(\frac{\partial \ln K}{\partial 1/T} \right)_p |_{T=\langle T \rangle} = - \frac{\langle \Delta H_r^0(\langle T \rangle) \rangle}{R} (1/T - 1/\langle T \rangle) \quad 21$$

with $\langle \Delta H_r^0(\langle T \rangle) \rangle$ being the average enthalpy of reaction at the average temperature of the study (this dependence is from now on omitted for simplicity, but it exists on the average enthalpy, entropy and Gibbs energy that appear until the end of the Section).

Using this relation and evaluating the first term in Equation 18 by using Equation 17, we get:

$$\ln K \approx -\frac{\langle \Delta G_r^0 \rangle}{R \langle T \rangle} - \sum_{i=0}^n \langle p_i \rangle \ln \langle p_i \rangle - \frac{\langle \Delta H_r^0 \rangle}{R} (1/T - 1/\langle T \rangle) \quad 22$$

where:

$$\langle p_i \rangle \equiv \frac{e^{-\Delta G_{r,i}^0/R\langle T \rangle}}{\sum_{i=0}^n e^{-\Delta G_{r,i}^0/R\langle T \rangle}} \quad 23$$

is the probability of each isomer evaluated at $\langle T \rangle$. Expanding $\langle \Delta G_r^0 \rangle = \langle \Delta H_r^0 \rangle - \langle T \rangle \langle \Delta S_r^0 \rangle$ in the first term in Equation 22 gives:

$$\ln K \approx \frac{\langle \Delta S_r^0 \rangle}{R} - \sum_{i=0}^n \langle p_i \rangle \ln \langle p_i \rangle - \frac{\langle \Delta H_r^0 \rangle}{RT} \quad 24$$

Therefore, a van 't Hoff plot in a system of this kind will give a slope which is $-\frac{\langle \Delta H_r^0 \rangle}{R}$, and an intercept which is $\frac{\langle \Delta S_r^0 \rangle}{R} - \sum_{i=0}^n \langle p_i \rangle \ln \langle p_i \rangle$. This applies as long as the Taylor expansion keeps only the first order term is legitimate – which happens when the temperatures are not too low and the temperature interval not too broad (in which case the linearity of the van 't Hoff plot is questionable even without the presence of isomers). We can then define:

$$S_{isom} = -R \sum_{i=0}^n \langle p_i \rangle \ln \langle p_i \rangle \quad 25$$

as the *entropy of isomerism* for this system. It shifts the equilibrium in favor of the direct reaction since it is a positive term on the entropy ($\ln p_i$ is the logarithm of a fraction and

thus is always negative). Note that p_i can also be evaluated based on the absolute Gibbs energy (G_i) or the Gibbs energy of formation ($\Delta G_{f,i}$) of the isomers, because the term $e^{-\Delta G_{r,i}^0/RT}$ is proportional to $e^{-\Delta G_{f,i}^0/RT}$ ($e^{-\Delta G_{r,i}^0/RT} = e^{-\Delta G_{f,i}^0/RT} e^{\Delta G_{f,A}^0/RT} e^{\Delta G_{f,B}^0/RT}$), $\Delta G_{f,A}^0$ being the Gibbs energy of formation of A and $\Delta G_{A,f}^0$ the Gibbs energy of formation of B), and this factor cancels in calculating p_i .

This new entropy term evaluates the distribution of isomers by their Gibbs energy, like the classical entropic term evaluates the distribution of microstates by their energy. It is the Gibbs entropy formula¹³, but with probabilities calculated based on their Gibbs energy – the natural energy for this system. It treats the isomers like states in an ensemble ruled by the Gibbs energy.

For the case where isomerism is present in the reactants, we have:

$$K = \frac{[AB]}{[A][B]} = \frac{[AB]}{\sum_{i=0}^n [A]_i [B]} = \frac{1}{\sum_{i=0}^n 1/K_i} = \frac{1}{\sum_{i=0}^n e^{\Delta G_{r,i}^0/RT}} \quad 26$$

where i is summing over each of n possible A isomers. Similarly to the above derivation:

$$\ln K = -\ln \left[e^{\langle \Delta G_r^0 \rangle / RT} \sum_{i=0}^n e^{(-\langle \Delta G_r^0 \rangle + \Delta G_{r,i}^0) / RT} \right] \quad 27$$

In this case we define:

$$\langle \Delta G_r^0 \rangle \equiv \sum_{i=0}^n p_i^{(+)} \Delta G_{r,i}^0 \quad 28$$

by defining $p_i^{(+)}$ as the fraction of each isomer i of the reactant in equilibrium:

$$p_i^{(+)} \equiv \frac{e^{\Delta G_{r,i}^0/RT}}{\sum_{i=0}^n e^{\Delta G_{r,i}^0/RT}} \equiv \frac{e^{\Delta G_{r,i}^0/RT}}{Z^{(+)}} = \frac{1/K_i}{\sum_{i=0}^n 1/K_i} = \frac{[A]_i}{[A]} \quad 29$$

where $Z^{(+)}$ is the *pseudo*-partition function of the system with $-\Delta G_{r,i}^0$ replaced by $+\Delta G_{r,i}^0$.

Working through a similar derivation as above, we get:

$$\ln K \approx \frac{\langle \Delta S_r^0 \rangle}{R} - \sum_{i=0}^n \langle p_i^{(+)} \rangle \ln \langle p_i^{(+)} \rangle - \frac{\langle \Delta H_r^0 \rangle}{RT} \quad 30$$

Thus, now the entropy of isomerism is a negative term (favoring the reverse reaction) and calculated using $p_i^{(+)}$ as given by Equation 29 (and likewise the average values $\langle \Delta S_r^0 \rangle$ and $\langle \Delta H_r^0 \rangle$ are calculated using $p_i^{(+)}$).

The above derivation is for reactions in solution, but, again, all of this holds for the gas phase as long as the equilibrium constants are written in terms of partial pressures and the standard state is the ideal gas at 1 bar.

This equation can be generalized if it so happens that the reaction coefficient for the species with isomers is not unitary. It can be easily shown that the intercept or total entropy of reaction (the entropy of reaction with the entropy of isomerism contribution) is:

$$\frac{\Delta S_{total}}{R} = \frac{\langle \Delta S_r^0 \rangle}{R} - a \sum_{i=0}^n \langle p_i \rangle \ln \langle p_i \rangle \quad 31$$

where a is the reaction coefficient for the species with isomers ($a > 0$ for products and $a < 0$ for reactants).

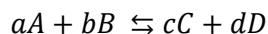
When there exist both isomers in multiple reactants and multiple products, and the whole system is in complete thermodynamic equilibrium, one can just add all entropy of isomerism contributions, given by Equation 9, for all species – obtaining a total entropy of isomerism for the system of

$$\frac{\Delta S_{total}}{R} = \frac{\langle \Delta S_r^0 \rangle}{R} - \sum_j n_j \sum_{i=0}^n \langle p_i \rangle \ln \langle p_i \rangle \quad 32$$

where n_j is the reaction coefficient for species j (which can be either a reactant or product: $n_j > 0$ for products and $n_j < 0$ for reactants).

2.4. Reaction kinetics and the Arrhenius equation

The rate of a reaction is defined as the “velocity” at which reactants are converted to products. Imagine for example a reaction:



In this case the rate of the reaction is defined as ^{11, 12}:

$$v = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt} \quad 33$$

These concentrations are not necessarily equilibrium concentrations. For each elementary step in a reaction, the rate of the direct reaction is also related to the concentration of the reactants by the reaction rate constant, k . Assuming this reaction is an elementary reaction ^{11, 12}:

$$v_1 = k_1[A]^a[B]^b \quad 34$$

where k_1 is the rate constant for the direct reaction. For the reverse reaction, the rate is:

$$v_{-1} = k_{-1}[C]^c[D]^d \quad 35$$

k_{-1} being the rate constant for the reverse reaction. In equilibrium, the forward and reverse rates are equal ($v_1 = v_{-1}$). One can, then, deduce that the ratio of the rate constants of the direct and reverse steps of a elementary reaction is equal to the equilibrium constant for the reaction:

$$\frac{k_1}{k_{-1}} = \frac{[C]_{eq}^c [D]_{eq}^d}{[A]_{eq}^a [B]_{eq}^b} = K_{eq} \quad 36$$

($c^0 = 1$ a. u. (the same units in which the concentrations are expressed)). Equilibrium is thus defined by the ratio of the velocities of the direct and reverse reactions.^{11, 12}

The temperature dependence of the k 's is given by the Arrhenius law or Arrhenius equation, an empirical equation proposed by Svante Arrhenius in 1889^{11, 12}:

$$k = Ae^{-E_a/RT} \quad 37$$

where A is the pre-exponential factor and E_a is the molar activation energy. This equation can (in principle) be valid for any type of reaction: since it is empirical it does not assume any special conditions. Though, the interpretation of the parameters can change depending on the type of reaction studied.^{11, 12} A fitting to the Arrhenius equation can always be made by plotting experimental $\ln k$ values as a function of $1/T$ – the slope is (if the equation applies) $-E_a/R$ and the intercept $\ln A$.

A physical interpretation can be given to the activation energy and pre-exponential factor: $e^{-E_a/RT}$ is akin to a Boltzmann factor which is proportional to the fraction of molecules which have enough energy to react (kinetic energy, in a hard-sphere collision view of reactivity¹¹). The pre-exponential factor can be interpreted as the number of “collisions” with the correct orientation between the reaction molecules (in the hard-sphere collision view) or, more generally, the “opportunities” to react, independently if they have sufficient energy or not. This interpretation makes sense since, for the case $E_a = 0$, the rate constant would simply be A – the total number of “collisions” or “opportunities”.^{11, 12} In the next section we will see a more modern interpretation of the Arrhenius equation.

2.5. Transition state theory

Transition state theory (TST) is an approximate theory for determining rate constants. It was developed independently by Pelzer and Wigner; Evans and Polanyi; and Eyring¹¹. In TST, a transition state (or activated complex) is a molecule whose configuration lies within a short distance from the highest point of the barrier in the potential energy surface – the saddle point – which is the equilibrium structure of said transition state. This barrier is a dividing surface that divides the potential energy surface in the product region and the reactant region (Fig. 15). In other words, during the reaction, the reactants “transform” into the transition state in a step that precedes the formation of the products. The reaction coordinate, then, unites these two regions, passing through the transition state. It is a vibrational coordinate of the transition state, along which the

reactants become more similar to the products. Nuclear motion along this coordinate transforms the transition state into the products.^{3, 11, 14}

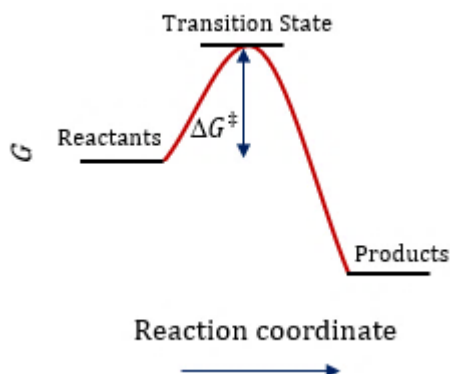
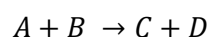


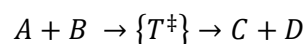
Fig. 15: Potential energy surface along a reaction coordinate for an exergonic ($\Delta G_r < 0$) reaction, illustrating a typical transition state and Gibbs energy of activation of reaction ($\Delta G^\ddagger$).

Transition state theory is a classical theory since it assumes that the system never returns to the transition state – all molecules that reach the transition state become products. It also assumes the reactants and the transition state obey a Boltzmann distribution. TST assumes a transition state in thermal equilibrium with the reaction system - even though it is not a stable species, but a stage in the transformation of reactants to products. Another assumption of the theory is that motion along the reaction coordinate can be treated classically.^{11, 14, 15}

Let us imagine the reaction:



which in TST formalism can also be written as:



where $T^\ddagger$ is the transition state, and the braces are used to remind us that this is not a stable reaction intermediary. In TST, one can define the ratio of concentrations between the transition state and the reactants (exactly like one would write an equilibrium constant) as:

$$K^\ddagger \equiv \frac{[T^\ddagger]}{[A][B]} \quad 38$$

where $[A]$ is the concentration of A in equilibrium (and similarly for B), and $[T^\ddagger]$ the “concentration” of the transition state. This is not an equilibrium constant, as the transition state is not in chemical equilibrium with the reactants. Under the assumptions of TST, one can write ^{3, 11, 15}:

$$K^\ddagger = \frac{k_B T}{h\nu} e^{-\frac{\Delta G^\ddagger}{RT}} \quad 39$$

where $\Delta G^\ddagger$ is the standard state activation Gibbs energy– the difference in Gibbs energy between the reactants and the transition state, k_B is the Boltzmann constant, h the Planck constant, and ν the frequency of motion along the reaction coordinate (the inverse time constant associated with motion along the reaction coordinate). For an elementary reaction of this type the rate is given by:

$$\frac{d[C]}{dt} = k[A][B] = k^\ddagger[T^\ddagger] \quad 40$$

where k is the rate constant for the reaction and $k^\ddagger$ the rate at which the transition state converts into the products. The last equality holds since the rate is limited by the number of molecules which have reached the transition state. Following the previous equation and using Equation 38:

$$k = k^\ddagger K^\ddagger \quad 41$$

But $k^\ddagger$ is simply the frequency of motion along the reaction coordinate (ν). Using Equation 39 one then obtains:

$$k = \frac{k_B T}{h} e^{-\frac{\Delta G^\ddagger}{RT}} (c^0)^{1-m} \quad 42$$

The last result is known as the Eyring equation, in homage to one of its developers. ^{3, 11,}

¹⁴ The factor $(c^0)^{1-m}$, where c^0 is the standard concentration and m is the sum of the

reaction coefficients of the reactants (in this example reaction $m = 2$), is needed for correct dimensionality (we omitted the standard concentrations in Equation 38 for simplicity, and thus attributed a dimensionality to $K^\ddagger$). To account for the limitation that some of the molecules that reach the transition state might return to the reactant state and not cross the barrier, a transmission coefficient κ can be added as a proportionality constant to the pre-exponential factor in Equation 42.^{11, 14}

This equation holds for reactions in the gas phase, where it is exact; and for chemically controlled reactions in dilute solutions of nonionic species.¹¹

By measuring the rate constant of the reaction at different temperatures, one can use the relation (assuming $c^0 = 1$ a. u.):

$$\ln \frac{k}{T} = -\Delta H^\ddagger / RT + \Delta S^\ddagger / R + \ln \left(\frac{k_B}{h} \right) \quad 43$$

to obtain the standard state enthalpy of activation $\Delta H^\ddagger$ and standard state entropy of activation $\Delta S^\ddagger$ for the reaction (since $\Delta G^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger$).

An important thing to note is if we calculate the activation parameters for the reverse reaction we get: $\Delta G_{reverse}^\ddagger = \Delta G_{direct}^\ddagger - \Delta G_r^0$ where ΔG_r^0 is the Gibbs energy of the reaction. This result is valid as long as the reverse and direct reaction occur via the same transition state. Also: $\Delta H_{reverse}^\ddagger = \Delta H_{direct}^\ddagger - \Delta H_r^0$, and $\Delta S_{reverse}^\ddagger = \Delta S_{direct}^\ddagger - \Delta S_r^0$.

11

When one is interpreting the direct reaction, one must note that the Gibbs energy of the step of the reaction that occurs after the transition state barrier (the transition state $\rightarrow$ products step) is $\Delta G_{TS \rightarrow products} = -\Delta G_{reverse}^\ddagger$. This is likewise true for $\Delta H_{TS \rightarrow products}$ and $\Delta S_{TS \rightarrow products}$. This is important when analyzing the whole process reactants $\rightarrow$ products, whose Gibbs energy (or likewise enthalpy or entropy) is the sum of the energy of the two steps: $\Delta G_r^0 = \Delta G_{reactants \rightarrow TS} + \Delta G_{TS \rightarrow products} = \Delta G_{direct}^\ddagger - \Delta G_{reverse}^\ddagger$.

Transition state theory is an approximate theory for interpreting the kinetics of reactions. It has some shortcomings and limitations: it can only be applied to single-step reactions, and even if applied to each step in a multi-step reaction it can fail; it fails if the transition state is exceptionally short living and the Boltzmann distribution assumption is not reached; it can fail at very low temperatures due to important tunneling effects and at very high temperatures due to complex motion of the molecules. Because the motion

along the reaction coordinate is treated classically, TST does not count with possible tunneling at any temperature, and thus the real reaction rate constant will usually be miscalculated by at least a small amount. Also, when there are multiple transition states, TST is not an exact theory.^{14, 15}

Relating TST in solution to the Arrhenius theory previously discussed, we can see that since $\frac{d \ln k}{d(1/T)} = -E_a/R$ in Arrhenius and $\frac{d \ln k}{d(1/T)} = -\Delta H^\ddagger/R - T$ in TST (for dilute non-ionic solutions):

$$E_a = \Delta H^\ddagger + RT \quad 44$$

Since $A = k e^{E_a/RT}$, one can also deduce, using Equation 42, that the pre-exponential factor in the Arrhenius equation is related to the activation entropy by:

$$A = \frac{k_B T}{h} e^{\frac{\Delta S^\ddagger}{R} + 1} (c^0)^{1-m} \quad 45$$

These results apply only for elementary reactions in dilute nonionic solutions.¹¹

2.6. Symmetry and entropy

For a long time, symmetrical molecules have been known to have higher melting points, lower solubility and lower volatility, when compared to less symmetric analogs. This is an indication that the crystal phase of symmetric molecules has a greater stability relative to its liquid and gas phases. This is translated into lower entropies of fusion ($\Delta_{fus}S$), sublimation ($\Delta_{sub}S$), and solubility ($\Delta_{sol}S$).¹⁶⁻²²

Molecular symmetry is numerically expressed by the external symmetry number (σ_{sym}). This symmetry number is defined as the number of possible transformations on the molecule that only permute identical atoms - thus bringing the molecule to a state indistinguishable from the original state.^{11, 23} These transformations must be able to occur on the rigid molecule. Rotations are the only type of transformations that do not require any bond breaking/deformation – they are the only type of transformations accounted for in the external symmetry number (also known as the rotational symmetry number or simply symmetry number).^{11, 23} Experimentally, the relation found between

the decrease in the entropies of fusion, sublimation and solubility and this symmetry number in rigid molecules is ¹⁶⁻²¹:

$$\Delta_{proc}S = -R \cdot \ln \sigma_{sym} \quad 46$$

where $\Delta_{proc}S^0$ is the entropy change of the process (fusion, sublimation or solubility). Thus, the difference in these entropy changes, $\Delta\Delta_{proc}S$, between two compounds (A and B) that (hypothetically) only differ in symmetry is:

$$\Delta\Delta_{proc}S = -R \cdot \ln \frac{\sigma_A}{\sigma_B} \quad 47$$

Although this corresponds to an ideal hypothetical situation, there are many examples of analogous molecules with different symmetry where other factors have a minor contribution to entropy and Equation 47 holds. ¹⁶⁻²¹

The question of which of the phases (solid vs liquid and gas) is affected by this symmetry effect is still unsolved. It could be that symmetry decreases the entropy of the liquid and gas phases, or that it increases the entropy of the crystal. Or even some combination of both. Still, two reasonable hypotheses have gained force in the literature. The first hypothesis (H1) (Fig. 16) is that the absolute entropy of the gas and liquid phases ($S(g)$ and $S(l)$) is reduced by symmetry, because of the introduction of the σ_{sym} in the rotational partition function of polyatomic gases to correct for the overcounting of microscopically indistinguishable rotational states. This arises from the parity requirements of the nuclear wavefunction, which, with respect to interchange of identical nuclei, must be antisymmetric for fermions and symmetric for bosons. ^{24, 25} This restricts the number of available rotational quantum states, which decreases the entropy of rotation of the molecule S_{rot} by $R \cdot \ln \sigma_{sym}$, which consequently lowers the total entropy of the molecule by the same factor. ^{24, 25} In the liquid phase molecular rotation is also allowed. Thus, it is assumed that symmetry also decreases the rotational entropy of molecules in the liquid phase or in solution.

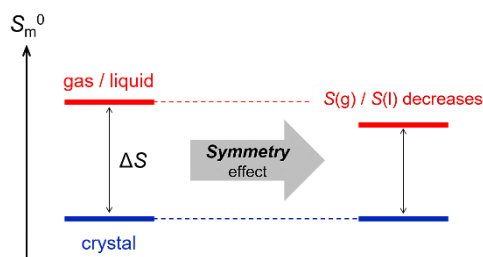


Fig. 16: Hypothesis 1 (H1). The entropy of the liquid and gas phases are decreased, making them less stable when compared to the solid phase.

The second hypothesis (H2) (Fig. 17) is that the absolute entropy of the crystal ($S(cr)$) increases with symmetry, because of the increase in the number of possible arrangements of the molecules in the crystal lattice. The atoms that make up molecules in a pure solid are not indistinguishable. This is because each particle has a very definite position in the crystal lattice. Hence, rotating a symmetrical molecule in the crystal lattice effectively interchanges particles that, although identical, have different sets of coordinates and are, therefore, distinguishable.^{26 12} Then, in the crystal of a symmetric molecule there are multiple identical energy microstates compatible with the crystal macrostate. These different microstates only involve rotations of the symmetric molecules (the same number of rotations that add up to σ_{sym}). Thus, the residual entropy of the crystal macrostate is increased by $k_B \cdot \ln \sigma_{sym}^N = N k_B \cdot \ln \sigma_{sym}$, where N is the number of molecules in the crystal and k_B the Boltzmann constant. In a mole of crystal molecules, we have the $R \cdot \ln \sigma_{sym}$.^{26 12} The geometric restrictions imposed by ordered and structured crystal lattices are what create the advantage of symmetry. In general, symmetry will increase the entropy of any system having orientationally ordering requirements. On the other hand, symmetry will have a smaller effect on the entropy of amorphous solids, where ordering requirements are much less strict.

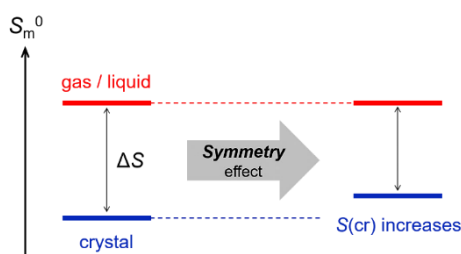
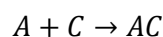


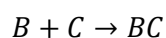
Fig. 17: Hypothesis 2 (H2). The entropy of the solid phase is increased, making it more stable when compared to the gas/liquid phase.

Both of these hypotheses are regularly evoked independently of each other.¹⁶⁻²² The current state-of-art is inconclusive with regards to which of the two hypothesis is the “real” one (the one that matches the experimental evidence).

If H1 is valid, when comparing the following reactions (as an example) in the gas phase or in solution:



and



the entropy difference due to symmetry ($\Delta_{sym}\Delta S_r$) between the entropy of reaction for reaction $A + C$ and for reaction $B + C$, is:

$$\begin{aligned}\Delta_{sym}\Delta S_r &= -R \cdot \ln \sigma_{AC} + R \cdot \ln \sigma_A + R \cdot \ln \sigma_C - (-R \cdot \ln \sigma_{BC} + R \cdot \ln \sigma_B + R \cdot \ln \sigma_C) \\ &= R \cdot \ln \frac{\sigma_A \sigma_{BC}}{\sigma_B \sigma_{AC}}\end{aligned}\quad 48$$

where σ_X is the symmetry number of species X .

In this work, one of the objectives of the study is to ascertain the validity of H1, in particular if symmetry influences reactions in solution. Fullerenes are a very useful tool for probing the presence of symmetry due to their high symmetry numbers (in particular C_{60} with $\sigma_{sym} = 60$). In Table 2 are presented the symmetry group and corresponding rotational symmetry number of the molecules studied in this thesis.

Table 2: Symmetry groups and symmetry numbers for the molecules studied in this thesis.

Molecule	Symmetry group	Symmetry number
C_{60}	I_h	60
C_{70}	D_{5h}	10
ACMA	C_{2v}	2
ICMA	C_s	1
AC ₇₀ MA <i>d</i>	C_{2v}	2
AC ₇₀ MA ^a	C_s	1
AICBA <i>trans</i> -1	C_s	1
AICBA ^a	C_1	1
anthracene	D_{2h}	4
9,10-dimethylantracene	D_{2h}	4

^a all isomers except those previously mentioned.

2.7. UV-Vis spectroscopy

UV-Visible spectroscopy is a type of electronic absorption spectroscopy in which light is absorbed by chemical species due to the transition of valence electrons to higher energy levels. These transitions occur in the UV and visible light range. The UV-Vis spectrophotometer is a device that measures the fraction of radiation absorbed by the sample, giving as an output the spectrum of absorption of light at different wavelengths.

11, 27

UV-Visible spectra of molecules are made up of bands (Fig. 18), because of the different vibrational and rotational levels possible in the initial and final states of the transitions. ^{11, 27}

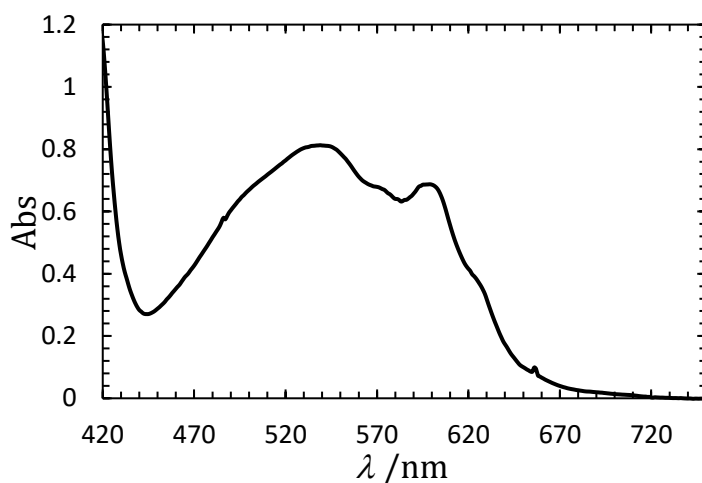


Fig. 18: UV-Vis spectra of a solution of C_{60} 1 mmol·L⁻¹ in *m*-xylene.

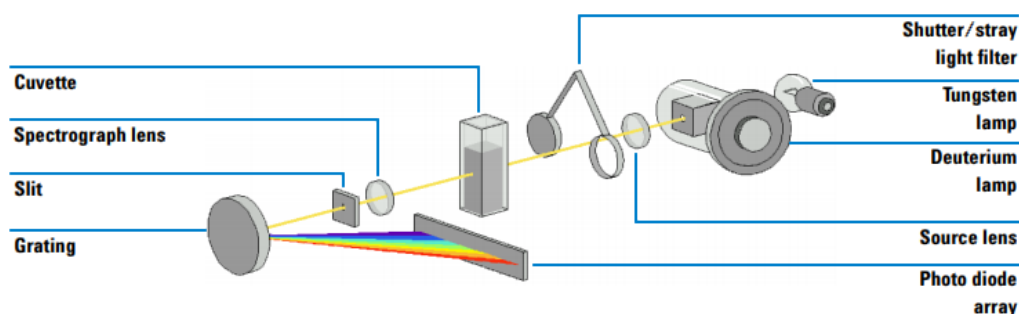


Fig. 19: Scheme of the diode array Agilent 8453 UV-Vis Spectrophotometer. Adapted from the apparatus' operator manual ²⁸.

In this work we used a diode array type UV-Vis spectrophotometer (from Agilent model 8453) (Fig. 20). Its optical system is schematized in Fig. 19 ²⁸. It is composed of:

- A **light source** made up of a Tungsten lamp (which emits in the range between 190 and 800 nm) and a Deuterium lamp (which emits between 370 to 1100 nm);
- the **source lens** which collimates the light from both lamps;
- a electromechanical **shutter** which opens to allow the beam to pass through the sample for measurements, closing between measurements to limit the exposure of the sample to light;
- a **stray light filter**, which corrects for stray light by having every measurement be done with and without the filter - with the filter active all the light measured below 400 nm is stray light. The intensity of the stray light is then subtracted to the whole spectrum giving a stray light corrected spectrum;
- the **cell holder** which is where the cuvette with the sample is placed. In our case the cell holder is temperature controlled by a circulating water bath (Fig. 20 and Fig. 21);
- the **spectrograph lens** – which refocuses the light that passed through the sample unabsorbed;
- a **slit** – a narrow aperture in a plate at the focus of the spectrograph lens. Its size is the same as each of the photodiodes in the diode array detector, and thus only the appropriate wavelengths will be projected onto each appropriate photodiode;
- a concave holographic **grating** that accomplishes the spectral imaging by dispersing the light at an angle linearly proportional to its wavelength;

- the **diode array** photodetector, a series of 1024 photodiodes and control circuits on a semiconductor chip. Its sampling resolution of about 0.9 nm.

The UV-Vis is coupled to a circulating water bath which keeps the cell holder at a fixed controlled temperature, defined by the interface monitor (Fig. 20 and Fig. 21).



Fig. 20: Setup of the Agilent 8453 UV-Vis Spectrophotometer (a). The apparatus is adjoined to a circulating water bath (b) which keeps the cell holder at a fixed designated temperature. The device is also connected to a pc interface (c) for data acquisition.



Fig. 21: Temperature control of the cell holder via a circulating water bath.

Since the cell and dispersion medium can absorb in the region under study, when using this spectroscopy one must first perform a blank spectrum, which will be discounted in the measured spectra.^{27, 28}

The Beer-Lambert law states that under certain conditions, the absorbance of incident light due to the presence of species X at a specific wavelength λ it absorbs in is proportional to its molar concentration:

$$\text{Abs}_{X,\lambda} = \varepsilon_{X,\lambda} l [X]$$

49

where $\varepsilon_{X,\lambda}$ is the species' molar absorptivity at the designated wavelength and l is the optical path length of the cell.^{11, 27} Using this law, we can turn the absorbance values obtained via UV-Vis spectroscopy - if we know $\varepsilon_{X,\lambda}$ and l - into the concentration of the species in the medium under study (in the case of this work, in solution).

$\varepsilon_{X,\lambda}$ can be obtained by preparing solutions of a precise concentration of X , and measuring their absorbance at the desired wavelength(s). A way to do this is to prepare a number of solutions of different concentrations and draw a plot of the absorbance as a function of concentration, the slope of which will be (as long as linearity is proven and holds) $\varepsilon_{X,\lambda} l$. This is known as a Beer-Lambert plot, and allows one to ascertain the validity of the law in the range of concentrations used.^{11, 27}

The Beer-Lambert law tends to fail for very high concentrations of the absorbing species, in particular in highly scattering materials. This can happen because the molecules are closer to each other, and interactions become important. This is especially true when chemical interactions are present, because they change the polarizability of the molecules. In general, for the Beer-Lambert law to be valid the absorbing of the different species must be independent from each other; the medium must be homogenous in the interaction (between the radiation and the sample) region; there must be no scattering of radiation; the incident light must be able to probe the sample non-invasively; and the incident radiation should be composed of parallel - preferentially monochromatic - rays.²⁷

In this thesis we use UV-Vis spectroscopy to study the Diels-Alder reaction between fullerenes and anthracene/9,10-dimethylantracene.

2.8. Spectra modeling and analysis - the *HypSpec* software

The Windows™ application *HypSpec*²⁹ is used for the determination of equilibrium constants (as well as unknown spectra of species in equilibrium) from spectrophotometric data. *HypSpec* processes UV-Vis, circular dichroism, IR, Raman, luminescence and fluorescence data - with the sole requirement that the spectral intensity of each chemical species should be proportional to the concentration of that species in solution (in the case of UV-Vis - the technique used in this work - this translates in the Beer-Lambert law being valid). It implements an algorithm to refine the

equilibrium constants and unknown molar absorptivities ε from given equilibrium spectra and (not obligatory) spectra of some of the species in equilibrium, as well as initial concentrations for the reactants.²⁹⁻³¹ In this thesis, this program was used to study the Diels-Alder reaction between fullerenes and anthracene, as well as determine the unknown spectra of the fullerene-anthracene adducts.

After scaling and correcting the spectra if needed, the algorithm uses the least-squares method to minimize the objective function (in matrix notation):

$$U = \mathbf{r}^T \mathbf{W} \mathbf{r} \quad 50$$

where $\mathbf{r}$ is the vector of residuals ($\mathbf{r} = \mathbf{y}^{experimental} - \mathbf{y}^{calculated}$), $\mathbf{y}$ being the vector of the response for the studied wavelengths (in the case of UV-Vis spectroscopy case it would be absorbance); and $\mathbf{W}$ is the weight matrix – one way to define the weights is by having the matrix be the inverse of the covariance matrix, which minimizes the variance of the weighted average.^{30, 31} To minimize the objective function, the Gauss-Newton-Marquardt method – a method used to solve non-linear least squares problems³² - is used:

$$(\mathbf{J}^T \mathbf{W} \mathbf{J} + \lambda \mathbf{D}) \Delta \mathbf{p} = \mathbf{J}^T \mathbf{W} \mathbf{r} \quad 51$$

where $\mathbf{J}$ is the Jacobian matrix, $\mathbf{D}$ is a matrix composed of the diagonal elements of $\mathbf{W}$, λ is the Marquardt parameter and $\Delta \mathbf{p}$ is the vector of shifts applied to the parameters. The Jacobian matrix is composed of the derivatives of the responses with respect to the refined parameters. The parameters are given initial values, calculated with the Beer-Lambert law and initial estimates of the concentrations by weighted linear least-squares – the weighting scheme can be chosen: we chose an absolute weighting scheme - which assumes the error in absorbance is related to the absorbance value^{30, 31}. In the case of this work (UV-Vis spectroscopy) it calculates the partial derivatives (for computing the Jacobian) of the absorbance at each studied wavelength λ with respect to the unknown molar absorptivities of species i ($\frac{\partial Abs_{\lambda}}{\partial \varepsilon_{i\lambda}}$) and with respect to the equilibrium constant ($\frac{\partial Abs_{\lambda}}{\partial K}$) based on the Beer-Lambert law written in terms of the equilibrium constant (assuming only one species as the product (and with a molecularity of 1), as is the case in this work):

$$Abs_{\lambda} = l \sum_j \varepsilon_{j\lambda} c_j + l \varepsilon_{p\lambda} K \prod_j c_j^{n_j} \quad 52$$

where l is the optical path length, $\varepsilon_{j\lambda}$ is the molar absorptivity of the j th reagent with equilibrium concentration c_j , at wavelength λ , $\varepsilon_{p\lambda}$ the molar absorptivity of the product at wavelength λ , K is the equilibrium constant for the reaction, and n_j is the molecularity of the reactant j in the reaction. This gives a set of non-linear equations.^{30, 31} The system is also constrained by the mass-balance equations:

$$c_i^0 = c_i + K n_i \prod_j c_j^{n_j} \quad 53$$

where c_i^0 is the initial concentration of species i , n_i is the molecularity of species i . The rest of the symbols have the same meaning as in the previous equation (j again is an index that goes over all other reactants in the reaction). To calculate the concentrations of the species, with an estimate of the equilibrium constant, the mass-balance equations are solved by the Newton-Raphson method.³⁰⁻³²

This algorithm is generalized for the possibility of multiple equilibrium constants, which is not the case in this work.^{30, 31}

For a detailed explanation of the least-squares method see³².

Note: References for the methods of analysis underlying this program^(30, 31) are for the precursor suit of programs HYPERQUAD, which work on the same basic principles, but may be a bit outdated as indicated by the authors of the program²⁹.

2.9. Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a thermal analysis technique which measures the heat-flow difference between the analyzed sample and a reference (Fig. 22). Both sample and reference are subjected to the same temperature program, which can include a fixed or variable heating (or cooling) rate.³³⁻³⁵

In DSC the analyzed sample is placed in a crucible in every way identical to the crucible used as reference, except it contains no sample. The signal obtained in the reference is subtracted from the signal of the sample – thus making the methodology

differential. This strategy gives a smoother baseline, as effects like temperature fluctuations, electrical spikes or moisture level are removed during the subtraction of the signals. Still, the system is never perfectly symmetric (due to differences in the furnace block, in the positioning of the temperature sensors, and due to differences in the crucibles themselves), and baseline corrections still need to be adopted.³³⁻³⁵

There are two types of DSC: power-compensated DSC and heat-flux DSC. In this work we use a heat-flux DSC. In heat-flux DSC, also known as quantitative or calorimetric DTA (differential temperature analysis), the sample and reference crucibles are placed on individual thermally conducting bases. The system directly measures, at each instant of time, the potential difference generated between the sensors (via the Seebeck effect) due to the temperature difference between sample and reference. This temperature difference is due to the heat exchange of the sample with the surrounding block (via the thermally conducting base) as a consequence of the process occurring on the sample. Integration of the potential difference signal, and use of the calibration constant, gives the total heat (absorbed or released) associated with the process.³³⁻³⁵

DSC can be used to analyze various kinds of processes, in particular thermal events like melting of solids, solid phase transformations, and glass transitions. It can also be used to determine heat capacities.³⁴

In this work we used DSC to obtain enthalpy values on the retro Diels-Alder reaction of crystalline ICMA and ICBA. For this, we used the Netzsch DSC 200 F3 Maia differential scanning calorimeter (Fig. 23). The scheme of this DSC model is in Fig. 22. The sample and reference are placed on individual heat-flux sensors. The apparatus contains two pairs of thermocouples, which both measure temperature differences in two different points of the reference and sample conducting bases (one in the center of the heat flux sensor, and the other further away). These are converted to heat fluxes (ϕ_1 and ϕ_2 , respectively). The difference in heat fluxes is related to the heat flowing into or from the sample cell - since a gradient of temperature at the conducting bases is created when the transfer of heat occurs. The difference in these heat fluxes is the signal given by the system in the thermograms.³⁶

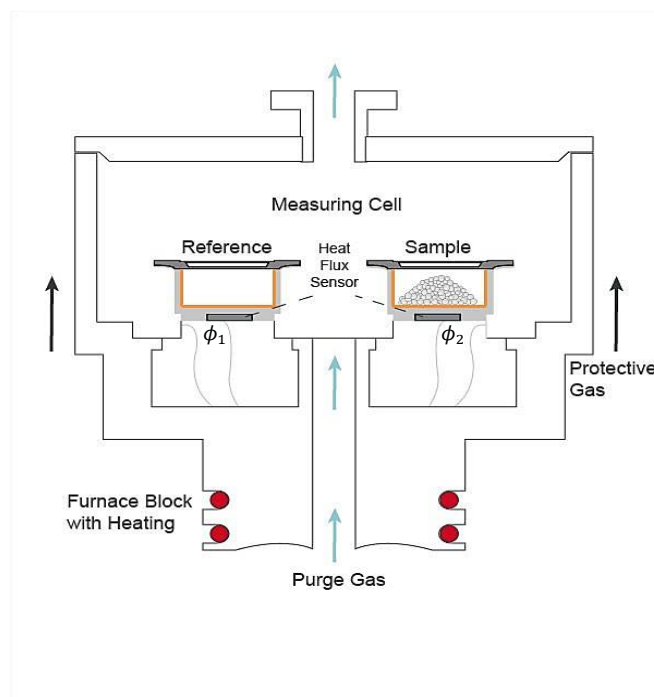


Fig. 22: Scheme of the Netzsch DSC 200 F3 Maia heat-flux differential scanning calorimeter.

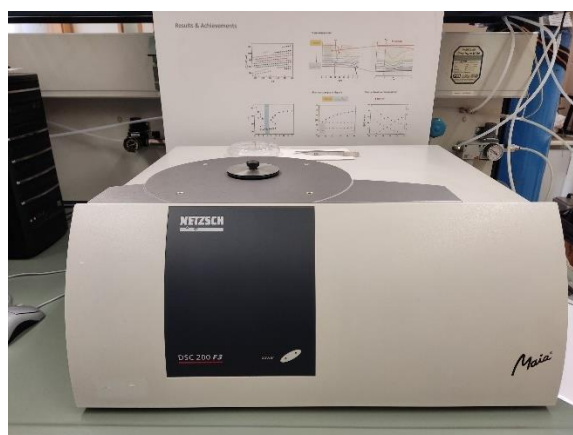


Fig. 23: Netzsch DSC 200 F3 Maia differential scanning calorimeter.

The scanning rate in DSC analysis is important and has several implications on the observed peaks. Altering the scanning rate changes the temperature at which the measured process occurs, and changes the shape of the peak(s). This is due to the fact that kinetics is a factor in these events - heat transfer and molecule diffusion require time. Increasing the scanning rate creates a temperature gradient in the sample and the instrument, and makes it more difficult for the sample to reach equilibrium. Thus, a higher scanning rate makes the peaks more pronounced, but the measurements might be less

accurate.³⁴ An example of the effect of the scanning rate on the DSC curve of a poly(ethylene terephthalate) (PET) sample is in Fig. 24.

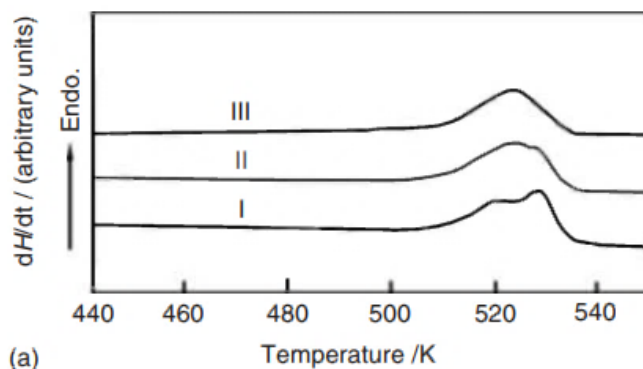


Fig. 24: Effect of the scanning rate on the DSC curve of a poly(ethylene terephthalate) (PET) sample. I – 10 K.min⁻¹; II – 20 K.min⁻¹; III – 40 K.min⁻¹. Adapted from Leng Y.³⁴

2.10. Thermogravimetric analysis

Thermogravimetric analysis (TGA) is based on thermogravimetry (TG) – a technique in which the mass of a sample is measured, as a function of time or temperature, using a thermobalance. A thermobalance (Fig. 26) is the combination of an electronic microbalance, the furnace and a temperature programmer. In TG the sample on a crucible is placed on the furnace - whose temperature is fixed (isothermal) or subjected to a fixed or variable scanning (heating or cooling) rate.^{33, 34} A typical thermogravimetric curve obtained with this technique is in Fig. 25.

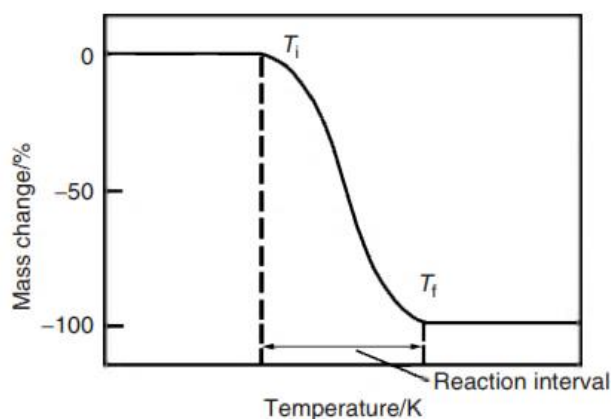


Fig. 25: Typical TG curve of mass loss as a function of temperature, with the mass loss occurring between temperatures T_i and T_f (reaction interval). Adapted from Leng Y.³⁴

TG can be used to analyze thermal stability and reactions that involve mass change, like dehydration, desorption, decomposition, and oxidation. Kinetics of these processes can be determined via the mass loss as a function of time – usually by performing the experiment under fixed temperature or isothermal intervals (in which case the kinetics can be determined for the temperature of the various intervals).^{33, 34}

In this work we used the Netzsch TG 209 F1 Iris³⁷ (Fig. 26 and Fig. 27) thermogravimetric balance for TGA, which is schematized in Fig. 26. In this work TG was used to study the kinetics of mass loss (release of indene) during the retro Diels-Alder reaction in crystalline ICMA and ICBA.

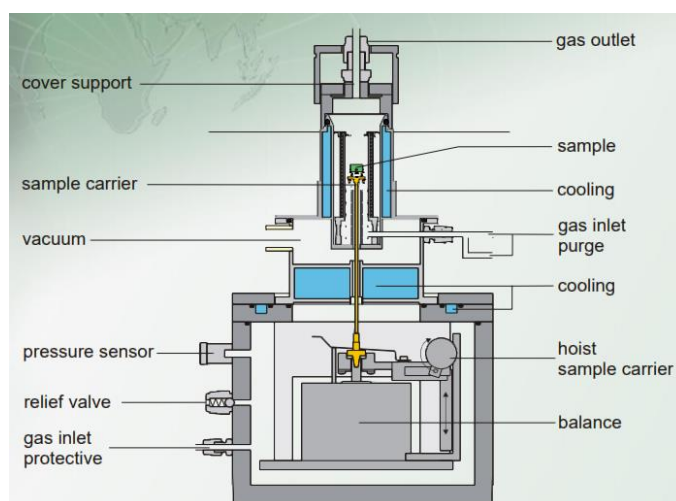


Fig. 26: Scheme of the Netzsch TG 209 F1 Iris TG apparatus.



Fig. 27: Netzsch TG 209 F1 Iris TG apparatus.

2.11. Theoretical chemistry methods

2.11.1. Density Functional Theory

Density Functional Theory (DFT) is a quantum chemical method for electronic structure calculations on many-body systems (atoms, molecules, or condensed phases – in this case we are mostly concerned with molecules) by making use of the electron density function.^{38, 39} The basic principle behind DFT is that the electron density function has a one-one correspondence with the electronic energy – the electron density function uniquely defines the ground-state of a molecule (more specifically, it uniquely defines the wavefunction of the system - this is known as the *Hohenberg–Kohn* theorem).^{38, 39} The electron density function only depends on the three spatial coordinates (for time independent problems) and, thus, with DFT the quantum mechanical problem is reduced to 3 coordinates - instead of $3N$ on the classical wavefunction methods, where N is the number of electrons of the system.^{38, 39} In DFT, the electronic energy of the system is expressed as a functional (a “function of other functions”) of the electron density.^{38, 39}

In the methods usually employed based on DFT, the most commonly used are based on the *Kohn-Sham* theory. In this theory the electron density function is constructed from a set of orbitals occupied by non-interacting electrons.^{38, 39} For atoms and molecules in the absence of external potentials, the electronic energy of the system in this theory is expressed as a functional of the electron density as^{38, 39}:

$$E[\rho] = T[\rho] + E_{ne}[\rho] + E_H[\rho] + E_{XC}[\rho] \quad 54$$

where $\rho = \rho(\mathbf{r})$ is the electron density function depending on the three spatial coordinates ($\mathbf{r}$); $T[\rho]$ is the Kohn-Sham kinetic energy (a functional of the electron density, as demonstrated by the bracket notation); $E_{ne}[\rho]$ is the electron-nucleus interaction energy (a functional of the electron density); $E_H[\rho]$ is the Hartree (or Coulomb) energy (the electrostatic interaction energy between the electrons) (a functional of the electron density); and $E_{XC}[\rho]$ is the exchange and correlation energy of the system (also a functional of the electron density).^{38, 39}

In Kohn-Sham DFT, finding the ground-state electronic energy from the electron density can be accomplished by employing a self-consistent iterative procedure based

on Equation 54.^{38, 39} But, the exact form of this energy functional is unknown. This is because there is an unknown term in the energy in Equation 54 – the exchange and correlation energy.^{38, 39} One must try to best describe this term by constructing appropriate exchange and correlation functionals - be them purely theoretical or empirical/semi-empirical.^{38, 39} Thus, many of these functionals, like B3LYP and M06-2X (both of which are used in this thesis), have been designed and optimized to be used in calculating the electronic energy in many-body systems,

Now follows a succinct description of the two functionals utilized in the thesis:

B3LYP:

B3LYP (Becke, 3-parameter, Lee–Yang–Parr) is a hybrid functional – a functional which is constructed with the energy as a linear combination of the Hartree-Fock exact exchange energy and other exchange and correlation functionals. The exchange and correlation energy is written as^{38, 39}:

$$E_{XC}^{B3LYP} = (1 - a)E_X^{LSDA} + aE_X^{HF} + b\Delta E_X^{B88} + (1 - c)E_C^{LSDA} + cE_C^{LYP} \quad 55$$

where E_X^{LSDA} and E_C^{LSDA} are the exchange energy and correlation energy in the local density approximation^{38, 39}, respectively; E_X^{HF} is the Hartree-Fock exchange energy^{38, 39}; ΔE_X^{B88} the B88 (Becke 88) functional exchange energy; and E_C^{LYP} the LYP (Lee-Yang-Parr) functional correlation energy. The a, b and c parameters are determined by fitting to experimental data ($a = 0.2$, $b = 0.72$ and $c = 0.81$)^{38, 39}.

B3LYP is the most widespread functional used in quantum chemistry calculations, due to its versatility and low computational cost.^{38, 39}

M06-2X:

M06-2X⁴⁰ is one of the M06 suite of functionals (Minnesota functionals). It includes 54% of the Hartree-Fock exchange energy and contains functionals which contemplate dispersion forces implicitly by empirical fitting to experimental data.³⁸⁻⁴⁰ This feature improves on one of the problems with standard DFT functionals – like B3LYP.^{38, 39} M06-2X is suitable for general thermochemistry and kinetics, and especially suitable for describing noncovalent interactions like dispersion forces.³⁸⁻⁴⁰ It is probably the

functional most competitive with B3LYP, in terms of applicability - except for transition metals and systems where weak interactions are of primary importance, where M06-2X has some limitations.³⁸⁻⁴⁰

For more information on DFT and the described functionals, as well as context on some of the nomenclature used, see:³⁸⁻⁴⁰.

Both these functionals based on Kohn-Sham DFT was used to study the Diels-Alder reaction of fullerenes with anthracene. M06-2X was used as the main computational method, while the B3LYP results were used for comparison and to evaluate the importance of dispersion forces in these reactions.

2.11.2. Solvent model based on density

The solvent model based on density (SMD) is a theoretical solvent model in which the solvent is described implicitly: as a continuum dielectric medium with surface tension at the solute-solvent boundary. It is a universal solvent model, meaning it can be applied to a system of charged or uncharged solute in any solvent or liquid medium for which a few descriptors are known: in particular the dielectric constant, the refractive index, the bulk surface tension, and the acidity and basicity parameters. It can also use the electronegative halogenicity and aromaticity descriptors. The density “part” comes from the fact that the electron density of the solute molecules in the solvent is used without considering partial atomic charges.⁴¹

This solvent model separates solvation energy into two components. The first component is the electrostatic contribution. It comes from the self-consistent reaction field treatment which involves solving the nonhomogeneous Poisson equation for electrostatics, in terms of the integral-equation formalism polarizable continuum model (IEF-PCM)^{38, 42}. The cavities for electrostatic calculation are defined as the superpositions spheres centered on the nucleus. The second component is the cavity dispersion solvent structure contribution. This contribution arises from short-range interactions between solute and solvent molecules in the first solvation shell - it is a sum of terms proportional to the solvent-accessible surface area of the solute atoms.⁴¹

SMD has been parametrized with various training sets of solvation data. The intrinsic atomic Coulomb radii and atomic surface tension coefficients of the model were optimized over various electronic structure methods. The SMD model has been tested

with a 6-31G(d) basis set and found to achieve errors of only 0.6–1.0 kcal·mol⁻¹ in solvation free energies of uncharged solutes.⁴¹

In this thesis SMD was used as the solvent model to simulate *m*-xylene, in order to theoretically study the Diels-Alder reactions of fullerenes with anthracene in solution.

2.12. A note on the coefficient of determination

The coefficient of determination R^2 is a parameter that allows us to evaluate how well a model explains a given set of data. In the case of this work we will use it to ascertain how good a linear equation fits the experimental data in a van 't Hoff, Arrhenius or Eyring plot, or how well a kinetical model fits to the experimental kinetic data.

The coefficient of determination can be defined as^{43, 44}:

$$R^2 = 1 - \frac{SS_{\text{res}}}{SS_{\text{tot}}} \quad 56$$

Let us assume we have a dataset of (y, x) experimental values and a model $f(x)$ which tries to calculate y from the x value. Then:

$$SS_{\text{res}} = \sum_i (y_i - f(x_i))^2 \quad 57$$

is the residual sum of square of the usage of the model to explain the experimental data - a sum over all data points of the square deviation of each data point y value (y_i) to the y value predicted by the model ($f(x_i)$) at the same data point x_i . Also:

$$SS_{\text{tot}} = \sum_i (y_i - \bar{y})^2 \quad 58$$

is the total sum of squares of the data, $\bar{y}$ being the average value of y over the whole data set. If SS_{res} is null, then there is no deviation from the y values predicted by the model to the experimental y values and $R^2 = 1$. If $SS_{\text{res}} = SS_{\text{tot}}$, $R^2 = 0$; if $SS_{\text{res}} < SS_{\text{tot}}$, R^2 will be between 0 and 1; and if $SS_{\text{res}} > SS_{\text{tot}}$, R^2 can even be negative.^{43, 44}

Since $1 - R^2$ is proportional to the residual sum of squares (Equation 56), it is the best indicator of the deviation of model predictions to experimental data. It tells us at which magnitude the model deviates from the experimental data, *i.e.* the smaller $1 - R^2$ is (and R^2 closer to unity) the better the model fits the experimental data. The degree of how good a fit is can only be visualized by looking at how small $1 - R^2$ is.^{43, 44}

In this work the values of R^2 presented will always be in such a way that $1 - R^2$ has one or two significant figures (*i.e.* $R^2 = 0.994$, $R^2 = 0.9993$, $R^2 = 0.99991$), to provide as much information as possible to the reader. Never will it be presented in a way that $1 - R^2$ would have no significant figures (presenting R^2 as 1.00 instead of 0.9993, for example, would make $1 - R^2 = 0.00$ and thus would convey limited information to the reader). Following this, the R^2 value for a fit will sometimes be presented with different decimal places even for cases where it was obtained from the same experimental methodology, purely to convey the most information possible. Since it is a purely mathematical concept, the significant figures of R^2 will be decided based on this logic, and not based on the limitations of the experimental methodology.

2.13. References

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Chapter 3:

Experimental Methodologies

3.1. Study of the Diels-Alder addition to fullerenes using UV-Vis spectroscopy

This section is organized as follows:

- In Section 3.1.1. the spectra of the studied fullerenes (C_{60} , C_{70} and ICMA) in *m*-xylene, and their temperature dependence, were determined. We will also present the equations describing the variation of molar absorptivities, at specific wavelengths, with temperature – which allows one to calculate the molar absorptivity for any temperature within and near the studied temperature range.
- In Section 3.1.2., a study to obtain Beer-Lambert plots for the same fullerenes is describe, and the obtained plots presented. This study was used to ascertain the validity of the Beer-Lambert law and as a tool to help us choose the wavelengths for the study.
- In Section 3.1.3. we give a succinct description of the tests performed and progressive optimization of the experimental methodologies used in the next sections, which includes a short explanation for the choice of dienes.
- In Sections 3.1.4 and 3.1.5. the main studies using UV-Vis spectroscopy are described – the kinetic study of the reaction of fullerenes with anthracene and the thermodynamic study with 9,10-dimethylantracene.
- In Section 3.1.6. the methodology to obtain the spectra of the adducts generated during the Diels-Alder reactions studied is described – a study of these reactions using various solution in a reactor oven (which is also a parallel way to determine the equilibrium constants for the reaction of C_{60} and C_{70} with anthracene, and consequently the equilibrium thermodynamic parameters - ΔH_r^0 and ΔS_r^0 .
- In Section 3.1.7. codes written in *Octave* to help with the data analysis are presented.
- In Sections 3.1.8. and 3.1.9. the temperature calibration of the UV-Vis temperature-controlled cell holder and of the reactor oven used for Section 3.1.6., respectively, are described, and the relationship obtained between setpoint temperatures and real measured temperatures presented.

In this work and in this Section, we opted to present some concentrations as molalities (mols per unit of solvent mass) - since the studies are not done at one single temperature and thus the molar concentration is not fixed (the volume of the solvent changes with temperature due to the temperature dependence of density). A prepared molar concentration (~ 25 °C) will sometimes be presented as complement. This is also

reflected in the need to measure rigorously the solvent mass added to each solution, so as to directly have a possibility to calculate molal concentrations without referring to the solvent density (as we did throughout this work). Still, a rigorous volume of the solvent was always added, so that we have information on both the mass weighted and the mass calculated by the rigorous volume added and the density of the solvent at the temperature of the lab when the addition was performed. These two values were compared and checked for consistency – and found to be consistent. All kinetic and equilibrium constants in this work are determined in the converted molarity values.

Temperatures in this Section will be presented as equipment setpoint temperatures. The temperature calibration of the UV-Vis and the reactor are presented in Sections 3.1.8. and 3.1.9, respectively. The following chapters of this thesis will, then, deal with the corrected temperatures only.

In this Section and the whole thesis, confidence intervals for the values are presented as the standard uncertainties, unless otherwise specified.

3.1.1. Fullerene spectra and temperature dependence

Solutions of the different fullerenes studied (C_{60} , C_{70} and ICMA) in *m*-xylene (Fig. 28) were prepared at concentrations of around $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. The solid fullerenes were weighted rigorously in a microbalance Mettler Toledo UMT2 (repeatability of 0.25 μg) and put in a flask. Solvent was then added using a $5.000 \pm 0.015 \text{ mL}$ volumetric pipette. The solutions were weighted in an analytic balance Mettler AE 163 (repeatability of 20 μg), before and after the addition, and the mass of solvent registered. This mass was used to convert the concentration to molar concentration at each studied temperature, using the density of the solvent at each temperature. The solid was dissolved with the help of ultrasounds. Care was taken to ensure complete solubilization and that a translucent solution was obtained.



Fig. 28: Solutions of various fullerenes in *m*-xylene: left – C₆₀, middle – ICMA, right – C₇₀.

An aliquot of the solution was then transferred to a UV-Vis quartz glass cell using a micropipette, and the cell then placed in the UV-Vis cell holder. This cell holder is temperature controlled by a circulating water bath (Section 2.7.). The spectra of the solutions was monitored as the temperature of the bath was changed, to obtain the variation of the spectra with temperature. The obtained spectra for the different temperatures studied for the three fullerenes are in Fig. 29.

This study allowed for the variation of molar absorptivity with temperature to be plotted and the parameters describing the temperature dependence obtained, which allows us to calculate the spectra of the fullerenes at any temperature and concentration – which was needed and performed in the further studies. In the temperature range studied the molar absorptivities at the desired wavelengths (the ones that will be used in the reaction studies) were found to obey a second order polynomial dependency with temperature (Fig. 30, for C₇₀ 677 nm and ICMA 705 nm). Table 3 presents the parameters a , b and c , as in $\varepsilon = aT^2 + bT + c$ - using the real, calibrated temperatures (Sections 3.1.8. and 3.1.9.). The parameters were calculated by least-squares fit. This equation predicts the behavior of change in molar absorptivities as a function of temperature for the chosen wavelengths for studying the reactions in this work – allowing one to calculate the molar absorptivities for any temperature within or near the temperature range.

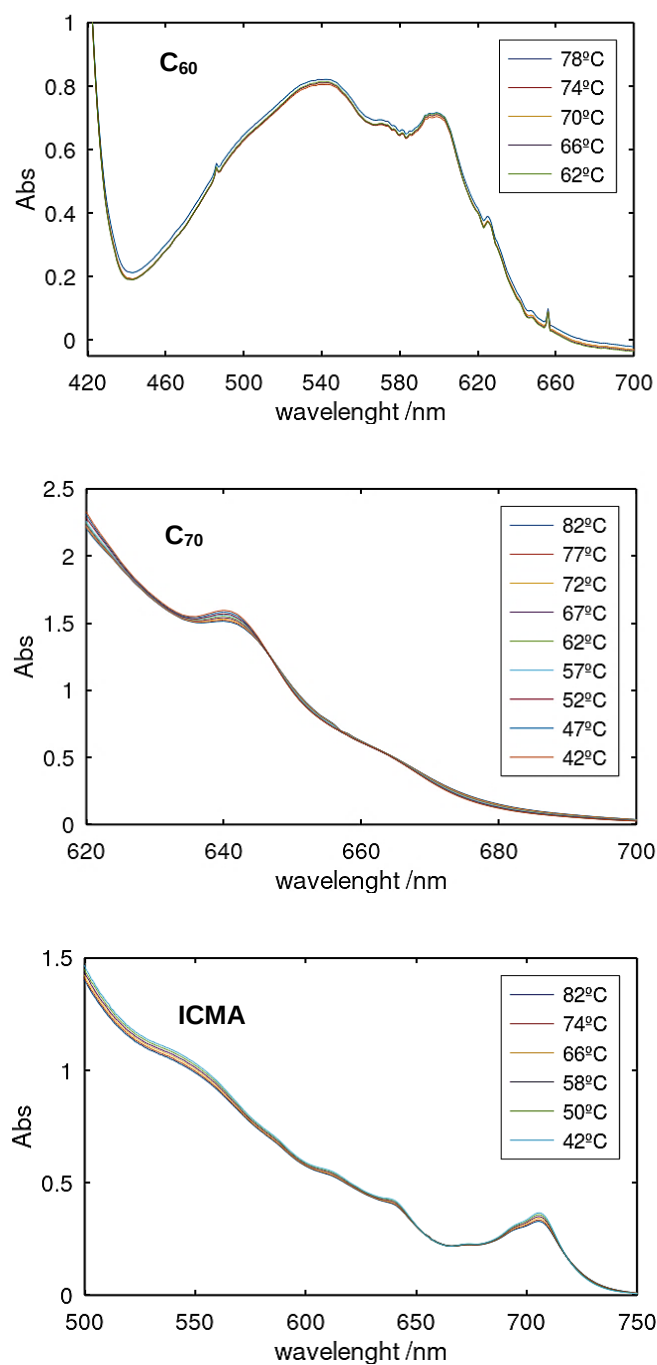


Fig. 29: Temperature dependence of the visible spectrum of C_{60} (top), C_{70} (middle) and ICMA (bottom) solutions. Temperatures presented are setpoint temperatures of the UV-Vis apparatus. Molal concentrations - C_{60} : $1.219 \text{ mol} \cdot \mu\text{g}^{-1}$; C_{70} : $1.209 \text{ mol} \cdot \mu\text{g}^{-1}$; ICMA: $1.266 \text{ mol} \cdot \mu\text{g}^{-1}$. Prepared molar concentrations (25°C): C_{60} : $1.1049 \text{ mmol} \cdot \text{L}^{-1}$; C_{70} : $1.040 \text{ mmol} \cdot \text{L}^{-1}$; ICMA: $1.089 \text{ mmol} \cdot \text{L}^{-1}$.

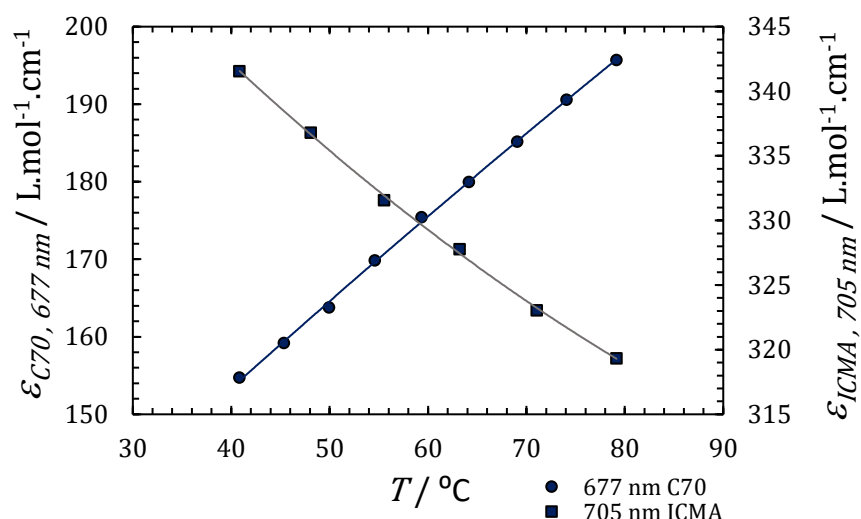


Fig. 30: Temperature dependence of the molar absorptivities for C_{70} 677 nm ($R^2 = 0.9992$) and ICMA 705 nm ($R^2 = 0.9993$), showing a polynomial relationship in the range of temperatures studied. Temperatures used are the real temperatures, not the uncalibrated setpoint temperatures given by the UV-Vis water bath apparatus.

Table 3: Parameters for the temperature dependence of the molar absorptivity for the studied wavelengths for C_{60} , C_{70} and ICMA. From these parameters one can use the polynomial dependence, of the type $\epsilon = aT^2 + bT + c$, to calculate the molar absorptivity at any temperature. These linear relationships do not contain the variation of solvent density with temperature, which has been previously accounted for when calculating the absorptivities.

Fullerene	Wavelength / nm	$a / \text{L.mol}^{-1}.\text{cm}^{-1}.\text{C}^{-2}$	$b / \text{L.mol}^{-1}.\text{cm}^{-1}.\text{C}^{-1}$	$c / \text{L.mol}^{-1}.\text{cm}^{-1}$
C_{60}	498	-1.57×10^{-2}	3.78	451
	705	-	-	-
C_{70}	665	4.95×10^{-4}	0.705	444
	677	-1.29×10^{-3}	1.24	106
ICMA	705	3.16×10^{-3}	-0.961	376

Most of the wavelengths, except for C_{60} , have small a parameters, and the b parameter is near unity - both which indicate a small variation of molar absorptivity with temperature, as could already be seen in the graphs. Though, the change in spectra has two contributions: the effect of change in concentration due to a change of the density of the solvent and the change in molar absorptivity, these can change the spectra in the same direction or in opposing directions, depending on the wavelength – the molar absorptivities can either increase or diminish with raising temperature, but the solution is always diluted when increasing temperature). In this study we calculated the molar absorptivities by accounting for the change in density of the solvent when changing the temperature, and thus are purely analyzing the change in molar absorptivity as a function

of temperature. From here on, these empirical functions are used to calculate the spectra of the fullerenes at any temperature when needed.

The dienes used in the reaction studies, 9,10-dimethylantracene and anthracene, do not absorb beyond 470 nm and 420 nm, respectively (spectra of the dienes at concentrations beyond the highest concentrations used in the studies, showing no absorption beyond 470 nm, are in Fig. A1 in Appendix A). Thus, they do not absorb in the regions of the spectra under study in this work (>500 nm), and no treatment of this kind was needed for them.

3.1.2. Beer-Lambert plots

To test the validity of the Beer-Lambert law (Section 2.7.) in solutions of the different studied fullerenes (C_{60} , C_{70} and ICMA), solutions of different concentrations were prepared by successive dilution of the most concentrated solution – which was prepared the same way as described in Section 3.1.1. The UV-Vis spectrum of each solution on a quartz glass cell was obtained. Variations due to the temperature are small, as can be seen in Section 3.1.1., and the spectra were obtained only at the average temperature for the studies performed – see Sections 3.1.4, 3.1.5 and 3.1.6. –; 70 °C for C_{70} and C_{60} , and 50 °C for ICMA (molar concentrations were calculated correcting for solvent density at the studied temperature). This allowed for determining the Beer-Lambert plots for different wavelengths (the ones which will be used to study the reactions, and some others), allowing us to ascertain which wavelengths were valid for studying solutions of these fullerenes, as well as understand the limits of applicability of the Beer-Lambert law for these systems.

The Beer-Lambert plots obtained are in Fig. 31, Fig. 32 and Fig. 33 for C_{60} , C_{70} and ICMA respectively. It was found that the Beer-Lambert law holds to (at least, as it wasn't tested for higher concentrations) near $3 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ for C_{60} , to near $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ for ICMA; and to near $2.5 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ in C_{70} (in this case a further concentrated solution deviated from the linearity of the law). As we work with concentrations of fullerene at around $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$, this validates the Beer-Lambert law in the concentration range used, for the studied wavelengths. It was also found that in the three fullerenes the linearity of the law holds to absorbances higher than 2 for some wavelengths. Thus, in this study it seems valid to surpass an absorbance of 1 (which is sometimes told to be the good limit for the use of Beer-Lambert law) for solutions of the fullerenes and, presumably, solutions of the fullerenes and their formed adducts,

as studied in this work in the following sections. Still, this was avoided whenever possible, and wavelengths with absorbance below 1 were mostly used, when possible. For every fullerene at least one wavelength with absorbances below 1 was used in the studies in Section 3.1.4. and 3.1.5. In the studies where we used a full range of spectra (to determine the spectra of the adducts, Section 3.1.6.), we tried to reduce high absorbance wavelengths as much as possible – while keeping a quality wavelength range and spectra, whilst also working under the same concentrations of fullerenes as in the other studies. Molar absorptivities for the three fullerenes at the studied wavelengths can, and were, determined from the slope of the Beer-Lambert plots (see Section 2.7.), and are presented in Table 4.

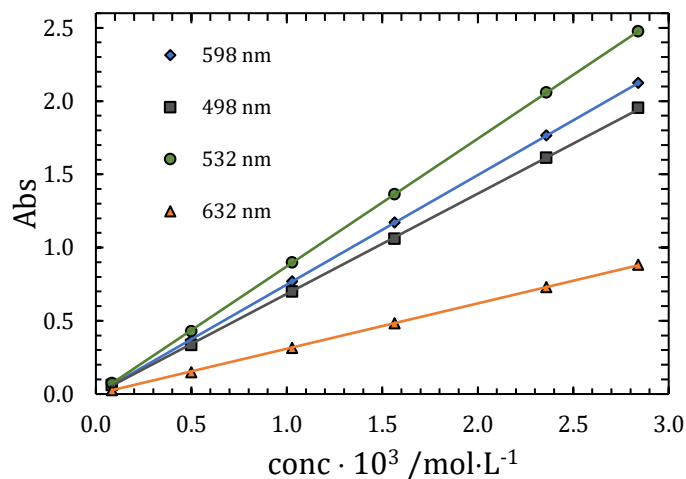


Fig. 31: Beer-Lambert plots at 498 nm, 532 nm, 598 nm and 632 nm for solutions of various concentrations of C_{60} in *m*-xylene at $T_{\text{setpoint}} = 70.0\text{ }^{\circ}\text{C}$ ($T_{\text{real}} = 67.1\text{ }^{\circ}\text{C}$) ($R^2 > 0.9999$ for all plots).

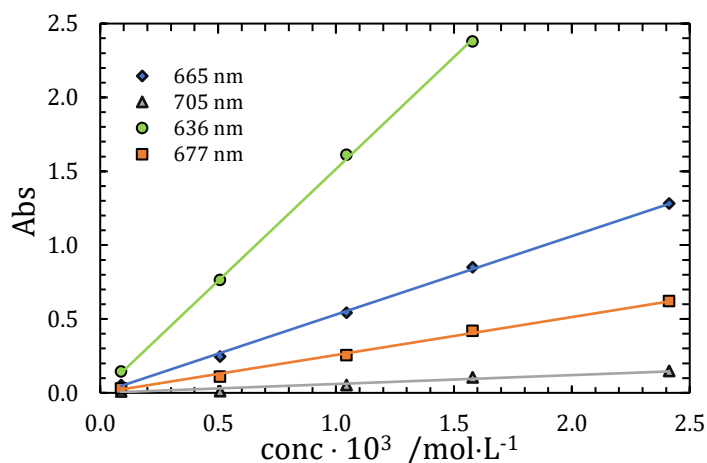


Fig. 32: Beer-Lambert plots at 636 nm ($R^2 = 0.9996$), 665 nm ($R^2 = 0.9993$), 675 nm ($R^2 = 0.997$), and 705 nm ($R^2 = 0.969$) for solutions of various concentrations of C_{70} in *m*-xylene at $T_{\text{setpoint}} = 70.0\text{ }^{\circ}\text{C}$ ($T_{\text{real}} = 67.1\text{ }^{\circ}\text{C}$).

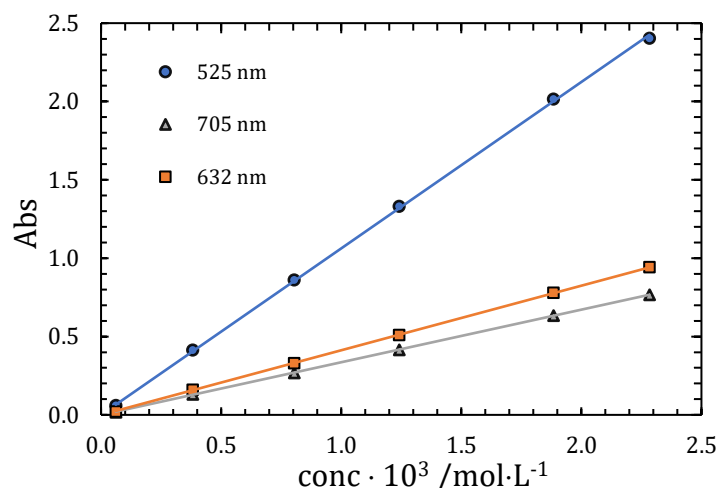


Fig. 33: Beer-Lambert plots at 525 nm, 632 nm and 705 nm for solutions of various concentrations of ICMA in *m*-xylene at $T_{\text{setpoint}} = 50.0\text{ }^{\circ}\text{C}$ ($T_{\text{real}} = 48.1\text{ }^{\circ}\text{C}$) ($R^2 > 0.9998$ for all plots).

Table 4: Molar absorptivities determined via the Beer-Lambert plots for C_{60} , C_{70} and ICMA. The wavelengths chosen are the ones used in the reaction studies. Setpoint temperatures are $70\text{ }^{\circ}\text{C}$ for C_{60}/C_{70} and $50\text{ }^{\circ}\text{C}$ for ICMA.

Fullerene	wavelength / nm	$\varepsilon / \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$
C_{60}	498	684 ± 3
	705	-
C_{70}	665	530 ± 8
	677	257 ± 9
ICMA	705	336 ± 1

3.1.3. Testing/Optimization of the experimental methodologies

Kinetic study of the reaction with anthracene and equilibrium study with DMA

The first task of studying the reaction kinetics of fullerene reactions was optimizing the procedure to find the best way to obtain the kinetical parameters using UV-Vis spectroscopy. At the start of the journey, we tried following the reaction between C_{60} and anthracene (around $1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ of each) by preparing a solution of both reactants in toluene in a flask and putting it in a temperature-controlled reactor oven. We tried this for $50\text{ }^{\circ}\text{C}$. We daily measured the spectra of an aliquot of the solution and determined the concentration of adduct from the deconvolution of the obtained spectra. The theoretical model would then be fitted to these experimental points. Using this approach,

we found that we ended up with a low number of experimental data points for the fit, and also that some of the toluene was evaporating from the flask.

In order to overcome these problems, we opted to study the reaction kinetics at higher temperatures, with a single run of the automated spectra acquisition in a fixed time interval with the solution in a temperature-controlled UV-Vis cell for the whole reaction time. This allowed us to obtain hundreds of experimental points and a better sampling of the whole reaction curve. Still, the reaction velocity was not as fast and the total change in spectrum not as pronounced as we wished, and thus we decided to also increase the concentration of diene to $20 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$ – which increases the rate of the reaction while also shifting equilibrium towards the products, with an increase in spectra change over the reaction period. This also allowed the theoretical model for the kinetics of the reaction to be simplified, since anthracene will be present in excess (as it is 20x more concentrated than the fullerenes).

To better cope with the solvent losses, we decided to change the solvent to *m*-xylene, which has lower vapor pressure than toluene, while still being an excellent solvent for the species in study. 1,2,3,4-tetrahydronaphthalene (THN) was also tested, as it has, according to the literature, an even higher solubility of fullerenes, and a lower vapor pressure than *m*-xylene. This solvent did not work as it was found to hydrogenate the fullerenes. So, we opted for *m*-xylene.

With these adjustments the optimization goal was achieved - a clean and robust spectra acquisition while following the reaction in real time, with a big set of data points, and without any significant losses of solvent. This same procedure was then used for the equilibrium study for the reactions with DMA.

Choice of conjugated dienes

From the dienes available, we tested four: anthracene, 9,10-dimethylantracene, tetracene, and indene. In the case of indene we found that it readily reacts to a great extent - giving polyadducts in the process. In the case of tetracene, trying to obtain van 't Hoff plots was a failed task. The reason for that we found to be that tetracene reacts significantly with dissolved oxygen. Despite purging the solvent before the experiment, the dissolved oxygen during the experiment was enough to ruin the study of the kinetics of the reactions with tetracene. Also, tetracene has low and difficult solubility in our solvent, making the task of preparing the solutions more strenuous. The solution of tetracene had to be previously heated to dissolve the diene – followed by a further mixing with a heated solution of the fullerene in the UV cell (which has possible complications

like sudden precipitation and the reaction starting before total mixing). Its low solubility also limits the concentrations achievable. Anthracene was found to be optimal for our experiments since it is stable, it reacts significantly but not too much extent that we detect the presence of bisadducts – we had at most undetectable traces of bisadducts. Anthracene also is readily and easily soluble in our solvent. 9,10-Dimethylantracene shared these properties, although its concentration cannot be as high since we found effects like sudden precipitation in solutions of DMA at high concentrations with fullerenes. With DMA, the kinetics of the reaction is very fast and equilibrium reached in minutes (depending on the fullerene), and it becomes a hard challenge to study the kinetics of its reaction. Though, this characteristic makes it an ideal diene for studying the equilibrium of the reaction, which is exactly what we decided to do as described in Section 3.1.5.

Adduct spectra determination and equilibrium study in the reactor

Initially, we tried to determine the spectra of the product adduct of the Diels-Alder reaction (using equilibrium spectra of solutions and the *HypSpec*¹ program) by using flasks with solutions of C₆₀ in toluene and different concentrations of anthracene, but the solvent losses were a major source of error in the study. We decided, then, to acquire 7 individual UV-Vis cells (with good vapor containment), which we placed in the reactor each with a different solution of the studied fullerene and anthracene, mimicking our previous idea, but with better execution (and this time in *m*-xylene), since the cells could be directly measured in the UV-Vis without any need to transfer the solution. In this scenario the solvent losses were minimal (as monitored by weighting the cells on an analytical balance before and after each measurement), and the study was able to be performed smoothly and successfully.

3.1.4. Kinetic study of the Diels-Alder reaction between fullerenes and anthracene

Solutions of fullerenes C₆₀ and C₇₀ with anthracene were prepared in *m*-xylene. The solid fullerene and anthracene were weighted rigorously in the microbalance Mettler Toledo UMT2 and put in a flask. Solvent was then added using a 5 mL volumetric pipette. The solution was weighted in the analytic balance Mettler AE 163, before and after the addition, and the mass of solvent registered. This mass was used to convert the concentration to molar concentration, using the density of the solvent at the studied

temperature. The solids were dissolved with the help of ultrasounds. Care was taken to ensure complete solubilization and that a translucent solution was obtained.

An aliquot of the solution was transferred to the quartz glass cell, using a micropipette. The mass of solvent was controlled by weighting the cell before and after the experiment. The cell containing the solution of fullerene and anthracene, which are very slow reacting at ambient temperatures, was then placed in the UV-Vis cell holder, which is temperature controlled by a circulating water bath (Section 2.7.). The change in spectra was then recorded as a function of time (*i.e.* the evolution of the reaction) (Fig. 34 gives an example of change in spectra for the C_{60} + anthracene (1:20 molar ratio) solution at $T_{setpoint} = 78\text{ }^{\circ}\text{C}$).

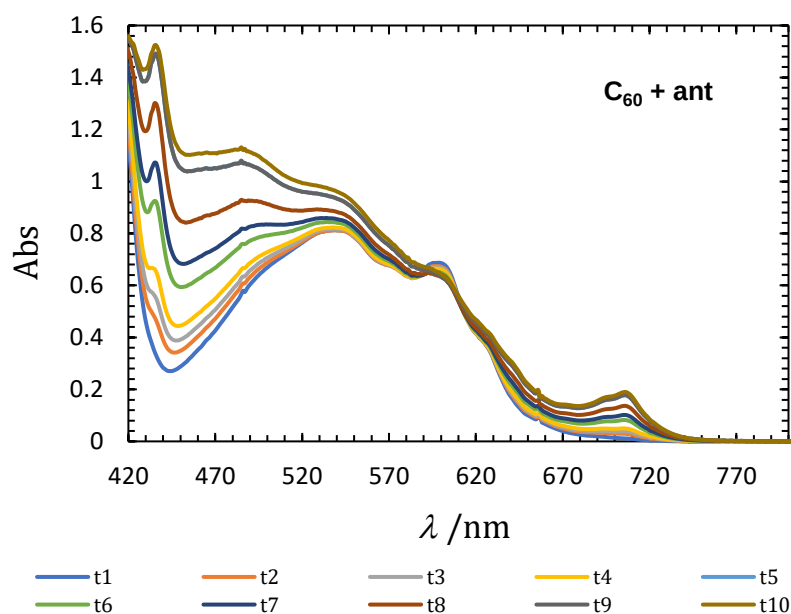


Fig. 34: Time evolution of C_{60} +anthracene solution spectrum at $T_{setpoint} = 78\text{ }^{\circ}\text{C}$.

The UV-Vis spectrophotometer (Agilent 8453) used in this work has a kinetic mode, which registers the absorbances for up to 6 wavelengths as a function of time. We used this mode to monitor various wavelengths, including isobestic points for the reaction (wavelengths at which there is no change in absorbance during the reaction – which are characteristic of occurring reactions, for example 596 nm in the C_{60} + anthracene reaction (Fig. 34)); a blank control chosen as a wavelength with no absorbance (later to be used as baseline to subtract to the absorbance values at the other wavelengths); and a wavelength to control for possible double additions (730 nm for C_{60} : the spectrum of the bisadducts generates a broad peak from 700-740 nm, having higher absorbance in that region when compared to monoadducts (Fig. 35), making the

absorbance at 730 nm increase when there is formation of bisadducts). In these studies we never found any absorbance at those wavelengths, and never a distortion of the 705 nm peak, which was confirmation of no detectable formation of bisadducts. Plus, we never found the isobestic points characteristic of the second addition reaction, thus also supporting that no significant double addition occurred. Note that the spectrum of the mixture of isomers in ACBA (anthracene- C_{60} bisadduct) and AICBA (indene,anthracene- C_{60} bisadduct) is probably different from the commercial available ICBA, and since different isomers have different spectra ², the spectrum of the mixture of bisadducts that one might obtain in these experiments will be slightly different from the ICBA spectrum. For C_{70} the situation is more complicated, since isobestic points are outside of our study range (in zones of too high absorbance), and we have no good estimative of the bisadducts spectra. Still, as happens with C_{60} we expect the bisadducts to show absorbance at a wavelength higher than the monoadduct, and thus we controlled wavelengths near the end of the region of absorption of the monoadduct. Also, we found (as we will see in the Results and Discussion Section) a much less reactive C_{70} +DMA system, so we expect that since no bisadducts were found for C_{60} , none will be present for the C_{70} system. For ICMA we also have no way to estimate the spectra of the trisadduct, but the reaction of DMA with ICMA is even less reactive than with C_{70} , and thus we can also assume that trisadducts will not form at a significant extent.

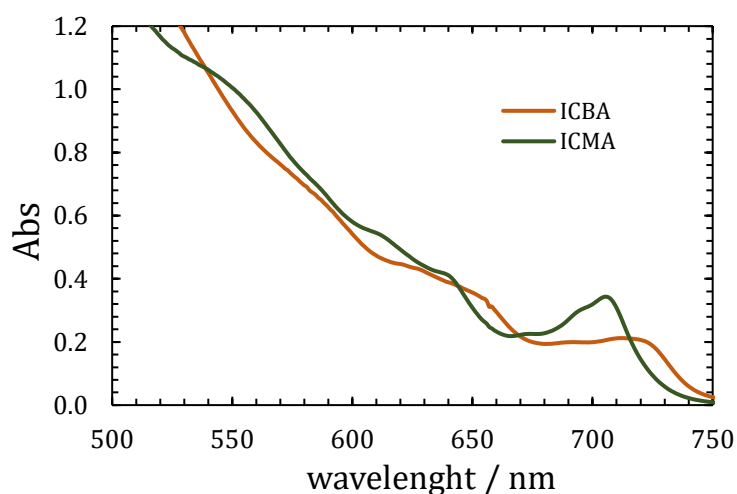


Fig. 35: UV-Vis spectrum of ICMA (green) and of ICBA (orange) in m-xylene at 66 °C. Concentrations are $\sim 1 \times 10^{-3} \text{ mol} \cdot \text{L}^{-1}$.

The Diels-Alder reaction is an elementary reaction. Thus, the rate law for the change in product concentration as a function of time is given by:

$$\frac{d|FA|}{dt} = k_1|F||A| - k_{-1}|FA| \quad 59$$

where $|FA|$ is the molar concentration of the adduct, $|F|$ the molar concentration of the fullerene, and $|A|$ the molar concentration of anthracene, all at time t . k_1 and k_{-1} are the rate constants for the forward and reverse reactions respectively. These rate constants depend on the temperature (Sections 2.4. and 2.5.). Solving this equation when anthracene is present in excess, one gets the following function for the time dependence of the adduct concentration:

$$|FA| = |FA|_{eq}[1 - e^{-(k_1|A|_0 + k_{-1})t}] \quad 60$$

where $|A|_0$ and $|F|_0$ are the anthracene and fullerene molar concentrations at $t = 0$, respectively; and $|FA|_{eq} = \frac{k_1|A|_0|F|_0}{k_1|A|_0 + k_{-1}}$.

Since the Beer-Lambert law (Section 2.7.) holds in our experiments (see Section 3.1.2.), and since $Abs = Abs_{FA} + Abs_F$, the sum of the absorbances of the adduct and fullerene (the conjugated diene does not absorb in the studied wavelength interval), Equation 60 can be converted to:

$$Abs(t) = (\varepsilon_{FA,\lambda} - \varepsilon_{F,\lambda})l[1 - e^{-(k_1|A|_0 + k_{-1})t}] + Abs_0 \quad 61$$

where $\varepsilon_{FA,\lambda}$ and $\varepsilon_{F,\lambda}$ are the molar absorptivity of the adduct and fullerene at the studied wavelength λ , respectively; and $Abs_0 = \varepsilon_{F,\lambda}l|F|_0$ is the absorbance at $t = 0$, before the start of the reaction (only due to the absorbance of the fullerene). The molar absorptivities of the fullerene for the studied wavelengths were calculated by the polynomial relationships described in Table 3 in Section 3.1.1. The molar absorptivities of the adducts were obtained via the methodology to be described in Section 3.1.6.

Equation 61 was then fitted to the experimental data of absorbance as a function of temperature (for the desired wavelengths), using the method of least-squares to optimize the rate constants (minimizing the square deviations of the model to the experimental data) (Fig. 36 illustrates this for $T_{setpoint} = 82$ °C in the C_{70} + anthracene system). This was done for the reaction at different temperatures, with the rate constants

determined at all temperatures studied. The equilibrium constants for the reaction were then determined for each studied temperature as (see Section 2.4.):

$$K_{eq} = \frac{k_1}{k_{-1}}$$

62

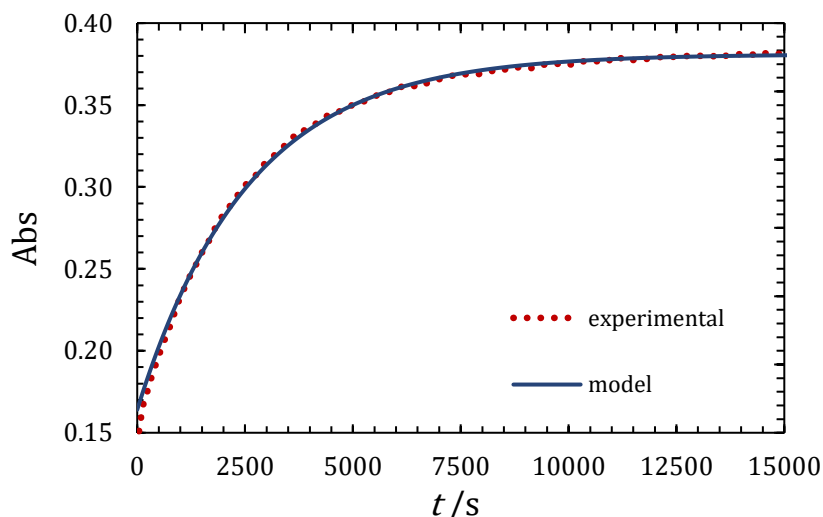


Fig. 36: Fit of the model (blue line) described by Equation 61 to the experimental data (red points) for C_{70} + anthracene (1:20 molar ratio) at 677 nm ($T_{setpoint} = 82\text{ }^{\circ}\text{C}$, $T_{real} = 79.2\text{ }^{\circ}\text{C}$). Fit $R^2 = 0.998$.

3.1.5. Thermodynamic study of the Diels-Alder reaction between fullerenes and 9,10-dimethylantracene

The reactions between fullerenes C_{60} , C_{70} and ICMA; and 9,10-dimethylantracene (DMA) were studied thermodynamically, by obtaining the equilibrium absorbances for various wavelengths at different temperatures. This procedure was chosen because the kinetics of reactions with DMA are much faster than with anthracene (in anthracene reactions would take a few hours, with DMA they took only minutes), making a kinetic study difficult, but facilitating studies at equilibrium. The procedure of preparing the solutions was in every way the same as the one used to prepare the solutions in Section 3.1.4., and the same quartz glass cell was used.

After introducing the UV-Vis cell with the desired solution, the temperature of the UV-Vis temperature-controlled cell holder was varied intervals, and the absorbances at equilibrium obtained for each temperature (Fig. 37 illustrates this process for the C_{70} +DMA system). The equilibrium absorbance was taken as an average over all data points in the equilibrium step - to reduce noise and effects due to random deviations on

the absorbance values. Like explained in Section 3.1.4., here we also use the kinetics mode of our UV-Vis system and again selected the studied wavelengths, isobestic points, and wavelengths for double addition control – in the case of ICMA triple addition control.

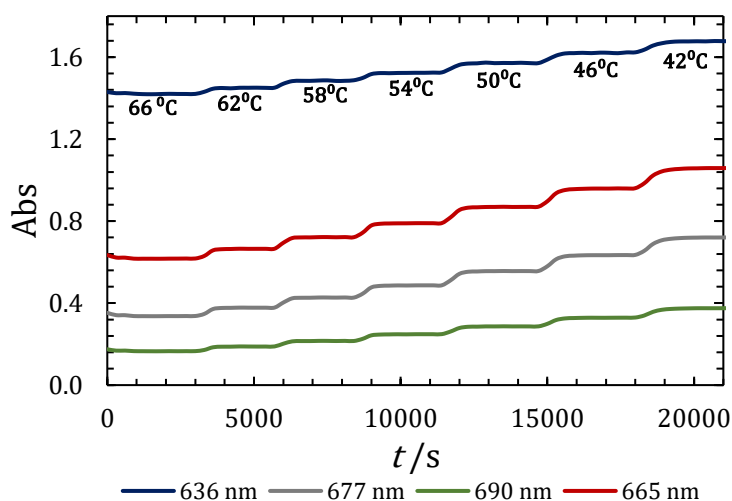


Fig. 37: Temperature dependence of the equilibrium absorbances for various wavelengths for the C_{70} +DMA system. Temperatures presented are setpoint temperatures. Since the Diels-Alder reaction is exothermic in this temperature range, lower temperatures mean a larger extent extension of the reaction and more formation of the adduct.

This experiment was performed for different solutions with different concentrations of DMA for each fullerene, which are shown in Table 5. The values are presented in molalities because the concentration per volume units varies with the temperature and thus is not fixed for each experiment. Fig. 38 contains the equilibrium spectra for a solution of each of the three fullerenes at different temperatures.

Table 5: Concentration of the samples studied for each Fullerene + DMA system.

Fullerene	Solution	$[F] / \text{mol} \cdot \mu\text{g}^{-1}$ ^a	$[\text{DMA}] / \text{mol} \cdot \mu\text{g}^{-1}$ ^b	$[\text{DMA}]/[F]$
C_{60}	1	1.1447	1.6195	1.4
	2	1.0999	2.8471	2.5
C_{70}	1	1.3575	2.3718	1.8
	2	1.0188	5.2543	5.2
ICMA	1	1.0257	10.550	10.3
	2	1.0177	17.100	16.8

^a The uncertainty on the fullerene concentration is $u(F)=0.0025 \cdot [F]$. ^b The uncertainty on the DMA concentration is $u(\text{DMA})=0.0025 \cdot [\text{DMA}]$.

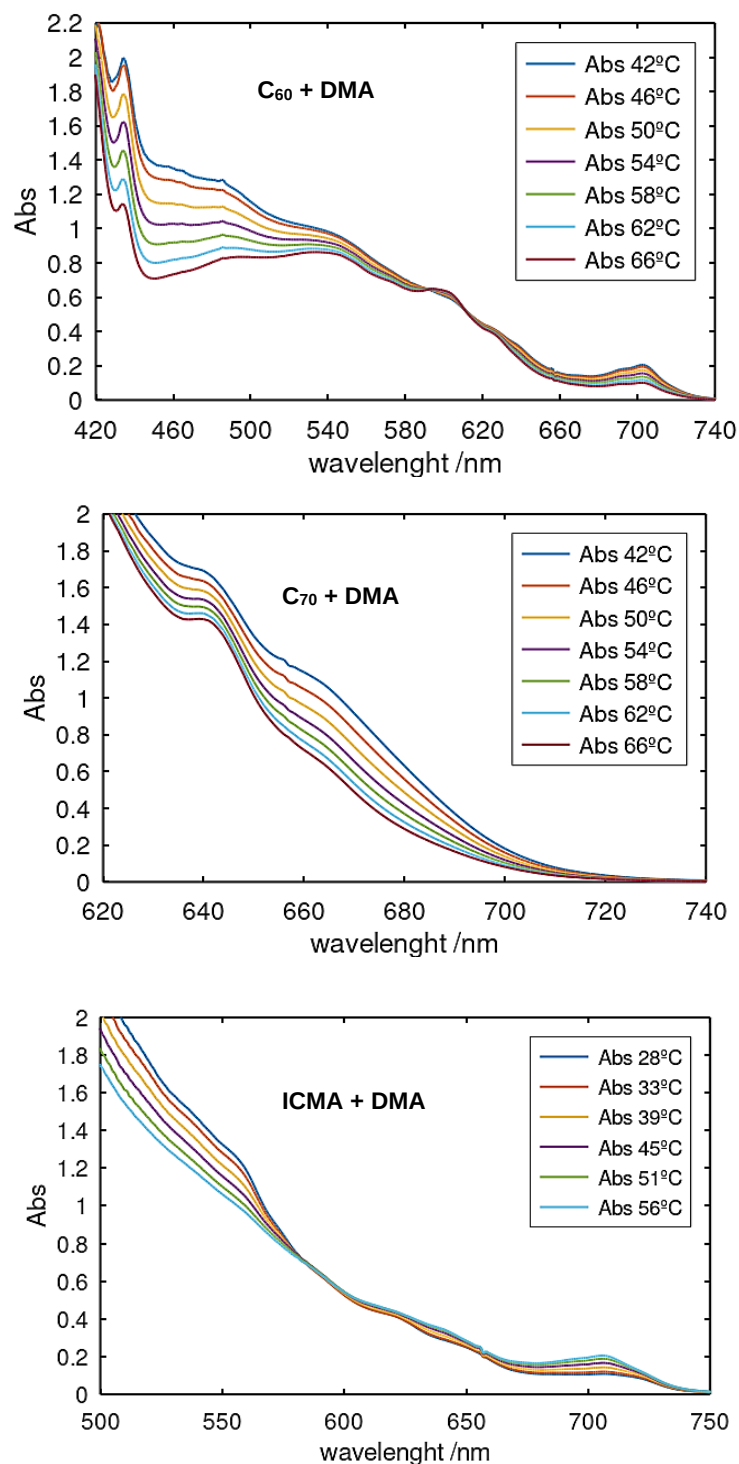


Fig. 38: Equilibrium spectra for various temperatures for the C₆₀+DMA (1:2.5 molar ratio) (top), C₇₀+DMA (1:5.2 molar ratio) (middle), and ICMA+DMA (1:16.8 molar ratio) (bottom) solutions. Temperatures presented are setpoint temperatures. Since the DA reaction is exothermic in this temperature range, lower temperatures mean a more extension of the reaction and more formation of the adduct.

The equilibrium molar concentration of the adduct was determined based on the fact that the absorbance at a given studied wavelength λ is given in terms of the molar concentrations as (since DMA does not absorb in the studied region):

$$\begin{aligned} \text{Abs}_{eq} &= \varepsilon_{FA,\lambda} l [FA]_{eq} + \varepsilon_{F,\lambda} l [F]_{eq} \\ &= \varepsilon_{FA,\lambda} l [FA]_{eq} + \varepsilon_{F,\lambda} l ([F]_0 - [FA]_{eq}) \end{aligned} \quad 63$$

Thus, knowing the equilibrium absorbance (Abs_{eq}), the molar absorptivities (for the studied wavelength) of the fullerene ($\varepsilon_{F,\lambda}$) and the adduct ($\varepsilon_{FA,\lambda}$), and the initial molar concentration of fullerene ($[F]_0$), one can easily calculate $[FA]_{eq}$. The molar absorptivities of the fullerenes were determined based on the linear relationships shown in Table 3 of Section 3.1.1. The molar absorptivities of the adducts C₆₀-DMA and C₇₀-DMA were assumed to be the same as for the C₆₀-anthracene and C₇₀-anthracene adducts, obtained from the study in Section 3.1.6., using the *HypSpec* program. For the ICMA-DMA adduct, the molar absorptivity was determined by an optimization procedure, minimizing the residual sum of squares (SS_{res} , Section 2.12) of the van 't Hoff plot. This generated a molar absorptivity $\varepsilon = 57 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$. This procedure was tested for the C₆₀ and C₇₀ reactions, and found to arrive at a molar absorptivity of the adduct very close to the one estimated from the spectra of the adducts obtained via *HypSpec*. Equilibrium constants were then determined, at the different temperatures studied, from the equilibrium molar concentration of adduct $[FA]_{eq}$ and the initial concentration of fullerene ($[F]_0$) and DMA ($[A]_0$), as:

$$K_{eq} = \frac{[FA]_{eq}}{([F]_0 - [FA]_{eq})([A]_0 - [FA]_{eq})} \quad 64$$

3.1.6. Determination of the spectra of the fullerene-anthracene adducts and equilibrium study in the reactor

To determine the UV-Vis spectra of the adducts of C_{60} and C_{70} with anthracene (ACMA and AC₇₀MA, respectively), multiple cells containing solutions of the fullerenes and different concentrations of anthracene were prepared. For C_{70} six cells were prepared, and for C_{60} seven (Fig. 39). A solution of the fullerenes was previously prepared by weighting the solid rigorously (using a microbalance Mettler Toledo UMT2) to a volumetric flask of 25.00 ± 0.03 mL. *m*-xylene was then added to the flask, making up the 25.00 mL. The flask was weighted (in an analytical balance Mettler AE 163) before and after addition of the solvent. The solutions in the optical glass cells were then prepared by weighting rigorously, using a microbalance, the different anthracene masses and adding, using a volumetric pipette, aliquots of the rigorous solution of fullerene previously prepared. The cells were weighted before and after the addition (using the Mettler AE 163 analytical balance), and the mass of solution added registered. All the cells were then placed under a temperature-controlled reactor oven, and allowed to reach equilibrium. Afterwards their equilibrium spectra were obtained and the temperature of the reactor changed. The order in which the cells were measured was defined by a random number generator. After every measurement the cell was weighted (using an analytical balance) to control and correct for the solvent loss. The variations were found to be minimal. This process was repeated for various temperatures.



Fig. 39: Optical glass cells with solutions of C_{60} and different anthracene initial concentrations prepared for the equilibrium study in the reactor.

In Table 6 and Table 7 are the prepared concentrations of the sample solutions for C_{60} and C_{70} , respectively; and in Fig. 40 and Fig. 41 are the equilibrium spectra of the samples at $T = 59\text{ }^{\circ}\text{C}$, for C_{60} and C_{70} , respectively.

Table 6: Samples prepared for the C_{60} +Anthracene system for study by UV-Vis in the reactor at different temperatures.

Solution	anthracene / $\text{mol} \cdot \mu\text{g}^{-1}$ ^a	C_{60} / $\text{mol} \cdot \mu\text{g}^{-1}$ ^b	ant/ C_{60}
1	0.58304		0.5
2	1.4931		1
3	1.8544		2
4	5.1612	1.2112	4
5	6.5551		5
6	13.027		11
7	23.314		19

^a The uncertainty on the anthracene concentration $[A]$ is $u(F)=0.0025 \cdot A$. ^b The uncertainty on the C_{60} concentration $[C_{60}]$ is $u(\text{DMA})=0.0025 \cdot [C_{60}]$.

Table 7: Samples prepared for the C_{70} +Anthracene system for study by UV-Vis in the reactor at different temperatures.

Solution	anthracene / $\text{mol} \cdot \mu\text{g}^{-1}$ ^a	C_{70} / $\text{mol} \cdot \mu\text{g}^{-1}$ ^b	ant/ C_{70}
1	5.1584		4
2	9.2526		8
3	15.419		13
4	18.582	1.2271	15
5	27.826		23
6	34.719		28

^a The uncertainty on the anthracene concentration $[A]$ is $u(F)=0.0025 \cdot [A]$. ^b The uncertainty on the C_{70} concentration $[C_{70}]$ is $u(\text{DMA})=0.0025 \cdot [C_{70}]$.

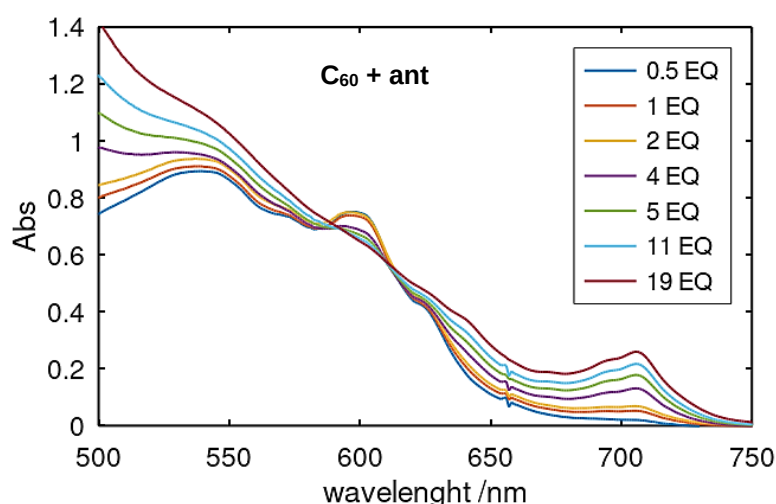


Fig. 40: Equilibrium spectra at $T_{\text{setpoint}} = 59\text{ }^{\circ}\text{C}$ ($T_{\text{real}} = 56.5\text{ }^{\circ}\text{C}$) for the different solutions used in the C_{60} + anthracene reactor study. The different anthracene equivalents are identified in the legend. $[\text{C}_{60}] = 1.2112\text{ mol}\cdot\mu\text{g}^{-1}$.

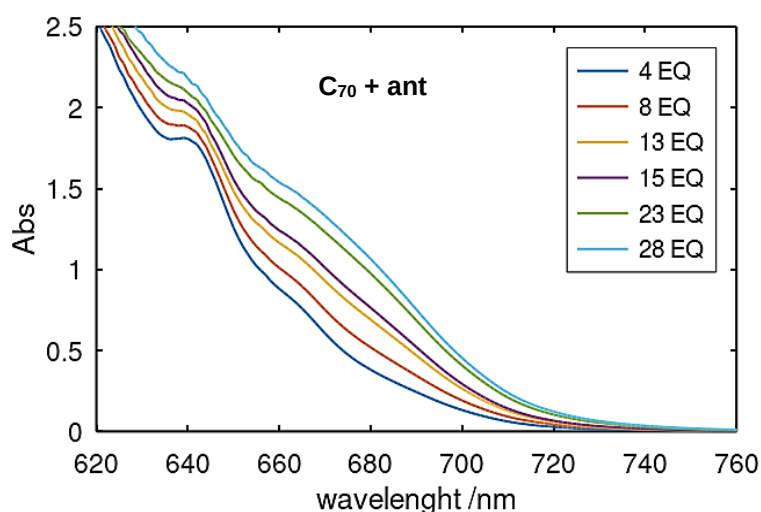


Fig. 41: Equilibrium spectra at $T_{\text{setpoint}} = 59\text{ }^{\circ}\text{C}$ ($T_{\text{real}} = 56.5\text{ }^{\circ}\text{C}$) for the different solutions used in the C_{70} + anthracene reactor study. The different anthracene equivalents are identified in the legend. $[\text{C}_{70}] = 1.2271\text{ mol}\cdot\mu\text{g}^{-1}$.

The equilibrium spectra for every cell was used to compute the equilibrium constant and the spectra of the product at each studied temperature, using the *HypSpec*¹ software: given the initial spectra for the desired temperature, calculated using the parameters obtained in Table 3 of Section 3.1.1.; and molar concentrations corrected for the temperature studied. This allowed us to obtain the equilibrium constants and the spectra of the mentioned adducts, for all the temperatures studied. ΔH_r^0 and ΔS_r^0 were then computed from the equilibrium constants at different temperatures using a van 't Hoff plot. Examples of the fits obtained using the adduct spectrum and the equilibrium

constant obtained by the program for the C_{60} +anthracene system are in Fig. 42. As we can see, the fits obtained were reasonably good, and give confidence to the spectra simulation and consequent equilibrium constant determination. Variations of the spectra of the adduct due to temperature could not be determined within the uncertainty of the method, and thus an average spectrum was used when needed. The obtained spectra of the adducts obtained in this study are in Fig. 43.

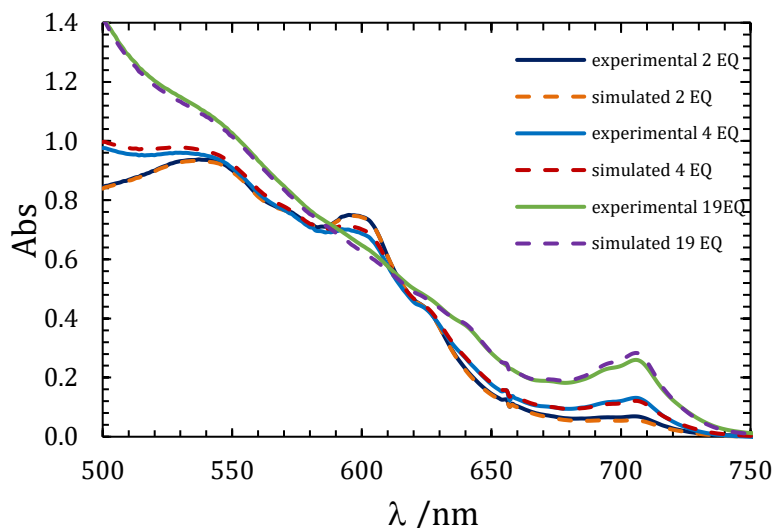


Fig. 42: Experimental equilibrium spectra at $T = 59\text{ }^{\circ}\text{C}$, and respective simulated spectra via *HypSpec* for the 2 eq, 5 eq and 19 eq solutions of C_{60} +anthracene. $[C_{60}] = 1.2112\text{ mol}\cdot\mu\text{g}^{-1}$.

Molar absorptivities obtained for the adducts of C_{60} and C_{70} with anthracene (ACMA and AC₇₀MA, respectively), for the studied wavelengths, as used in the thesis, are compiled in Table 8. The presented absorptivity values are average values of the absorptivities obtained for each temperature (resolution of the method does not allow one to discern any temperature dependence). Uncertainties are the standard deviations between those values.

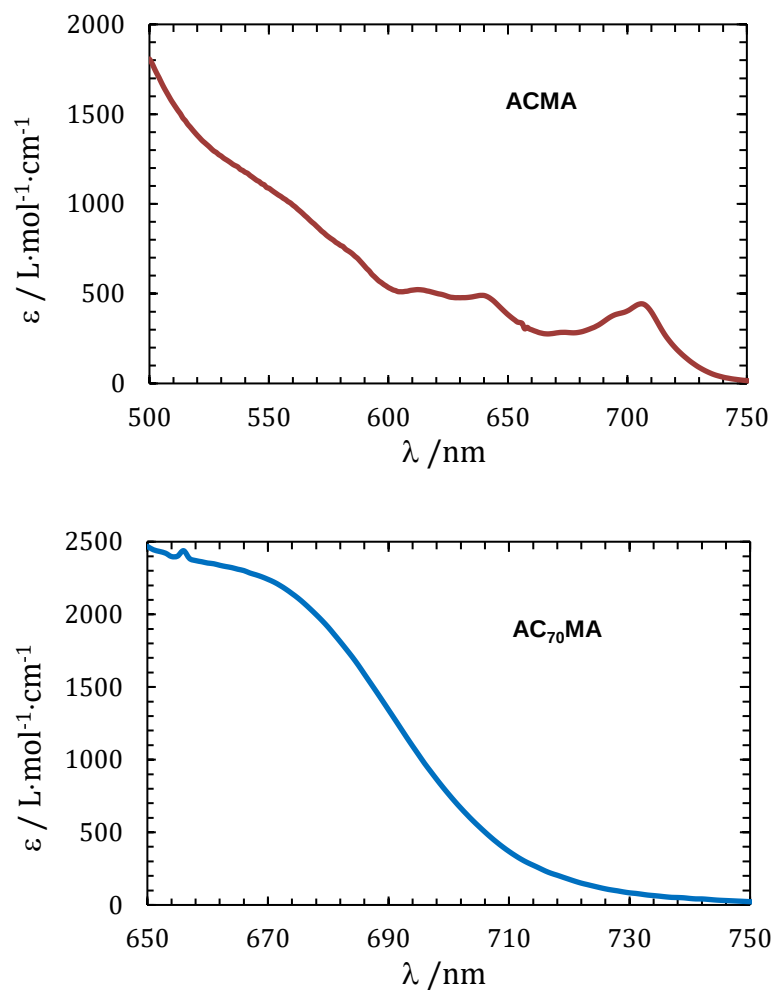


Fig. 43: Spectrum of the C₆₀-anthracene adduct (ACMA) (top) and C₇₀-anthracene adduct (AC₇₀MA) (bottom) - in *m*-xylene -, for the region under study, simulated using the *HypSpec* program.

Table 8: Molar absorptivities determined for the adducts of C₆₀ and C₇₀ with anthracene (ACMA and AC₇₀MA, respectively). Absorptivity values presented are average values of the absorptivities obtained for each temperature (resolution of the method does not allow one to discern any temperature dependence). Uncertainties are the standard deviations between those values.

Adduct	Wavelength / nm	$\epsilon / \text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$
ACMA	498	$(1.894 \pm 0.051) \times 10^{-3}$
	705	$(0.453 \pm 0.011) \times 10^{-3}$
AC ₇₀ MA	665	$(2.08 \pm 0.20) \times 10^{-3}$
	677	$(2.33 \pm 0.19) \times 10^{-3}$

3.1.7. Spectra analysis and correction

Two codes in Octave ³ were programmed. One to read spectra files, correct the spectra for the baseline, compile the data and plot it for a first visualization of the spectra. This was used in the reactor study and the study of the reactions with DMA. The code follows with annotations for clarification (marked by #, and in green). This example has the code read data from the spectra obtained in the reactor experiments for various temperatures and concentrations of diene (equivalents), with the concentrations compiled in the same sheet for each temperature.

```
-----
pkg load io

##### variables to be edited between experiments:

#what are the dienes, dienophiles,
#diene/dienophile equivalents and temperatures
#of the data?
dienophile={"C60"};
diene={"Ant"};
equivalents=[1,2,3,4,5,6,7];
temperatures=[69,66,62,59,55];
#####

#read edited csv files of the type
#dienophile_diene_equivalents_temperatures.csv

for n=1:columns(temperatures),
    for j=1:columns(equivalents),
        #first the wavelength column and the first spectrum
        filename=[char(dienophile) "_" char(diene) "_" ...
            num2str(equivalents(j)) "EQ_" num2str(temperatures(n)) "C.csv"];
        D=csvread(filename);
        #correction for 190 turning into 0
        D(1,1)=190;
        #write a flag for keeping track of the loops
        message = ["n=" num2str(n) " j=" num2str(j)]

        #correct spectra with the baseline...
        D(:,2)=D(:,2)-mean(D(761:811,2));

        #create a matrix VT
        #for variable names and for all equivalents
        #to appear in the same final sheet
        c=rows(D);
        VT([2:c+1],j+1,n)=D(:,2);
        VT([2:c+1],1,n)=D(:,1);
        #create a matrix V of class cell for xls writing
        #and adding variable names
        V(:,j+1)=num2cell(VT(:,j+1,n));
        #add equivalent names according to the j variable
        V(1,j+1)=[num2str(equivalents(j)) " EQ"] ;

    endfor
endfor
```

```

#add the wavelengths which don't need to be inside the for loop
V(1,1)="wavelength /nm";
V([2:c+1],1)=num2cell(D(:,1));

#save results for each temperatures to xls file
filename=[char(dienophile) "_" char(diene) "_" num2str(temperatures(n)) "C_" ...
num2str(equivalents(j)) "EQ_REACTOR_DATA.xlsx"];
xlswrite(filename,V);

#make plot from 3d VT matrix

#position and size of the figure
figure(n,"position",[0,0,480,296])
#data to be plotted and linewidth chosen
plot(VT([2:c+1],1,n),VT([2:c+1],2:(columns(equivalents)+1),n),"linewidth", 1)

#range of x and y
xlim([500,750]);
ylim([0,1.4]);
#axis labels
xlabel("wavelength /nm");
ylabel("Abs");
#legend with the column of V that contains the equivalents
legend((V(1,2:(columns(equivalents)+1)))));

#where tick marks are located (xmin,delta,xmax)
xticks(500:50:750);
yticks(0:0.2:1.4);
#choose fontsize and linewidth for the rest of the graph
set(gca,"fontsize", 11, "linewidth", 1)

#save plot in tif format for this temperature
#with name as variable name
aux=figure(n);
name=[char(dienophile) "_" char(diene) "_REACTOR_" ...
num2str(temperatures(n)) "C"];
saveas(aux,name,"tif");

endfor
-----

```

For each temperature, the code outputs a xls file of the type shown in Fig. 44, and the resulting graphical plots of absorbance (Fig. 45) for each concentration of diene.

	A	B	C	D	E	F	G	H
1	wavelength /nm	1 EQ	2 EQ	3 EQ	4 EQ	5 EQ	6 EQ	7 EQ
2	190	-0.78347	-0.49368	-1.24851	-0.88628	-1.12256	-1.27417	-0.96875
3	191	-1.28812	-0.38924	-1.87008	-1.5213	-1.79974	-1.90312	-1.57499
4	192	-0.67831	-0.12975	-1.1076	-0.75358	-1.04695	-1.12779	-0.78177
5	193	-1.28088	-1.00448	-1.76275	-1.42343	-1.69886	-1.79583	-1.554
6	194	-1.37752	-1.06263	-1.94114	-1.62077	-1.85722	-1.96848	-1.66384
7	195	-1.03545	-0.48192	-1.62686	-1.18667	-1.53891	-1.66059	-1.43794
8	196	-0.75386	-0.295	-1.30743	-0.89276	-1.23441	-1.31605	-1.05631
9	197	-0.95642	-0.68113	-1.41537	-1.06198	-1.37904	-1.4578	-1.2174
10	198	-0.75155	-0.46743	-1.31027	-0.89057	-1.23253	-1.31383	-1.0816
11	199	-1.1341	-0.70143	-1.57223	-1.22226	-1.52475	-1.62956	-1.31999
12	200	-0.87968	-0.57052	-1.34806	-1.04014	-1.304	-1.37053	-1.16277
13	201	-0.39387	0.281121	-0.89712	-0.52307	-0.79996	-0.88318	-0.58826
14	202	-0.95649	-0.49801	-1.44559	-1.03383	-1.39315	-1.45454	-1.22421
15	203	-0.45122	-0.11038	-0.98179	-0.61855	-0.911	-1.00865	-0.77483
16	204	-0.84804	-0.12987	-1.28921	-0.90729	-1.28253	-1.33799	-1.00445
17	205	-0.94901	-0.44027	-1.43646	-1.05055	-1.37098	-1.43787	-1.2703
18	206	-0.61246	-0.31084	-1.2101	-0.8804	-1.17453	-1.21593	-0.9857
19	207	-1.17667	-0.87979	-1.62825	-1.26508	-1.57226	-1.65203	-1.41388
20	208	-0.81175	-0.22202	-1.41045	-1.0934	-1.34376	-1.41576	-1.18327
21	209	-1.14135	-0.82596	-1.65308	-1.29591	-1.6115	-1.69286	-1.42272
22	210	-1.37238	-0.98432	-1.82357	-1.52923	-1.78381	-1.84661	-1.63054

Fig. 44 : X/s file produced for each temperature by the spectra analysis code.

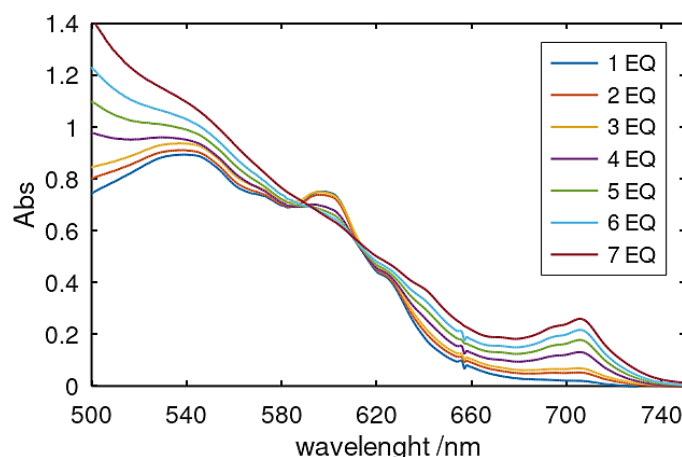


Fig. 45: Graphical plot produced for each temperature by the spectra analysis code.

The only change needed to make to the code for different experiments is to edit the “variables to be changed between experiments” field (the fullerene, diene, temperatures and equivalents of the data). Of course, one temperature can be analyzed individually by just introducing one value in the *temperatures* variable. If there are multiple temperatures for the same equivalents of diene (as in the DMA study), instead of multiple equivalents for the same temperature (as in the reactor study), then the variable “*temperatures*” and “*equivalents*” can be switched, preserving the basis of the code.

The other code was programmed to read kinetic data (data of absorbance as a function of time for various wavelengths), and also automatically corrects the absorbances with the wavelength chosen as the baseline. This was used for the study of the kinetics, and also for the DMA step study which was performed using the same

kinetic mode (Section 3.1.5.). The code follows, as an example for a kinetic experiment between C₆₀ and anthracene:

```
-----
pkg load io
```

```
####variables to be edited between experiments:
```

```
#A contains the wavelengths studied
```

```
A=[428,456,538,705,730,780];
```

```
l=columns(A);
```

```
#what are the dienes, dienophiles,
```

```
#diene/dienophile equivalents and temperature
```

```
#of the data?
```

```
dienophile={"C60"};
```

```
diene={"ANT"};
```

```
equivalents={"20"};
```

```
temperature={"70"};
```

```
#####
```

```
#read edited csv files of the type
```

```
#dienophile_diene_equivalents_temperature_wavelength.csv
```

```
#first the time column and the first wavelength
```

```
filename=[char(dienophile) "_" char(diene) "_" ...
```

```
char(equivalents) "EQ_" char(temperature) "C_" num2str(A(1)) ".csv"];
```

```
D=csvread(filename);
```

```
#all other wavelengths using a for loop,
```

```
# stored in matrix D
```

```
for i=2:l,
```

```
    filename=[char(dienophile) "_" char(diene) "_" ...
```

```
    char(equivalents) "EQ_" char(temperature) "C_" num2str(A(i)) ".csv"];
```

```
    T=csvread(filename);
```

```
    D(:,i+1)=T(:,2);
```

```
endfor
```

```
#correct all wavelengths with the blank...
```

```
 #(assumed as the highest wavelength)
```

```
for i=2:l,
```

```
    D(:,i)=D(:,i)-D(:,l+1);
```

```
endfor
```

```
#create a new matrix VT with an empty row
```

```
#for variable names
```

```
c=rows(D);
```

```
VT=zeros(c+1,l+1);
```

```
VT([2:c+1],:)=D;
```

```
#create a matrix V of class cell for xls
```

```
writing
```

```
#and adding variable names
```

```
V=num2cell(VT);
```

```
#add variable names
```

```

V(1,1)="t /s";

#using a for loop for labeling the wavelengths
for i=1:l-1,
    name=[num2str(A(i)) " nm"];
    V(1,i+1)=name;
endfor

#now the blank wavelength
name=["Blank " num2str(A(l)) " nm"];
V(1,l+1)=name;

#save to xls file
filename=[char(dienophile) "_" char(diene) "_" ...
char(equivalents) "EQ_" char(temperature) "C_KINETICS_DATA.xlsx"];
xlswrite(filename,V);

```

In this case the wavelengths are manually edited between experiments, when changing the fullerene involved in the reaction. In the case of DMA, the data has different temperatures in it, which do not need to be explicitly mentioned – in that case the temperature variable can be deleted from the code. For the kinetics with anthracene, the data is for one temperature only. For both there is only one equivalent for each experiment.

The code outputs a *xls* file of the type of Fig. 46.

	A	B	C	D	E	F	G
1	t/s	428 nm	456 nm	538 nm	705 nm	730 nm	Blank 780 nm
2	0	0.313696	0.193987	0.714753	0.011277	0.001335	0.261886
3	122	0.397336	0.248341	0.743388	0.024228	0.011104	0.16328
4	242	0.461413	0.280855	0.714368	0.0149	0.0059	0.0303
5	362	0.459317	0.272856	0.702975	0.0104	0.0019	0.0141
6	482	0.466391	0.27769	0.702324	0.0119	0.0018	0.0139
7	602	0.473628	0.281651	0.700151	0.0139	0.0023	0.0185
8	722	0.485864	0.290383	0.701381	0.016	0.0027	0.0174
9	841.9	0.49588	0.297105	0.701427	0.018	0.003	0.0185
10	961.9	0.508882	0.306334	0.70335	0.0201	0.0033	0.0171
11	1081.9	0.521575	0.314865	0.704069	0.022	0.0036	0.0173
12	1201.9	0.532474	0.322901	0.705202	0.024	0.004	0.0171
13	1321.9	0.543828	0.330811	0.705974	0.0257	0.0042	0.0169
14	1441.9	0.555135	0.33865	0.70613	0.0277	0.0046	0.0187
15	1561.9	0.565214	0.34567	0.706408	0.0299	0.0051	0.0211
16	1681.9	0.576561	0.35364	0.707864	0.0313	0.0051	0.0198
17	1801.9	0.588449	0.362091	0.709309	0.0333	0.0054	0.019
18	1921.9	0.600696	0.371017	0.711259	0.0352	0.0058	0.0179
19	2041.9	0.609616	0.376326	0.71022	0.0369	0.0062	0.0226
20	2161.9	0.621017	0.383985	0.711907	0.0386	0.0064	0.0202
21	2281.9	0.630669	0.391496	0.712672	0.0405	0.0068	0.0207
22	2401.9	0.642646	0.400241	0.714286	0.0421	0.0071	0.0197

Fig. 46: *Xls* file produced for each temperature by the kinetics experiment analysis code.

3.1.8. Temperature calibration of the UV-Vis

Temperature calibration of the UV-Vis' temperature-controlled cell holder was performed by measuring the temperature of the inside of a UV-Vis cell filled with *m*-xylene, with a custom Omron thermistor wrapped in aluminum foil, and submersed in the liquid. For various setpoint temperatures of the water bath, the temperature of the sensor was recorded and plotted against the setpoint temperatures. The data was fitted to a second order polynomial function by a least-squares fit. The obtained plot is in Fig. 47. The function found to better describe the relation between the two variables is Equation 65 (for T in Celsius). This function was used to convert the setpoint temperatures to real temperatures in the studies performed in this work.

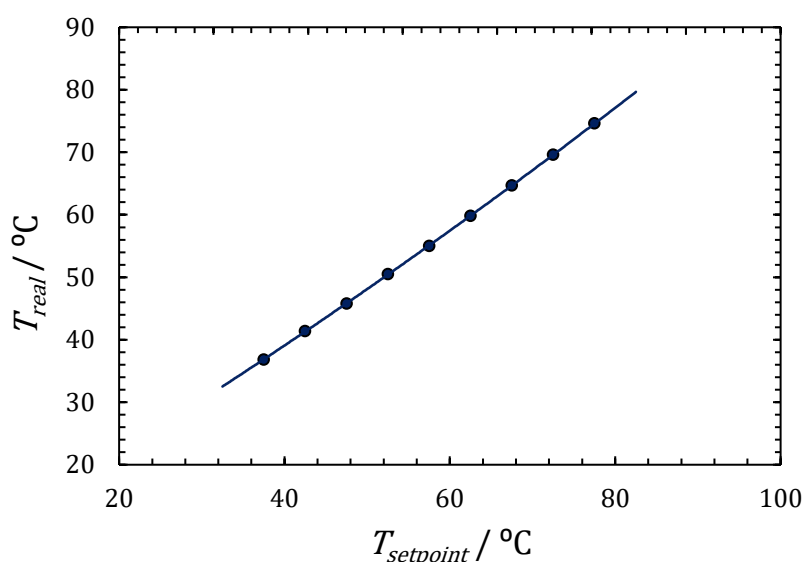


Fig. 47: Measured temperature vs setpoint temperature for the UV-Vis cell holder temperature calibration. The equation found to best describe was an order 2 polynomial. The temperature interval chosen was the temperature interval used for the UV-Vis studies. Fit $R^2 = 0.99998$.

$$T_{real}(^{\circ}\text{C}) = 1.61 \times 10^{-3} \times T_{setpoint}^2 + 0.758 \times T_{setpoint} + 6.18 \quad 65$$

3.1.9. Temperature calibration of the reactor

Temperature calibration of the reactor used in the study of Section 3.1.6. was performed by measuring the temperature inside the reactor, by fixing the measuring unit of the thermometer to the sample support shown in Fig. 39. The temperature was measured using a TD110 VWR Pt1000. For various setpoint temperatures of the reactor

oven, the temperature of the sensor was recorded and plotted against the setpoint temperatures. The data was fitted to a linear function by a least-squares fit. The obtained plot is in Fig. 47. The function found to better describe the relation between the two variables is Equation 65 (for T in Celsius). This function was used to convert the setpoint temperatures to real temperatures in the studies performed in this work. This function was used to convert the setpoint temperatures of the reactor to real temperatures for the study described in Section 3.1.6.

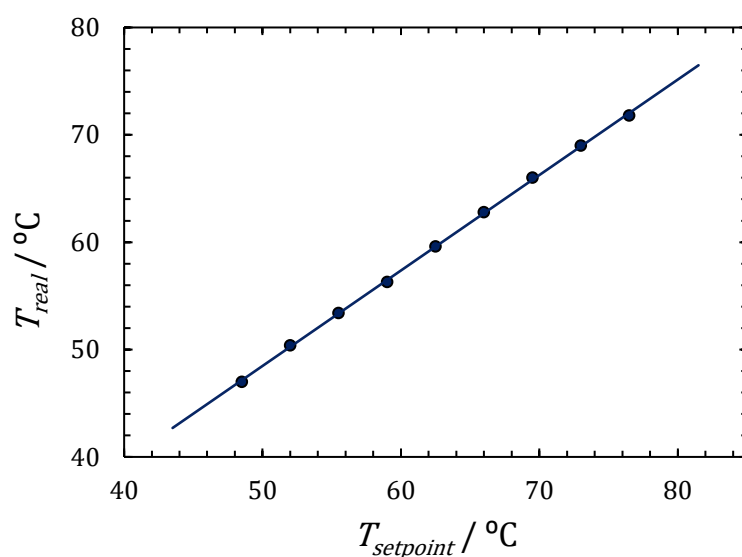


Fig. 48: Measured temperature vs setpoint temperature of the reactor obtained for the temperature calibration. The equation found to best describe was a linear function. The temperature interval chosen was the temperature interval used for the study. Fit $R^2 = 0.9997$.

$$T_{real}(^{\circ}\text{C}) = 0.889 \times T_{setpoint}(^{\circ}\text{C}) - 4.02$$

66

3.2. Quantum chemistry study of the reactions between fullerenes and conjugated dienes

To evaluate effects on the reactivity of fullerenes (in particular isomerism), and to have computational support for the experimental studies, a study of the reaction between fullerenes and anthracene (with some results also for indene and 9,10-dimethylantracene) (the reaction of C_{60} with indene was also studied to evaluate the differences in thermodynamical reactivity and stability predicted by the computational

method due changing the diene) was performed using quantum chemistry methods. All calculations in this work were performed using the *Gaussian 09* software package ⁴.

First, electronic energies at $T = 0$ K for the fullerenes C_{60} , C_{70} and ICMA; dienes anthracene and indene and for the possible adducts were calculated using Density Functional Theory with the M06-2X functional and a 6-31+G(d) basis. Their respective geometries were optimized, and their respective electronic energies at $T = 0$ K calculated (in vacuum). For C_{70} and ICMA, since there are different possible isomers for the adduct with anthracene, the geometry of each possible isomer was optimized individually.

For $AC_{70}MA$ (anthracene- C_{70} monoadduct), there are 4 distinguishable [6,6] isomers as possible products, whose structures are in Fig. 49. Isomer **a** has the anthracene addend bonded in the edge of the fullerene, where it is locally most similar to C_{60} , while isomer **d** has the anthracene bonded on the equatorial belt of C_{70} (in which it differs most from C_{60}). Thus, going from **a** to **d**, the similarity to C_{60} is decreased, and we are closer to the center of the C_{70} (chosen to be where its local diameter is smaller).

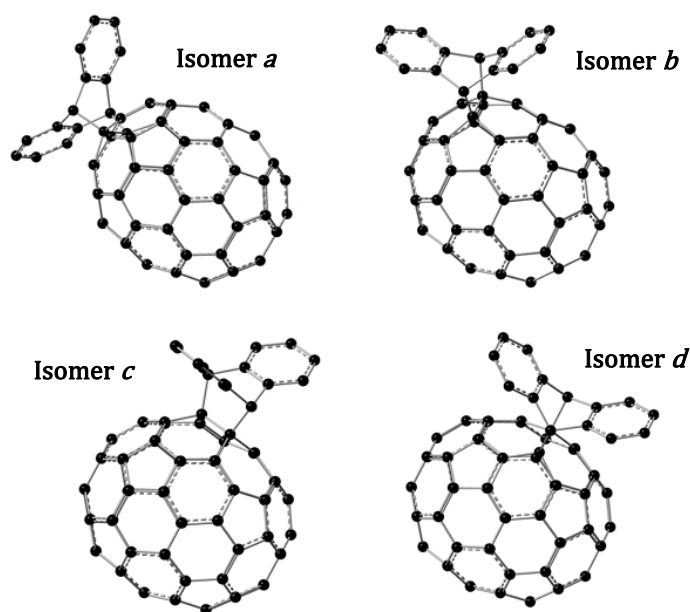


Fig. 49: Optimized structures for the possible isomers of the C_{70} -anthracene adduct, and their respective nomenclature.

For AICBA (anthracene,indene- C_{60} bisadduct) 14 isomers (Fig. 50) were optimized using this method. There are a total of 29 isomers for this reaction, composed of the 14 optimized isomers and their enantiomer pairs - except for the *trans*-1 and the *e*-face **a** and **b** isomers, which do not have enantiomer pairs -, and the *cis*-1 type of

isomers, which were not optimized. This adds up to the 29 total isomers that correspond to the 29 possible bonds where the anthracene group can add, 30 bonds in the C_{60} structure minus the one in which indene is already bonded. The enantiomer pairs are similar adducts that only differ in being non-superimposable mirror images of each other, as exemplified in Fig. 51. These pairs don't need to be optimized individually as their energy is the same by definition. The *cis*-1 isomers are clearly unstable due to the overlap of the addends, which generate very strong repulsive forces. Thus, these isomers were not studied and not even optimized, as their contribution to the reactions will be nonexistent. In fact, all isomers with both addends on the same side of the C_{60} (all *cis* isomers) can be predicted to be relatively unstable when compared to the other isomers. Still, the *cis*-2 and *cis*-3 isomers were studied to confirm this hypothesis. The **a** and **b** nomenclature here is related with the orientation of the indene group, and both would be undistinguishable if indene were replaced by a symmetric group like anthracene. **a** means the anthracene group is closer to the aromatic ring of indene, and **b** means it is closer to the shorter side of indene (Fig. 50).

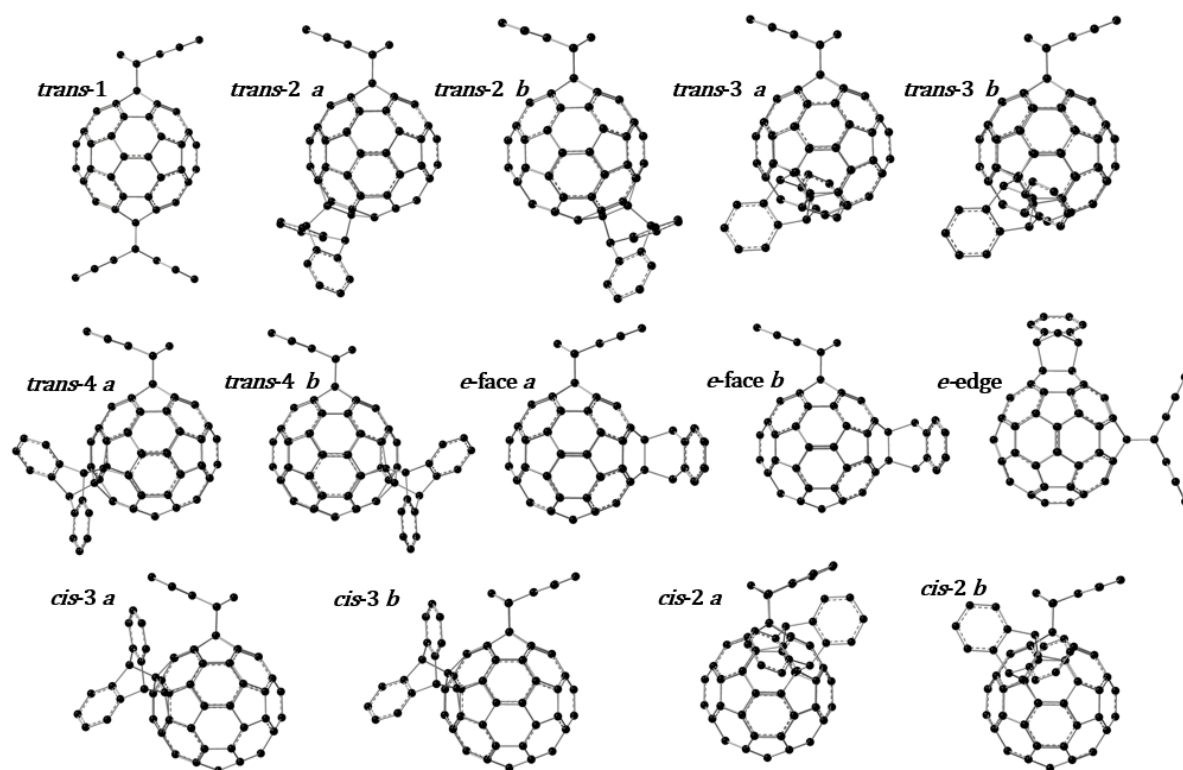


Fig. 50: Optimized structures for the possible isomers of the ICMA-anthracene adduct, and their respective nomenclature.

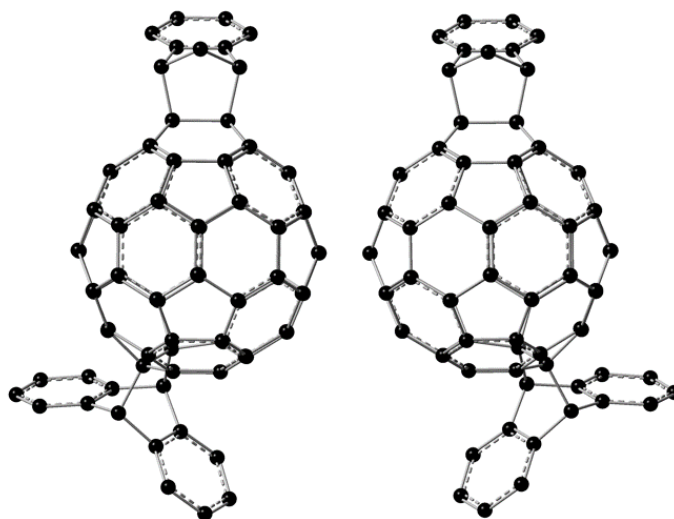


Fig. 51: Enantiomer pair for the anthracene-ICMA adduct *trans*-2 **a** isomer.

We assume in this work that the optimal geometries found in the study closely match the real equilibrium structures of the molecules - the potential energy surface should not contain very different local minima due to the low flexibility of these fullerene molecules. To better ascertain that the structures of these molecules are absolute minima and not geometries of local minima in the potential energy the optimizations were repeated for the *trans*-2 **a** and *trans*-2 **b** isomer of AICBA, with slightly different starting geometries. The energies found this way were the same, thus supporting our assumptions. Also, on some molecules frequency calculations were performed that confirmed we were at the presence of absolute minima for those structures, since no imaginary frequencies were found.

Afterwards, the optimized geometries were used for single-point calculations of energy at the M06-2X/6-311++G(2d,p) level (to evaluate the effect of changing the basis, with this basis being more complete but computationally more expensive) and at the B3LYP/6-31+G(d) level (to evaluate the effect of changing the DFT functional – in this case B3LYP is expected to pale in evaluating the reactivity, when compared to M06-2X, because it is “blind” to dispersion interactions). With these two methods the energies of the two most stable isomers of anthracene- C_{70} adduct (isomer **a** and isomer **b**) were calculated, while for ICMA the calculations were performed only on some representative isomers. The chosen isomers of AICBA were the *trans*-1, *trans*-3 **a**, *e*-face **a**, and *cis*-2 **b** isomers. MP2/cc-pVDZ calculations were also performed on the C_{60} +Anthracene system to evaluate the effect of changing the theoretical method (changing to a post-Hartree-Fock method: Møller–Plesset perturbation theory to second order (MP2) ⁵).

Owing to the very high demand for computational resources, the MP2 was not used to study the other reactions.

Afterwards, the optimized geometries were used to calculate the electronic energies of the species in solution, using SMD - Solvation Model based on Density ⁶ (Section 2.11.2.) to simulate *m*-xylene, at the M06-2X/6-31+G(d) level of theory. Given the relatively low flexibility of the molecules studied (i.e., they do not possess low frequency vibrational modes like those associated to internal rotation) and the absence of any obvious conformational equilibria, we assume that the preferred geometry in the weakly polar *m*-xylene shall not be significantly different from that in the gas phase. Geometry optimizations in solution at the 6-31+G(d) level were performed on some representative species and very similar energies were found, supporting this hypothesis.

Finally, vibrational frequency calculations were performed at the M06-2X/6-31+G(d) level of theory on some representative molecules to obtain the enthalpy and entropies of reaction in the gas phase, at $T = 298$ K and 1 bar. These calculations were performed only for the most stable isomer in the reactions in which isomers are present (C₇₀-ant and ICMA-ant adduct). No imaginary frequencies were found, confirming that the structures correspond to true minima.

3.3. High-performance liquid chromatography study

In this thesis we had plans to have HPLC studies performed on equilibrated solutions of fullerenes and the different dienes. This study was/would be done in collaboration with Mónica Válega from the University of Aveiro. We had a first batch analyzed which compared the reactivity of C₆₀ and ICMA when subject to Diels-Alder addition with anthracene. Due to technical complications, we were unable to conclude the study and only this first batch was analyzed. The procedure of preparation and analysis of this first batch is herein explained. The results for this analysis are presented in Section 4.4.

Using *orto*-terphenyl as an internal standard (always at $\sim 1 \times 10^{-3}$ mol · L⁻¹, like anthracene), six solutions were prepared (in toluene) and analyzed: one standard solution of each only C₆₀ (solution A) / anthracene (B) and ICMA (C) with internal standard; two mixtures of each C₆₀ (D) / ICMA (E) with anthracene (with internal standard); and the other a mixture of all three C₆₀, ICMA and anthracene (F) (also with internal standard). The concentrations of C₆₀ and ICMA were $\sim 0.5 \times 10^{-3}$ mol · L⁻¹. The solutions were prepared as described in Section 3.1.4., weighting all the species in the microbalance and dissolving them together in a flask with the help of ultrasounds (only

when fullerenes were present in the solution, not needed for anthracene and *orto*-terphenyl. The concentrations of the solutions at 25 °C are in Table 9. The internal standard was used with the intention of using the method as a quantitative analysis, but sadly only a qualitative analysis was possible in the end, making the internal standard unimportant.

Table 9: Concentrations of the species in the six solutions analyzed in HPLC to compare the reactivity of C₆₀ and ICMA with anthracene. Concentrations are for 25 °C.

Solution	concentration / mmol·L ⁻¹			
	anthracene	C ₆₀	ICMA	<i>orto</i> -terphenyl
A	-	0.4596	-	1.131
B	0.9251	-	-	1.262
C	-	-	0.5355	1.259
D	1.078	0.5050	-	0.9981
E	1.011	-	0.5509	1.056
F	0.8858	0.5242	0.5128	0.9314

Prior to the HPLC measurements, the solutions were kept at 70 °C for two weeks to ensure equilibrium was reached. The measurements were then performed on the equilibrated solutions at 70 °C. Measurements were performed using a UV-Vis detector in the range 190-700 nm, with specific wavelengths for following the elution at 336 nm, 435 nm, 285 nm, and 314 nm. The mobile phase was composed of a mixture of toluene 5% and acetonitrile 95%, except between 30 and 40 minutes of elution, where 85%/15% toluene/acetonitrile was used.

3.4. Study of the retro Diels-Alder reaction in C₆₀-indene adducts

3.4.1. Study of the retro Diels-Alder using differential scanning calorimetry

The thermal study of crystalline ICMA and ICBA was carried out in a heat flux differential scanning calorimeter (Netzsch DSC 200 F3 Maia). All measurements were performed under a constant flow of nitrogen (50 mL·min⁻¹), using varying heating rates,

sealed aluminum crucibles with a small hole punctured on the top lid, and samples of about 5 mg in each experiment. The temperature and heat flux scales were calibrated by measuring the temperature and the enthalpy of melting of some reference materials (*o*-terphenyl, benzoic acid, 1,3,5-triphenylbenzene, perylene, *p*-quaterphenyl). The sample crucible was weighted rigorously before (with and without compound) and after the DSC experiment - to quantify the mass loss during the process.

The DSC scans of ICMA were performed for scanning rates of 5 and 20 K·min⁻¹, the former being repeated on 3 different experiments. DSC scans of ICBA were performed for scanning rates of 5, 10, 20 and 50 K·min⁻¹. The peaks of heat absorbed during the retro Diels-Alder reaction (loss of indene by the adducts) were then integrated, using a tangential baseline for the regions before and after the peak; and used to obtain the ΔH_r^0 for the process.

3.4.3. Study of the retro Diels-Alder via thermogravimetric analysis

The kinetic study of the Retro-Diels-Alder reactions (release of indene) in solid samples of ICMA and ICBA was carried out in a Netzsch TG 209 F1 Iris. Prior to the kinetic experiments, the thermal behavior of the samples was evaluated by performing dynamic TG runs for each compound, using a heating rate of 2 K·min⁻¹, for large temperature intervals. The kinetic experiments for both crystalline fullerenes consisted of three isothermal periods: first an isothermal step for stabilization was performed at a lower temperature (230 °C for ICMA and 195 °C for ICBA). Then, the reaction rate, at a given studied temperature, was determined by measuring the total mass loss of indene during a long (1 hour to 5 hours) isothermal step. After stabilization of the baseline, the remaining solid was heated for 30 min (at a temperature 40 K higher than the isothermal temperature of the study), to ensure that all indene was released. This procedure was repeated for various temperatures, in intervals of 5 K.

3.5. References

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Chapter 4:

Results and Discussion

This Results and Discussion section is organized as follows:

- In Section 4.1. the results pertaining the quantum chemistry calculation results are presented – including the analysis of electronic energies of reaction; effect of the theoretical method and basis set; analysis of reaction energies in solution and of the solvation energies for the different species; values of enthalpy and entropy of reaction at 298 K; and HOMA (harmonic oscillator model of aromaticity) analysis of the optimized structures in vacuum. This is chosen to be presented first as to give a theoretical support for the analysis of the results in the next sections.
- In Section 4.2. the kinetic and thermodynamic results for the reactions of C_{60}/C_{70} with anthracene are presented and analyzed – including the results of the kinetic study and of the equilibrium study in the reactor.
- In Section 4.3. the thermodynamic results for the reactions of $C_{60}/C_{70}/ICMA$ with 9,10-dimethylanthracene are presented and analyzed.
- In Section 4.4. the HPLC results comparing the reactivity of C_{60} and ICMA with anthracene are presented and analyzed.
- In Section 4.5. the kinetic and thermodynamic results pertaining the thermal analysis studies performed on the retro Diels-Alder reaction on solid ICMA and ICBA are presented and interpreted.

All kinetic and equilibrium constants in this Section and the whole thesis are determined in molarity values, with the solvent volume adjusted for the corresponding temperature. Also, in this Section, confidence intervals for the values are also presented as standard uncertainties. The standard state for the thermodynamic quantities presented in this thesis is $1 \text{ mol}\cdot\text{L}^{-1}$ for solutes in solution, the ideal gas at 1 bar for gases and the pure solid at 1 bar for solids.

4.1. Quantum chemistry results for the reactions between fullerenes and conjugated dienes

The results exposed in this section have been published by our group in MDPI's *Organics* journal. The article is entitled: **Theoretical Study on the Diels–Alder Reaction of Fullerenes: Analysis of Isomerism, Aromaticity, and Solvation** (Rodrigues, D. J.; Santos, L. M.; Melo, A.; Lima, C. F., *Theoretical Study on the Diels–Alder Reaction of Fullerenes: Analysis of Isomerism, Aromaticity, and Solvation. Organics* 2022, 3 (4), 364-379). ¹ The article is open access and can be found at <https://www.mdpi.com/2673-401X/3/4/25>.

4.1.1. Optimized geometries and electronic energies of reaction in vacuum

The optimized geometries for the different isomers of the C₇₀-anthracene adduct and ICMA-anthracene adduct are in Fig. 52 and Fig. 53, respectively.

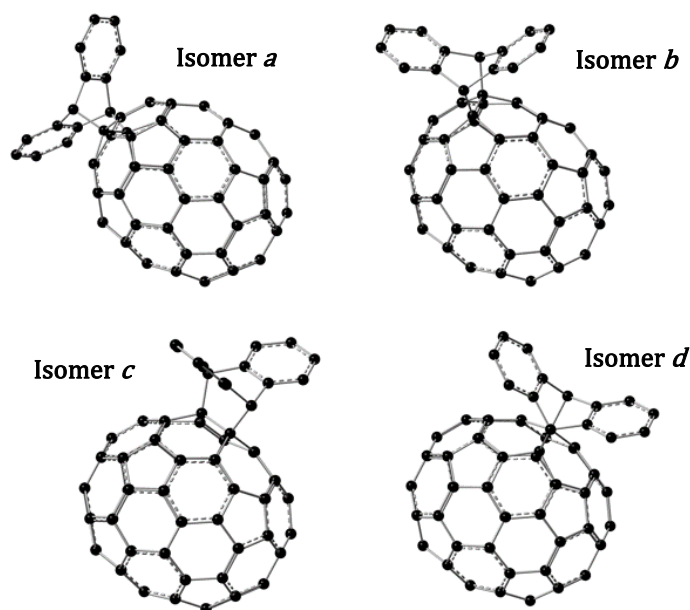


Fig. 52: Optimized structures for the possible isomers of the C₇₀-anthracene adduct, and their respective nomenclature.

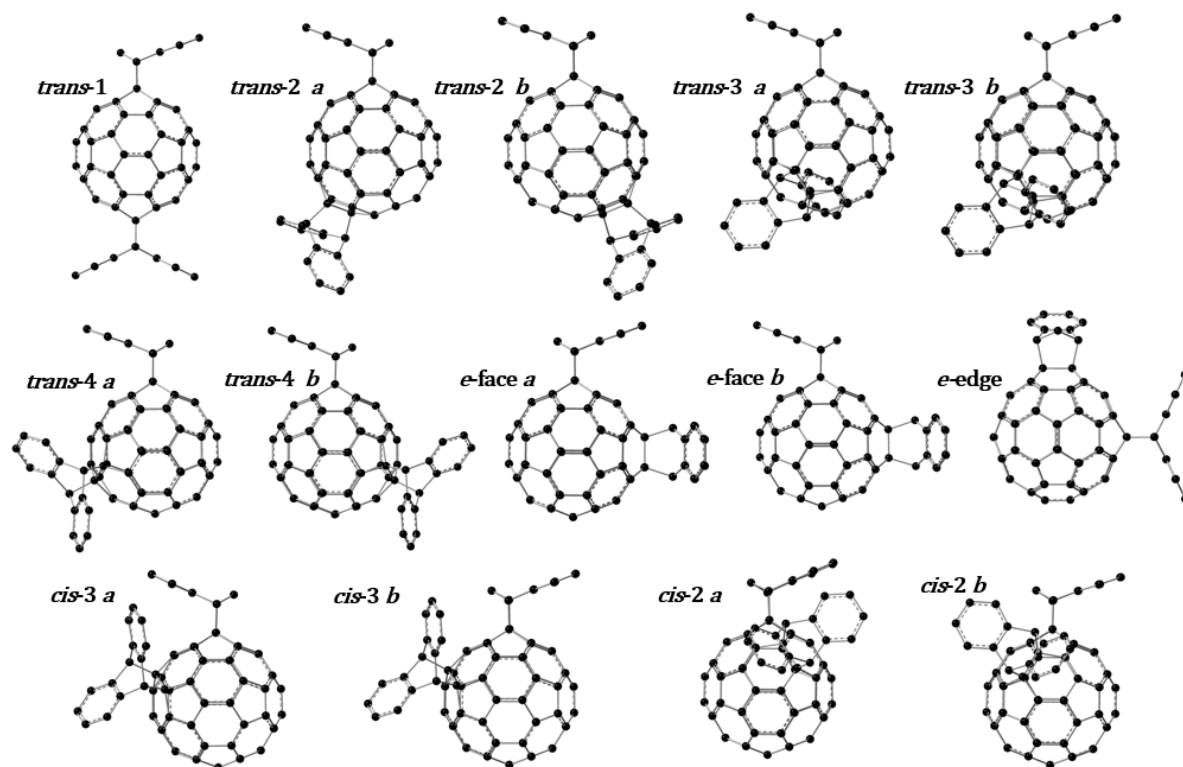


Fig. 53: Optimized structures for the possible isomers of the ICMA-anthracene adduct, and their respective nomenclature.

Using the electronic energies E_{el} of the species calculated using the M06-2X/6-31+G(d) method, reaction energies ($\Delta_r E_{el}$) were computed based on Equation 67. For all possible isomers for the Diels-Alder addition of anthracene to C_{70} and ICMA, the probability according to a Boltzmann distribution (assuming an ensemble at $T = 330\text{ K}$) of each isomer i of n possible isomers at $T = 330\text{ K}$ (an average of the temperatures studied experimentally for these reactions) was calculated by Equation 68. The average electronic energy of reaction was then computed by using Equation 69, $\Delta_r E_{el_i}$ being the electronic energy of reaction for isomer i . This is an approximation, as in an ensemble of the isomers as a product of the reaction at T , the probabilities of each isomer are calculated based on their Gibbs energy of reaction and not electronic energies of reaction (Section 2.3.). Still, the corrections to the enthalpy are, in principle, similar for all isomers, and the same is true for their entropies (their vibrational structure is similar), and the main differences should come from differences in the electronic energy).

$$\Delta_r E_{el} = E_{el}^{adduct} - E_{el}^{fullerene} - E_{el}^{anthracene}$$

$$p_i = \frac{\exp\left(-\frac{\Delta_r E_{el_i}}{RT}\right)}{\sum_{i=0}^n \exp\left(-\frac{\Delta_r E_{el_i}}{RT}\right)} \quad 68$$

$$\langle \Delta_r E_{el} \rangle_{T=330K} = \sum_{i=0}^n (p_i \Delta_r E_{el_i})_{T=330K} \quad 69$$

The results obtained are presented in Table 10 for the possible C₇₀-Ant adduct isomers and in Table 11 for the possible ICMA-anthracene adduct isomers (the probabilities present are in this case for each enantiomer pair when is the case that there are enantiomers). The compiled results using for comparing the (thermodynamical) reactivity of the fullerenes with the various different theoretical methods referred in Section 3.2. are in Table 12 (including the results for the reaction of C₆₀ with indene and DMA (in this case only for M06-2X/6-31+G(d)).

The obtained values of the electronic energies at all theoretical levels predict a higher thermodynamical reactivity of indene in cycloaddition to C₆₀, as expected because it is known indene is a stronger diene in Diels-Alder reactions². It also predicts a higher thermodynamical reactivity with DMA than with anthracene, and close to indene. This difference can be due to dispersive interactions between the extra CH₃ groups in DMA and the surface of the fullerene. The position of DMA as an addend is optimal for this kind of interaction.

Table 10: Electronic energies for $T = 0$ K for the reaction between C₇₀ and anthracene using M06-2X/6-31+G(d). The fraction of each adduct isomer present in an ensemble that follows the Boltzmann distribution at $T = 330$ K is also present (neglecting the differences due to the vibrational and rotational structures of the molecules, and corrections to the electronic energy at this temperature).

AC ₇₀ MA isomer	$\Delta_r E_{el}$ /kJ · mol ⁻¹	$p_i/\%$ ($T = 330$ K)
<i>a</i>	− 96.6	86
<i>b</i>	− 91.6	14
<i>c</i>	− 19.5	≈ 0
<i>d</i>	95.5	≈ 0
average	−95.9	-

Table 11: Electronic energies for $T = 0$ K for the reaction between ICMA and anthracene using M06-2X/6-31+G(d). The fraction of each adduct isomer present in an ensemble that follows the Boltzmann distribution at $T = 330$ K is also present (neglecting the differences due to the vibrational and rotational structures of the molecules, and corrections to the electronic energy at this temperature). The probabilities calculated are for both enantiomers (when a pair of enantiomers exist) for the case of ICMA.

AICBA Isomer	$\Delta_r E_{el}$ /kJ · mol ⁻¹	$p_i/\%$ ($T = 330$ K)
<i>trans</i> -1	- 91.2	2
<i>trans</i> -2 <i>a</i>	- 91.9	5
<i>trans</i> -2 <i>b</i>	- 92.1	5
<i>trans</i> -3 <i>a</i>	- 95.9	20
<i>trans</i> -3 <i>b</i>	- 95.0	15
<i>trans</i> -4 <i>a</i>	- 91.3	4
<i>trans</i> -4 <i>b</i>	- 91.2	4
<i>e</i> -face <i>a</i>	- 96.5	13
<i>e</i> -face <i>b</i>	- 96.1	11
<i>e</i> -edge	- 96.1	22
<i>cis</i> -3 <i>a</i>	- 79.9	≈0
<i>cis</i> -3 <i>b</i>	- 79.7	≈0
<i>cis</i> -2 <i>a</i>	- 64.9	≈0
<i>cis</i> -2 <i>b</i>	- 77.9	≈0
average	-95.2	-

Table 12: Electronic energies of reaction obtained using different methods and/or basis for the reactions between the studies fullerenes and anthracene/indene/DMA. For C₇₀, the average electronic energy was calculated using Equation 69. Electronic energies of reaction values are in kJ·mol⁻¹. In parenthesis in the MP2 results is the Hartree-Fock energy.

Fullerene	$\Delta_r E_{el}(T = 0 \text{ K})/\text{kJ} \cdot \text{mol}^{-1}$			
	B3LYP 6-31+G(d)	M06-2X 6-31+G(d)	M06-2X 6-311++G(2d,p)	MP2 cc-pVDZ
C ₆₀ + Ind -> ICMA	- 31.0	- 116.6	- 106.4	-
C ₆₀ + DMA -> DCMA	-	- 114.1	-	-
C ₆₀ + Ant -> ACMA	7.8	- 95.4	- 85.4	- 165.5 (-30.2)
C ₇₀ + Ant -> AC ₇₀ MA ^a	8.3	- 95.9	- 85.8	-
<i>a</i>	8.2	-96.6	- 86.4	-
<i>b</i>	20.9	-91.6	- 80.4	-
<i>c</i>	-	-19.5	- 9.2	-
<i>d</i>	-	95.5	105.6	-
ICMA + Ant -> AICBA				
<i>trans</i> -1	14.6	- 91.2	- 81.1	-
<i>trans</i> -3 <i>a</i>	8.6	- 95.9	- 86.1	-
<i>e</i> -face <i>a</i>	9.3	- 96.5	- 86.3	-
<i>cis</i> -2 <i>b</i>	32.6	- 77.9	- 67.8	-

^a average value calculated using the Boltzmann distribution for the isomers at $T = 330$ K.

The electronic energies of reaction found predict that only two isomers of the C₇₀-anthracene adduct should exist in an ensemble of C₇₀ and anthracene in equilibrium with its products, which are isomer **a** and isomer **b**. These are the [6,6] additions which occur nearest to the edges of the fullerene, where it is more similar to C₆₀ in local curvature and size of the bonds. This goes according to the state of the art (see Section 1.2.). The bonds more similar to C₆₀ are more curved and their higher strain release makes the addition to these bonds preferable. Also, at 330 K, if the differences in stability were only due to the differences in $T = 0$ K electronic energies (thus neglecting the differences due to the vibrational and rotational structures of the molecules, and corrections to the electronic energy at this temperature), isomer **a** should exist at about 86 %. It is thus predicted that it should be the major product of this reaction at this temperature. An average of the electronic energy for the Diels-Alder reaction of C₇₀ with anthracene - using the same fraction of each isomers as calculated in Table 10 - gives an electronic energy of reaction $\Delta_r E_{el} = 95.9 \text{ kJ} \cdot \text{mol}^{-1}$, which is very close to $\Delta_r E_{el}$ obtained for C₆₀. Thus, the computational method does not predict a significant difference in reaction energy due to electronic structure differences between C₆₀ and C₇₀ when reacting with anthracene (which is the most significant contribution to the enthalpy of the reactions).

For the reaction of ICMA with anthracene the isomers found to be most stable were the *trans*-3 and *e* (equatorial) isomers. There are 4 *trans*-3 isomers (the two isomers optimized and their enantiomer) and four equatorial isomers (isomers *e*-face **a**, *e*-face **b** and the enantiomer pair for *e*-edge), which gives 8 predominant isomers, each with the respective Boltzmann probabilities given in Table 11. There are also 9 residual isomers (the other isomers and their enantiomer pairs, excluding all *cis* isomers, which are practically nonexistent in equilibrium, due to strong repulsive forces between both addends.). The predicted stability goes by the following ordering: equatorial > *trans*-3 > *trans*-2 $\approx$ *trans*-4 $\approx$ *trans*-1 > *cis*-3 > *cis*-2. Still, *trans*-3 **a** and *e*-edge will exist in 20% and 22%, respectively, due to existing in two different enantiomers (these probabilities are the sum of the probabilities of each enantiomer).

Doing the same average electronic energy of reaction calculation as before for ICMA, one gets $\Delta_r E_{el} = 95.2 \text{ kJ} \cdot \text{mol}^{-1}$, which is close to both the reaction energy for C₆₀ and the average reaction energy calculated for C₇₀. Thus, no difference in thermodynamical reactivity is predicted between the 3 fullerenes in these theoretical calculations. The average energy for ICMA is within $0.1 \text{ kJ} \cdot \text{mol}^{-1}$ of the energy of reaction obtained for C₆₀, which means a second addition in the presence of the various

isomers is predicted to be equally as reactive (in terms of electronic energy) by the theoretical results.

The probabilities calculated allows one to calculate the entropy of isomerism contribution (Section 2.3.) for the reactions. This gives, at 330 K, for AC₇₀MA a $S_{isom} = 3.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ and for AICBA (ICMA-ant adduct) a $S_{isom} = 21.5 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which will increase the entropy of reaction by these same amounts. The reactions are favored in entropy due to the presence of the isomers, with the reaction of ICMA being largely favored in this specific contribution.

4.1.2. Effect of the theoretical method and basis set

Looking at the values in Table 12, we can see that, when compared to the dispersion-corrected M06-2X, the B3LYP functional predicts the fullerenes to be much less reactive towards Diels-Alder addition. In fact, Solà and co-workers have shown that inclusion of dispersion corrections is essential for the study of the chemical reactivity of fullerenes^{3, 4}. Moreover, as verified experimentally (see the next sections and Section 1.2.) these reactions are significantly exothermic, thus proving that M06-2X describes energetics better. A great fraction of the B3LYP destabilization is due to the inability of this functional to describe London dispersion forces. B3LYP probably “sees” the interaction between the anthracene “wings” (the rings in a diagonal position, see Fig. 53, for example) with the fullerene surface as highly repulsive. Interestingly, the differences, Δ , between the values of $\Delta_r E_{el}$ calculated using M06-2X and B3LYP (both with 6-31+G(d)) nicely support this reasoning. The smallest difference is observed for the reaction of C₆₀ with indene ($\Delta = 86 \text{ kJ} \cdot \text{mol}^{-1}$). It gives a smaller value than the reaction of C₆₀ with anthracene ($\Delta = 103 \text{ kJ} \cdot \text{mol}^{-1}$). This makes sense considering indene is smaller than anthracene and has only one “wing” to overlap with the C₆₀ surface. For the two AC₇₀MA isomers, Δ is greater for isomer **b** (113 as compared to 105 $\text{kJ} \cdot \text{mol}^{-1}$ for isomer **a**). Moreover, for isomer **a**, Δ is similar to Δ for C₆₀ + anthracene and for three representative isomers of AICBA (*trans*-1, *trans*-3 **a**, and e-face **a**); for *cis*-2 **b** Δ is slightly larger (of the four it is the only isomers to have significant interactions between both addends, which explains its differentiation from the other isomers). This is easily understood by recalling that in isomer **a** of AC₇₀MA, anthracene binds to the place where the local curvature is more similar to C₆₀, thus giving a similar Δ . In isomer **b** of AC₇₀MA, Δ is larger because one “wing” of anthracene overlaps with the flatter surface of C₇₀ closer to the equatorial belt of hexagons, which increases the magnitude of the dispersive π --- π interactions. In the *cis*-2 **b** isomer of AICBA, Δ is larger because there is

an additional intramolecular contact between the two addends. Still, B3LYP, like M06-2X, predicted the same thermodynamical reactivity for C₆₀, C₇₀ and the most stable isomers of ICMA, as well as predicting that the *trans*-3 and equatorial isomers are more stable than *trans*-1 and *cis*-2 isomers.

Using M06-2X with a larger basis set, 6-311++G(2d,p), a less negative electronic energy of reaction was found for all fullerenes studied. It is known that using a more complete basis set lowers the energy of a molecular species, approximating it to the variational limit ⁵ (the calculated electronic energies for each species are compiled in Appendix B). Still, the electronic energies were lowered more in favor of the reactants, making the reactions less favorable. The differences between the two basis sets are very constant for all reactions ($\Delta \approx 10 \text{ kJ}\cdot\text{mol}^{-1}$). One possible contribution for this is the lower basis set superposition error (BSSE) when using the larger 6-311++G(2d,p) basis ⁶, which corrects for some overestimation of the interaction energy between the fullerene surface and the addend in adduct molecules. Using this more complete basis, the order of thermodynamical reactivity for C₆₀, C₇₀ and the most stable isomers of ICMA is the same. It also predicts that the *trans*-3 and equatorial isomers are more stable than *trans*-1 and *cis*-2 isomers.

The MP2/cc-pVDZ result for C₆₀ + anthracene corroborates the importance of correlation energy in the fullerenes, with the uncorrelated Hartree-Fock (HF) method ⁵ predicting a substantially less negative electronic energy of reaction. This correlation is manifested in both electronic conjugation effects and London dispersive interactions, although MP2/cc-pVDZ probably overestimates the correlation energy.

Together, these results highlight the importance of intramolecular interactions with a significant contribution from London dispersion, such as $\pi\cdots\pi$ interactions, involving the aromatic addends at the surface of the fullerene.

The results at the three theoretical levels predict indene to be more reactive than anthracene towards Diels-Alder reaction with C₆₀. It is known that indene is a diene that favors Diels-Alder reaction when compared to anthracene. ²

4.1.3. Solvation energies and electronic energies of reaction in *m*-xylene

The solvation energies for the species in a solution of *m*-xylene were calculated according to Equation 70, and are presented in Table 13. The electronic energy of reaction ($T = 0 \text{ K}$) in *m*-xylene (calculated according to Equation 67); and the probabilities

of each isomer and average energy of reaction as calculated in Section 4.1.1. are presented in Table 14.

$$\begin{aligned}\Delta_{\text{solv}}E_{\text{el}}^{6-31+G(d)}(m-\text{xylene}) \\ = E_{\text{el}}^{6-31+G(d)}(m-\text{xylene}) - E_{\text{el}}^{6-31+G(d)}(\text{vacuum})\end{aligned}\quad 70$$

Table 13: Electronic energies of solvation in *m*-xylene, at $T = 0$ K, for the compounds involved in the Diels-Alder cycloadditions of the fullerenes studied, calculated using M06-2X/6-31+G(d) (single-point energy calculations on the M06-2X/6-31+G(d) optimized geometries in vacuum).

Molecule	$\Delta_{\text{solv}}E_{\text{el}}(m\text{-xylene}) / \text{kJ}\cdot\text{mol}^{-1}$
Indene	– 29.7
Anthracene	– 42.3
C ₆₀	– 145.3
C ₇₀	– 164.2
ICMA	– 157.3
ACMA	– 166.1
AC ₇₀ MA	
<i>a</i>	– 186.4
<i>b</i>	– 187.0
AICBA ^a	
<i>trans</i> -1	– 179.9
<i>trans</i> -2 <i>a</i>	– 180.8
<i>trans</i> -2 <i>b</i>	– 180.3
<i>trans</i> -3 <i>a</i>	– 180.8
<i>trans</i> -3 <i>b</i>	– 180.4
<i>trans</i> -4 <i>a</i>	– 179.4
<i>trans</i> -4 <i>b</i>	– 179.1
<i>e</i> -face <i>a</i>	– 180.2
<i>e</i> -face <i>b</i>	– 179.6
<i>e</i> -edge	– 181.4
<i>cis</i> -3 <i>a</i>	– 178.8
<i>cis</i> -3 <i>b</i>	– 180.7
<i>cis</i> -2 <i>a</i>	– 178.5
<i>cis</i> -2 <i>b</i>	– 180.0

^a The AICBA regioisomers are ordered up-to-down by increasing proximity of Ant from Ind.

In general, solvation energies for the diene and fullerene found are more negative than the corresponding adducts – this means that the solvent solvates the reagents better than the products, favoring the reverse the reaction (the electronic energy of reaction in *m*-xylene will thus be less negative). This makes sense considering the fact that the available surface area for solvation is higher in the reactants. In the regioisomers of AICBA the effect of solvation also shows almost no noticeable dependence on the

addends' position. Still, in solution, the anthracene-ICMA adduct has one different most stable isomer - the *e*-edge isomer (instead of the *e*-face *a*, as in vacuum). In this case the *e*-edge isomer exists at about 30% (at 330 K, considering only the electronic energy differences) as a racemic mixture of two enantiomers, being a clear major isomer in solution. In short, solvation by *m*-xylene, as simulated by SMD, makes the reaction $\approx 20 \text{ kJ}\cdot\text{mol}^{-1}$ less exothermic but has little distinguishing effect on the possible isomers of the reactions (and this is also true for the isomers of AC₇₀MA) - solvation is almost independent of the dienophile, diene, and position of the addends.

Table 14: Electronic energies of reaction in *m*-xylene ($T = 0 \text{ K}$) for the reactions between C₆₀, C₇₀, ICMA and anthracene/indene at the M06-2X/6-31+G(d) level of theory. The fraction of each possible isomer present in an ensemble that follows the Boltzmann distribution at $T = 330 \text{ K}$ is also present (neglecting the differences due to the vibrational and rotational structures of the molecules, and corrections to the electronic energy at this temperature). The probabilities calculated are for both enantiomers (when a pair of enantiomers exist) for the case of ICMA.

Reaction	$\Delta_r E_{el}(m\text{-xylene})$ / $\text{kJ}\cdot\text{mol}^{-1}$	$p_i / \%$ ($T = 330\text{K}$)
R1. C ₆₀ + Ind → ICMA	− 98.8	-
R2. C ₆₀ + Ant → ACMA	− 74.0	-
R3. C ₇₀ + Ant → AC ₇₀ MA ^a	− 76.4	-
<i>a</i>	− 77.1	88
<i>b</i>	− 71.5	12
R4. ICMA + Ant → AICBA ^a	− 76.4	-
<i>trans</i> -1	− 71.6	1
<i>trans</i> -2 <i>a</i>	− 73.1	5
<i>trans</i> -2 <i>b</i>	− 72.8	4
<i>trans</i> -3 <i>a</i>	− 77.1	22
<i>trans</i> -3 <i>b</i>	− 75.9	14
<i>trans</i> -4 <i>a</i>	− 71.2	3
<i>trans</i> -4 <i>b</i>	− 70.7	2
<i>e</i> -face <i>a</i>	− 77.1	11
<i>e</i> -face <i>b</i>	− 76.1	7
<i>e</i> -edge	− 78.0	30
<i>cis</i> -3 <i>a</i>	− 59.1	≈ 0
<i>cis</i> -3 <i>b</i>	− 60.8	≈ 0
<i>cis</i> -2 <i>a</i>	− 43.9	≈ 0
<i>cis</i> -2 <i>b</i>	− 58.3	≈ 0

^a average values calculated using the Boltzmann distribution for the isomers at $T = 330 \text{ K}$.

In solution we have, at 330 K, for C₇₀ a $S_{isom} = 3.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ and for ICMA a $S_{isom} = 20.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, very close to the values obtained for the reactions in vacuum.

4.1.4. Enthalpies and entropies of reaction at $T = 298$ K

The previous calculations ignore the contributions from the zero-point vibrational energies and the thermal enthalpy contribution due to having $T > 0$ K, allowing for excitations of the vibrational, rotational and translational modes. Thus, we calculated the enthalpies of the reaction (and entropies) by performing vibrational frequency calculations on the species. The translational and rotational degrees of freedom are considered to be in the equipartition limit in these calculations, and the vibrational modes treated as an approximated harmonic oscillator.

Standard enthalpies and entropies of reaction at $T = 298$ K were calculated from the obtained absolute enthalpies and entropies of the species (also at $T = 298$ K) as $\Delta H_r^0 = H_{adduct}^0 - H_{fullerene}^0 - H_{diene}^0$ and $\Delta S_r^0 = S_{adduct}^0 - S_{fullerene}^0 - S_{diene}^0$ (considering $\sigma_{sym} = 1$ for all species). Enthalpies of the reaction in solution were then estimated based on Equation 71:

$$\Delta H_r^0(\text{gas}) = \Delta_r E_{el}^{6-311++G(2d,p)} + \Delta_r E_{solv}^{6-31+G(d)} + \Delta H_r^{corr} \quad 71$$

where:

$$\Delta H_r^{corr} = \Delta H_r(\text{gas}) - \Delta_r E_{el}^{6-31+G(d)} \quad 72$$

where $\Delta_r E_{el}^{6-311++G(2d,p)}$ is the reaction electronic energy calculated using the basis 6-311++G(2d,p), $\Delta_r E_{el}^{6-31+G(d)}$ is the reaction electronic energy calculated using the basis 6-31+G(d), $\Delta_r E_{solv}^{6-31+G(d)}$ is the solvation energy of the reaction at the 6-31+G(d) basis, ΔH_r^{corr} is the thermal correction to the reaction enthalpy (in the gas phase, at $T = 298$ K), and $\Delta H_r^0(\text{gas})$ the reaction enthalpy calculated for the reaction in the gas phase at $T = 298$ K. This equation ignores the contributions of solvation to the rotational and vibrational structure of the molecules, and corrections to the electronic energy as we deviate at $T = 0$ K. The standard enthalpies and entropies of reaction obtained; and the estimated enthalpies of reaction in *m*-xylene are present in Table 15.

Table 15: Standard enthalpies of reaction in the gas phase, at $T = 298.15$ K; estimated standard enthalpies of reaction in *m*-xylene, at $T = 298.15$ K – calculated by Equations 71 and 72; and standard entropies of reaction in the gas phase; for the Diels–Alder cycloadditions of the fullerenes studied with indene and anthracene, calculated at the M06–2X/6–31+G(d) level of theory.

Reaction	ΔH_r^0 (gas, 298.15 K) / $\text{kJ}\cdot\text{mol}^{-1}$	ΔH_r^0 (<i>m</i> -xylene, 298.15 K) / $\text{kJ}\cdot\text{mol}^{-1}$	ΔS_r^0 (gas, 298.15 K) / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
R1. $\text{C}_{60} + \text{Ind} \rightarrow \text{ICMA}$	– 105.4	– 77	– 211
R2. $\text{C}_{60} + \text{Ant} \rightarrow \text{ACMA}$	– 85.6	– 54	– 215
R3. $\text{C}_{70} + \text{Ant} \rightarrow \text{AC}_{70}\text{MA}$			
Isomer <i>a</i>	– 82.5	– 53	– 213
R4. $\text{ICMA} + \text{Ant} \rightarrow \text{AICBA}$			
Isomer <i>e</i> -face <i>a</i>	– 82.5	– 53	– 214

The calculated enthalpies are similar for the most stable isomer of the adduct of the three fullerenes. Thus, their reactivity is expected to be similar in enthalpy. The zero-point energies and thermal corrections for enthalpies make the reaction less exothermic by $\cong 10 \text{ kJ}\cdot\text{mol}^{-1}$. Given the stoichiometry of the Diels-Alder reactions, it follows that this decrease in exothermicity must come from the vibrational component, as the translational and rotational components which are equal for all molecules (as they are in the equipartition limit at this temperature) actually should favor the direct reaction making it more exothermic. This probably results from the lower frequency modes that appear in the adduct associated to single bonds and addend flipping – lower frequency modes have higher occupation of excited states and thus increase the overall energy of the system, in this case the energy of the adduct. The same effect of the vibrations as found in the enthalpies will affect the entropies of reaction as a higher occupation of excited states leads to a higher entropy. This is a contribution that makes the entropy more favorable for the direct reaction.

The entropies are predicted to be similar for every reaction, independently of the diene or fullerene. When comparing to experimental results, the entropy values must be corrected by adding the entropy of isomerism and entropy of symmetry term (if it applies). This gives an expected ΔS_r^0 at 330 K (with the isomerism calculated in solution, assuming the entropy of symmetry contribution, and neglecting both the change in entropy of reaction due to using slightly different temperatures ($T = 298$ K for the entropy term vs $T = 330$ K for the entropy of isomerism term) and the effect of solvation on the entropy of

reaction; also, assuming the ΔS_r^0 for the isomer studied for each reaction is similar to the entropy of reaction averaged over all possible isomers and their Boltzmann weights) of $-177 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for R1, $-175 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for R2, $-179 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for R3, $-182 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for R4. The entropy of isomerism contributions (ΔS_{isom}) for the various reactions are compiled in Table 16, jointly with the possible symmetry contributions (ΔS_{sym}), calculated using the symmetry numbers of all species in the reaction (Section 2.6.). Their sum is also presented, which will be compared with experimental differences in reactivity in the further sections.

Since $\left(\frac{\partial S_{isom}}{\partial T}\right)_p = -\frac{\text{var}(\Delta H_r^0)}{RT^3} + \frac{\text{cov}(\Delta H_r^0, \Delta S_r^0)}{RT^2}$ (Section 2.3.), it is expected that S_{isom} for these cases varies slowly with temperature. This is true assuming the differences in entropy between the different isomers to be negligible (making $\text{cov}(\Delta H_r^0, \Delta S_r^0) = 0$), and the main difference in the enthalpies to be due to the electronic energy (thus $\text{var}(\Delta H_r^0) = \text{var}(\Delta_r E_{el})$) (both assumptions which are justifiable since the relevant isomers for the studies should have similar vibrational structures). Since $\text{var}(\Delta_r E_{el})$ is small for the systems under study (Section 3.1.3., $\frac{\text{var}(\Delta_r E_{el})}{RT^3}$ (for $T \approx 330 \text{ K}$) is $1 \times 10^{-8} \text{ J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$ for the C_{70} system and $2 \times 10^{-8} \text{ J}\cdot\text{K}^{-2}\cdot\text{mol}^{-1}$ for the ICMA system), $\frac{\partial S_{isom}}{\partial T}$ is small. Thus, the choice of temperature for the evaluation of the entropy of isomerism does not significantly influence the results, and we take these values evaluated at $T = 330 \text{ K}$ as a good estimate of the entropy of isomerism for the different further experiments in this thesis, even when the average temperature of those experiments is slightly different from 330 K .

Table 16: Entropy of isomerism (evaluated at $T = 330 \text{ K}$) and entropy of symmetry contributions to the ΔS_r^0 for the different reactions studied (and their sum).

Reaction	ΔS_{isom} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	ΔS_{sym} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	ΔS_{sum} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$
R1. $\text{C}_{60} + \text{Ind} \rightarrow \text{ICMA}$	0	34.0	34.0
R2. $\text{C}_{60} + \text{Ant} \rightarrow \text{ACMA}$	0	39.8	39.8
R3. $\text{C}_{70} + \text{Ant} \rightarrow \text{AC}_{70}\text{MA}$	3.0	30.7	33.7
R4. $\text{ICMA} + \text{Ant} \rightarrow \text{AICBA}$	20.7	11.5	32.2

4.1.5. HOMA analysis of aromaticity

The question of aromaticity in fullerenes is still controversial, but some authors advocate that, contrary to the non-aromatic pentagons, the hexagons can be slightly aromatic^{7,8}. Assuming aromaticity, formation of the least stable AC₇₀MA isomers, **c** and **d**, implies the disruption of aromaticity in three and four hexagons, respectively, while in isomers **a** and **b** only two hexagons are sacrificed. The differentiation between *trans*- and *e*- isomers in AICBA, however, is harder to rationalize. All isomers are close in energy and bond topology in the C₆₀ framework is less diverse than in C₇₀.⁹ We investigated the possibility that, after binding of the diene, the four hexagons adjacent to the bond (not those directly bonded, which become non-aromatic) become more aromatic. This makes sense considering that the release of strain upon addition allows for some geometry adjustment of the surrounding fullerene surface.⁷ A quick inspection of the ICMA and ACMA vacuum optimized structures supports this hypothesis, with the four hexagons adjacent to the addend showing more aromatic character, as suggested by shorter bonds (on average) and smaller bond-length alteration, in comparison to C₆₀. Following this reasoning we employed the Harmonic Oscillator Model of Aromaticity (HOMA)^{10,11} on the optimized M06-2X/6-31+G(d) vacuum fullerene structures to gain some insight about the aromatic character of relevant hexagons. The bond lengths used in the calculation of HOMA indices were taken from the M06-2X optimized structures. HOMA indices were calculated using the refined model of HOMA¹⁰:

$$\text{HOMA} = 1 - \left[\alpha (r_{\text{opt}} - r_{\text{av}})^2 + \alpha/n \cdot \sum (r_{\text{av}} - r_i)^2 \right] = 1 - \text{EN} - \text{GEO}$$

73

where n is the number of bonds considered in the summation ($n = 6$ for the case of hexagons), r_{opt} stands for the optimal value of a specific bond length in a fully aromatic system (for C-C bonds $r_{\text{opt}} = 1.388 \text{ \AA}$)¹¹, r_{av} is the average bond length of the n bonds, r_i is the bond length of bond i , and $\alpha = 257.7 \text{ \AA}^{-2}$ is a normalization constant. The term EN is closely related to de-aromatization due to bond energies and GEO is attributed to de-aromatization due to geometric contributions, namely bond length alternation.

In our HOMA analysis we have distinguished between three types of hexagons (see Fig. 54): Type-I (the normal hexagons of C₆₀), Type-II (the four hexagons adjacent to an addend), and Type-III (the superposition of two Type-II hexagons). This distinction is based on the different bond topology and calculated HOMA indices, which increase HOMA (higher aromaticity) in the order: Type-I < Type-II < Type-III. The detailed results

of our HOMA analysis are presented in Table 17. In C_{70} there are three types of hexagons: Ia, the hexagons in the edges of C_{70} ; Ib, the hexagons in the center of the equatorial belt of C_{70} ; and Ic, the rings adjacent to Ib in the equatorial belt (see Fig. 55 for a visual display). This, analogously to before, gives rise to three different Type-II rings in C_{70} adducts: IIa, IIb, and IIc.

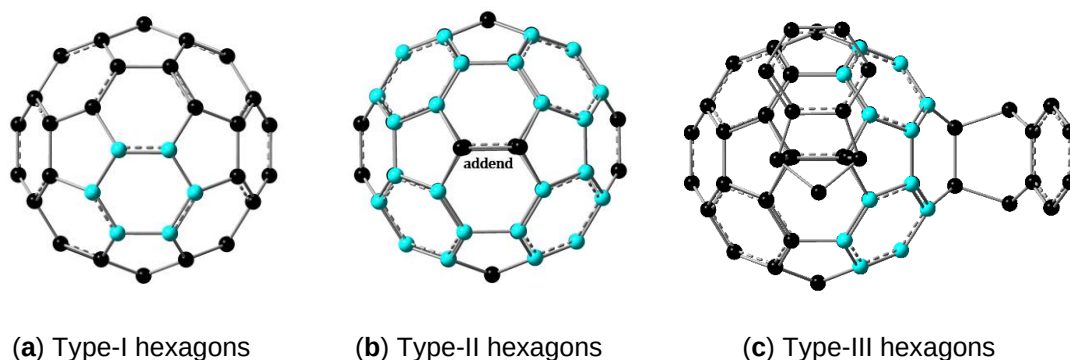


Fig. 54: Schematic view of the three types of hexagons considered in the HOMA analysis (in blue): (a) regular hexagons in C_{60} ; (b) and (c) adjacent hexagons to the addends in fullerene adducts, which, due to release of bond strain, can become more aromatic. In the case of (c) they are simultaneously adjacent to two addends. Structures taken from the optimized M06-2X/6-31+G(d) geometries.

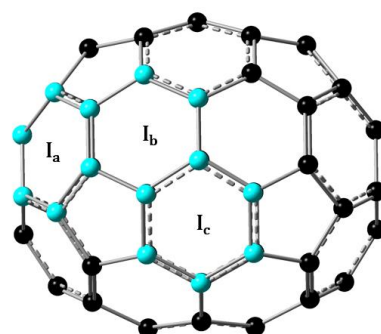


Fig. 55: Designated types of rings in C_{70} . The same logic applies to Type-II rings, except they are adjacent to an addend. Structure taken from the optimized M06-2X/6-31+G(d) geometries.

Table 17 shows the average HOMA results for each type of hexagon in the fullerenes studied; the detailed results for each individual hexagon are presented in Appendix B1. We chose to present the average values for a question of simplicity and because the HOMA values do not vary significantly within the same type of hexagon. Also of note is the fact that addition of the addend only alters the aromaticity of the four adjacent hexagons; all the others remain similar to the Type-I hexagons in the parent C_{60} or C_{70} . The results reveal a clear gain in aromaticity in the four hexagons adjacent to the adduct, in the C_{60} adducts HOMA increases from ~ 0.2 (Type-I) to 0.4 - 0.5 (Type-II). This increase of aromaticity is manifested by a decrease of both EN and GEO

parameters, although according to HOMA, de-aromatization in fullerenes has a stronger contribution from bond length alternation. In the case of the bisadducts, the aromaticity gain is even larger if the ring is simultaneously adjacent to both addends (Type-III), in which case the HOMA value is ~ 0.7 . All three equatorial isomers of AICBA have two such hexagons, which can help explaining their higher stability. However, aromaticity changes do not seem enough to explain the relative stability of *trans*-3 isomers, which remains to be explained. The same trend upon addend addition is observed in C_{70} . Although aromaticity has also a contribution for $\Delta_r E_{el}$, the differentiation between $AC_{70}MA$ isomers is better explained by bond curvature and release of strain.

Table 17: HOMA analysis of aromaticity, including the average EN and GEO values, for the hexagons in fullerenes and hexagons adjacent to the addend in the respective adducts, rings in which there is an increase in aromaticity after the diene binds. The average values were calculated by averaging over all adjacent rings of the same type.

Molecule	<EN>	<GEO>	<HOMA>	Hexagon Type (Qty.) ^a
C_{60} ^b	0.267	0.529	0.204	I (20)
C_{70}	0.219	0.462	0.319	Ia (10)
	0.473	0.705	-0.177	Ib (10)
	0.253	0.259	0.489	Ic (5)
ICMA	0.162	0.366	0.471	II (4)
ACMA ^c	0.158	0.368	0.474	II (4)
$AC_{70}MA$ isomer <i>a</i>	0.126	0.299	0.575	IIa (2)
	0.330	0.585	0.085	IIb (2)
$AC_{70}MA$ isomer <i>b</i>	0.118	0.306	0.576	IIa (2)
	0.178	0.199	0.624	IIc (2)
AICBA <i>trans</i> -1	0.160	0.354	0.486	II (8)
AICBA <i>trans</i> -2 <i>a</i>	0.163	0.363	0.474	II (8)
AICBA <i>trans</i> -2 <i>b</i>	0.163	0.363	0.474	II (8)
AICBA <i>trans</i> -3 <i>a</i>	0.168	0.368	0.464	II (8)
AICBA <i>trans</i> -3 <i>b</i>	0.167	0.367	0.465	II (8)
AICBA <i>trans</i> -4 <i>a</i>	0.080	0.217	0.703	III (1)
	0.163	0.369	0.468	II (6)
AICBA <i>trans</i> -4 <i>b</i>	0.083	0.228	0.690	III (1)
	0.166	0.377	0.457	II (6)
AICBA <i>e</i> -face <i>a</i>	0.084	0.222	0.694	III (2)
	0.158	0.356	0.486	II (4)
AICBA <i>e</i> -face <i>b</i>	0.086	0.232	0.682	III (2)
	0.160	0.356	0.484	II (4)
AICBA <i>e</i> -edge	0.085	0.226	0.689	III (2)
	0.159	0.358	0.483	II (4)

^a Type of hexagon and quantity of each type. ^b All 20 hexagons are equivalent. ^c All four hexagons adjacent to the addend are equivalent.

Another important remark is the difference in aromaticity found for C₇₀ hexagons – while Type-Ia (edge hexagons) have an aromaticity value not much different than C₆₀ hexagons, Type-Ic (equatorial hexagons) have a much higher HOMA value (~0.5), thus being more aromatic; and Type-Ib (hexagons adjacent to Type-Ic hexagons) are slightly anti-aromatic.

4.2. Kinetics and thermodynamics of the Diels-Alder reaction between fullerenes and anthracene

4.2.1. Equilibrium study in the reactor

The equilibrium constants determined by the study in the reactor explained in Section 3.1.6. are presented in Table 18, with the respective standard uncertainties. In this temperature range, the equilibrium constants for C₆₀ are more than twice the equilibrium constants for C₇₀. This is due to, as we will see forward, a significantly less exothermic reaction counterbalanced by a lower entropic loss (less negative entropy of reaction) in C₆₀.

Table 18: Equilibrium constants and respective standard errors for the C₆₀/C₇₀ + anthracene reaction study in the reactor, obtained using the *HypSpec* program. The standard state is $c^0 = 1 \text{ mol}\cdot\text{L}^{-1}$.

$T / ^\circ\text{C}$	K_{eq}	
	C ₆₀ + ant $\rightarrow$ C ₆₀ -ant	C ₇₀ + ant $\rightarrow$ C ₇₀ -ant
49.9	108.9 ± 2.3	45.8 ± 0.9
53.2	93.4 ± 1.5	40.3 ± 0.4
56.5	81.7 ± 1.5	29.2 ± 0.3
59.8	63.5 ± 0.9	24.3 ± 0.1
63.2	58.4 ± 0.8	19.1 ± 0.2
66.6	46.8 ± 0.6	14.8 ± 0.5

The obtained van 't Hoff plots (explained in Section 2.2. and 2.3.) from plotting the obtained equilibrium constants for the various studied temperatures are in Fig. 56. The values of enthalpy and entropy of reaction obtained from the plots are in Table 19. One data point was excluded from the C₇₀ van 't Hoff plot for being an outlier.

Interpreting these values, we see that C_{70} has a more exothermic reaction (more negative enthalpy change, which makes the reaction more favorable) and a more negative entropy change (which makes the reaction less favorable).

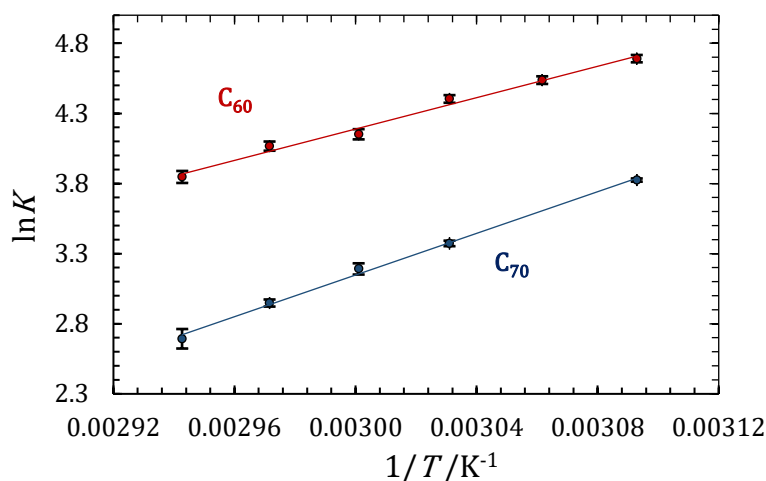


Fig. 56: Van 't Hoff plots for C_{60} + anthracene (red) ($R^2 = 0.989$) and C_{70} + anthracene (blue) ($R^2 = 0.997$) UV-Vis study of equilibrium on a reactor at different temperatures, with respective uncertainties of the data points shown as error bars. Uncertainties presented are 2 times the standard error.

Table 19: Thermodynamic parameters obtained for the reaction between C_{60}/C_{70} and anthracene in the UV-Vis study of equilibrium on a reactor at different temperatures. The standard state is $c^0 = 1 \text{ mol} \cdot \text{L}^{-1}$.

Reaction	$\Delta H_r^0 / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta S_r^0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
$C_{60} + \text{Ant} \rightarrow \text{ACMA}$	-46 ± 3	-105 ± 8
$C_{70} + \text{Ant} \rightarrow \text{AC}_{70}\text{MA}$	-62 ± 2	-159 ± 6

If we assume the presence of the entropy of symmetry in solution, there is an expected difference in the entropy terms only due to this contribution of $R \cdot \ln \frac{\sigma_{C_{60}} \sigma_{C_{70}-ant}}{\sigma_{C_{70}} \sigma_{C_{60}-ant}} = R \cdot \ln \frac{60}{10 \times 2} \approx 9.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. We also have to account for the entropy of isomerism (estimated in Section 4.1.3., using electronic energies of reaction, in solution, for C_{70}) of $3.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. These two contributions add to a total difference of $6.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The experimental difference obtained ($54 \pm 10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$) is much larger than this, and thus, the results using this method show a significant entropic difference not explained solely by symmetry and isomerism. Still, when compared with the theoretical results (in the absence of symmetry and isomerism contributions), one finds a big entropic difference where the theory predicts none. The manifestation of symmetry in these reactions in solution partially explains this difference.

In regard to the higher exothermicity of the reaction with C_{70} , since these differences are not predicted by the theoretical methods employed, and in the predominant isomer of C_{70} (isomer **a**) the diene interacts mostly in the local zone of the fullerene structure in which it is most similar to C_{60} (see Section 4.1.1.) – we cannot explain such a significant difference in enthalpy of reaction by simply looking at the molecules. The most plausible explanation seems to be solvation effects (which can also explain differences unpredicted theoretically in the entropies of reaction). The major difference between C_{60} and C_{70} is the equatorial belt of hexagons in the latter. The interaction of these hexagons with the solvent is different from the edges of C_{70} that are similar to C_{60} . If these interactions of the solvent with the C_{70} belt are partially disrupted by the introduction of addends, it could explain the difference in enthalpy if the interaction of the solvent molecules with the hexagons in the equatorial belt of C_{70} were less favorable than with the rest of the molecule and with C_{60} . These interactions would be dispersive π -- π interactions between the aromatic hexagons of the molecules and the benzene rings of *m*-xylene. The solvent model used in the theoretical study is implicit (meaning there are no explicit solvent molecules), and thus it would not (as in fact it did not) predict these differences.

The results for C_{70} in this Section give values higher than found for the kinetic study of the reaction with anthracene (results of which are presented in the next Section). In fact, both enthalpy and entropy of reaction for C_{70} in this scenario seem a little too high (in absolute value). In this study we used solutions up to a concentration of about $3 \times 10^{-2} \text{ mol} \cdot \text{L}^{-1}$ of anthracene, and used a region of the spectra with absorbances that reach a value of 2. The spectral range used is also limited, in order to avoid even higher values of absorbance being taken into consideration by *HypSpec*. Thus, it could be that the values are off because of one or a combination of these factors, and the results (for C_{70}) should be regarded with care.

4.2.2. Kinetic study

The obtained rate constants and consequent equilibrium constants obtained from the kinetic study of the reaction between C_{60}/C_{70} and anthracene (explained in Section 3.1.4.) are in Table 20. The rate constants obtained for the two different wavelengths of C_{70} show reproducible values. For the studied temperatures, the direct reaction in C_{70} is significantly slower (about two times slower) than the reaction with C_{60} . The reverse reaction, though, is more than two times faster for C_{70} . This makes the overall DA reaction favorable (in terms of equilibrium) in C_{60} . Though, we have to keep in mind that a factor

of 2 in these values corresponds only to a difference of $RT\ln(2)$ (around $2 \text{ kJ} \cdot \text{mol}^{-1}$ at the studied temperatures) in the activation Gibbs energy. Thus, these factors, as interpreted by looking at rate constants or equilibrium constants, might seem much more preponderate than they really are. Also, this is very dependent on temperature, and thus looking at the activation parameters gives one a better interpretation of the reaction.

Table 20: Direct and reverse reaction rate constants obtained for the different wavelengths studied for the reaction of C_{60} and C_{70} with anthracene.

$T/^{\circ}\text{C}$	C_{60} (705 nm)		C_{70} (665 nm)		C_{70} (677 nm)	
	$k_1 \times 10^3 / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_{-1} \times 10^5 / \text{s}^{-1}$	$k_1 \times 10^3 / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_{-1} \times 10^5 / \text{s}^{-1}$	$k_1 \times 10^3 / \text{L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$	$k_{-1} \times 10^5 / \text{s}^{-1}$
59.4	1.59	1.82	0.767	3.54	0.791	3.68
63.2	2.11	3.70	0.953	5.84	0.902	5.61
67.1	2.76	4.96	1.35	9.33	1.42	9.75
71.1	3.33	6.26	1.57	14.9	1.59	15.0
75.1	4.02	8.97	2.20	21.8	2.34	22.8
79.2	5.02	14.4	2.71	33.7	2.84	34.5

The equilibrium constants, obtained using Equation 4 of Section 3.1.4., are in Table 21. As a consequence of the differences in the rate constants, the equilibrium constants for C_{60} in this temperature range are about 4 times bigger than the equilibrium constants for the reaction with C_{70} . This comes as a consequence of the equilibrium constant being the ratio of the direct and reverse rate constants, the former being two times larger for C_{60} and the latter 2 times smaller for C_{60} .

Table 21: Equilibrium constants obtained for the different wavelengths studied for the reaction of C₆₀ and C₇₀ with anthracene. The standard state is $c^0 = 1 \text{ mol}\cdot\text{L}^{-1}$.

$T / ^\circ\text{C}$	K_{eq}		
	C ₆₀ (705 nm)	C ₇₀ (665 nm)	C ₇₀ (677 nm)
59.4	87.5	20.4	21.7
63.2	57.1	16.1	16.3
67.1	55.6	14.1	14.4
71.1	53.3	10.3	10.6
75.1	44.8	9.8	10.1
79.2	37.0	7.9	8.1

Plotting the rate constants obtained for the direct and reverse reactions as a function of $1/T$, the standard state activation entropy ($\Delta S^\ddagger$) and standard state activation enthalpy ($\Delta H^\ddagger$) for the direct and reverse reactions were obtained, using the Eyring equation (see Section 2.5.):

$$\ln \frac{k}{T} = -\Delta H^\ddagger / RT + \Delta S^\ddagger / R + \ln \left(\frac{k_B}{h} \right) \quad 74$$

where k is the rate constant (for the direct or reverse reaction), k_B is the Boltzmann constant and h the Planck constant. The thermodynamic parameters ΔH_r^0 and ΔS_r^0 can then be derived by Equation 75 (exemplified for ΔH_r^0 but analogous for ΔS_r^0 , see Section 2.5.). Obtained plots are in Fig. 57 and the obtained kinetic and thermodynamic parameters in Table 22 and Table 23.

$$\Delta H_r^0 = \Delta H_{direct}^\ddagger - \Delta H_{reverse}^\ddagger \quad 75$$

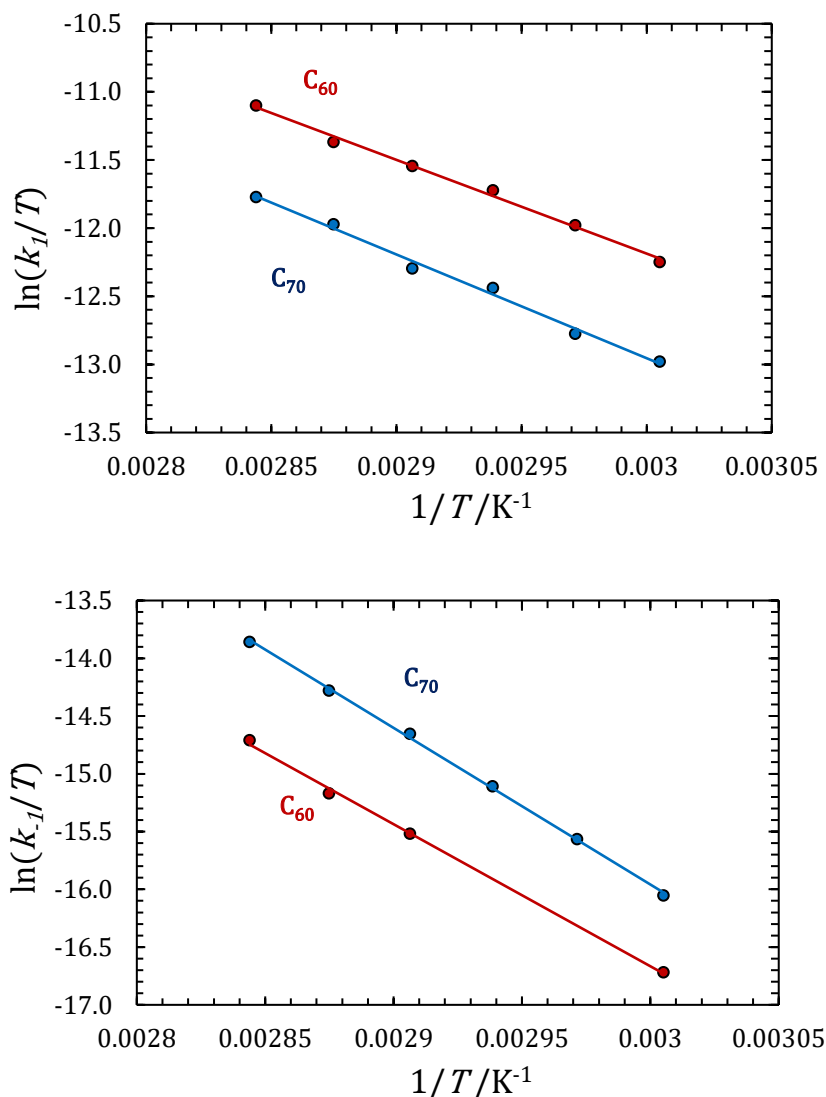


Fig. 57: Plots obtained for the direct (top) and reverse (bottom) Diels-Alder reactions. C_{60} +Ant is represented in red ($\lambda=705$ nm), C_{70} +Ant in blue ($\lambda=677$ nm). Direct reactions – C_{60} : $R^2 = 0.995$, C_{70} : $R^2 = 0.993$. Reverse reactions – C_{60} : $R^2 = 0.999$, C_{70} : $R^2 = 0.9985$.

Two points ($T = 63.37$ °C and 67.14 °C) were excluded from the reverse plot of C_{60} for being clear outliers. The parameters obtained for both wavelengths of C_{70} are, within the associated uncertainty, the same. The results show that C_{70} has a higher enthalpy barrier in the direct and reverse reaction, and a less negative entropy of activation for both direct and reverse reaction, also. This also manifests itself in the equilibrium entropy of reaction – with the entropy of C_{60} being less negative (favoring the reaction) than C_{70} . This entropic difference goes according to the tendency found for the equilibrium parameters in these reactions (Sections 4.2.1. and 4.3.). In the equilibrium enthalpy of reaction, no significant difference outside the experimental uncertainties could be found. The obtained equilibrium parameters for C_{60} are close to the ones found for the same

reaction in the previous Section. The equilibrium parameters for C_{70} are, though, considerably less negative (both entropy and enthalpy) than the ones obtained in the previous Section.

Table 22: Standard state activation enthalpies obtained from the Eyring equation for the reactions of C_{60} and C_{70} with anthracene. The standard state is $c^0 = 1 \text{ mol}\cdot\text{L}^{-1}$.

	Direct Reaction	Reverse Reaction	Equilibrium
Fullerene	$\Delta H^\ddagger / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta H^\ddagger / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta H_r^0 / \text{kJ} \cdot \text{mol}^{-1}$
C_{60} (705 nm)	57 ± 2	102 ± 3	-45 ± 4
C_{70} (665 nm)	65 ± 2	114 ± 1	-48 ± 3
C_{70} (677 nm)	63 ± 3	113 ± 2	-49 ± 4
C_{70} (average)	63 ± 2	113 ± 1	-48 ± 3

Table 23: Standard state activation entropies obtained from the Eyring equation for the reactions of C_{60} and C_{70} with anthracene. The standard state is $c^0 = 1 \text{ mol}\cdot\text{L}^{-1}$.

	Direct Reaction	Reverse Reaction	Equilibrium
Fullerene	$\Delta S^\ddagger / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta S^\ddagger / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	$\Delta S_r^0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$
C_{60} (705 nm)	-127 ± 6	-29 ± 8	-98 ± 10
C_{70} (665 nm)	-110 ± 7	10 ± 4	-120 ± 8
C_{70} (677 nm)	-115 ± 8	8 ± 5	-123 ± 9
C_{70} (average)	-113 ± 6	9 ± 3	-122 ± 6

The direct and reverse activation entropy is more positive for C_{70} when compared to C_{60} . This difference is bigger in the reverse reaction, and only in that case is it as expected following a symmetry loss between the transition state and the products. Since we suspect that (Section 3.2.1. and Section 3.3.) symmetry loss (in solution) in C_{60} plays a role in making its reaction entropically different from C_{70} – we interpret this huge difference in reverse reaction activation entropies between the two fullerenes as the symmetry breaking occurring in the transition state $\rightarrow$ products step (thus manifesting itself in the reverse reaction). For this to be the case - assuming symmetry manifests itself in the entropy of the transition state the same way as it does for species in equilibrium^{12, 13} -, the transition state needs to be symmetric. In this scenario the activation entropy for the reactants $\rightarrow$ transition state step (manifested in the direct reaction) is not affected by any symmetry loss, but the transition state $\rightarrow$ products step

is increased in C_{60} when compared to C_{70} (assuming transition states with full preservation of symmetry for both C_{60} and C_{70}) by $R \cdot \ln \frac{\sigma_{C_{60}} \sigma_{C_{70}-ant}}{\sigma_{C_{70}} \sigma_{C_{60}-ant}} = R \cdot \ln \frac{60}{10 \times 2} \approx 9.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The experimental difference obtained for this step, given by $-(\Delta S_{C_{60}}^{\ddagger} - \Delta S_{C_{70}}^{\ddagger})$ of the reverse reaction (see Section 2.5.), is $38 \pm 11 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which suggests a significant contribution from symmetry breaking.

Noting that the bigger entropic loss happens in the reactants $\rightarrow$ products step (with a largely negative entropy of activation), and is small in the retro reaction, we can conclude that the transition state should be an intermolecular complex in which the molecules are partially bonded (as expected of the classic transition state of the Diels-Alder reaction, and which explains the large lowering of entropy), but in which the symmetry number of the fullerene is preserved. Our explanation for a transition state that accommodates both these findings is a complex in which the anthracene migrates from one possible bond to another in the fullerene – and as such in a wave function view the anthracene is $1/30$ (in the case of C_{60}) located and bonded to each of the 30 possible [6,6] bonds in which it can bind. The transition state bond migration process would have to have a small activation energy, with the bond having a very short lifetime (much smaller than the lifetime of the transition state), allowing the migration to all the possible [6,6] bonds to occur to an extent such that it reaches the statistical limit where it spends the same time on each possible binding spot. This is a complicated requirement, but can be possible depending on the reaction coordinate associated with the anthracene migration.

Assuming a Boltzmann distribution for possible isomers in the transition state of C_{70} , with the same probabilities as obtained for the products in Section 4.1.3., the entropy of isomerism would increase the direct reaction's entropy of activation for C_{70} when compared to C_{60} by $3.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (estimated in Section 4.1.3.). This, within the experimental uncertainties, cannot be excluded. If this were the case, the transition state could not be, for C_{70} , as conjectured above, as the presence of isomers rules out the possibility of anthracene wandering through every [6,6] bond – it could only migrate between topologically equal [6,6] bonds, and only a partial symmetry of C_{70} would be maintained ($\sigma_{sym} = 5$) (except in isomer **d**, where all symmetry would be maintained (but this isomer is almost nonexistent)). Thus, to this value we have to add the symmetry breaking of C_{70} in the direct step ($R \cdot \ln 10 = 19.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$), giving an expected value due to this contribution and the isomerism contribution of $(\Delta S_{C_{60}}^{\ddagger} - \Delta S_{C_{70}}^{\ddagger}) = -22.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ for the direct reaction, which is not far from the experimental

difference ($-14 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$). Also, we would have to exclude this symmetry loss value from the reverse step, ending up with an expected value due to entropy of $-(\Delta S_{\text{C}_{60}}^{\ddagger} - \Delta S_{\text{C}_{70}}^{\ddagger}) = 28.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ in this scenario, which is close to the experimental difference of $38 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. In this scenario of a symmetric C_{60} transition state but an unsymmetric C_{70} transition state we obtain predicted values of difference in entropy due to symmetry and isomerism close to the experimental ones.

On the other hand, if isomers were not present in the transition state - as would be the case if the transition state is as conjectured - then, the entropy of activation of the reverse reaction would be decreased by $3.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, making $-(\Delta S_{\text{C}_{60}}^{\ddagger} - \Delta S_{\text{C}_{70}}^{\ddagger}) = 6.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ in total, adding both symmetry and isomerism contributions. This value is very small when compared to the activation entropy found experimentally. Still, some other contributions that cause a difference in entropy between this step for both fullerenes can exist (for example differences in the solvation of the transition state, and the differences in entropy of reaction found that are not explained by symmetry or isomerism), and as such our experimental resolution does not allow us to confirm (with complete confidence) this hypothesis. A deeper study of these reactions, with different methodologies, would be needed to confirm our transition state hypothesis.

In this analysis we assumed no significant entropy differences between C_{60} and C_{70} , besides contribution due to symmetry and isomerism. This is in a way supported by other results obtained in this thesis, and by the computational results which predict entropies of reaction equal (within the quantum uncertainty) for both fullerenes (Section 4.1.). Still these confirmations are based on equilibrium and thus only the fullerene and the adducts, and are being extended to the transition states as our assumption only. When compared to the theoretical results, which predict no significant difference in entropy, the large entropic difference found for the reverse reaction and in the equilibrium entropies of reaction seem to support that, in fact, symmetry manifests itself in these reactions in solution. Other differences due to solvation effects (in particular on the transition state) are certainly also present, which help explain the differences found for both kinetic and thermodynamic parameters of the two fullerenes.

4.3. Thermodynamics of the Diels-Alder reaction between fullerenes and 9,10-dimethylantracene

The equilibrium constants obtained in the study of the reactions of C_{60}/C_{70} and ICMA with DMA (explained in Section 3.1.5.) are presented in Table 24. In this temperature range, the equilibrium constants take the following ordering of magnitude $C_{60} \gg C_{70} > \text{ICMA}$. This is due to, as we will see forward, a significantly less loss of entropy in C_{60} , compared to the other two; while C_{70} , even though it is the less favored in entropy, it has a more exothermic reaction (more negative enthalpy of reaction).

Table 24: Equilibrium constants for the $C_{60}/C_{70}/\text{ICMA} + \text{DMA}$ reaction equilibrium study. For C_{60} solution 1 at 705 nm is presented, for C_{70} solution 2 at 665 nm, and for ICMA solution 2 at 705 nm. The standard state is $c^0 = 1 \text{ mol}\cdot\text{L}^{-1}$.

$T / ^\circ\text{C}$	K_{eq}		
	$C_{60} + \text{DMA} \rightarrow C_{60}\text{-DMA}$	$C_{70} + \text{DMA} \rightarrow C_{70}\text{-DMA}$	$\text{ICMA} + \text{DMA} \rightarrow \text{ICMA-DMA}$
37.3	-	-	128
40.9	-	166	90
44.5	474	127	69
48.1	381	98	-
49.9	-	-	53
51.8	304	75	-
55.6	242	58	37
59.4	193	46	-
63.2	160	36	23

The obtained van 't Hoff plots (explained in Section 2.2 and 2.3) (from plotting the obtained equilibrium constants for the various studied temperatures) are in Fig. 58. The values of enthalpy and entropy of reaction obtained from the plots are in Table 25. The average of the obtained values for the different solutions and for the different wavelengths studied are also presented.

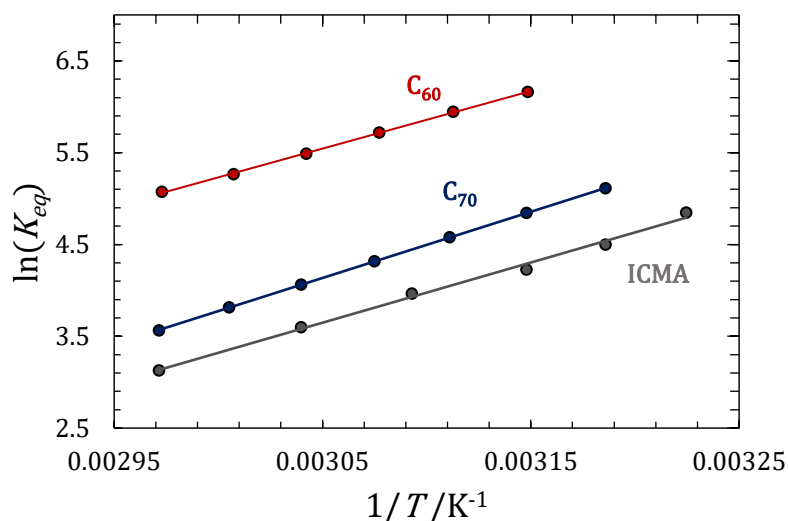


Fig. 58: Van 't Hoff plots for the C₆₀ (red)/C₇₀ (blue)/ICMA (gray) + DMA system. For C₆₀ this plot corresponds to solution 1 at $\lambda=705$ nm; for C₇₀ to solution 2 at $\lambda=665$ nm; and for ICMA to solution 2 at $\lambda=705$ nm. C₆₀: $R^2 = 0.9995$, C₇₀: $R^2 = 0.99997$, ICMA: $R^2 = 0.995$.

The results for the reaction with DMA show slightly more exothermic and more negative entropy of reactions than the reactions with anthracene. This was also found theoretically in the electronic energies of reaction (Section 4.1.1.). They also show a clear difference in the entropy of reaction, favoring C₆₀, as also found in the previous sections for the reactions with anthracene. This difference of entropies of reaction in this study is $29 \pm 11 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. This can contemplate the difference due to symmetry (symmetry in the fullerene-DMA adducts in the same as in fullerene-anthracene adducts) and isomerism contributions ($6.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, assuming the isomer distribution of the fullerene-DMA adduct isomers will be similar to the distribution of isomers in fullerene-anthracene adducts), paired with some other entropic contributions (as also found in the equilibrium study for the reactions with anthracene).

Table 25: Thermodynamic parameters obtained for the reactions with C₆₀, C₇₀ and ICMA with DMA for the various samples and wavelengths studied. Uncertainties of the average values are the standard deviation of all individual values, except for the case of ICMA in which it was calculated as the propagation of uncertainty formula for the average (one half of the square root of the sum of the squared uncertainties of the two values). The standard state is $c^0 = 1 \text{ mol} \cdot \text{L}^{-1}$.

Fullerene	wavelength / nm	$\Delta H_r^0 / \text{kJ} \cdot \text{mol}^{-1}$	$\Delta S_r^0 / \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	Sample
C ₆₀	498	-52.5 ± 0.7	-113.7 ± 2.2	1
		-57.4 ± 0.5	-129.1 ± 1.4	2
	705	-51.9 ± 0.5	-112.0 ± 1.6	1
		-50.7 ± 1.2	-109.0 ± 3.7	2
average	-	-53 ± 3	-116 ± 9	-
C ₇₀	665	-59.8 ± 0.4	-150.4 ± 1.1	1
		-59.7 ± 0.1	-147.6 ± 0.4	2
	677	-57.6 ± 0.6	-144.6 ± 1.9	1
		-56.1 ± 0.4	-138.1 ± 1.2	2
average	-	-58 ± 2	-145 ± 5	-
ICMA	705	-53.6 ± 0.7	-133.7 ± 2.0	1
		-54.5 ± 2.0	-135.9 ± 6.2	2
average	-	-54 ± 1	-135 ± 3	-

For the reaction of ICMA with DMA, the enthalpy change is similar to the reaction between C₆₀ and DMA – the mono and bisadduct formation is similar in enthalpy terms. In terms of entropy, the first addition (the reaction of C₆₀) is favored when compared to the second addend addition (the reaction of ICMA). An expected difference due to the entropy of symmetry for C₆₀ when compared to ICMA ($R \cdot \ln(\sigma_{C_{60}}/\sigma_{C_{60}-ant}) = R \cdot \ln(60/2) = 28.3 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (since ICMA has no symmetry and neither do its adducts); and due the entropy of isomerism contribution for ICMA, calculated in Section 4.1.3., ($20.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$); is $8.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. The experimental difference is $19 \pm 10 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$. Thus, it is plausible within the uncertainties of the methodology, that the major differences in entropy are due to the manifestation of symmetry in solution and isomerism. Also, this is supported by the theoretical calculations, which find no entropic or enthalpic distinction on the thermodynamical reactivity of C₆₀ vs ICMA (first vs second addition) (Section 4.1.4). Thus, we can say that symmetry explains the higher (thermodynamical) reactivity of the first Diels-Alder addition in fullerenes, when compared to the second addition (for systems where the entropy of isomerism contribution is not much higher than in this case – which happens if many isomers are equally stable). This can also change if the dienes have some kind of stabilizing

interaction when as addends. But, independent of the case, and generally (according to our studies) - symmetry seems to be a factor at play in comparing reactivity.

Comparing ICMA with C_{70} , their symmetry and isomerism contributions are very similar and thus are expected to cancel out (ICMA has $\sigma_{sym} = 1$ and thus the expected symmetry difference is $R \cdot \ln(\sigma_{C_{70}}/\sigma_{C_{70}-DMA}) = R \cdot \ln(10) = 19.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ (since the major isomers of C_{70} do not have symmetry)). The estimated entropy of isomerism of C_{70} is $3.0 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which when added to the symmetry value gives a total contribution of $22.1 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, which is very close to the $20.7 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ of entropy of isomerism of ICMA estimated in Section 4.1.2. Thus, only a very small difference in entropy due to these contributions is expected. The experimental difference is $10 \pm 6 \text{ kJ} \cdot \text{mol}^{-1}$, which should be due to other entropic contributions.

Again, in this study we find entropic contributions which can partially be explained by the manifestation of the effects of symmetry in entropy for reactions in solution. Still, the entropy of isomerism is estimated theoretically and we've seen solvation is insufficiently described by the computational method. If the "real" solvation makes a different distribution of isomers in ICMA that gives a lower entropy of isomerism, part of these entropic differences found that are not explained by symmetry and isomerism could actually be justified with this refined isomerism.

4.4. Results of the high-performance liquid chromatography study

The chromatograms for the six solutions A,B,C,D,E and F are in Fig. 59 to Fig. 64. This analysis is qualitative only, as we didn't use the peak areas to quantify the reactivity.

Comparing the chromatograms, we see that, since unlike in solutions with C_{60} and anthracene, there is no noticeable new peak (not present in the standard solutions of only one of the species) corresponding to the formed ICMA-anthracene (AICBA) adduct. Thus, ICMA does not, or reacts to a very reduced extent with anthracene - when compared to C_{60} . This agrees with the results found for the reaction with DMA, in which the reaction of anthracene with ICMA should be disfavored in relation to C_{60} in entropy. The equilibrium constant of C_{60} at 70°C is, according the results we found, more than 6x as big as for ICMA. Admitting this is also the case with anthracene (as appears to be and is expected to be, because the dienes are not much different), then it is expected that in equilibrium there should exist significantly less ICMA-anthracene than C_{60} -anthracene, which explains why it isn't even detectable. This is another evidence, confirming our

findings, that, in general, (but which might change for special dienes) monoadducts are formed more extensively than bisadducts. Also, only one new peak shows when in the solutions where C_{60} reacts with anthracene (D and F), thus this confirms that only the first addition and formation of the monoadduct is significant, confirming previous results (in this case the molar ratio of anthracene/fullerene was 2:1).

Every peak (except for C_{60} in solution A) exhibited an unexplained splitting. Still, this does not affect any of the (qualitative) conclusions.

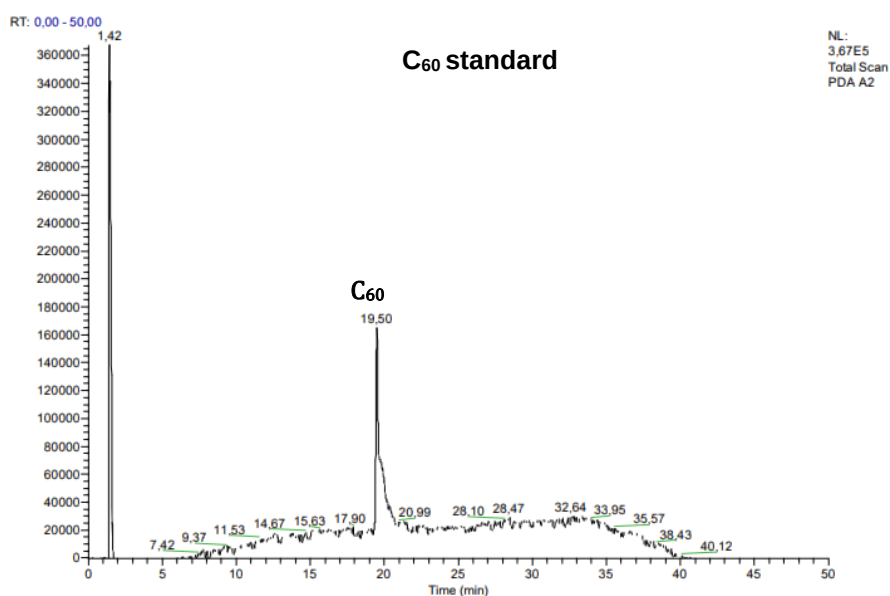


Fig. 59: Chromatogram of solution A showing the peak corresponding to C_{60} at 19.50 minutes of elution.

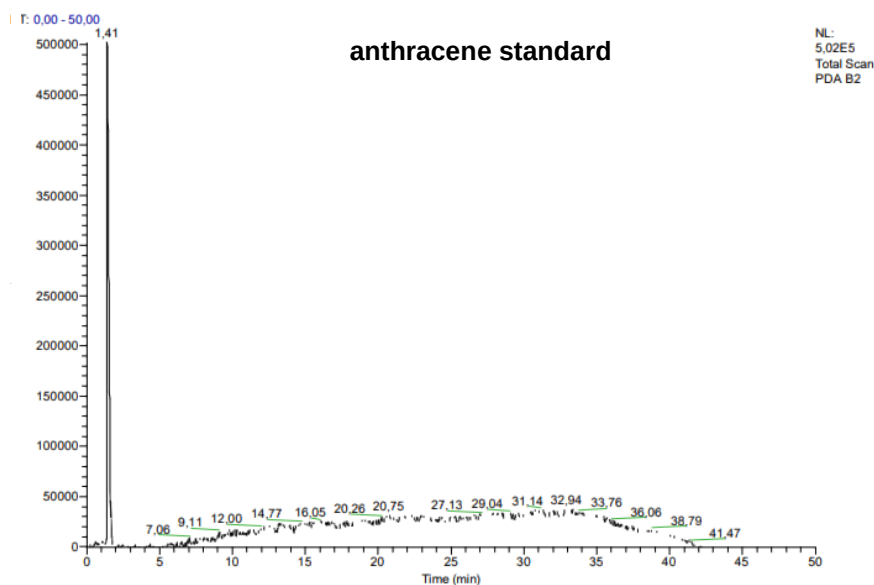


Fig. 60: Chromatogram of solution B showing no peaks corresponding to anthracene or *ortho*-terphenyl (they are mixed in the solvent peak).

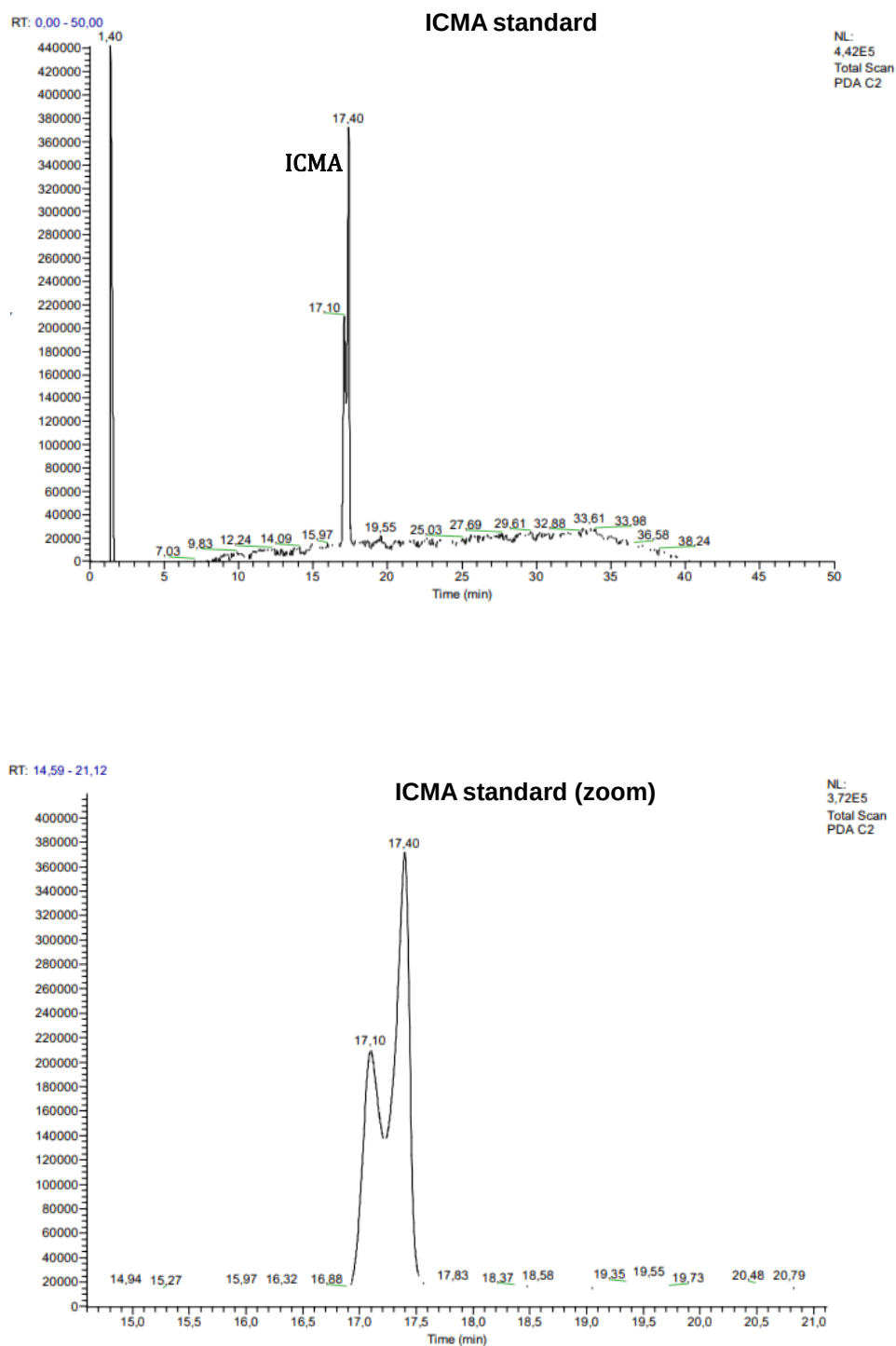


Fig. 61: Chromatogram of solution C showing the peak corresponding to ICMA at 17.10/17.40 (splitted) minutes of elution.

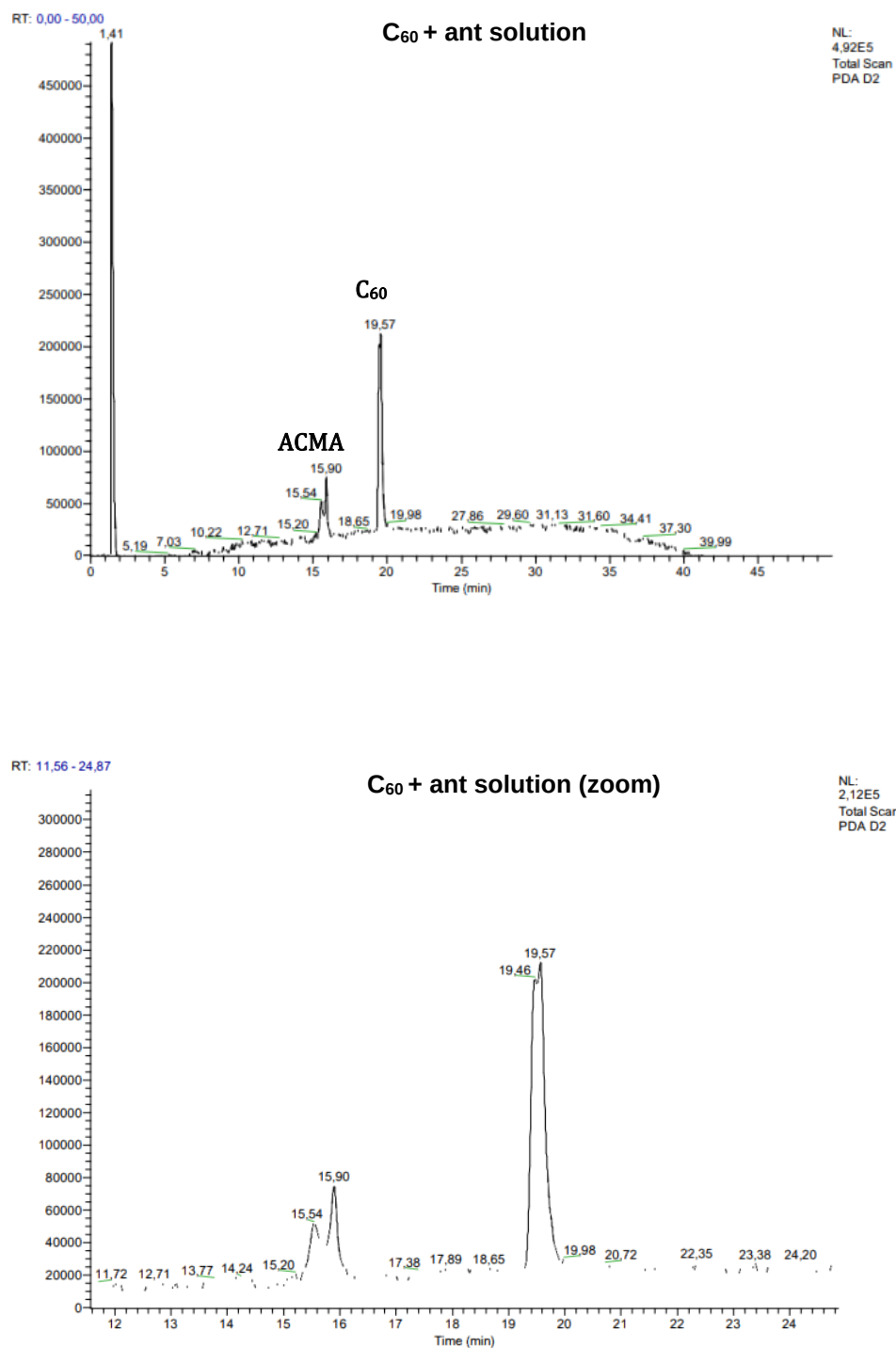


Fig. 62: Chromatogram of solution D showing the peaks corresponding to C₆₀ at 19.5 (splitted) minutes of elution, and another peak which must correspond to the a single adduct - ACMA (15.24/15.90 min, splitted).

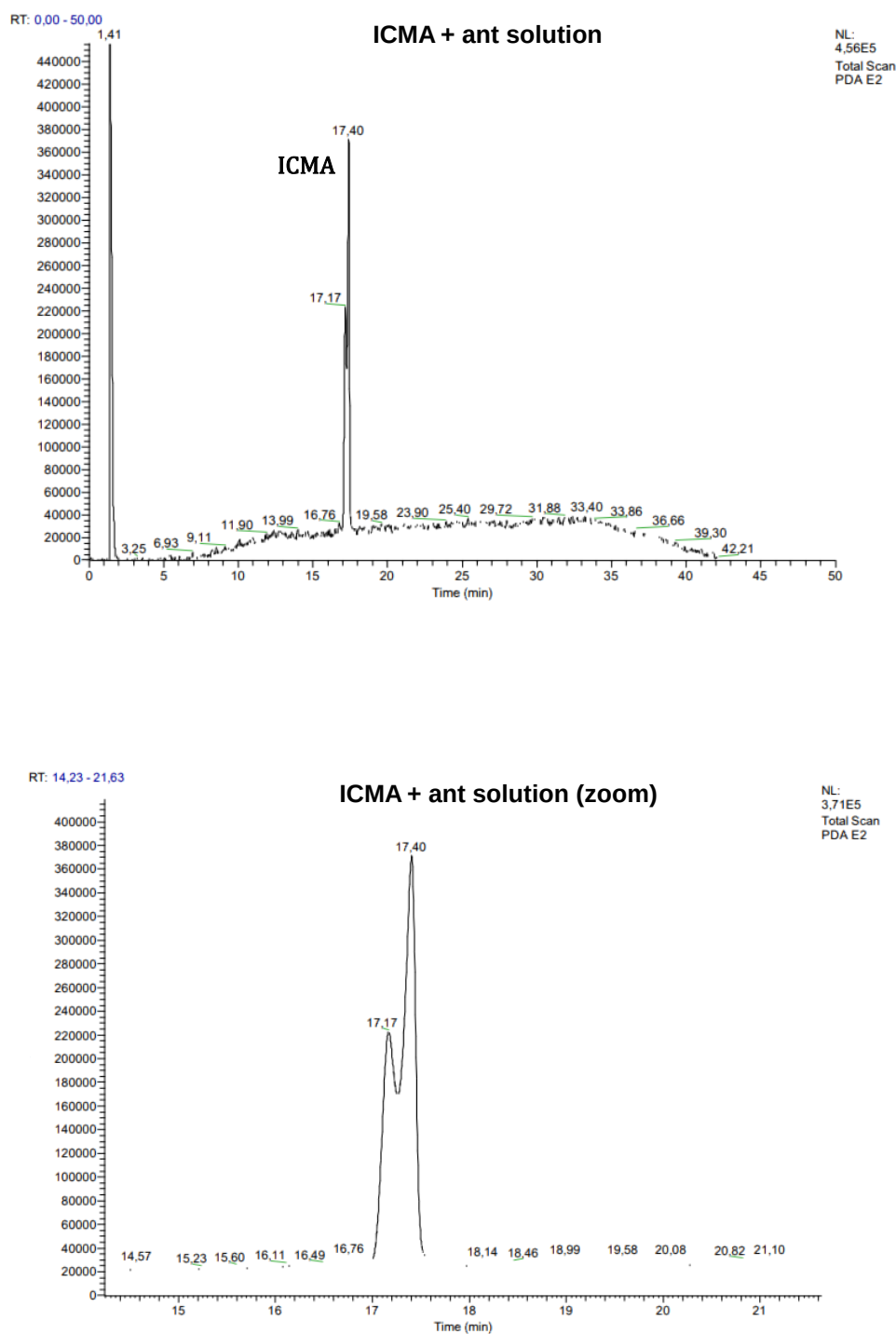


Fig. 63: Chromatogram of solution E showing the peak corresponding to ICMA at 17.17/17.40 (splitted) minutes of elution, and no significant detectable peak of the adduct with anthracene (AICBA).

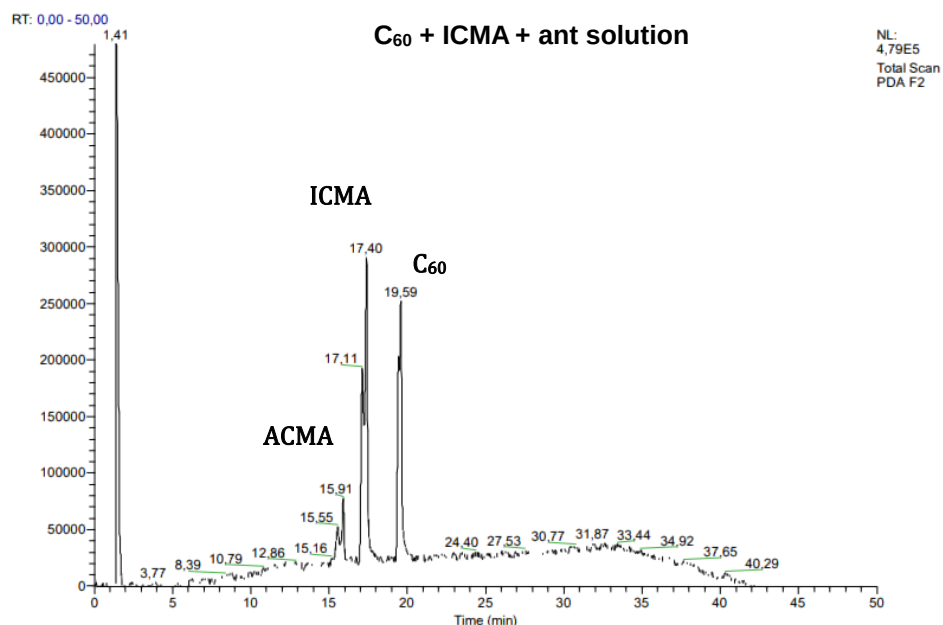


Fig. 64: Chromatogram of solution F showing the peak of C₆₀ at 19.59 min of elution, the peak of ICMA at 17.11/17.40 min, the peak of the C₆₀-anthracene adduct (ACMA) at 15.55/15.91 min, and again no peak of the ICMA-anthracene adduct.

In the chromatograms of solutions of C₆₀ and anthracene, we see the presence of a new peak (a peak not present in the standard solutions of only one of the species), which corresponds to the C₆₀-ant adduct formed by Diels-Alder reaction. In the case of chromatograms of solutions that contain ICMA and anthracene, we see that there is no noticeable new peak corresponding to the formed ICMA-anthracene (AICBA) adduct. Thus, ICMA does not, or reacts to a very reduced extent with anthracene - when compared to C₆₀. This agrees with the results found for the reaction with DMA, in which the reaction of anthracene with ICMA should be disfavored in relation to C₆₀ in entropy. The equilibrium constant of C₆₀ at 70 °C is, according to the results found for DMA, more than 6x as big as for ICMA. Admitting this is also the case with anthracene, then it is expected that in equilibrium there should exist significantly less ICMA-anthracene than C₆₀-anthracene, which explains why it isn't even detectable. This is another evidence, confirming our findings, that, in general, (but which might change for special dienes) monoadducts are formed more extensively than bisadducts. Also, only one new peak appears in the solutions where C₆₀ reacts with anthracene (D and F). Thus this confirms that only the first addition and formation of the monoadduct is significant, confirming previous results (in this case the molar ratio of anthracene/fullerene was 2:1).

Every peak (except for C_{60} in solution A) exhibited an unexplained splitting. Still, this does not affect any of the (qualitative) conclusions.

4.5. Global results on the Diels-Alder addition to fullerenes in solution

The global results on the Diels-Alder addition to fullerenes in solution are summarized in Table 26. Globally, we found the following conclusions on the reactivity towards Diels-Alder addition to fullerenes in solution:

- Thermodynamical reactivity of the fullerenes studied towards Diels-Alder cycloaddition at the studied temperatures varies according to: $C_{60} \gg C_{70} > \text{ICMA}$. In terms of kinetics, C_{60} as a faster forward and slower reverse rate at the temperatures studied.
- The exothermicity of the reaction with C_{70} is higher for both anthracene and DMA. This wasn't predicted by the theoretical methods employed, and can be explained by dispersive $\pi-\pi$ interactions with the solvent molecules, which are different in the C_{70} equatorial belt.
- The results support of the influence of symmetry on these reactions in solution – thus supporting hypothesis 1 (H1) introduced in Section 2.6., and that in fact its extension from the gas phase to solutions is valid.
- Symmetry and isomerism are the biggest factors in distinguishing first addition and formation of monoadducts from second additions and formation of bisadducts. Globally, the addition to C_{60} is more favorable than the addition to ICMA because of the effect of symmetry, which makes C_{60} much more reactive (even though the addition to ICMA has isomerism which compensates a part of this). This was also supported by the HPLC qualitative results.
- The symmetry breaking on these reactions occurs in the TS $\rightarrow$ products step. This finding also led us to hypothesize that the transition state for these reactions does not have isomers.
- C_{70} has a higher forward and reverse enthalpy of activation than C_{60} . It also has a less negative entropy of activation for both the direct and reverse reaction. This means that the rates for the reverse and direct reactions in C_{70} (when compared to C_{60}) are disfavored (slower) by enthalpy of activation and favored (faster) by entropy of activation.

- Diels-Alder reaction of fullerenes with DMA are more exothermic and show more negative entropy of reactions than the Diels-Alder reactions of fullerenes with anthracene.

- As seen in Table 26 the experimental and theoretical results for the enthalpies of reaction have a reasonable agreement.

Table 26: Compilation of experimental UV-Vis results comparing the different fullerenes and dienes studied. The standard state is $c^0 = 1 \text{ mol}\cdot\text{L}^{-1}$ for reactions in solution and $p = 1 \text{ bar}$ for gas phase reactions (computational results only).

Method ^a	Fullerene	Diene	$\Delta H_r^0 / \text{kJ}\cdot\text{mol}^{-1}$	$\Delta S_r^0 / \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ^b
Computational	C ₆₀	Ant	– 54	– 175
Equilibrium - Reactor	C ₆₀	Ant	– 46 ± 3	– 105 ± 8
Kinetics - UV	C ₆₀	Ant	– 45 ± 4	– 98 ± 10
Equilibrium - UV	C ₆₀	DMA	– 53 ± 3	– 116 ± 9
Computational	C ₇₀	Ant	– 53	– 179
Equilibrium - Reactor	C ₇₀	Ant	– 62 ± 2	– 159 ± 6
Kinetics - UV	C ₇₀	Ant	– 48 ± 3	– 122 ± 6
Equilibrium - UV	C ₇₀	DMA	– 58 ± 2	– 145 ± 5
Computational	ICMA	Ant	– 53	– 182
Equilibrium - UV	ICMA	DMA	– 54 ± 1	– 135 ± 3

^a The computational results presented are for the most stable isomer only. ^b The computational entropy results are considering the entropy of symmetry and entropy of isomerism, and are for the gas phase reaction.

4.6. Results on the retro Diels-Alder reaction of C₆₀-indene adducts

Concerning the DSC results, comparatively to the usual DSC peaks for a well-defined phase transition (e.g. melting), both ICMA and ICBA show broad peaks, spanning quite large temperature intervals. This is understandable since the process of indene release under the conditions of these DSC experiments is a non-reversible process that does not occur at a well-defined temperature. For ICBA, the retro Diels-Alder (RDA) indene release heat absorption peak was found to occur at a much lower temperature when compared to ICMA. The indene release in ICBA also occurs in a broader peak (as seen in Fig. 65, for 20 K·min^{–1} of scanning rate). The broader peak can be explained by the fact that there are two different indene groups to be released in ICBA

(while ICMA has only one), which can result in two different (in this case overlapping) peaks if the release of both indenenes does not happen simultaneous, but in two different steps; and due to the fact that the first loss of indene in ICBA molecules occurs in different isomers that make up the crystalline phase, which is expected to give a broader peak.

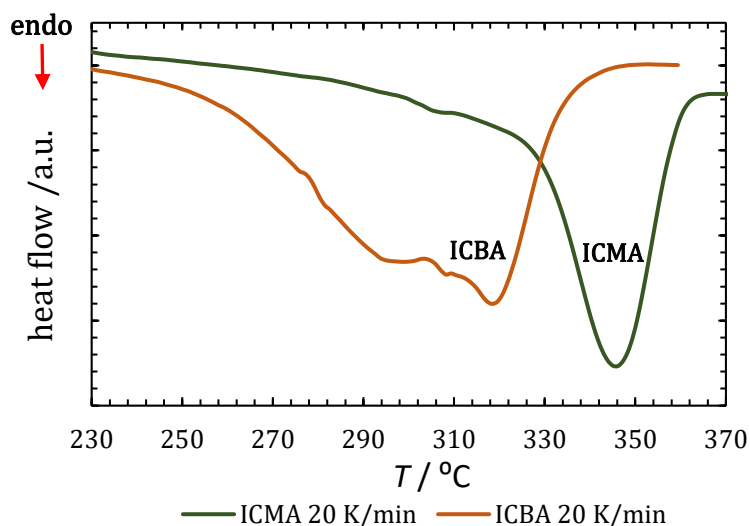


Fig. 65: DSC thermograms for ICMA (green) and ICBA (orange) for a scanning rate of 20 K·min⁻¹.

To have a better interpretation of these ICBA peaks, we tried changing the scanning and seeing the effects it had on the peaks, since higher scanning rates make the peaks more pronounced (see Section 2.9. for the effect of scanning rates on the obtained peaks for thermal events). The different peaks obtained for 10, 20 and 50 K·min⁻¹ scanning rates are in Fig. 66. As can be seen, increasing the scanning rate helps to better discern the presence of a first broad peak followed by a second sharper peak – which correspond to the first indene loss in the presence of isomers, and the second indene loss akin to ICMA (but in a, presumably, different crystalline structure), respectively. Thus, the retro Diels-Alder indene loss in ICBA occurs in two different steps, giving two different (but overlapping) peaks.

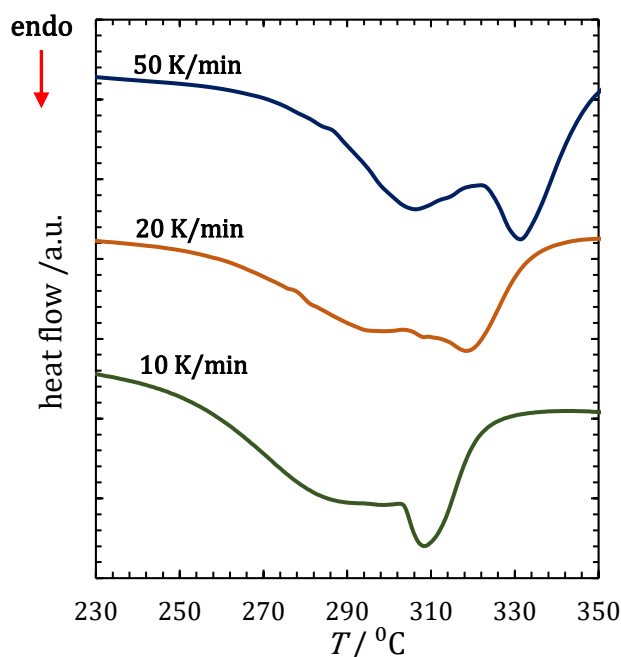


Fig. 66: DSC thermograms for ICBA for various scanning rates. The heat flows were divided by the scanning rate to facilitate the comparison.

The lower temperature of loss of both indene groups of ICBA when compared to the loss of indene in ICMA can be explained by the different crystalline phases. The structure of ICBA has, on most isomers, a more challenging packing which will lower the dispersion interactions on the crystalline structure when compared to ICMA, which can explain a lower temperature of loss of indene. This effect is also present on the second indene loss in ICBA, where the peak still does not occur at the same temperature as ICMA because the crystal does not have enough time to adjust to an ICMA structure (and also the two losses overlap, which means there is never a moment where the crystalline phase is composed only of ICMA; what happens, presumably, is the following: $\text{ICBA} \rightarrow \text{ICMA} + \text{ICBA} \rightarrow \text{ICMA} + \text{ICBA} + \text{C}_{60} \rightarrow \text{C}_{60}$).

In Table 27 and Table 28 we present the information and ΔH_r^0 for each experiment performed, and the average values obtained, for ICMA and ICBA respectively. The calibration constants used were chosen at the mean temperature of the peak. ΔH_r^0 were calculated based on Equation 76.

$$\Delta H_r^0 = \frac{\varphi \cdot M}{S}$$

where φ is the peak heat flow area divided by the sample mass, M the molar mass of the compound and S is the DSC sensitivity constant for mean temperature of the process, determined by previous calibration of the DSC. The calibrated $T_{onset,real}$ was calculated from the experimental $T_{onset,exp}$ as:

$$T_{onset,real} = 0.99701 \cdot T_{onset,exp} + 1.5089 \quad 77$$

as determined by previous calibration of the DSC. $T_{onset,real}$ is presented on the table as T_{onset} . Given the large peak widths observed in the DSC thermograms of both fullerenes, the enthalpies for the Retro Diels-Alder reactions, ΔH_r^0 , measured by DSC can only be regarded as semi-quantitative. Moreover, the ICBA peak is too large and is the overlap of two individual peaks. Hence, in this case it would be incorrect to report a value of T_{onset} considering the beginning of the peak since it would be unrepresentative of the whole process. In this way, we chose to report the average temperature of the peak, calculated as: $\langle T_{peak} \rangle = T_{final} - (w_{peak} / 2)$, where w_{peak} is the peak width in Kelvin units. However, despite these limitations, most DSC experiments show concordant results, even if comparing the ΔH_r^0 values for ICBA obtained at different scanning rates.

Table 27: Conditions and results for the ICMA retro Diels-Alder DSC experiments. ΔH_r^0 values were calculated based on Equation 76.

Exp.	Heating rate / K·min ⁻¹	<i>m</i> / mg	<i>T</i> _{onset} / K	<i>T</i> _{final} / K	<i>S</i> / μV·s·J ⁻¹	φ / μV·s·mg ⁻¹	ΔH_r^0 / kJ·mol ⁻¹
1	20	1.8549	602.84	632.31	3.06	366.0	100.2
2	5	1.8041	587.17	615.31	3.17	353.3	93.3
3	5	1.9191	587.73	615.37	3.17	361.3	95.5
4	5	1.7374	587.70	615.35	3.17	354.1	93.6
5	5	1.4960	587.75	615.30	3.17	353.4	93.4
average ^a			587.6 ± 0.2				93.9 ± 0.5

^a Average values refer only to the experiments performed at the heating rate of 5 K·min⁻¹. Uncertainties quoted as the standard deviation of the mean.

Table 28: Conditions and results for the ICBA retro Diels-Alder DSC experiments. ΔH_r^0 values were calculated based on Equation 76.

Exp.	Heating rate / K·min ⁻¹	<i>m</i> / mg	$\langle T_{\text{peak}} \rangle^a$ / K	T_{final} / K	S / μV·s·J ⁻¹	φ / μV·s·mg ⁻¹	ΔH_r^0 / kJ·mol ⁻¹
1	2	2.2746	551.29	572.38	3.41	608.0	170.0
2	5	2.3197	562.94	584.69	3.33	594.5	169.9
3	10	2.6730	570.77	594.72	3.28	578.1	167.9
4	20	2.0008	581.66	606.41	3.21	588.3	174.7
5	50	3.2666	595.82	621.62	3.11	562.9	172.6
average ^b							171.0 ± 1.2

^a Since the DSC peak spans a very large temperature interval (40 to 50 K depending on the heating rate), instead of T_{onset} we report the average temperature of the peak, $\langle T_{\text{peak}} \rangle$ calculated as: $\langle T_{\text{peak}} \rangle = T_{\text{final}} - (w_{\text{peak}} / 2)$, where w_{peak} is the peak width in Kelvin units. ^b Average values refer to all experiments. Uncertainties quoted as the standard deviation of the mean.

The found enthalpy change for the process in ICBA is slightly lower than twice the enthalpy for the process in ICMA (1.8x). This can be explained by the difference in crystalline structure mentioned before, which should make the release of indene in ICBA less endothermic. Intermolecular forces involving the indene group are also broken in the Retro Diels-Alder reactions studied and thus they are a direct contribution to ΔH_r^0 . In this way, weaker cohesive energy of the solid fullerene adducts decreases ΔH_r^0 . The differences in bond energy for the bisadducts when compared to monoadducts was predicted in this thesis (experimentally and theoretically) to not differ significantly, and thus that should not contribute to this difference found. The ΔH_r^0 for the retro Diels-Alder predicted computationally for ICMA (the reverse of the studied C₆₀ + indene reaction) in the gas phase is 105 kJ·mol⁻¹ at $T = 298.15$ K, and this value should become slightly smaller with increasing temperature (and the temperature of the enthalpy obtained in the DSC is higher). This gives a value close to the one found for the loss of indene in ICMA in the solid phase (Table 27). However, the process in the solid phase is significantly different from the gas phase, and intermolecular interactions - which can be expressed as molar enthalpies of sublimation ($\Delta_{\text{sub}}H$) have a direct contribution to the total energy of the reaction. This can be easily visualized in the thermodynamic cycle shown in Fig. 67. On one hand, indene interacts with the neighboring molecules, increasing its binding energy to the solid (total binding energy = C₆₀–Indene bond + intermolecular interactions), and thus increasing ΔH_r^0 ($\Delta_{\text{RDA}}H$). On the other hand, the cohesive energies of the two solids (ICMA and C₆₀) directly affect ΔH_r^0 . Given the similarity between ΔH_r^0 in the gas phase and in the solid state, one can conclude that the C₆₀ solid obtained after the retro Diels-Alder reaction and ICMA have similar $\Delta_{\text{sub}}H$, despite the larger molecular

size of ICMA. Its irregular structure probably hampers the establishment of optimal intermolecular contacts, reducing the packing efficiency when compared to the solid C_{60} in the reaction product (which differs from the most stable crystalline form of C_{60} at those temperatures, because the crystal did not adjust to its most stable structure, and is in a metastable state). This was verified by the color and shape of the crystal obtained after the process.

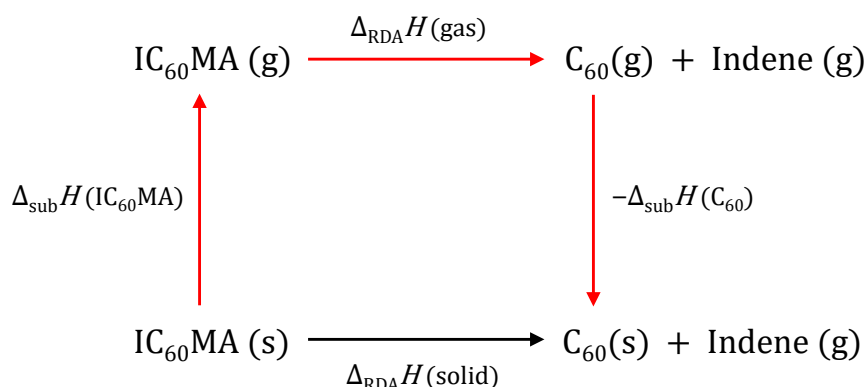


Fig. 67: Thermodynamic cycle showing the relation between the retro Diels-Alder (RDA) reaction in solid and gas phases and the sublimation of the fullerenes.

We have thus far assumed that the final product of the process, solid C_{60} , is in the same thermodynamic state in both ICMA and ICBA Retro Diels-Alder reactions. This may not be necessarily true since the solids can be formed in somewhat distinct structures and have no time to rearrange to the equilibrium structure of crystalline C_{60} . However, this contribution of slightly different solid phases of the product C_{60} is probably less significant than the crystal packing in the ICMA and ICBA solids. Remember that our ICBA sample is a mixture of isomers. If these isomers are co-crystallized that surely contributes for some loosening of the packed molecules, or even a significant loss of crystallinity, weakening intermolecular interactions. If each isomer crystallizes as a pure compound, this also contributes to larger variance of possible bond energies (considering both the molecular differentiation between them and the different crystal arrangements). Moreover, as more indene molecules bind to the symmetrical C_{60} core the molecular structure of the resulting fullerene becomes more irregular (with exception of some symmetrical isomers), and more C_{60} surface is inhibited from establishing intermolecular interactions. The most probable consequence of these factors is the decrease the cohesive energy density of the solid, and thus a decrease in the total binding energy of indene to the condensed state. A thermodynamic cycle for ICBA, similar to that in Fig. 67, suggests that (assuming the same enthalpy of reaction in the

gas phase for generating the bisadducts from C_{60} is twice the one found for the generation of ICMA), despite its large size, the $\Delta_{sub}H$ of ICBA is significantly lower than $\Delta_{sub}H$ of C_{60} .

Concerning the TG results, in Fig. 68 is the TG curve for ICMA and ICBA for a constant heating rate of $2\text{ K}\cdot\text{min}^{-1}$. The mass loss occurs at a much lower temperature for ICBA and spans a much larger temperature interval, confirming the results also found in the DSC experiments. The mass loss in ICBA corresponds to approx. 2 molar equivalents of indene, double that of ICMA, as expected.

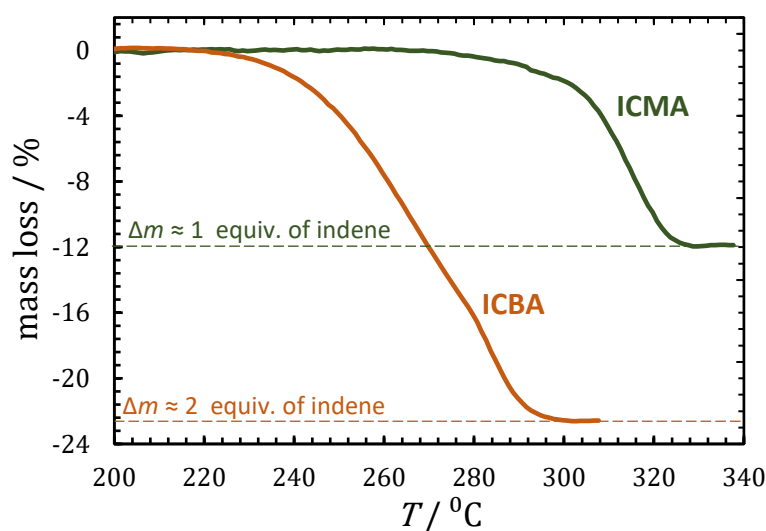


Fig. 68: Plot of the mass loss as a function of temperature for the TG experiments of ICMA (green) and ICBA (orange). Both experiments were carried at a constant heating rate of $2\text{ K}\cdot\text{min}^{-1}$.

The TG curve for one selected temperature in the ICMA and ICBA isothermal kinetic experiments are presented in Fig. 69. In ICMA (Fig. 69A) the $m = f(t)$ curve observed follows a regular exponential decay. However, in ICBA (Fig. 69B) the curve is clearly more complex, as it was expected from the overlap of two consecutive processes. A more detailed look into the ICBA curve suggests the superposition of a fast process (the major contribution in the initial period) and a slower process (which is more preponderant in the final period when the initial faster process has virtually ended). Similar curves were obtained at all the temperatures studied.

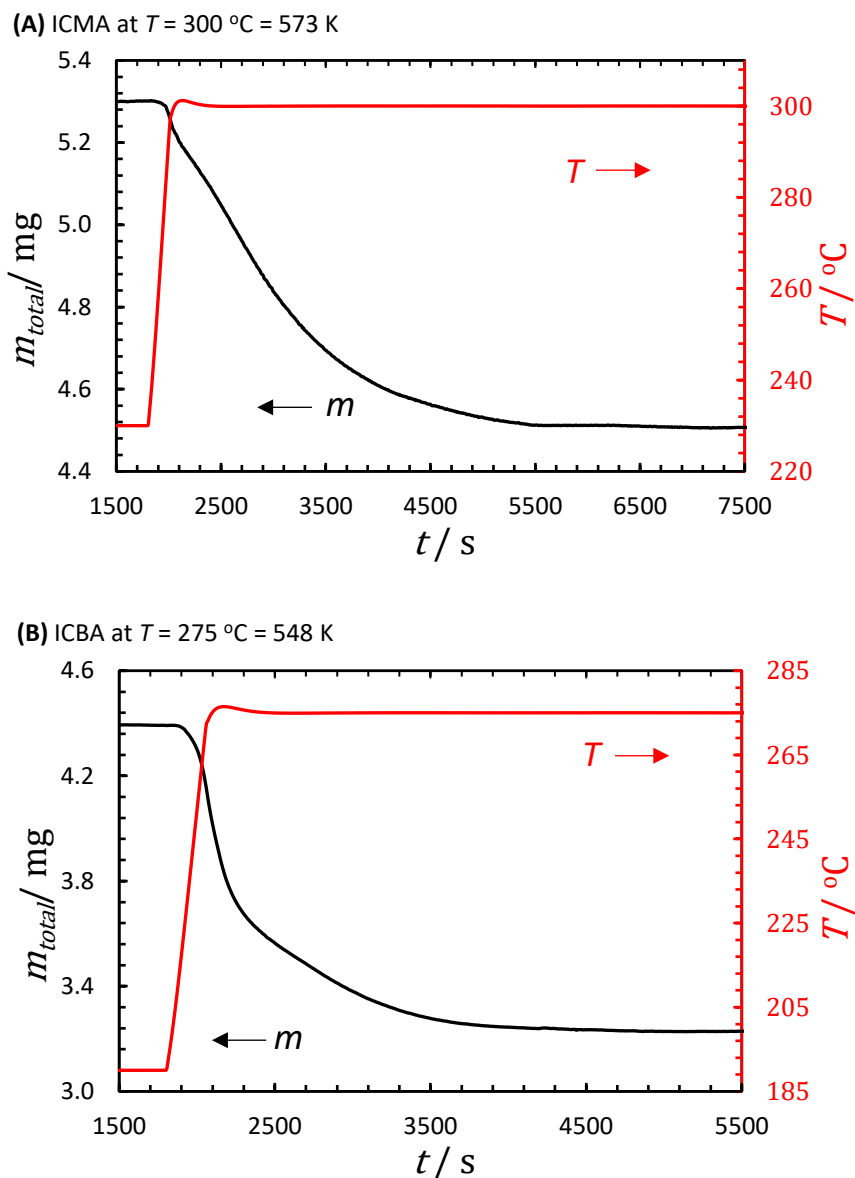
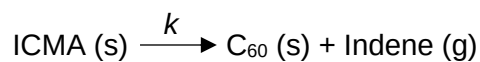


Fig. 69: Isothermal TG curves, $m = f(t)$, for the Retro Diels-Alder reaction (with loss of indene) in solid (A) ICMA and (B) ICBA, at the selected temperatures; m_{total} is the total mass of sample in the crucible.

In ICMA, and in accordance with the DSC and TG results, the kinetics of the process is easily described by the well-defined first-order reaction:



where k is the rate constant for the reaction and for which the rate law with respect to the moles of ICMA reacted is given by the following equation:

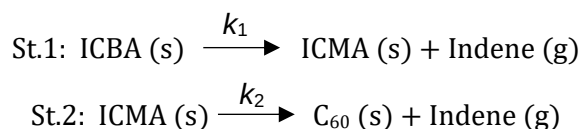
$$\frac{d n(\text{ICMA})}{dt} = -k \cdot n(\text{ICMA}) \quad 78$$

where $n(\text{ICMA})$ is the number of moles of ICMA. After integration, Equation 78 becomes:

$$\ln[n(\text{ICMA})] = -kt + \ln[n_0] \quad 79$$

where n_0 is the number of moles of ICMA at the beginning of the reaction, $t = 0$. The values of k at various temperatures were obtained from the slope of the linear regression of $\ln[n(\text{ICMA})] = f(t)$ on the experimental ICMA TG isothermal curves. The k values obtained for the temperatures studied are presented in Table 29.

However, the kinetics of Retro Diels-Alder in ICBA follow a more complex behavior. The DSC results, in particular the deconvolution of the DSC peak into 2 individual contributions, and the dynamic TG experiments; give strong indications that the observed mass loss in the kinetic TG experiments corresponds to the combination of the two consecutive steps:



where k_1 and k_2 are the rate constants for the first, St.1, and second, St.2, reaction steps, respectively, and $k_1 > k_2$ at the temperature intervals studied. In this way, we can express the rate law of indene formation as two consecutive first order reactions:

$$\frac{d n(\text{Ind})}{dt} = k_1 \cdot n(\text{ICBA}) + k_2 \cdot n(\text{ICMA}) \quad 80$$

where $n(\text{Ind})$ and $n(\text{ICBA})$ are the number of moles of indene and ICBA, respectively. Knowing that each individual step is a first order reaction, Equation 80 rearranges to ¹⁴:

$$\frac{d n(\text{Ind})}{dt} = k_1 \cdot n_0(\text{ICBA}) \cdot e^{-k_1 \cdot t} + \frac{k_1 \cdot k_2 \cdot n_0(\text{ICBA})}{k_2 - k_1} \cdot e^{-k_1 \cdot t} - \frac{k_1 \cdot k_2 \cdot n_0(\text{ICBA})}{k_2 - k_1} \cdot e^{-k_2 \cdot t} \quad 81$$

After integration and some rearrangement, Equation 81 becomes:

$$n(\text{Ind}) = n_{\text{total}}(\text{Ind}) - n_0(\text{ICBA}) \cdot e^{-k_1 \cdot t} - \frac{k_2 \cdot n_0(\text{ICBA})}{k_2 - k_1} \cdot e^{-k_1 \cdot t} + \frac{k_1 \cdot n_0(\text{ICBA})}{k_2 - k_1} \cdot e^{-k_2 \cdot t} \quad 82$$

where $n_{\text{total}}(\text{Ind})$ is the total indene mass released during the process. The values of k_1 and k_2 for the two-step reaction are presented in Table 29, at each temperature studied. They were obtained by fitting (via least-squares) Equation 82 to the experimental ICBA TG isothermal curves; the fitting parameters being k_1 , k_2 , $n_0(\text{ICBA})$ and $n_{\text{total}}(\text{Ind})$. The results are presented in Table 29. The experimental isothermal TG curves for ICBA were successfully fitted to Equation 82 for all the temperatures studied, with a small sum of residuals obtained between the model and the experimental curve. This supports that the Retro Diels-Alder reaction in ICBA can be perfectly described by a consecutive process of two first order reactions.

Table 29: Global results for the DSC (thermodynamics) and TG (kinetics) experiments of the Retro Diels-Alder reactions in the solid fullerenes ICMA and ICBA; $\langle T \rangle$ is the average temperature of the TG experiments.

	T / K^a	$k \cdot 10^3 / \text{s}^{-1}^b$		T / K^a	$k_1 \cdot 10^3 / \text{s}^{-1}$	$k_2 \cdot 10^3 / \text{s}^{-1}$
ICMA	563.2	0.496	ICBA	518.2	0.862	-
	568.2	0.792		523.1	1.52	0.110
	573.2	1.24		528.2	2.61	0.192
	578.1	2.00		533.2	3.80	0.336
	583.1	3.13		538.2	6.55	0.530
	588.2	4.94		543.2	11.6	0.921
				548.2	17.6	1.46
				553.3	-	2.38

^a The standard uncertainty of the temperature is $u(T/K) = 0.4 \text{ } ^\circ\text{C}$. ^b The standard uncertainty of k is $u(k/\text{s}^{-1}) = 0.002 \cdot k$.

The Arrhenius plots, $\ln k = f(1/T)$, of the reaction rate constants obtained for ICMA and for the two reaction steps for ICBA are presented in Fig. 70. The good linear fittings are further support that the Retro Diels-Alder reactions in the fullerenes studied are well described by our kinetic model. The thermodynamic (by DSC) and kinetic (by TG) parameters obtained in this study are compiled in Table 30, for comparison purposes.

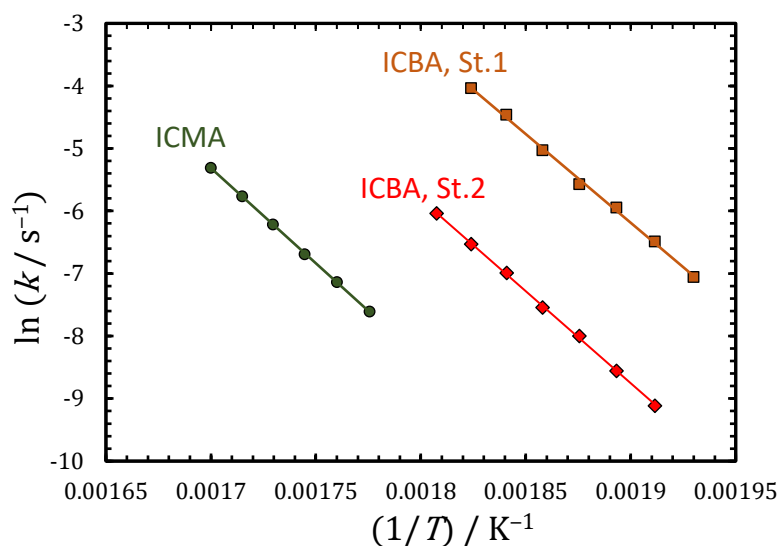


Fig. 70: Plot of $\ln k = f(1/T)$ for the Retro Diels-Alder reactions in solid ICMA (green dots, $R^2=0.9999$); and the first (St.1) (orange losangles, $R^2=0.9981$) and second (St.2) (red squares $R^2=0.9996$) reaction steps in solid ICBA, as measured by TG.

Table 30: Global results for the DSC (thermodynamics) and TG (kinetics) experiments of the Retro Diels-Alder reactions in the solid fullerenes ICMA and ICBA.

Compound	DSC results			TG results	
	T_{onset} / K	$\Delta H_r^0 / kJ \cdot mol^{-1}$	$\langle T \rangle^b / K$	$E_a / kJ \cdot mol^{-1}$	$\ln(A / s^{-1})$
ICMA	587.6 ± 0.2	94 ± 1	576 ± 1	253 ± 2	46.5 ± 0.3
ICBA ^a	567.3 ± 0.3	172 ± 2	St.1	533 ± 1	236 ± 5
			St.2	538 ± 1	245 ± 2

^a The TG results for the two individual steps (St. 1 and St. 2) of the Retro Diels-Alder reaction of ICBA are shown. ^b $\langle T \rangle$ is the average temperature of the TG experiments.

The kinetic TG results show that both steps of the ICBA reaction display a slightly lower E_a than ICMA. The transition state for the Retro Diels-Alder reaction certainly

involves the breaking of the C₆₀–indene bond, and the relatively large magnitude of E_a corroborates this assumption. The larger E_a for ICMA is probably resulting from the extra cohesive energy around indene in the crystal lattice that must be overcome to reach the transition state. The same applies to explain the greater E_a for St.2 of ICBA, relative to St.1. After release of the first indene the newly formed ICMA can rearrange to some extent in the lattice, achieving a more tightly packed state that will impose additional restraints to the release of the second indene. In ICBA k_2 is relatively small and the difference between k_1 and k_2 is large enough to allow for some fast crystal rearrangements after the loss of the first indene. However, due to the superposition of the two consecutive reaction steps, the solid is never pure ICMA during the Retro Diels-Alder reaction. Moreover, these rearrangements are probably not fast enough to allow for transient zones in the crystal to be packed like the equilibrium structure of pure ICMA, thus explaining why E_a is lower for St.2 of ICBA than for ICMA. Another possible contribution to the different magnitudes of activation energy for the first and second steps in ICBA is a different local environment of the two indene groups in the crystal lattice, which makes one more tightly bound to the crystal than the other.

The lower rate of Retro Diels-Alder for ICMA (and consequent higher decomposition temperature) is both the result of higher E_a and smaller A . The smaller pre-exponential factor, A , of ICMA can also be the result of its tighter packing, which imposes more steric constraints to the reaction path – the path to the transition state is narrower. The greater A for St.1 (relative to St.2 in ICBA and to ICMA), although somewhat masked by the experimental uncertainty, can be due to ICBA having twice the number of indene adducts. This doubles the probability, over time, of excess energy being concentrated on a C–Indene bond vibration that will lead to bond breaking and consequent release of indene.

Alternatively, we also analyze the kinetic data using Transition State Theory and the Eyring equation (Section 2.5.). The applicability of the TST to these solid phase reactions is questionable. These solid-phase reactions may be composed of more than one step, and are not guaranteed to be elementary, since the bond breaking/formation steps might not be the only steps needed for the reaction to occur, due to the complexity of the system. Unless this reaction has a step whose barrier is much more pronounced than the barrier of the other steps (making them negligible), the application of TST should be taken with a grain of salt, and only as semi-qualitative. If it is the case that one step is more important, the results of TST will approximately describe that step. In this case, it makes sense that the Diels-Alder bond breaking step is the defining step for these reactions. The magnitude of the individual $\Delta H^\ddagger$ and $\Delta S^\ddagger$ values are also significantly

affected by approximations used to derive the Eyring equation (which does not include any solid-state interactions or environments). Still, the relative comparison of the values for the two fullerenes can give us some insight – the Retro Diels-Alder reaction for ICMA and ICBA is a similar phenomenon (similar crystal environment, same nature of the transition state), and any inconsistencies in applying TST should cancel out to a large extent if comparing between the two.

The advantage of using TST relative to Arrhenius is the derivation of kinetic parameters, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, that can be easily interpreted on a chemical perspective. The discussion of the TST results (presented in Table 31) draws similar conclusions to the Arrhenius interpretation. The difference in $\Delta S_m^\ddagger$ between St.1 and St.2 of ICBA, $\Delta\Delta S^\ddagger \approx R \cdot \ln(2) \approx 5.8 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$, is precisely what is expected for a process of concentrating enough energy on a specific bond vibration, with twice the probability of occurring – due to ICBA having twice the number of reactive bonds relative to ICMA. This suggests a near-equivalency of both indene groups in the crystal lattice, which means the significant differences found in the activation energy of the two steps must be mostly due to rearrangement of the solid. The difference in $\Delta S^\ddagger$ between St.1 for ICBA and ICMA has margin for including this statistical contribution, plus some additional effect that probably comes from differences in crystal packing. Curiously, the ICMA/ICBA ratios for $\Delta H^\ddagger$ [248 / (231 + 240)], as determined by TG, and for ΔH_r^0 (94 / 172), as determined by DSC, are similar, ~ 0.54 , suggesting that crystal packing has a comparable effect on both phenomena.

Table 31: Enthalpies, entropies and Gibbs energies of activation, at the average temperature of the TG experiments, $\langle T \rangle$, for the Retro Diels-Alder reactions in the solid fullerenes ICMA and ICBA. The values were obtained using the Eyring equation.

TG results					
Compound		$\langle T \rangle / \text{K}$	$\Delta H^\ddagger$	$\Delta S^\ddagger$	$\Delta G^\ddagger$
			/ $\text{kJ} \cdot \text{mol}^{-1}$	/ $\text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$	/ $\text{kJ} \cdot \text{mol}^{-1}$
ICMA		576 ± 1	248 ± 2	128 ± 3	175 ± 2
ICBA ^a	St.1	533 ± 1	231 ± 5	139 ± 9	158 ± 7
	St.2	538 ± 1	240 ± 2	134 ± 4	168 ± 3

^a The TG results for the two individual steps (St. 1 and St. 2) of the Retro Diels-Alder reaction of ICBA are shown.

4.7. References

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Chapter 5:

Conclusions and Future Perspectives

In this thesis we proposed to scrutinize and compare the reactivity of fullerenes. We set out to figure how symmetry, isomerism, nature and presence of addends, solvation and other factors play a role in determining the reactivity of fullerenes. Our computational study predicted (when excluding symmetry and isomerism) no difference in thermodynamical reactivity of C_{60} , C_{70} and ICMA towards Diels-Alder cycloaddition. It indicated the presence of two major isomers for the C_{70} -anthracene adduct. We found that, besides the *cis* isomers, which are much more unstable due to repulsive forces between the addends, the isomers of AICBA are only slightly differentiated both in vacuum and in solution. We found no significant difference in (thermodynamical) reactivity between the Diels-Alder reaction of C_{60} and the Diels-Alder reactions generating the most stable isomers of C_{70} and ICMA. We found that aromaticity increases in the adjacent rings to which the addend binds, helping to stabilize the adducts. Equatorial isomers of AICBA are especially stabilized by this effect because they contain rings that are simultaneously adjacent to both addends. This helps explaining why the equatorial isomers are the most stable isomers of AICBA. Also, the effect of computational method and basis set suggests the existence of stabilizing dispersive interactions between the addend and the fullerene's surface.

We found experimentally that the thermodynamical reactivity of the fullerenes towards Diels-Alder cycloaddition (in the temperature ranges studied) goes according to: $C_{60} >> C_{70} > ICMA$. The higher reactivity of C_{60} compared to C_{70} and ICMA was found experimentally to have a significant contribution from the influence of molecular symmetry in the entropy of species in solution. This supports the hypothesis that predicts an influence of symmetry in the gas phase and solution, lowering the entropy of symmetrical species and making them entropically more reactive. It also supports that the hypothesis is indeed extendable from the gas phase to solution (at least for these systems), because the species have rotational motion and thus the reduced number of rotational levels compatible with its permutation symmetry play a role in decreasing the entropy of the solvated species. This result is import also in differentiating the first addition (and generation of monoadducts) from subsequent additions. The first addition is entropically favored when compared to the second addition (and generation of bisadducts), because of symmetry. However, the existence of isomers in the bisadducts can somewhat dilute this preference. The exothermicity of the Diels-Alder reaction of C_{70} with both anthracene and 9,10-dimethylantracene is higher than for the Diels-Alder reaction of C_{60} /ICMA. This wasn't predicted by the theoretical methods employed and was tentatively explained by dispersive interactions with solvent molecules. The solvent *m*-xylene probably interacts strongly with the equatorial belt of C_{70} than with C_{60} and the

edges of C_{70} (where it is locally similar to C_{60}), and such different solvation patterns can alter the relative reactivity of the fullerenes. This different solvent interaction can also contribute to make the entropy change for C_{70} less negative than for C_{60} and ICMA.

The results from the kinetic studies suggested that symmetry breaking occurs in the TS $\rightarrow$ products step – thus slowing down the reverse reaction. Moreover, we postulate a transition state, compatible with the experimental findings, where the addend partially binds to every possible [6,6] bond in the fullerene. It was found that C_{70} has a higher forward and reverse enthalpy of activation than C_{60} . It also has a less negative direct and reverse entropy of activation. Regarding the dienes, it was found, experimentally and computationally, that the Diels-Alder reaction of fullerenes with DMA is more exothermic and shows more negative entropies of reaction than the reactions with anthracene. This is probably due to the establishment of C-H $\cdots\pi$ interactions between the methyl groups of DMA and the surface of C_{60} . Good agreement was found between the experimental and theoretical values for the Diels-Alder reaction of fullerenes with anthracene in solution.

This combined computational and experimental approach showed that differences in reactivity of fullerenes is ruled by symmetry and isomerism effects, as well as solvation interactions.

In the retro Diels-Alder studies of crystalline ICMA and ICBA, the reaction was found to occur at a significantly lower temperature in ICBA, owing in part to the less efficient crystal packing in ICBA. In ICBA we found that this reaction occurs in two consecutive steps – the first loss of indene, with a faster rate; and the second loss with a slower rate. The first step occurs in a broader temperature range because of the presence of different isomers in the ICBA crystal. We also found, for ICBA, the enthalpy of the retro Diels-Alder reaction is slightly less than twice the one found for ICMA. This also supports the less efficient packing of ICBA. The activation energies found take the following order: ICMA > ICBA step 2 > ICBA step 1. This is mainly due to stronger solid-state interactions and better crystal packing in the same sequence. The first step of indene loss in ICBA shows a greater pre-exponential factor (A) than the second step and the indene loss in ICMA; partially due to the fact that it has two identical bonds which can break to generate the products. This was confirmed by a difference of $R \cdot \ln(2)$ observed between the activation entropy for the two steps in ICBA, which is exactly the factor predicted by this effect.

In the future, deeper studies in fullerene reactivity are still needed and would nicely complement the results of this thesis. The generation of bisadducts by C_{70} wasn't

evaluated in this work. Also, there is a panoply of possible other higher fullerenes to study, as well as C₂₈, the smaller stable fullerene. It would also be interesting to study third and subsequent additions, evaluating trisadducts and higher. The evaluation of reactions generating trisadducts is already ongoing on our laboratory. There is also the curious case of endohedral fullerenes – evaluating the differences in reactivity due to the presence of the caged molecule is important, because caging of molecules by fullerenes have found diverse applications – and there is the possibility of broken symmetry in these fullerenes, which would significantly alter their reactivity. Also, a study of the presence of symmetry in the dissolution energy of fullerene solids would help clear this symmetry effect even further. And, of course, there are many other possible dienes to study. In this thesis the diene effect wasn't deeply evaluated, but it is an important part in determining reactivity in this type of reaction. Another area we would like to better probe is the solvent effect. We saw many interesting effects in *m*-xylene, and studying the reactions in other mediums would make for interesting studies.

Appendix

Appendix A – UV-Vis spectra for concentrated solutions of anthracene and DMA.

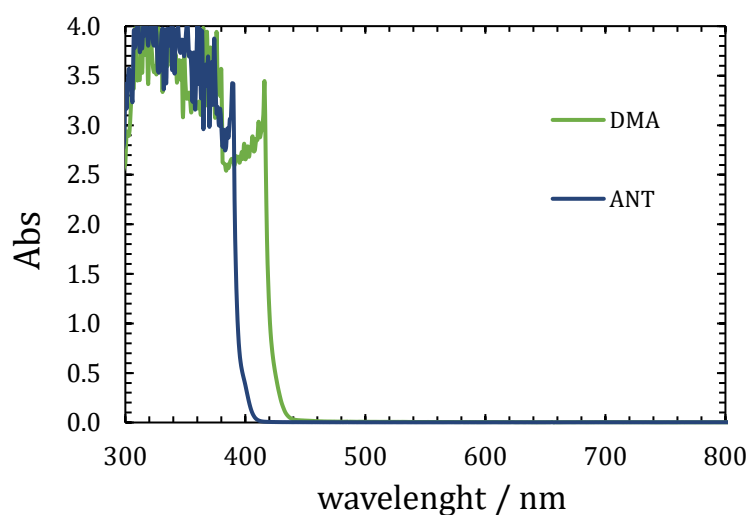


Fig. A1: UV-Vis spectra of 9,10-dimethylantracene (DMA, green) and anthracene (ANT, blue). In our region of interest (498 nm to 800 nm), there is no absorption of light due to either species. Concentrations – DMA: 0.0200 mol.L⁻¹; anthracene: 0.0238 mol.L⁻¹. These concentrations are beyond the highest concentration used in our studied.

Appendix B – Supplementary information for the theoretical calculations

Appendix B1 – Electronic energies for the species and discriminated HOMA values

Table B1: Electronic energies obtained (in vacuum) for the various species studied at different theoretical levels. M06-2X/6-311++G(2d,p), B3LYP/6-31+G(d), and MP2/cc-pVDZ are single point energy calculations on the optimized M06-2X/6-31+G(d) geometries.

Species	E_{el} / Hartree			
	M06-2X/ 6-31+G(d)	M06-2X/ 6-311++G(2d,p)	B3LYP/ 6-31+G(d)	MP2/ cc-pVDZ ¹
anthracene	-539.308194	-539.444350	-539.548294	-537.848034 (-536.038262)
indene	-347.614828	-347.704859	-347.775603	-
C ₆₀	-2285.492704	-2285.994963	-2286.220335	-2279.675979 (-2271.964664)
AC ₆₀ MA	-2824.837241	-2825.471834	-2825.765670	-2817.587061 (-2808.014434)
C ₇₀	-2666.503092	-2667.089136	-2667.356359	-
AC ₇₀ MA <i>a</i>	-3205.848078	-3206.566391	-3206.901523	-
AC ₇₀ MA <i>b</i>	-3205.846171	-3206.564118	-3206.896679	-
AC ₇₀ MA <i>c</i>	-3205.818709	-	-	-
AC ₇₀ MA <i>d</i>	-3205.774922	-	-	-
ICMA	-2633.151952	-2633.740334	-2634.007738	-
AICBA <i>trans</i> -1	-3172.494885	-3173.215574	-3173.550477	-
AICBA <i>trans</i> -2 <i>a</i>	-3172.495132	-	-	-
AICBA <i>trans</i> -2 <i>b</i>	-3172.495216	-	-	-
AICBA <i>trans</i> -3 <i>a</i>	-3172.496658	-	-	-
AICBA <i>trans</i> -3 <i>b</i>	-3172.496348	-3173.217473	-3173.552751	-
AICBA <i>trans</i> -4 <i>a</i>	-3172.494920	-	-	-
AICBA <i>trans</i> -4 <i>b</i>	-3172.494882	-	-	-
AICBA <i>e</i> -face <i>a</i>	-3172.496894	-3173.217558	-3173.552494	-
AICBA <i>e</i> -face <i>b</i>	-3172.496743	-	-	-
AICBA <i>e</i> -edge	-3172.496762	-	-	-

AICBA <i>cis</i> -3 <i>a</i>	-3172.490488	-	-	-
AICBA <i>cis</i> -3 <i>b</i>	-3172.490574	-	-	-
AICBA <i>cis</i> -2 <i>a</i>	-3172.489805	-	-	-
AICBA <i>cis</i> -2 <i>b</i>	-3172.484859	-3173.210505	-3173.543610	-

¹ The calculated Hartree-Fock energy is shown in parenthesis.

Table B2. Electronic energies obtained for the species in *m*-xylene, simulated using SMD – Solvent Model based on Density. The energies were obtained through single point calculations on the optimized geometries obtained in vacuum, at the M06-2X/6-31+G(d) level.

Species	$E_{el}^{m-xylene}$ / Hartree
anthracene	-539.324296
indene	-347.626159
C ₆₀	-2285.548057
AC ₆₀ MA	-2824.900524
C ₇₀	-2666.503092
AC ₇₀ MA <i>a</i>	-3205.919287
AC ₇₀ MA <i>b</i>	-3205.917180
ICMA	-2633.211855
AICBA <i>trans</i> -1	-3172.563408
AICBA <i>trans</i> -2 <i>a</i>	-3172.564002
AICBA <i>trans</i> -2 <i>b</i>	-3172.563872
AICBA <i>trans</i> -3 <i>a</i>	-3172.565535
AICBA <i>trans</i> -3 <i>b</i>	-3172.565046
AICBA <i>trans</i> -4 <i>a</i>	-3172.563268
AICBA <i>trans</i> -4 <i>b</i>	-3172.565046
AICBA <i>e</i> -face <i>a</i>	-3172.565521
AICBA <i>e</i> -face <i>b</i>	-3172.565133
AICBA <i>e</i> -edge	-3172.565868
AICBA <i>cis</i> -3 <i>a</i>	-3172.559316
AICBA <i>cis</i> -3 <i>b</i>	-3172.558671
AICBA <i>cis</i> -2 <i>a</i>	-3172.558345
AICBA <i>cis</i> -2 <i>b</i>	-3172.552854

Table B3: Thermal corrections to enthalpy (including ZPE) from $T = 0$ to 298.15 K, ΔH_f^{corr} , and absolute enthalpies, at $T = 298.15$ K, obtained from optimization and frequencies calculations for the various species using M06-2X/6-31+G(d).

Species	ΔH_f^{corr} / Hartree	$H(T = 298.15 \text{ K})$ / Hartree
Indene	0.150539	-347.4642888
Anthracene	0.206977	-539.1012174
C ₆₀	0.399011	-2285.093693
C ₇₀	0.465784	-2666.037308
IC ₆₀ MA	0.553810	-2632.598142
AC ₆₀ MA	0.609736	-2824.227505
AC ₇₀ MA <i>a</i>	0.678131	-3205.169947
AIC60BA <i>e</i> -face <i>a</i>	0.766103	-3171.730791

Table B4: HOMA analysis, decomposed in EN and GEO values, for the hexagon rings in C₆₀ and C₇₀, and hexagons adjacent to the addends in the respective adducts.

Species	EN	GEO	HOMA	Ring Type
C ₆₀ ¹	0.267	0.529	0.204	I
AC ₆₀ MA ²	0.158	0.368	0.474	II
IC ₆₀ MA	0.162	0.363	0.475	II
	0.162	0.363	0.475	II
	0.163	0.369	0.468	II
	0.163	0.369	0.468	II
AICBA <i>trans</i> -1	0.161	0.349	0.490	II
	0.161	0.349	0.490	II
	0.158	0.355	0.488	II
	0.158	0.355	0.488	II
	0.165	0.364	0.470	II
	0.165	0.364	0.470	II
	0.156	0.349	0.495	II
	0.156	0.349	0.495	II
AICBA <i>trans</i> -2 <i>a</i>	0.159	0.351	0.490	II
	0.174	0.382	0.444	II
	0.155	0.353	0.492	II
	0.165	0.373	0.462	II
	0.159	0.349	0.492	II
	0.166	0.359	0.475	II
	0.165	0.366	0.469	II
	0.162	0.371	0.467	II
AICBA <i>trans</i> -2 <i>b</i>	0.162	0.366	0.472	II
	0.169	0.379	0.453	II
	0.170	0.370	0.460	II
	0.164	0.347	0.489	II
	0.160	0.369	0.472	II
	0.155	0.352	0.493	II
	0.164	0.373	0.463	II
	0.160	0.349	0.491	II
AICBA <i>trans</i> -3 <i>a</i>	0.170	0.371	0.459	II
	0.176	0.388	0.436	II

	0.170	0.375	0.455	II
	0.163	0.346	0.491	II
	0.182	0.392	0.426	II
	0.160	0.357	0.483	II
	0.157	0.345	0.498	II
	0.164	0.367	0.469	II
AICBA <i>trans</i> -3 <i>b</i>	0.167	0.365	0.469	II
	0.167	0.361	0.472	II
	0.164	0.356	0.479	II
	0.187	0.403	0.410	II
	0.162	0.366	0.471	II
	0.161	0.358	0.481	II
	0.154	0.344	0.502	II
	0.176	0.387	0.437	II
AICBA <i>trans</i> -4 <i>a</i>	0.080	0.217	0.703	III
	0.160	0.363	0.477	II
	0.173	0.377	0.449	II
	0.168	0.377	0.454	II
	0.160	0.363	0.477	II
	0.152	0.353	0.495	II
	0.163	0.381	0.456	II
AICBA <i>trans</i> -4 <i>b</i>	0.083	0.228	0.690	III
	0.165	0.378	0.457	II
	0.163	0.384	0.454	II
	0.165	0.378	0.457	II
	0.175	0.391	0.434	II
	0.157	0.351	0.492	II
	0.169	0.384	0.448	II
AICBA <i>e</i> -face <i>a</i>	0.084	0.222	0.694	III
	0.084	0.222	0.694	III
	0.161	0.365	0.474	II
	0.161	0.365	0.474	II
	0.156	0.347	0.497	II
	0.156	0.347	0.497	II
AICBA <i>e</i> -face <i>b</i>	0.086	0.232	0.682	III
	0.086	0.232	0.682	III
	0.159	0.354	0.487	II
	0.159	0.354	0.487	II
	0.160	0.359	0.481	II
	0.160	0.359	0.481	II
AICBA <i>e</i> -edge	0.084	0.220	0.696	III
	0.086	0.232	0.682	III
	0.164	0.362	0.474	II
	0.165	0.353	0.483	II
	0.155	0.361	0.484	II
	0.154	0.357	0.489	II
C ₇₀ ³	0.219	0.462	0.319	Ia
	0.473	0.705	-0.177	Ib
	0.253	0.259	0.489	Ic
AC ₇₀ MA <i>a</i>	0.126	0.299	0.575	IIa
	0.126	0.299	0.575	IIa
	0.330	0.585	0.085	IIb
	0.330	0.585	0.085	IIb
AC ₇₀ MA <i>b</i>	0.118	0.306	0.576	IIa
	0.118	0.306	0.576	IIa
	0.178	0.199	0.624	IIc

0.178	0.199	0.624	IIc
¹ All 20 hexagons are equivalent.			
² All 4 four hexagons adjacent to the addend are equivalent.			
³ Ia and Ib hexagons exist in 10 equivalent unities and Ic rings in 5 equivalent unities.			

Appendix B2 – M06-2X/6-31+G(d) Optimized Geometries

Anthracene

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.652663	0.714593	-0.000019
2	6	0	2.475821	1.405672	0.000041
3	6	0	1.219600	0.718406	0.000033
4	6	0	1.219602	-0.718405	0.000018
5	6	0	2.475822	-1.405671	-0.000018
6	6	0	3.652664	-0.714592	-0.000058
7	6	0	0.000000	1.400640	0.000026
8	6	0	0.000001	-1.400641	0.000027
9	6	0	-1.219601	-0.718406	0.000022
10	6	0	-1.219602	0.718405	0.000010
11	6	0	-2.475821	1.405671	-0.000025
12	1	0	-2.470912	2.493147	-0.000062
13	6	0	-3.652663	0.714592	-0.000054
14	6	0	-3.652663	-0.714592	-0.000008
15	6	0	-2.475821	-1.405672	0.000027
16	1	0	-0.000005	2.489468	0.000039
17	1	0	4.598900	1.247714	-0.000049
18	1	0	2.470909	2.493147	0.000087
19	1	0	2.470910	-2.493147	-0.000025
20	1	0	4.598897	-1.247719	-0.000116
21	1	0	-0.000003	-2.489468	0.000042
22	1	0	-4.598898	1.247718	-0.000086
23	1	0	-4.598898	-1.247718	-0.000025
24	1	0	-2.470913	-2.493147	0.000064

Indene

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.229273	-0.686185	0.000045
2	6	0	-1.663420	-1.156195	0.000032
3	6	0	-0.211136	0.720159	-0.000036
4	6	0	-2.436045	0.140941	0.000024
5	6	0	-1.601730	1.194800	-0.000163
6	6	0	0.955768	-1.408064	0.000094
7	6	0	0.997046	1.414277	-0.000058
8	6	0	2.168267	-0.712014	0.000067
9	6	0	2.186769	0.684998	-0.000008
10	1	0	-1.896160	-1.768092	-0.881467
11	1	0	-1.896149	-1.767921	0.881654
12	1	0	-3.519346	0.186958	0.000044
13	1	0	-1.890978	2.240588	-0.000263
14	1	0	0.946677	-2.495516	0.000143
15	1	0	1.014951	2.501053	-0.000137
16	1	0	3.104918	-1.261990	0.000090
17	1	0	3.138628	1.208614	-0.000040

C₆₀

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.922830	-1.753120	-0.959790
2	6	0	3.240993	-0.397478	-1.370838
3	6	0	3.468725	0.582444	-0.414105
4	6	0	3.388865	0.251837	0.997712
5	6	0	3.085783	-1.044804	1.390662
6	6	0	2.847166	-2.069469	0.389655
7	6	0	1.939362	-2.283939	-1.886619
8	6	0	1.649904	-1.256635	-2.870820
9	6	0	2.453940	-0.090174	-2.551636
10	6	0	1.928901	1.183238	-2.723839
11	6	0	2.919433	1.914396	-0.594194
12	6	0	2.789966	1.379089	1.689995
13	6	0	1.913369	1.160776	2.744289
14	6	0	1.595928	-0.195325	3.154159
15	6	0	2.169032	-1.273392	2.493286
16	6	0	1.364526	-2.439438	2.174214
17	6	0	1.784002	-2.931546	0.874419
18	6	0	0.843336	-3.439273	-0.011656
19	6	0	0.922899	-3.108257	-1.423087
20	6	0	0.355759	-1.098126	-3.347041
21	6	0	-0.707340	-1.960557	-2.863109

22	6	0	-0.430401	-2.943371	-1.922390
23	6	0	-1.346698	-3.170435	-0.819052
24	6	0	-0.559372	-3.477467	0.361486
25	6	0	-0.960482	-3.007300	1.604720
26	6	0	0.023023	-2.476014	2.530920
27	6	0	-0.575293	-1.348865	3.222907
28	6	0	0.193480	-0.233921	3.526741
29	6	0	2.499845	2.406197	0.705620
30	6	0	-1.939363	2.283939	1.886618
31	6	0	-0.922900	3.108256	1.423085
32	6	0	-0.843336	3.439272	0.011657
33	6	0	-1.784003	2.931546	-0.874419
34	6	0	-2.847166	2.069470	-0.389656
35	6	0	-3.240993	0.397478	1.370838
36	6	0	-2.453939	0.090174	2.551637
37	6	0	-1.649904	1.256633	2.870820
38	6	0	-0.355760	1.098125	3.347042
39	6	0	0.707342	1.960557	2.863109
40	6	0	0.430403	2.943371	1.922389
41	6	0	0.559372	3.477466	-0.361486
42	6	0	0.960482	3.007300	-1.604719
43	6	0	-0.023023	2.476013	-2.530920
44	6	0	-1.364527	2.439438	-2.174215
45	6	0	-2.169033	1.273394	-2.493286
46	6	0	-3.085783	1.044804	-1.390663
47	6	0	-3.388865	-0.251836	-0.997712
48	6	0	-3.468725	-0.582443	0.414106
49	6	0	-1.928900	-1.183239	2.723840
50	6	0	-2.166995	-2.208174	1.723380
51	6	0	-2.919432	-1.914396	0.594194
52	6	0	-2.499844	-2.406197	-0.705618
53	6	0	-2.789966	-1.379088	-1.689995
54	6	0	-1.913369	-1.160775	-2.744288
55	6	0	-1.595928	0.195325	-3.154160
56	6	0	-0.193481	0.233922	-3.526741
57	6	0	0.575292	1.348866	-3.222907
58	6	0	1.346698	3.170434	0.819053
59	6	0	2.166996	2.208173	-1.723380
60	6	0	-2.922829	1.753121	0.959790

AC₆₀MA

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.467649	-0.000003	-0.800841
2	6	0	2.467647	0.000009	0.800840
3	6	0	1.709899	1.170131	1.427746
4	6	0	1.284379	2.277091	0.740834
5	6	0	1.284379	2.277079	-0.740875
6	6	0	1.709906	1.170111	-1.427771
7	6	0	0.966108	0.725386	-2.573810
8	6	0	0.966107	-0.725412	-2.573734
9	6	0	1.709898	-1.170124	-1.427753
10	6	0	1.284383	-2.277085	-0.740838
11	6	0	1.284381	-2.277070	0.740876
12	6	0	1.709901	-1.170101	1.427775
13	6	0	0.966106	-0.725369	2.573807
14	6	0	0.966108	0.725428	2.573796
15	6	0	-0.150359	1.422936	3.026837
16	6	0	-0.591442	2.590399	2.307782
17	6	0	0.110575	2.996514	1.175453
18	6	0	-0.614117	3.442077	-0.000030
19	6	0	0.110575	2.996493	-1.175504
20	6	0	-0.591442	2.590362	-2.307827
21	6	0	-0.150359	1.422886	-3.026862
22	6	0	-1.323346	0.693571	-3.480309
23	6	0	-1.323347	-0.693617	-3.480296
24	6	0	-0.150359	-1.422925	-3.026836
25	6	0	-0.591440	-2.590386	-2.307783
26	6	0	0.110576	-2.996502	-1.175452
27	6	0	-0.614117	-3.442067	0.000030
28	6	0	0.110576	-2.996480	1.175502
29	6	0	-0.591441	-2.590348	2.307828
30	6	0	-0.150360	-1.422874	3.026861
31	6	0	-1.323348	-0.693558	3.480309
32	6	0	-1.323347	0.693630	3.480297
33	6	0	-2.495540	1.421129	3.031411
34	6	0	-2.042018	2.594032	2.303320
35	6	0	-2.732817	3.018828	1.175820
36	6	0	-2.001908	3.459333	-0.000030
37	6	0	-2.732817	3.018808	-1.175870
38	6	0	-2.042018	2.593995	-2.303364
39	6	0	-2.495539	1.421079	-3.031435
40	6	0	-3.617801	0.726215	-2.598740
41	6	0	-3.617801	-0.726248	-2.598727
42	6	0	-2.495540	-1.421117	-3.031412
43	6	0	-2.042016	-2.594019	-2.303319
44	6	0	-2.732815	-3.018815	-1.175820
45	6	0	-2.001907	-3.459319	0.000030
46	6	0	-2.732816	-3.018795	1.175871
47	6	0	-2.042018	-2.593981	2.303364
48	6	0	-2.495541	-1.421066	3.031436
49	6	0	-3.617802	-0.726203	2.598739
50	6	0	-3.617802	0.726260	2.598727
51	6	0	-4.339512	1.173923	1.422042

52	6	0	-3.905450	2.295505	0.727063
53	6	0	-3.905450	2.295492	-0.727102
54	6	0	-4.339511	1.173898	-1.422063
55	6	0	-4.786460	0.000001	-0.694365
56	6	0	-4.339513	-1.173910	-1.422042
57	6	0	-3.905448	-2.295491	-0.727063
58	6	0	-3.905448	-2.295478	0.727101
59	6	0	-4.339513	-1.173886	1.422062
60	6	0	-4.786460	0.000013	0.694364
61	6	0	3.976746	-0.000012	-1.292606
62	1	0	3.995995	-0.000028	-2.387293
63	6	0	4.620878	-1.229634	-0.699657
64	6	0	5.131062	-2.313644	-1.402693
65	1	0	5.116971	-2.316652	-2.490138
66	6	0	5.657456	-3.398071	-0.697009
67	1	0	6.064735	-4.247372	-1.237750
68	6	0	5.657534	-3.398015	0.697070
69	1	0	6.064839	-4.247292	1.237829
70	6	0	5.131162	-2.313556	1.402721
71	1	0	5.117093	-2.316499	2.490167
72	6	0	4.620942	-1.229582	0.699655
73	6	0	3.976749	0.000024	1.292597
74	1	0	3.996015	0.000041	2.387284
75	6	0	4.620889	1.229631	0.699646
76	6	0	5.131145	2.313597	1.402697
77	1	0	5.117029	2.316585	2.490142
78	6	0	5.657710	3.397940	0.697026
79	1	0	6.065094	4.247200	1.237763
80	6	0	5.657739	3.397922	-0.697054
81	1	0	6.065147	4.247155	-1.237806
82	6	0	5.131291	2.313508	-1.402721
83	1	0	5.117242	2.316469	-2.490167
84	6	0	4.620959	1.229582	-0.699669

C₇₀

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.201751	3.091604	1.547133
2	6	0	0.000205	3.441961	0.884986
3	6	0	-1.201494	3.091714	1.546979
4	6	0	-1.201400	2.204703	2.663771
5	6	0	-0.000035	1.637623	3.152965
6	6	0	1.201688	2.204341	2.663699
7	6	0	2.440369	1.447541	2.635216
8	6	0	3.219795	1.882746	1.497261
9	6	0	2.440501	2.892961	0.816459
10	6	0	2.440786	2.953077	-0.562238
11	6	0	1.201992	3.215218	-1.273475
12	6	0	0.000184	3.505970	-0.583464
13	6	0	-1.201551	3.215279	-1.273427
14	6	0	-2.440079	2.953488	-0.562471
15	6	0	-2.440026	2.893103	0.816207
16	6	0	-3.219629	1.883112	1.497279
17	6	0	-2.440171	1.447798	2.635114
18	6	0	-2.440212	0.117982	3.004049
19	6	0	-1.201739	-0.516110	3.418378
20	6	0	-0.000063	0.221385	3.545606
21	6	0	1.201629	-0.516185	3.418378
22	6	0	2.440141	0.117545	3.003885
23	6	0	3.219454	-0.842420	2.253553
24	6	0	3.966919	-0.432413	1.155980
25	6	0	3.966908	0.965438	0.767930
26	6	0	3.967283	1.028417	-0.680749
27	6	0	3.220345	2.005798	-1.327847
28	6	0	2.440418	1.670740	-2.499156
29	6	0	1.201736	2.427147	-2.462032
30	6	0	0.000159	1.905105	-2.998832
31	6	0	-1.201410	2.427208	-2.462036
32	6	0	-2.440134	1.670910	-2.499127
33	6	0	-3.220001	2.006204	-1.328174
34	6	0	-3.966873	1.028804	-0.680689
35	6	0	-3.966553	0.965832	0.767877
36	6	0	-3.967178	-0.431941	1.155913
37	6	0	-3.219625	-0.842144	2.253421
38	6	0	-2.440478	-2.059070	2.190516
39	6	0	-1.202059	-1.852208	2.919544
40	6	0	-0.000123	-2.492578	2.531963
41	6	0	1.201540	-1.852357	2.919454
42	6	0	2.440244	-2.059392	2.190703
43	6	0	2.440197	-2.821589	1.039991
44	6	0	3.219380	-2.404014	-0.104560
45	6	0	3.966334	-1.232904	-0.053369
46	6	0	3.966915	-0.330556	-1.188261
47	6	0	3.220022	-0.643527	-2.317803
48	6	0	2.440307	0.377869	-2.981647
49	6	0	1.201502	-0.217464	-3.450294
50	6	0	0.000071	0.528911	-3.512929
51	6	0	-1.201547	-0.217248	-3.450313
52	6	0	-2.440233	0.378040	-2.981761
53	6	0	-3.219986	-0.643144	-2.317843
54	6	0	-3.966875	-0.329952	-1.188269
55	6	0	-3.966687	-1.232597	-0.053528
56	6	0	-3.219789	-2.403562	-0.104581
57	6	0	-2.440727	-2.821462	1.040039
58	6	0	-1.201749	-3.411100	0.565324

59	6	0	-0.000226	-3.304117	1.306725
60	6	0	1.201179	-3.411245	0.565287
61	6	0	1.201133	-3.348915	-0.859650
62	6	0	2.439833	-2.719709	-1.281142
63	6	0	2.440506	-1.861000	-2.361570
64	6	0	1.201564	-1.591707	-3.069492
65	6	0	-0.000041	-2.263768	-2.739327
66	6	0	-1.201630	-1.591443	-3.069724
67	6	0	-2.440493	-1.860634	-2.361623
68	6	0	-2.440271	-2.719547	-1.281323
69	6	0	-1.201672	-3.348769	-0.859629
70	6	0	-0.000233	-3.178785	-1.589228

AC₇₀MA isomer a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.338292	2.559794	1.660906
2	6	0	2.018900	3.070936	1.687297
3	6	0	1.171860	2.559010	2.700050
4	6	0	1.537865	1.410561	3.462159
5	6	0	2.762557	0.734992	3.231494
6	6	0	3.705115	1.410515	2.421362
7	6	0	4.722504	0.689810	1.674819
8	6	0	5.001278	1.412649	0.454390
9	6	0	4.129827	2.565257	0.442690
10	6	0	3.565420	2.994505	-0.741258
11	6	0	2.182324	3.434704	-0.763041
12	6	0	1.415253	3.517859	0.423730
13	6	0	0.010494	3.406534	0.271315
14	6	0	-0.839369	2.964298	1.357854
15	6	0	-0.273356	2.561145	2.556362
16	6	0	-0.804086	1.416910	3.233025
17	6	0	0.320664	0.689604	3.783756
18	6	0	0.320650	-0.689961	3.783667
19	6	0	1.537898	-1.410858	3.462082
20	6	0	2.762547	-0.735233	3.231410
21	6	0	3.705134	-1.410678	2.421258
22	6	0	4.722502	-0.689896	1.674762
23	6	0	5.001265	-1.412613	0.454280
24	6	0	5.269675	-0.724174	-0.724996
25	6	0	5.269620	0.724262	-0.724929
26	6	0	4.674077	1.73209	-1.968252
27	6	0	3.843588	2.287877	-1.972527
28	6	0	2.616706	2.278407	-2.737897
29	6	0	1.601474	2.995565	-1.989468
30	6	0	0.235711	2.631741	-2.068054
31	6	0	-0.571324	2.970622	-0.954512
32	6	0	-1.794813	2.258546	-0.651901
33	6	0	-1.970925	2.263611	0.809251
34	6	0	-2.489810	1.166867	1.452389
35	6	0	-1.878928	0.722773	2.671139
36	6	0	-1.878891	-0.723092	2.671107
37	6	0	-0.804091	-1.417286	3.232982
38	6	0	-0.273316	-2.561451	2.556199
39	6	0	1.171903	-2.559241	2.699854
40	6	0	2.018953	-3.071096	1.687088
41	6	0	3.338323	-2.559898	1.660695
42	6	0	4.129878	-2.565271	0.442498
43	6	0	3.565464	-2.994421	-0.741476
44	6	0	3.843643	-2.287714	-1.972697
45	6	0	4.674117	-1.173054	-1.968343
46	6	0	4.308574	0.000121	-2.740328
47	6	0	3.131353	0.000114	-3.478046
48	6	0	2.269300	1.162749	-3.474969
49	6	0	0.890886	0.713599	-3.490757
50	6	0	-0.129215	1.449017	-2.841256
51	6	0	-1.272254	0.712775	-2.433616
52	6	0	-2.140465	1.159051	-1.377729
53	6	0	-2.971107	-0.000074	-0.845568
54	6	0	-3.175762	-0.000056	0.742804
55	6	0	-2.489899	-1.167145	1.452395
56	6	0	-1.970840	-2.263688	0.809096
57	6	0	-0.839279	-2.964437	1.357612
58	6	0	0.010550	-3.406620	0.271069
59	6	0	1.415315	-3.517907	0.423461
60	6	0	2.182385	-3.434662	-0.763290
61	6	0	1.601529	-2.995426	-1.989680
62	6	0	2.616745	-2.278266	-2.738106
63	6	0	2.269348	-1.162523	-3.475045
64	6	0	0.890899	-0.713433	-3.490859
65	6	0	-0.129145	-1.448871	-2.841315
66	6	0	-1.272202	-0.712629	-2.433672
67	6	0	-2.140266	-1.158985	-1.377767
68	6	0	-1.794868	-2.258654	-0.652064
69	6	0	-0.571320	-2.970641	-0.954731
70	6	0	0.235720	-2.631696	-2.068232
71	6	0	-4.405873	-0.000053	-1.526994
72	1	0	-4.285902	0.000122	-2.615160
73	6	0	-5.119912	1.229589	-1.020746
74	6	0	-5.537652	2.312808	-1.783449
75	1	0	-5.386956	2.315165	-2.860502
76	6	0	-6.148527	3.398033	-1.150315

Kinetics and Thermodynamics of the Diels-Alder Addition to Fullerenes

77	1	0	-6.482609	4.247433	-1.738766
78	6	0	-6.324042	3.398934	0.232767
79	1	0	-6.795807	4.248307	0.717831
80	6	0	-5.890698	2.314893	0.999987
81	1	0	-6.014214	2.318423	2.080487
82	6	0	-5.296590	1.230084	0.367473
83	6	0	-4.732500	0.000030	1.036884
84	1	0	-4.891450	-0.000064	2.119957
85	6	0	-5.296922	-1.229819	0.367374
86	6	0	-5.891558	-2.314377	0.999860
87	1	0	-6.015239	-2.317804	2.080344
88	6	0	-6.324865	-3.398464	0.232723
89	1	0	-6.796903	-4.247666	0.717821
90	6	0	-6.149090	-3.397801	-1.150339
91	1	0	-6.483291	-4.247222	-1.738692
92	6	0	-5.537828	-2.312825	-1.783470
93	1	0	-5.386931	-2.315268	-2.860493
94	6	0	-5.119945	-1.229610	-1.020822

75	1	0	-5.004892	2.930721	-2.490610
76	6	0	-5.306526	4.102007	-0.697197
77	1	0	-5.526740	5.017560	-1.238070
78	6	0	-5.306611	4.102017	0.697083
79	1	0	-5.526838	5.017589	1.237918
80	6	0	-5.019603	2.931155	1.403083
81	1	0	-5.004959	2.930802	2.490538
82	6	0	-4.748862	1.764175	0.699782
83	6	0	-4.374632	0.426938	1.290903
84	1	0	-4.387580	0.429952	2.385412
85	6	0	-5.263685	-0.639866	0.699552
86	6	0	-5.990300	-1.592336	1.402937
87	1	0	-5.976642	-1.598684	2.490353
88	6	0	-6.733693	-2.541295	0.697180
89	1	0	-7.309075	-3.286760	1.238140
90	6	0	-6.733642	-2.541363	-0.697090
91	1	0	-7.308988	-3.286873	-1.238026
92	6	0	-5.990208	-1.592463	-1.402877
93	1	0	-5.976495	-1.598897	-2.490292
94	6	0	-5.263655	-0.639922	-0.699521

AC₇₀MA isomer *b*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.302069	0.486928	3.439516
2	6	0	0.942505	0.107683	3.529681
3	6	0	0.671887	-1.279216	3.436912
4	6	0	1.666218	-2.199079	3.003312
5	6	0	2.965520	-1.760595	2.640889
6	6	0	3.300763	-0.434662	3.001802
7	6	0	4.311148	0.316229	2.278551
8	6	0	3.944538	1.715702	2.288432
9	6	0	2.688166	1.814717	2.996917
10	6	0	1.722720	2.704404	2.570355
11	6	0	0.326456	2.304733	2.567301
12	6	0	-0.078610	1.054638	3.065289
13	6	0	-1.289059	0.538794	2.523648
14	6	0	-1.575224	-0.885048	2.537213
15	6	0	-0.622641	-1.776908	2.996390
16	6	0	-0.428015	-3.012746	2.297533
17	6	0	0.995334	-3.267646	2.283067
18	6	0	1.587042	-3.812432	1.161466
19	6	0	2.876318	-3.317889	0.712636
20	6	0	3.595671	-2.344972	1.449967
21	6	0	4.512973	-1.557232	0.713363
22	6	0	4.907220	-0.233907	1.161905
23	6	0	5.163500	0.588959	0.000009
24	6	0	4.810398	1.933044	0.000019
25	6	0	4.184898	2.511662	1.174004
26	6	0	3.169908	3.444599	0.725462
27	6	0	1.964661	3.535875	1.413415
28	6	0	0.714999	3.620756	0.689533
29	6	0	-0.294683	2.865999	1.408653
30	6	0	-1.354489	2.210349	0.740826
31	6	0	-1.924187	1.107332	1.406150
32	6	0	-2.899565	0.107909	0.791314
33	6	0	-2.407264	-1.191204	1.415967
34	6	0	-2.223495	-2.370920	0.740560
35	6	0	-1.206006	-3.297835	1.174520
36	6	0	-0.580317	-3.869761	-0.000021
37	6	0	0.786765	-4.130199	-0.000016
38	6	0	1.587051	-3.812431	-1.161505
39	6	0	2.876321	-3.317877	-0.712655
40	6	0	3.595681	-2.344973	-1.449980
41	6	0	4.512978	-1.557223	-0.713372
42	6	0	4.907216	-0.233898	-1.161892
43	6	0	4.311160	0.316244	-2.278541
44	6	0	3.944538	1.715722	-2.288394
45	6	0	4.184901	2.511680	-1.173975
46	6	0	3.169911	3.444614	-0.725416
47	6	0	1.964667	3.535876	-1.413371
48	6	0	0.714982	3.620768	-0.689496
49	6	0	-0.294678	2.866011	-1.408619
50	6	0	-1.354501	2.210363	-0.740810
51	6	0	-1.924203	1.107363	-1.406157
52	6	0	-2.899561	0.107910	-0.791342
53	6	0	-2.407237	-1.191187	-1.415981
54	6	0	-2.223489	-2.370919	-0.740605
55	6	0	-1.205999	-3.297825	-1.174560
56	6	0	-0.428004	-3.012734	-2.297572
57	6	0	0.995346	-3.267630	-2.283092
58	6	0	1.666235	-2.199057	-3.003338
59	6	0	2.965525	-1.760577	-2.640899
60	6	0	3.300776	-0.434637	-3.001788
61	6	0	2.302079	0.486955	-3.439498
62	6	0	2.688178	1.814743	-2.996893
63	6	0	1.722727	2.704422	-2.570315
64	6	0	0.326462	2.304753	-2.567284
65	6	0	-0.078602	1.054662	-3.065267
66	6	0	-1.289057	0.538816	-2.523652
67	6	0	-1.575208	-0.885021	-2.537229
68	6	0	-0.622623	-1.776883	-2.996399
69	6	0	0.671896	-1.279189	-3.436919
70	6	0	0.942521	0.107710	-3.529678
71	6	0	-4.374638	0.426879	-1.290899
72	1	0	-4.387619	0.429866	-2.385410
73	6	0	-4.748865	1.764144	-0.699815
74	6	0	-5.019554	2.931108	-1.403155

AC₇₀MA isomer *c*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	2.302069	0.486928	3.439516
2	6	0	0.942505	0.107683	3.529681
3	6	0	0.671887	-1.279216	3.436912
4	6	0	1.666218	-2.199079	3.003312
5	6	0	2.965520	-1.760595	2.640889
6	6	0	3.300763	-0.434662	3.001802
7	6	0	4.311148	0.316229	2.278551
8	6	0	3.944538	1.715702	2.288432
9	6	0	2.688166	1.814717	2.996917
10	6	0	1.722720	2.704404	2.570355
11	6	0	0.326456	2.304733	2.567301
12	6	0	-0.078610	1.054638	3.065289
13	6	0	-1.289059	0.538794	2.523648
14	6	0	-1.575224	-0.885048	2.537213
15	6	0	-0.622641	-1.776908	2.996390
16	6	0	-0.428015	-3.012746	2.297533
17	6	0	0.995334	-3.267646	2.283067
18	6	0	1.587042	-3.812432	1.161466
19	6	0	2.876318	-3.317889	0.712636
20	6	0	3.595671	-2.344972	1.449967
21	6	0	4.512973	-1.557232	0.713363
22	6	0	4.907220	-0.233907	1.161905
23	6	0	5.163500	0.588959	0.000009
24	6	0	4.810398	1.933044	0.000019
25	6	0	4.184898	2.511662	1.174004
26	6	0	3.169908	3.444599	0.725462
27	6	0	1.964661	3.535875	1.413415
28	6	0	0.714999	3.620756	0.689533
29	6	0	-0.294683	2.865999	1.408653
30	6	0	-1.354489	2.210349	0.740826
31	6	0	-1.924187	1.107332	1.406150
32	6	0	-2.899565	0.107909	0.791314
33	6	0	-2.407264	-1.191204	1.415967
34	6	0	-2.223495	-2.370920	0.740560
35	6	0	-1.206006	-3.297835	1.174520
36	6	0	-0.580317	-3.869761	-0.000021
37	6	0	0.786765	-4.130199	-0.000016
38	6	0	1.587051	-3.812431	-1.161505
39	6	0	2.876321	-3.317877	-0.712655
40	6	0	3.595681	-2.344973	-1.449980
41	6	0	4.512978	-1.557223	-0.713372
42	6	0	4.907216	-0.233898	-1.161892
43	6	0	4.311160	0.316244	-2.278541
44	6	0	3.944538	1.715722	-2.288394
45	6	0	4.184901	2.511680	-1.173975
46	6	0	3.169911	3.444614	-0.725416
47	6	0	1.964667	3.535876	-1.413371
48	6	0	0.714982	3.620768	-0.689496
49	6	0	-0.294678	2.866011	-1.408619
50	6	0	-1.354501	2.210363	-0.740810
51	6	0	-1.924203	1.107363	-1.406157
52	6	0	-2.899561	0.107910	-0.791342
53	6	0	-2.407237	-1.191187	-1.415981
54	6	0	-2.223489	-2.370919	-0.740605
55	6	0	-1.205999	-3.297825	-1.174560
56	6	0	-0.428004	-3.012734	-2.297572
57	6	0	0.995346	-3.267630	-2.283092
58	6	0	1.666235	-2.199057	-3.003338
59	6	0	2.965525	-1.760577	-2.640899
60	6	0	3.300776	-0.434637	-3.001788
61	6	0	2.302079	0.486955	-3.439498
62	6	0	2.688178	1.814743	-2.996893
63	6	0	1.722727	2.704422	-2.570315
64	6	0	0.326462	2.304753	-2.567284
65	6	0	-0.078602	1.054662	-3.065267
66	6	0	-1.289057	0.538816	-2.523652
67	6	0	-1.575208	-0.885021	-2.537229
68	6	0	-0.622623	-1.776883	-2.996399
69	6	0	0.671896	-1.279189	-3.436919
70	6	0	0.942521	0.107710	-3.529678
71	6	0	-4.374638	0.426879	-1.290899
72	1	0	-4.387619	0.429866	-2.385410

73	6	0	-4.748865	1.764144	-0.699815
74	6	0	-5.019554	2.931108	-1.403155
75	1	0	-5.004892	2.930721	-2.490610
76	6	0	-5.306526	4.102007	-0.697197
77	1	0	-5.526740	5.017560	-1.238070
78	6	0	-5.306611	4.102017	0.697083
79	1	0	-5.526838	5.017589	1.237918
80	6	0	-5.019603	2.931155	1.403083
81	1	0	-5.004959	2.930802	2.490538
82	6	0	-4.748862	1.764175	0.699782
83	6	0	-4.374632	0.426938	1.290903
84	1	0	-4.387580	0.429952	2.385412
85	6	0	-5.263685	-0.639866	0.699552
86	6	0	-5.990300	-1.592336	1.402937
87	1	0	-5.976642	-1.598684	2.490353
88	6	0	-6.733693	-2.541295	0.697180
89	1	0	-7.309075	-3.286760	1.238140
90	6	0	-6.733642	-2.541363	-0.697090
91	1	0	-7.308988	-3.286873	-1.238026
92	6	0	-5.990208	-1.592463	-1.402877
93	1	0	-5.976495	-1.598897	-2.490292
94	6	0	-5.263655	-0.639922	-0.699521

70	6	0	0.235720	-2.631696	-2.068232
71	6	0	-4.405873	-0.000053	-1.526994
72	1	0	-4.285902	0.000122	-2.615160
73	6	0	-5.119912	1.229589	-1.020746
74	6	0	-5.537652	2.312808	-1.783449
75	1	0	-5.386956	2.315165	-2.860502
76	6	0	-6.148527	3.398033	-1.150315
77	1	0	-6.482609	4.247433	-1.738766
78	6	0	-6.324042	3.398934	0.232767
79	1	0	-6.795807	4.248307	0.717831
80	6	0	-5.890698	2.314893	0.999987
81	1	0	-6.014214	2.318423	2.080487
82	6	0	-5.296590	1.230084	0.367473
83	6	0	-4.732500	0.000030	1.036884
84	1	0	-4.891450	-0.000064	2.119957
85	6	0	-5.296922	-1.229819	0.367374
86	6	0	-5.891558	-2.314377	0.999860
87	1	0	-6.015239	-2.317804	2.080344
88	6	0	-6.324865	-3.398464	0.232723
89	1	0	-6.796903	-4.247666	0.717821
90	6	0	-6.149090	-3.397801	-1.150339
91	1	0	-6.483291	-4.247222	-1.738692
92	6	0	-5.537828	-2.312825	-1.783470
93	1	0	-5.386931	-2.315268	-2.860493
94	6	0	-5.119945	-1.229610	-1.020822

AC₇₀MA isomer *d*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	3.338292	2.559794	1.660906
2	6	0	2.018900	3.070936	1.687297
3	6	0	1.171860	2.559010	2.700050
4	6	0	1.537865	1.410561	3.462159
5	6	0	2.762557	0.734992	3.231494
6	6	0	3.705115	1.410515	2.421362
7	6	0	4.722504	0.689810	1.674819
8	6	0	5.001278	1.412649	0.454390
9	6	0	4.129827	2.565257	0.442690
10	6	0	3.565420	2.994505	-0.741258
11	6	0	2.182324	3.434704	-0.763041
12	6	0	1.415253	3.517859	0.423730
13	6	0	0.010494	3.406534	0.271315
14	6	0	-0.839369	2.964298	1.357854
15	6	0	-0.273356	2.561145	2.556362
16	6	0	-0.804086	1.416910	3.233025
17	6	0	0.320664	0.689604	3.783756
18	6	0	0.320650	-0.689961	3.783667
19	6	0	1.537898	-1.410858	3.462082
20	6	0	2.762547	-0.735233	3.231410
21	6	0	3.705134	-1.410678	2.421258
22	6	0	4.722502	-0.689896	1.674762
23	6	0	5.001265	-1.412613	0.454280
24	6	0	5.269675	-0.724174	-0.724996
25	6	0	5.269620	0.724262	-0.724929
26	6	0	4.674077	1.173209	-1.968252
27	6	0	3.843588	2.287877	-1.972527
28	6	0	2.616706	2.278407	-2.737897
29	6	0	1.601474	2.995565	-1.989468
30	6	0	0.235711	2.631741	-2.068054
31	6	0	-0.571324	2.970622	-0.954512
32	6	0	-1.794813	2.258546	-0.651901
33	6	0	-1.970925	2.263611	0.809251
34	6	0	-2.489810	1.166867	1.452389
35	6	0	-1.878928	0.722773	2.671139
36	6	0	-1.878891	-0.723092	2.671107
37	6	0	-0.804091	-1.417286	3.232982
38	6	0	-0.273316	-2.561451	2.556199
39	6	0	1.171903	-2.559241	2.699854
40	6	0	2.018953	-3.071096	1.687088
41	6	0	3.338323	-2.559898	1.660695
42	6	0	4.129878	-2.565271	0.442498
43	6	0	3.565464	-2.994421	-0.741476
44	6	0	3.843643	-2.287714	-1.972697
45	6	0	4.674117	-1.173054	-1.968343
46	6	0	4.308574	0.000121	-2.740328
47	6	0	3.131353	0.000114	-3.478046
48	6	0	2.269300	1.162749	-3.474969
49	6	0	0.890886	0.713599	-3.490757
50	6	0	-0.129215	1.449017	-2.841256
51	6	0	-1.272254	0.712775	-2.433616
52	6	0	-2.140465	1.159051	-1.377729
53	6	0	-2.971107	-0.000074	-0.845568
54	6	0	-3.175762	-0.000056	0.742804
55	6	0	-2.489899	-1.167145	1.452395
56	6	0	-1.970840	-2.263688	0.809096
57	6	0	-0.839279	-2.964437	1.357612
58	6	0	0.010550	-3.406620	0.271069
59	6	0	1.415315	-3.517907	0.423461
60	6	0	2.182385	-3.434662	-0.763290
61	6	0	1.601529	-2.995426	-1.989680
62	6	0	2.616745	-2.278266	-2.738106
63	6	0	2.269348	-1.162523	-3.475045
64	6	0	0.890899	-0.713433	-3.490859
65	6	0	-0.129145	-1.448871	-2.841315
66	6	0	-1.272202	-0.712629	-2.433672
67	6	0	-2.140266	-1.158985	-1.377767
68	6	0	-1.794868	-2.258654	-0.652064
69	6	0	-0.571320	-2.970641	-0.954731

ICMA

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	4.194329	-1.418024	1.131578
2	1	0	4.303092	-1.763086	2.162095
3	6	0	5.102585	-0.290164	0.700824
4	6	0	5.798218	0.673012	1.414833
5	1	0	5.786340	0.685682	2.501864
6	6	0	6.525270	1.630075	0.697353
7	1	0	7.093735	2.384852	1.232949
8	6	0	6.525434	1.629740	-0.697852
9	1	0	7.094019	2.384271	-1.233663
10	6	0	5.798495	0.672350	-1.415015
11	1	0	5.786779	0.684481	-2.502056
12	6	0	5.102657	-0.290414	-0.700661
13	6	0	4.194320	-1.418350	-1.131124
14	1	0	4.303166	-1.763779	-2.161502
15	6	0	4.440727	-2.436254	0.000393
16	1	0	5.464576	-2.819420	0.000381
17	1	0	3.731930	-3.271332	0.000516
18	6	0	-0.351861	-3.233664	1.176208
19	6	0	0.971423	-2.853007	0.741621
20	6	0	1.681636	-1.903050	1.431801
21	6	0	1.081937	-1.275503	2.577748
22	6	0	-0.181954	-1.647842	3.027543
23	6	0	-0.919261	-2.654689	2.308508
24	6	0	-1.168546	-3.470324	0.000349
25	6	0	-0.351840	-3.233936	-1.175544
26	6	0	0.971440	-2.853170	-0.741002
27	6	0	1.681662	-1.903383	-1.431389
28	6	0	2.715506	-0.971787	0.803275
29	6	0	1.470139	0.122323	2.578937
30	6	0	0.578304	1.092248	3.029096
31	6	0	-0.747455	0.703576	3.480654
32	6	0	-1.118370	-0.632605	3.480753
33	6	0	-2.442516	-1.020038	3.031474
34	6	0	-2.318327	-2.271502	2.304452
35	6	0	-3.096862	-2.497527	1.176683
36	6	0	-2.510041	-3.116291	0.000297
37	6	0	-0.919194	-2.655174	-2.307978
38	6	0	-2.318258	-2.271979	-2.304032
39	6	0	-3.096822	-2.497776	-1.176236
40	6	0	-4.034559	-1.488835	-0.727037
41	6	0	-4.034584	-1.488687	0.727248
42	6	0	-4.152737	-0.291034	1.420985
43	6	0	-3.338936	-0.051159	2.598239
44	6	0	-2.950161	1.348326	2.597861
45	6	0	-1.682687	1.717473	3.031088
46	6	0	2.308319	0.352138	1.435303
47	6	0	-0.660977	3.548335	-0.000363
48	6	0	0.670522	3.158682	-0.000301
49	6	0	1.250119	2.536374	-1.176109
50	6	0	0.465598	2.333348	-2.309085
51	6	0	-0.931362	2.725039	-2.304326
52	6	0	-2.805935	2.936698	-0.727456
53	6	0	-2.805955	2.936848	0.726792
54	6	0	-1.483071	3.319441	1.175848
55	6	0	-0.931423	2.725522	2.303763
56	6	0	0.465534	2.333836	2.308643
57	6	0	1.250087	2.536629	1.175651
58	6	0	2.190466	1.530332	-0.741481
59	6	0	2.308370	0.351832	-1.435293
60	6	0	1.470223	0.121783	-2.578900
61	6	0	0.578381	1.091620	-3.029262
62	6	0	-0.747362	0.702858	-3.480802
63	6	0	-1.682605	1.716842	-3.031467
64	6	0	-2.950097	1.347792	-2.598201
65	6	0	-3.524966	1.972131	-1.422000
66	6	0	-3.525003	1.972423	1.421518
67	6	0	-4.269710	0.960093	0.693982
68	6	0	-4.269691	0.959950	-0.694274

Kinetics and Thermodynamics of the Diels-Alder Addition to Fullerenes

69	6	0	-4.152697	-0.291328	-1.421020
70	6	0	-3.338861	-0.051690	-2.598302
71	6	0	-2.442434	-1.020657	-3.031313
72	6	0	-1.118270	-0.633326	-3.480634
73	6	0	-0.181868	-1.648485	-3.027222
74	6	0	1.082000	-1.276037	-2.577452
75	6	0	2.190454	1.530485	0.741246
76	6	0	2.715536	-0.971935	-0.802955
77	6	0	-1.483041	3.319199	-1.176558

AICBA *trans*-1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.680698	0.887427	1.131000
2	1	0	-5.840507	1.211652	2.161654
3	6	0	-6.405875	-0.366476	0.700881
4	6	0	-6.937223	-1.429328	1.414911
5	1	0	-6.921806	-1.440718	2.501945
6	6	0	-7.499669	-2.491472	0.697766
7	1	0	-7.940204	-3.327753	1.233038
8	6	0	-7.499659	-2.491557	-0.697456
9	1	0	-7.940196	-3.327894	-1.232634
10	6	0	-6.937160	-1.429503	-1.414695
11	1	0	-6.921705	-1.440986	-2.501731
12	6	0	-6.405802	-0.366606	-0.700742
13	6	0	-5.680645	0.887252	-1.131077
14	1	0	-5.840633	1.211288	-2.161761
15	6	0	-6.078811	1.855493	-0.000108
16	1	0	-7.148776	2.079987	-0.000193
17	1	0	-5.502991	2.787198	-0.000132
18	6	0	-1.454740	3.363047	1.177086
19	6	0	-2.705986	2.791218	0.741272
20	6	0	-3.269991	1.747378	1.432654
21	6	0	-2.587188	1.217872	2.580551
22	6	0	-1.393587	1.775967	3.034075
23	6	0	-0.811059	2.879183	2.312987
24	6	0	-0.680042	3.710985	-0.000247
25	6	0	-1.454726	3.362908	-1.177547
26	6	0	-2.705958	2.791095	-0.741666
27	6	0	-3.270047	1.747275	-1.432968
28	6	0	-4.150961	0.670264	0.803198
29	6	0	-2.758599	-0.223008	2.581553
30	6	0	-1.731054	-1.047767	3.035703
31	6	0	-0.480455	-0.463168	3.486716
32	6	0	-0.316339	0.913287	3.486604
33	6	0	0.933688	1.497985	3.032879
34	6	0	0.629006	2.707324	2.312812
35	6	0	1.368963	3.025620	1.176537
36	6	0	0.698054	3.547240	-0.000229
37	6	0	-0.811049	2.878871	-2.313380
38	6	0	0.629017	2.707016	-2.313162
39	6	0	1.368964	3.025466	-1.176924
40	6	0	2.450151	2.176666	-0.741278
41	6	0	2.450124	2.176736	0.741005
42	6	0	2.745711	1.026895	1.428767
43	6	0	1.959649	0.672796	2.575699
44	6	0	1.788276	-0.768164	2.575898
45	6	0	0.596030	-1.326723	3.033429
46	6	0	-3.549275	-0.576490	1.437622
47	6	0	-0.119299	-3.261049	0.000218
48	6	0	-1.496940	-3.094430	0.000206
49	6	0	-2.167828	-2.572127	-1.176301
50	6	0	-1.427366	-2.256384	-2.313131
51	6	0	0.012779	-2.429881	-2.313262
52	6	0	1.907886	-2.345363	-0.740872
53	6	0	1.907897	-2.345308	0.741183
54	6	0	0.656324	-2.914371	1.177576
55	6	0	0.012778	-2.429584	2.313585
56	6	0	-1.427368	-2.256103	2.313426
57	6	0	-2.167836	-2.571985	1.176639
58	6	0	-3.249696	-1.722897	-0.741619
59	6	0	-3.549235	-0.576668	-1.437555
60	6	0	-2.758593	-0.223312	-2.581553
61	6	0	-1.731028	-1.048140	-3.035545
62	6	0	-0.480419	-0.463625	-3.486658
63	6	0	0.596057	-1.327138	-3.033271
64	6	0	1.788314	-0.768554	-2.575810
65	6	0	2.468102	-1.298697	-1.428333
66	6	0	2.467994	-1.298453	1.428462
67	6	0	3.358513	-0.225147	0.800511
68	6	0	3.358532	-0.225196	-0.800474
69	6	0	2.745614	1.026683	-1.428868
70	6	0	1.959627	0.672418	-2.575779
71	6	0	0.933679	1.497576	-3.033052
72	6	0	-0.316349	0.912834	-3.486732
73	6	0	-1.393599	1.775587	-3.034362
74	6	0	-2.587199	1.217572	-2.580743
75	6	0	-3.249701	-1.722788	0.741839
76	6	0	-4.150979	0.670106	-0.803275
77	6	0	0.656326	-2.914506	-1.177184
78	6	0	4.857025	-0.402304	1.292031
79	1	0	4.875729	-0.404216	2.386668
80	6	0	5.642010	0.742979	0.699750
81	6	0	6.274232	1.760679	1.402949
82	1	0	6.259387	1.765644	2.490370
83	6	0	6.922828	2.777109	0.697181

84	1	0	7.425056	3.574010	1.237674
85	6	0	6.922831	2.777157	-0.696925
86	1	0	7.425067	3.574096	-1.237356
87	6	0	6.274214	1.760789	-1.402764
88	1	0	6.259361	1.765820	-2.490183
89	6	0	5.641991	0.743041	-0.699631
90	6	0	4.857030	-0.402210	-1.291959
91	1	0	4.875704	-0.404178	-2.386600
92	6	0	5.354425	-1.698225	-0.699679
93	6	0	5.737672	-2.833496	-1.402627
94	1	0	5.723475	-2.834770	-2.490095
95	6	0	6.136578	-3.971409	-0.697081
96	1	0	6.442586	-4.861611	-1.238713
97	6	0	6.136532	-3.971469	0.696975
98	1	0	6.442491	-4.861722	1.238552
99	6	0	5.737620	-2.833597	1.402583
100	1	0	5.723352	-2.834933	2.490050
101	6	0	5.354422	-1.698271	0.699695

AICBA *trans*-2 a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.747329	0.037750	-0.575875
2	1	0	-6.185779	-0.701316	-1.249888
3	6	0	-5.954768	1.489207	-0.943666
4	6	0	-6.253710	2.115370	-2.143796
5	1	0	-6.437790	1.540907	-3.048316
6	6	0	-6.317206	3.513586	-2.161697
7	1	0	-6.566757	4.028198	-3.085100
8	6	0	-6.058486	4.256023	-1.008993
9	1	0	-6.109252	5.340383	-1.047538
10	6	0	-5.730637	3.620960	0.194313
11	1	0	-5.510277	4.201596	1.086652
12	6	0	-5.697106	2.235313	0.214631
13	6	0	-5.333340	1.242743	1.293317
14	1	0	-5.394861	1.600501	2.323423
15	6	0	-6.213708	0.042439	0.892736
16	1	0	-7.281198	0.257575	0.990750
17	1	0	-5.969287	-0.878503	1.432890
18	6	0	-2.586233	-3.403149	0.899620
19	6	0	-3.497239	-2.282399	0.897761
20	6	0	-3.816933	-1.648405	-0.277313
21	6	0	-3.214842	-2.097862	-1.503068
22	6	0	-2.349900	-3.190195	-1.525226
23	6	0	-2.027558	-3.863160	-0.290799
24	6	0	-1.771168	-3.328459	2.096420
25	6	0	-2.171642	-2.152676	2.846517
26	6	0	-3.233538	-1.494228	2.124848
27	6	0	-3.300495	-0.122470	2.090200
28	6	0	-4.192654	-0.172620	-0.387777
29	6	0	-2.931970	-0.934535	-2.320667
30	6	0	-1.796788	-0.909057	-3.129506
31	6	0	-0.886071	-2.042941	-3.135852
32	6	0	-1.158509	-3.154681	-2.350593
33	6	0	-0.090209	-3.803108	-1.611084
34	6	0	-0.632002	-4.246281	-0.337089
35	6	0	0.148637	-4.175255	0.810368
36	6	0	-0.437130	-3.711811	2.057327
37	6	0	-1.211641	-1.408411	3.530703
38	6	0	0.182606	-1.798457	3.475611
39	6	0	0.562193	-2.923227	2.755818
40	6	0	1.753835	-2.893801	1.930417
41	6	0	1.501251	-3.664534	0.738060
42	6	0	2.016619	-3.223136	-0.479057
43	6	0	1.201280	-3.296648	-1.675689
44	6	0	1.489685	-2.132877	-2.493995
45	6	0	0.464330	-1.524965	-3.217803
46	6	0	-3.358793	0.230182	-1.596684
47	6	0	0.928636	1.834633	-1.810378
48	6	0	-0.413322	2.202153	-1.767142
49	6	0	-0.982490	2.664080	-0.529001
50	6	0	-0.169670	2.737940	0.603739
51	6	0	1.225529	2.368763	0.534492
52	6	0	2.939007	0.961605	-0.758163
53	6	0	2.413412	0.034358	-1.855591
54	6	0	1.336370	0.663302	-2.564100
55	6	0	0.385960	-0.086885	-3.252669
56	6	0	-1.015203	0.295761	-3.203868
57	6	0	-1.408526	1.409741	-2.467677
58	6	0	-2.335980	2.167213	-0.434610
59	6	0	-2.835943	1.759641	0.775776
60	6	0	-1.993799	1.806689	1.938342
61	6	0	-0.693095	2.298279	1.869912
62	6	0	0.371235	1.645232	2.610543
63	6	0	1.566110	1.679243	1.802292
64	6	0	2.424344	0.609497	1.795060
65	6	0	3.307099	0.216338	0.610430
66	6	0	2.481366	-1.336154	-1.815405
67	6	0	2.815596	-2.022451	-0.546398
68	6	0	3.061926	-1.291797	0.587145
69	6	0	2.505256	-1.723643	1.838325
70	6	0	2.112537	-0.547039	2.588303
71	6	0	0.979590	-0.583848	3.400030
72	6	0	0.085466	0.542342	3.409830
73	6	0	-1.272234	0.030690	3.484488
74	6	0	-2.288773	0.646127	2.758612

75	6	0	-2.604749	1.376232	-1.660764
76	6	0	-3.899500	0.683295	0.939733
77	6	0	1.765815	1.934436	-0.646725
78	6	0	4.829490	0.516765	0.940155
79	1	0	5.098550	0.010497	1.872866
80	6	0	4.961167	2.017322	1.034097
81	6	0	5.305800	2.746709	2.165114
82	1	0	5.540884	2.235031	3.095553
83	6	0	5.342077	4.141377	2.092762
84	1	0	5.616353	4.719830	2.969986
85	6	0	5.021826	4.793491	0.902952
86	1	0	5.047901	5.878223	0.856638
87	6	0	4.660527	4.059150	-0.229387
88	1	0	4.396292	4.565706	-1.154771
89	6	0	4.638401	2.672060	-0.159973
90	6	0	4.234985	1.725694	-1.264835
91	1	0	4.001132	2.245329	-2.199706
92	6	0	5.311871	0.681935	-1.433747
93	6	0	5.928010	0.317454	-2.624155
94	1	0	5.666053	0.820332	-3.552200
95	6	0	6.882161	-0.702815	-2.614187
96	1	0	7.373753	-0.990960	-3.538764
97	6	0	7.200980	-1.357052	-1.425079
98	1	0	7.939440	-2.153556	-1.427044
99	6	0	6.570415	-0.998738	-0.231108
100	1	0	6.807369	-1.516521	0.695445
101	6	0	5.632737	0.026109	-0.239759

AICBA trans-2 b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.283707	-0.474739	-1.758655
2	1	0	-5.300297	0.018620	-2.750694
3	6	0	-6.547567	-0.491625	-0.810619
4	6	0	-7.701566	0.218196	-0.549483
5	1	0	-7.927244	0.969356	-1.049972
6	6	0	-8.517549	-0.223028	0.482953
7	1	0	-9.310746	0.225558	0.663891
8	6	0	-8.270478	-1.424946	1.190924
9	1	0	-8.914206	-1.703474	1.800158
10	6	0	-7.193584	-2.252965	0.906117
11	1	0	-7.095987	-3.074425	1.331955
12	6	0	-6.274333	-1.820815	-0.027680
13	6	0	-4.917101	-2.258152	-0.708162
14	1	0	-4.613744	-3.321229	-0.783406
15	6	0	-5.010112	-1.878655	-2.134493
16	1	0	-5.734390	-2.250962	-2.513795
17	1	0	-4.183705	-1.931653	-2.512872
18	6	0	-0.718417	-0.717745	-3.218004
19	6	0	-2.042527	-0.962715	-2.643814
20	6	0	-2.861926	0.103508	-2.313520
21	6	0	-2.404089	1.475651	-2.538498
22	6	0	-1.151639	1.707332	-3.081637
23	6	0	-0.285360	0.580121	-3.430847
24	6	0	0.202717	-1.716671	-2.673336
25	6	0	-0.552074	-2.578976	-1.762490
26	6	0	-1.939749	-2.113003	-1.744227
27	6	0	-2.661899	-2.134840	-0.562996
28	6	0	-3.787984	-0.015290	-1.094034
29	6	0	-2.884605	2.300563	-1.428721
30	6	0	-2.086676	3.312538	-0.922186
31	6	0	-0.762580	3.557484	-1.496427
32	6	0	-0.308073	2.777196	-2.546133
33	6	0	1.079560	2.311202	-2.564406
34	6	0	1.093594	0.953344	-3.111194
35	6	0	1.964884	0.008489	-2.596006
36	6	0	1.507049	-1.363658	-2.370984
37	6	0	0.038301	-3.041594	-0.598557
38	6	0	1.417225	-2.668388	-0.278888
39	6	0	2.131181	-1.852737	-1.140456
40	6	0	2.974757	-0.782871	-0.604946
41	6	0	2.871969	0.367424	-1.504536
42	6	0	2.858692	1.651805	-0.987322
43	6	0	1.937569	2.650723	-1.532003
44	6	0	1.457043	3.475673	-0.422236
45	6	0	0.144514	3.916451	-0.404938
46	6	0	-3.639403	1.438284	-0.517870
47	6	0	-0.783449	2.568384	2.918666
48	6	0	-2.087778	2.215382	2.616327
49	6	0	-2.545603	0.843247	2.841314
50	6	0	-1.674310	-0.101603	3.356523
51	6	0	-0.295382	0.271615	3.676196
52	6	0	1.461786	1.814429	2.889116
53	6	0	1.358999	2.964730	1.989534
54	6	0	-0.028621	3.430720	2.007800
55	6	0	-0.618982	3.893334	0.843860
56	6	0	-1.997948	3.520095	0.524166
57	6	0	-2.711916	2.704463	1.385744
58	6	0	-3.452662	0.484304	1.749829
59	6	0	-3.439399	-0.800051	1.232607
60	6	0	-2.518252	-1.798990	1.777265
61	6	0	-1.660261	-1.459466	2.809694
62	6	0	-0.272661	-1.925455	2.791444
63	6	0	0.570899	-0.855599	3.326945
64	6	0	1.823335	-0.623903	2.783776

65	6	0	2.281172	0.748233	2.558782
66	6	0	2.081178	2.986580	0.808298
67	6	0	2.947439	1.859370	0.459064
68	6	0	3.044664	0.771330	1.309961
69	6	0	3.058702	-0.586539	0.763158
70	6	0	2.303879	-1.448841	1.674037
71	6	0	1.505974	-2.460814	1.167519
72	6	0	0.181869	-2.705758	1.741741
73	6	0	-0.725201	-3.064686	0.650287
74	6	0	-2.037733	-2.623911	0.667561
75	6	0	-3.555450	1.634629	0.850243
76	6	0	-3.613231	-1.138612	-0.311723
77	6	0	0.137665	1.569494	3.463344
78	6	0	4.412186	-0.981198	-1.391183
79	1	0	4.345751	-1.133377	-2.484752
80	6	0	5.072722	-2.139566	-0.679843
81	6	0	5.497204	-3.342048	-1.262692
82	1	0	5.406629	-3.490885	-2.349299
83	6	0	6.047479	-4.346268	-0.446409
84	1	0	6.402912	-5.284500	-0.897540
85	6	0	6.160139	-4.148851	0.940742
86	1	0	6.602470	-4.934579	1.571019
87	6	0	5.718169	-2.948246	1.528843
88	1	0	5.798462	-2.795020	2.615785
89	6	0	5.179080	-1.944459	0.714613
90	6	0	4.604620	-0.623821	1.173948
91	1	0	4.702070	-0.472278	2.265153
92	6	0	5.204383	0.508160	0.371584
93	6	0	5.755612	1.690167	0.881073
94	1	0	5.831421	1.840990	1.968622
95	6	0	6.214679	2.676875	-0.012375
96	1	0	6.666364	3.600216	0.379548
97	6	0	6.107913	2.485432	-1.400618
98	1	0	6.478440	3.257488	-2.091012
99	6	0	5.542936	1.303209	-1.911683
100	1	0	5.455281	1.148611	-2.997768
101	6	0	5.099855	0.313851	-1.022936

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Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.446324	-1.112061	-0.654702
2	1	0	-6.226730	-0.367516	-0.483394
3	6	0	-5.535377	-2.379240	0.162945
4	6	0	-6.168924	-2.674639	1.359820
5	1	0	-6.778488	-1.933797	1.871186
6	6	0	-6.007104	-3.958619	1.893345
7	1	0	-6.509173	-4.221979	2.819772
8	6	0	-5.205484	-4.903027	1.251557
9	1	0	-5.090521	-5.891784	1.686141
10	6	0	-4.544598	-4.591217	0.057663
11	1	0	-3.906027	-5.323543	-0.430118
12	6	0	-4.731500	-3.328425	-0.483359
13	6	0	-4.151057	-2.644207	-1.699934
14	1	0	-3.753243	-3.297107	-2.479888
15	6	0	-5.305448	-1.694193	-2.075067
16	1	0	-6.201345	-2.232651	-2.395495
17	1	0	-5.030476	-0.948121	-2.828317
18	6	0	-2.608538	2.511182	-2.318105
19	6	0	-3.236952	1.218936	-2.158875
20	6	0	-3.870096	0.896085	-0.984626
21	6	0	-3.874876	1.846279	0.093743
22	6	0	-3.299075	3.106688	-0.050123
23	6	0	-2.651044	3.450211	-1.288880
24	6	0	-1.394379	2.336988	-3.086313
25	6	0	-1.257355	0.926312	-3.403078
26	6	0	-2.389061	0.220422	-2.847078
27	6	0	-2.232064	-1.037186	-2.320012
28	6	0	-3.998256	-0.521974	-0.435387
29	6	0	-3.723692	1.115808	1.337338
30	6	0	-2.995229	1.671718	2.387301
31	6	0	-2.377873	2.980526	2.228748
32	6	0	-2.529978	3.682609	1.041180
33	6	0	-1.399957	4.384307	0.464319
34	6	0	-1.475118	4.239077	-0.979207
35	6	0	-0.311007	4.070325	-1.719548
36	6	0	-0.270777	3.101911	-2.803479
37	6	0	0.005422	0.340974	-3.412991
38	6	0	1.179537	1.131456	-3.102436
39	6	0	1.044685	2.488996	-2.813127
40	6	0	1.804742	3.056911	-1.734733
41	6	0	0.974056	4.040048	-1.053860
42	6	0	1.047051	4.177256	0.324958
43	6	0	-0.164648	4.353460	1.101840
44	6	0	-0.006827	3.618075	2.344707
45	6	0	-1.092538	2.946314	2.894050
46	6	0	-3.633615	-0.281950	1.024566
47	6	0	0.458903	-0.394534	3.098431
48	6	0	-0.679946	-1.139226	2.802313
49	6	0	-0.642373	-2.087406	1.720370
50	6	0	0.539423	-2.242869	0.993734
51	6	0	1.717390	-1.489130	1.316736
52	6	0	2.306224	0.747210	2.185208
53	6	0	1.467055	1.713156	2.856780
54	6	0	0.333300	1.014926	3.426152
55	6	0	-0.917857	1.615408	3.453280

Kinetics and Thermodynamics of the Diels-Alder Addition to Fullerenes

56	6	0	-2.103714	0.837505	3.144318
57	6	0	-1.986168	-0.512380	2.813921
58	6	0	-1.923764	-2.075460	1.048527
59	6	0	-1.989225	-2.218689	-0.312827
60	6	0	-0.773251	-2.352932	-1.068883
61	6	0	0.472015	-2.377540	-0.438484
62	6	0	1.610921	-1.714411	-1.012903
63	6	0	2.615255	-1.362680	0.085078
64	6	0	3.295309	0.075341	-0.087430
65	6	0	2.933279	1.075497	1.010734
66	6	0	1.302152	2.995220	2.333336
67	6	0	1.949253	3.335274	1.093864
68	6	0	2.729825	2.380353	0.446001
69	6	0	2.659014	2.239731	-0.996216
70	6	0	2.822392	0.850648	-1.317480
71	6	0	2.092800	0.308034	-2.345174
72	6	0	1.465093	-1.022676	-2.185277
73	6	0	0.180160	-0.971732	-2.847525
74	6	0	-0.924050	-1.631551	-2.305733
75	6	0	-2.770491	-1.076641	1.739937
76	6	0	-3.078707	-1.606913	-1.182415
77	6	0	1.674629	-0.580682	2.342554
78	6	0	3.769666	-2.450750	0.140928
79	1	0	3.320243	-3.441745	0.261270
80	6	0	4.661303	-2.072262	1.299547
81	6	0	4.875563	-2.812881	2.455028
82	1	0	4.401897	-3.783974	2.579135
83	6	0	5.702493	-2.294831	3.454848
84	1	0	5.881329	-2.869250	4.359072
85	6	0	6.294375	-1.041767	3.300738
86	1	0	6.932163	-0.644348	4.084789
87	6	0	6.066945	-0.292024	2.144622
88	1	0	6.515764	0.691540	2.026807
89	6	0	5.256511	-0.814628	1.145054
90	6	0	4.867759	-0.128797	-0.141693
91	1	0	5.349830	0.846698	-0.262166
92	6	0	5.143475	-1.059211	-1.297628
93	6	0	5.854612	-0.752924	-2.450748
94	1	0	6.301816	0.230823	-2.573190
95	6	0	5.985263	-1.720606	-3.449856
96	1	0	6.545666	-1.492021	-4.351535
97	6	0	5.395165	-2.974546	-3.297024
98	1	0	5.498821	-3.720280	-4.079647
99	6	0	4.667194	-3.276025	-2.143277
100	1	0	4.194548	-4.248567	-2.026654
101	6	0	4.550428	-2.317800	-1.144253

AICBA *trans*-3 b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-5.179444	-0.773473	-1.906577
2	1	0	-5.770374	0.068267	-2.274453
3	6	0	-5.848714	-1.673386	-0.892723
4	6	0	-6.908736	-1.476057	-0.021055
5	1	0	-7.465386	-0.542242	-0.014099
6	6	0	-7.248654	-2.515625	0.852388
7	1	0	-8.085979	-2.392746	1.533312
8	6	0	-6.522593	-3.707255	0.863713
9	1	0	-6.803014	-4.499180	1.552279
10	6	0	-5.435385	-3.891632	0.002308
11	1	0	-4.857653	-4.812308	0.025996
12	6	0	-5.119163	-2.870266	-0.879550
13	6	0	-4.000143	-2.703836	-1.880414
14	1	0	-3.515733	-3.620423	-2.224209
15	6	0	-4.683654	-1.810366	-2.933498
16	1	0	-5.505909	-2.320210	-3.442712
17	1	0	-3.989396	-1.395566	-3.672088
18	6	0	-1.133851	1.711062	-3.131874
19	6	0	-2.076456	0.636557	-2.919593
20	6	0	-3.149321	0.810456	-2.080047
21	6	0	-3.309817	2.066109	-1.400352
22	6	0	-2.426077	3.122233	-1.613329
23	6	0	-1.310226	2.941155	-2.500099
24	6	0	0.193197	1.139379	-3.237342
25	6	0	0.085589	-0.287534	-3.086229
26	6	0	-1.307512	-0.629203	-2.893398
27	6	0	-1.660846	-1.634216	-2.031910
28	6	0	-3.807167	-0.310338	-1.277436
29	6	0	-3.804172	1.794586	-0.064255
30	6	0	-3.405077	2.591927	1.005901
31	6	0	-2.473711	3.685972	0.785253
32	6	0	-1.993781	3.943655	-0.491455
33	6	0	-0.596404	4.264567	-0.691303
34	6	0	-0.169665	3.635954	-1.931299
35	6	0	1.098270	3.077228	-2.020810
36	6	0	1.289103	1.803452	-2.692059
37	6	0	1.085999	-0.976052	-2.397747
38	6	0	2.226644	-0.291252	-1.858070
39	6	0	2.319408	1.069841	-1.996023
40	6	0	2.764404	1.904179	-0.858711
41	6	0	2.002243	3.131645	-0.891346
42	6	0	1.597470	3.746951	0.292722
43	6	0	0.268584	4.316175	0.395630
44	6	0	-0.233172	4.046781	1.732514

45	6	0	-1.575872	3.738529	1.922110
46	6	0	-3.945711	0.372850	0.075750
47	6	0	-1.076330	0.525201	3.661309
48	6	0	-2.152459	-0.146420	3.096873
49	6	0	-1.948913	-1.415029	2.419162
50	6	0	-0.666934	-1.951976	2.331339
51	6	0	0.461249	-1.245523	2.904811
52	6	0	1.178835	1.047149	3.349143
53	6	0	0.425324	2.293184	3.324240
54	6	0	-0.971608	1.968817	3.521896
55	6	0	-1.953877	2.675372	2.837663
56	6	0	-3.085554	1.972457	2.265021
57	6	0	-3.177631	0.585805	2.384216
58	6	0	-2.854215	-1.484741	1.295608
59	6	0	-2.455973	-2.081364	0.124874
60	6	0	-1.125465	-2.609282	0.022130
61	6	0	-0.239856	-2.563703	1.100070
62	6	0	1.157203	-2.255812	0.890307
63	6	0	1.596928	-1.421918	2.030795
64	6	0	2.476293	-0.389289	1.824489
65	6	0	2.251142	0.867985	2.477701
66	6	0	0.787348	3.308164	2.449695
67	6	0	1.916465	3.126674	1.551429
68	6	0	2.624386	1.926932	1.559901
69	6	0	3.077954	1.318937	0.340711
70	6	0	3.286436	-0.181927	0.544464
71	6	0	2.811587	-1.084658	-0.688120
72	6	0	1.627888	-1.999970	-0.369936
73	6	0	0.715709	-2.023757	-1.481002
74	6	0	-0.634250	-2.331930	-1.302815
75	6	0	-3.623745	-0.220725	1.270783
76	6	0	-2.971877	-1.682397	-1.251837
77	6	0	0.258972	-0.034873	3.566551
78	6	0	4.819215	-0.487294	0.815589
79	1	0	5.160860	0.121855	1.658712
80	6	0	5.553189	-0.171042	-0.464722
81	6	0	6.508682	0.821442	-0.642805
82	1	0	6.814976	1.442167	0.195984
83	6	0	7.066095	1.012762	-1.909448
84	1	0	7.818956	1.781305	-2.057070
85	6	0	6.656382	0.225597	-2.984743
86	1	0	7.091839	0.382707	-3.967172
87	6	0	5.682881	-0.760939	-2.807485
88	1	0	5.351492	-1.366098	-3.648173
89	6	0	5.139394	-0.959335	-1.544447
90	6	0	4.054123	-1.943248	-1.177404
91	1	0	3.746985	-2.566443	-2.023461
92	6	0	4.510576	-2.756596	0.009353
93	6	0	4.498390	-4.141703	0.114619
94	1	0	4.167858	-4.751370	-0.723164
95	6	0	4.911685	-4.739460	1.307660
96	1	0	4.911100	-5.821773	1.397473
97	6	0	5.318015	-3.953556	2.385125
98	1	0	5.632230	-4.425806	3.311343
99	6	0	5.318294	-2.560464	2.281980
100	1	0	5.621390	-1.944454	3.125369
101	6	0	4.921753	-1.967916	1.089830

AICBA *trans*-4 a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-4.008165	2.510058	-1.926050
2	1	0	-3.879308	2.655190	-3.000911
3	6	0	-3.903697	3.747418	-1.064093
4	6	0	-3.302186	4.979862	-1.267925
5	1	0	-2.820823	5.220798	-2.212540
6	6	0	-3.332431	5.910851	-0.223290
7	1	0	-2.884485	6.890425	-0.363645
8	6	0	-3.928451	5.595824	0.998171
9	1	0	-3.938800	6.333432	1.795625
10	6	0	-4.509188	4.340052	1.210033
11	1	0	-4.955683	4.090359	2.169437
12	6	0	-4.499752	3.430147	0.164329
13	6	0	-4.964071	1.996465	0.058765
14	1	0	-5.704027	1.669100	0.792388
15	6	0	-5.345626	1.924235	-1.432461
16	1	0	-6.198112	2.563616	-1.767984
17	1	0	-5.532430	0.904847	-1.786929
18	6	0	-2.690777	-2.170351	-2.541314
19	6	0	-3.359477	-0.981752	-2.066244
20	6	0	-2.801301	0.256014	-2.268584
21	6	0	-1.531326	0.348443	-2.935889
22	6	0	-0.886068	-0.780810	-3.425985
23	6	0	-1.479253	-2.076017	-3.224677
24	6	0	-2.886455	-3.224897	-1.566667
25	6	0	-3.682203	-2.697219	-0.475485
26	6	0	-3.984682	-1.313014	-0.762872
27	6	0	-4.006196	-0.386220	0.247153
28	6	0	-2.992628	1.454048	-1.339181
29	6	0	-0.767914	1.401818	-2.288491
30	6	0	0.616130	1.268615	-2.141189
31	6	0	1.286776	0.079295	-2.638721
32	6	0	0.557722	-0.918319	-3.275783
33	6	0	0.846350	-2.296515	-2.983110
34	6	0	-0.411846	-3.018803	-2.945459
35	6	0	-0.604928	-4.026532	-2.007204

36	6	0	-1.871164	-4.138215	-1.310534
37	6	0	-3.433135	-3.112493	0.829547
38	6	0	-2.367207	-4.058122	1.101331
39	6	0	-1.601184	-4.558026	0.055331
40	6	0	-0.168361	-4.693697	0.204802
41	6	0	0.448874	-4.358441	-1.068698
42	6	0	1.647166	-3.655682	-1.094602
43	6	0	1.854187	-2.601653	-2.068602
44	6	0	2.620547	-1.550494	-1.443061
45	6	0	2.349589	-0.236504	-1.726388
46	6	0	-1.557865	1.955986	-1.244769
47	6	0	1.778996	0.877339	1.744960
48	6	0	0.760344	1.753958	1.475519
49	6	0	-0.508020	1.634470	2.155617
50	6	0	-0.700467	0.639205	3.115205
51	6	0	0.361108	-0.294953	3.388653
52	6	0	2.236829	-1.366575	2.208714
53	6	0	2.873892	-1.038252	0.961869
54	6	0	2.867743	0.475785	0.749227
55	6	0	2.574531	0.926027	-0.757867
56	6	0	1.258314	1.682402	-0.942363
57	6	0	0.484389	2.172611	0.085022
58	6	0	-1.566581	1.973674	1.233123
59	6	0	-2.766131	1.308276	1.279003
60	6	0	-2.942951	0.244460	2.230884
61	6	0	-1.948916	-0.078013	3.150569
62	6	0	-1.665655	-1.471666	3.451566
63	6	0	-0.229673	-1.606760	3.600285
64	6	0	0.413105	-2.743041	3.128537
65	6	0	1.678869	-2.624354	2.426415
66	6	0	2.891621	-1.965544	-0.046244
67	6	0	2.285637	-3.262615	0.146967
68	6	0	1.702127	-3.599004	1.365672
69	6	0	0.446316	-4.324721	1.395233
70	6	0	-0.351025	-3.797424	2.488381
71	6	0	-1.727725	-3.667310	2.344831
72	6	0	-2.398178	-2.477845	2.836527
73	6	0	-3.448615	-2.139373	1.892472
74	6	0	-3.709909	-0.804864	1.592313
75	6	0	-0.939097	2.307848	-0.064456
76	6	0	-3.668450	1.091952	0.071483
77	6	0	1.562800	-0.180415	2.695163
78	6	0	3.788548	1.819101	-1.248941
79	1	0	3.603738	2.135770	-2.280545
80	6	0	5.031044	0.973348	-1.114187
81	6	0	5.852753	0.544169	-2.148639
82	1	0	5.641605	0.839067	-3.173977
83	6	0	6.948604	-0.271648	-1.856717
84	1	0	7.600211	-0.606907	-2.658273
85	6	0	7.205892	-0.661695	-0.543310
86	1	0	8.057454	-1.299234	-0.324462
87	6	0	6.370031	-0.241573	0.494165
88	1	0	6.560168	-0.555480	1.518015
89	6	0	5.288598	0.580948	0.204090
90	6	0	4.262601	1.094562	1.185286
91	1	0	4.479426	0.797252	2.216450
92	6	0	4.137453	2.590537	1.026784
93	6	0	4.205033	3.536909	2.041364
94	1	0	4.393984	3.227837	3.066882
95	6	0	4.025145	4.886510	1.728898
96	1	0	4.084137	5.634234	2.514426
97	6	0	3.765825	5.277226	0.415986
98	1	0	3.621669	6.328176	0.183017
99	6	0	3.684880	4.322985	-0.601081
100	1	0	3.468521	4.621972	-1.624108
101	6	0	3.879016	2.982909	-0.291412

AICBA *trans*-4 b

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-3.644677	-3.380478	-0.776271
2	1	0	-3.233520	-4.045944	-1.538401
3	6	0	-5.047584	-2.872740	-1.013733
4	6	0	-5.812722	-2.746933	-2.162682
5	1	0	-5.441596	-3.089294	-3.125456
6	6	0	-7.083431	-2.170646	-2.050805
7	1	0	-7.710958	-2.079344	-2.932690
8	6	0	-7.553355	-1.710170	-0.820365
9	1	0	-8.541761	-1.264278	-0.756462
10	6	0	-6.765917	-1.812786	0.332230
11	1	0	-7.127529	-1.436226	1.285830
12	6	0	-5.519845	-2.410348	0.222585
13	6	0	-4.405787	-2.634134	1.218911
14	1	0	-4.687175	-2.618285	2.274154
15	6	0	-3.772268	-3.923688	0.660590
16	1	0	-4.446679	-4.781854	0.724733
17	1	0	-2.809569	-4.171481	1.120800
18	6	0	0.954307	-2.286655	0.522491
19	6	0	-0.454736	-2.567239	0.584262
20	6	0	-1.244631	-2.471460	-0.540447
21	6	0	-0.644089	-2.034723	-1.754705
22	6	0	0.724938	-1.759089	-1.813494
23	6	0	1.545914	-1.911014	-0.661595
24	6	0	1.342791	-1.621027	1.783791
25	6	0	0.156509	-1.501020	2.598672
26	6	0	-0.959607	-2.079789	1.886385

27	6	0	-2.209987	-1.523784	1.981423
28	6	0	-2.730367	-2.118091	-0.529100
29	6	0	-1.585506	-1.175434	-2.453020
30	6	0	-1.125965	-0.091273	-3.191974
31	6	0	0.301649	0.194829	-3.254405
32	6	0	1.202712	-0.616638	-2.574142
33	6	0	2.323462	-0.060692	-1.869136
34	6	0	2.784752	-1.021316	-0.771476
35	6	0	3.199785	-0.301401	0.596937
36	6	0	2.285056	-0.625996	1.778364
37	6	0	-0.031258	-0.380865	3.407997
38	6	0	0.947274	0.675420	3.392690
39	6	0	2.066114	0.552714	2.573588
40	6	0	2.547316	1.695657	1.825536
41	6	0	3.065946	1.220757	0.571030
42	6	0	2.867754	1.964164	-0.561820
43	6	0	2.482276	1.300845	-1.829690
44	6	0	1.540398	2.162679	-2.502883
45	6	0	0.472314	1.622408	-3.218692
46	6	0	-2.771944	-1.085930	-1.649201
47	6	0	-2.216267	3.470423	-1.505970
48	6	0	-3.150618	2.442613	-1.482590
49	6	0	-3.751405	2.034879	-0.227333
50	6	0	-3.400540	2.683944	0.953934
51	6	0	-2.417355	3.750709	0.933198
52	6	0	-0.418577	4.418410	-0.333006
53	6	0	0.079326	3.931674	-1.609764
54	6	0	-1.034435	3.355865	-2.337943
55	6	0	-0.843794	2.227595	-3.126247
56	6	0	-1.828451	1.161153	-3.114599
57	6	0	-2.955847	1.260516	-2.299619
58	6	0	-3.934844	0.601528	-0.255648
59	6	0	-3.742984	-0.139525	0.882253
60	6	0	-3.336928	0.521761	2.093242
61	6	0	-3.187516	1.905423	2.147526
62	6	0	-2.076268	2.486466	2.880213
63	6	0	-1.598984	3.630880	2.126458
64	6	0	-0.236979	3.902878	2.065079
65	6	0	0.366845	4.307453	0.808261
66	6	0	1.335278	3.342028	-1.684233
67	6	0	2.152350	3.217804	-0.492474
68	6	0	1.681276	3.699841	0.725979
69	6	0	1.886615	2.918492	1.918777
70	6	0	0.705095	3.040853	2.754761
71	6	0	0.246700	1.946817	3.475737
72	6	0	-1.173508	1.663677	3.540100
73	6	0	-1.338097	0.219544	3.496184
74	6	0	-2.391813	-0.336941	2.776986
75	6	0	-3.434143	0.114310	-1.563545
76	6	0	-3.271586	-1.586824	0.886456
77	6	0	-1.835845	4.134172	-0.269164
78	6	0	4.027105	-1.868369	-1.276985
79	1	0	3.760671	-2.366991	-2.214540
80	6	0	4.361349	-2.844241	-0.174661
81	6	0	4.296406	-4.229705	-0.250656
82	1	0	4.006861	-4.714345	-1.180287
83	6	0	4.605131	-4.990670	0.879710
84	1	0	4.563715	-6.074720	0.827893
85	6	0	4.959944	-4.365516	2.074191
86	1	0	5.194614	-4.963731	2.949688
87	6	0	5.012807	-2.971770	2.152554
88	1	0	5.277755	-2.480260	3.085888
89	6	0	4.721018	-2.216874	1.023470
90	6	0	4.694797	-0.710350	0.934057
91	1	0	4.994503	-0.227499	1.869900
92	6	0	5.535388	-0.272645	-0.241058
93	6	0	6.538923	0.687611	-0.226190
94	1	0	6.807978	1.184456	0.703098
95	6	0	7.193537	1.009388	-1.417684
96	1	0	7.984250	1.754061	-1.414606
97	6	0	6.833155	0.384336	-2.610537
98	1	0	7.343758	0.644166	-3.533144
99	6	0	5.813568	-0.570347	-2.626576
100	1	0	5.519349	-1.049227	-3.557714
101	6	0	5.173468	-0.899911	-1.438604

AICBA e-face a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-0.865136	4.704651	-1.130755
2	1	0	-1.143346	4.933967	-2.161724
3	6	0	0.521179	5.124429	-0.700863
4	6	0	1.676081	5.403448	-1.414941
5	1	0	1.682578	5.387011	-2.501968
6	6	0	2.837879	5.712990	-0.697706
7	1	0	3.750566	5.957056	-1.233782
8	6	0	2.837821	5.713185	0.697686
9	1	0	3.750469	5.957388	1.233766
10	6	0	1.675974	5.403797	1.414908
11	1	0	1.682390	5.387590	2.501941
12	6	0	0.521146	5.124532	0.700809
13	6	0	-0.865157	4.704670	1.130695
14	1	0	-1.143415	4.934025	2.161642
15	6	0	-1.716719	5.314187	-0.000048
16	1	0	-1.691361	6.407278	-0.000037
17	1	0	-2.755387	4.966821	-0.000050

Kinetics and Thermodynamics of the Diels-Alder Addition to Fullerenes

18	6	0	1.448065	-2.333277	-1.170817	9	1	0	-7.679411	-3.221831	1.233035
19	6	0	0.591160	-3.393039	-0.726116	10	6	0	-5.542613	-3.432951	1.414954
20	6	0	-0.567848	-3.728748	-1.423901	11	1	0	-5.543055	-3.412350	2.501957
21	6	0	-0.930164	-2.972653	-2.592750	12	6	0	-4.363185	-3.575702	0.700831
22	6	0	-0.111703	-1.921790	-3.003460	13	6	0	-2.916947	-3.663510	1.130739
23	6	0	1.099307	-1.608363	-2.282325	14	1	0	-2.734372	-3.975076	2.161581
24	6	0	2.262215	-1.782922	-0.000009	15	6	0	-2.331837	-4.531901	-0.000074
25	6	0	1.448062	-2.333251	1.170810	16	1	0	-2.737911	-5.547106	0.000021
26	6	0	0.591158	-3.393021	0.726125	17	1	0	-1.236966	-4.569366	-0.000123
27	6	0	-0.567847	-3.728709	1.423926	18	6	0	1.494796	-1.526027	-1.169138
28	6	0	-1.782418	-4.052465	-0.693585	19	6	0	0.321076	-2.219831	-0.738028
29	6	0	-2.372289	-2.814204	-2.596769	20	6	0	-0.866925	-2.127854	-1.431311
30	6	0	-2.937374	-1.618710	-3.025807	21	6	0	-0.924973	-1.270384	-2.568218
31	6	0	-2.084982	-0.529829	-3.468396	22	6	0	0.210162	-0.580321	-2.998230
32	6	0	-0.707180	-0.677786	-3.450666	23	6	0	1.442976	-0.721023	-2.283322
33	6	0	0.141232	0.412834	-3.001323	24	6	0	2.452107	-1.310804	-0.000001
34	6	0	1.251838	-0.137317	-2.284846	25	6	0	1.494777	-1.525980	1.169111
35	6	0	1.731138	0.510910	-1.169615	26	6	0	0.321056	-2.219770	0.737999
36	6	0	2.419045	-0.189893	-0.000017	27	6	0	-0.866875	-2.127945	1.431364
37	6	0	1.099316	-1.608336	2.282322	28	6	0	-2.251248	-2.270087	-0.802341
38	6	0	1.251848	-0.137289	2.284828	29	6	0	-2.219849	-0.614818	-2.578087
39	6	0	1.731130	0.510916	1.169574	30	6	0	-2.331761	0.698705	-3.024595
40	6	0	1.124708	1.731120	0.738197	31	6	0	-1.147230	1.418576	-3.467208
41	6	0	1.124711	1.731119	-0.738252	32	6	0	0.090328	0.795796	-3.449370
42	6	0	0.078292	2.296970	-1.435888	33	6	0	1.266432	1.517175	-3.003536
43	6	0	-0.437498	1.608789	-2.570286	34	6	0	2.114724	0.596666	-2.282623
44	6	0	-1.880868	1.760149	-2.577037	35	6	0	2.801779	1.016159	-1.171786
45	6	0	-2.687946	0.717947	-3.022879	36	6	0	3.187811	0.111990	-0.000006
46	6	0	-2.900895	-3.482766	-1.421282	37	6	0	1.442968	-0.721021	2.283327
47	6	0	-4.747260	0.470775	0.000000	38	6	0	2.114721	0.596665	2.282642
48	6	0	-4.914409	-0.908375	0.000006	39	6	0	2.801775	1.016146	1.171795
49	6	0	-4.556477	-1.682022	1.175560	40	6	0	2.656387	2.371330	0.726070
50	6	0	-4.052415	-1.041227	2.302001	41	6	0	2.656389	2.371340	-0.726054
51	6	0	-3.893668	0.401804	2.305630	42	6	0	1.864182	3.281858	-1.423209
52	6	0	-3.914000	2.238287	0.741727	43	6	0	1.149679	2.844186	-2.593122
53	6	0	-3.391410	2.238286	-0.741758	44	6	0	-0.148523	3.492313	-2.596586
54	6	0	-4.227981	1.143495	-1.174625	45	6	0	-1.272426	2.795621	-3.025262
55	6	0	-3.893679	0.401772	-2.305632	46	6	0	-2.958262	-1.079493	-1.436362
56	6	0	-4.052426	-1.041259	-2.301986	47	6	0	-3.317304	3.272253	-0.000014
57	6	0	-4.556482	-1.682043	-1.175536	48	6	0	-3.924554	2.023363	-0.000023
58	6	0	-3.969606	-2.927297	0.727133	49	6	0	-3.855657	1.175614	1.174766
59	6	0	-2.900896	-3.482756	1.421330	50	6	0	-3.173105	1.617702	2.306496
60	6	0	-2.372284	-2.814173	2.596808	51	6	0	-2.522791	2.916307	2.302213
61	6	0	-2.937357	-1.618670	3.025828	52	6	0	-1.427340	4.454608	0.727337
62	6	0	-2.084966	-0.529783	3.468398	53	6	0	-1.427334	4.454609	-0.727340
63	6	0	-2.687938	0.717990	3.022877	54	6	0	-2.596557	3.727769	-1.175342
64	6	0	-1.880864	1.760183	2.577007	55	6	0	-2.522782	2.916322	-2.302241
65	6	0	-2.247628	2.550767	1.432748	56	6	0	-3.173105	1.617724	-2.306536
66	6	0	-2.247625	2.550736	-1.432778	57	6	0	-3.855660	1.175624	-1.174812
67	6	0	-1.000175	3.166323	-0.802548	58	6	0	-3.748681	-0.198085	0.741560
68	6	0	-1.000150	3.166332	0.802497	59	6	0	-2.958235	-1.079484	1.436310
69	6	0	0.078280	2.296972	1.435826	60	6	0	-2.219838	-0.614853	2.578055
70	6	0	-0.437493	1.608819	2.570244	61	6	0	-2.331757	0.698689	3.024536
71	6	0	0.141246	0.412871	3.001294	62	6	0	-1.147243	1.418570	3.467197
72	6	0	-0.707165	-0.677745	3.450669	63	6	0	-1.272447	2.795615	3.025255
73	6	0	-0.111690	-1.921755	3.003469	64	6	0	-0.148543	3.492308	2.596584
74	6	0	-0.930159	-2.972620	2.592776	65	6	0	-0.228709	4.340687	1.422119
75	6	0	-3.969615	-2.927317	-0.727092	66	6	0	-0.228699	4.340687	-1.422115
76	6	0	-1.782421	-4.052440	0.693624	67	6	0	1.019315	4.212399	-0.693568
77	6	0	-4.227979	1.143512	1.174614	68	6	0	1.019309	4.212397	0.693578
78	6	0	3.969218	0.151352	-0.000001	69	6	0	1.864166	3.281844	1.423219
79	1	0	4.094243	1.239155	-0.000015	70	6	0	1.149659	2.844180	2.593133
80	6	0	4.552674	-0.501344	-1.229382	71	6	0	1.266416	1.517168	3.003540
81	6	0	5.128314	0.148151	-2.314138	72	6	0	0.090309	0.795774	3.449362
82	1	0	5.217960	1.232068	-2.317593	73	6	0	0.210149	-0.580346	2.998258
83	6	0	5.584912	-0.605870	-3.397754	74	6	0	-0.924969	-1.270427	2.568226
84	1	0	6.042803	-0.107563	-4.247180	75	6	0	-3.748667	-0.198087	-0.741603
85	6	0	5.450220	-1.993576	-3.396810	76	6	0	-2.251310	-2.270073	0.802270
86	1	0	5.801872	-2.572069	-4.246059	77	6	0	-2.596571	3.727769	1.175329
87	6	0	4.857290	-2.644117	-2.312035	78	6	0	4.754335	-0.144323	-0.000027
88	1	0	4.737072	-3.725005	-2.314824	79	1	0	5.273553	0.819619	-0.000073
89	6	0	4.416519	-1.894192	-1.228992	80	6	0	5.056465	-0.967865	-1.229704
90	6	0	3.715868	-2.420374	0.000019	81	6	0	5.834135	-0.581011	-2.314217
91	1	0	3.627956	-3.511705	0.000015	82	1	0	6.321115	0.391471	-2.320022
92	6	0	4.416498	-1.894171	1.229033	83	6	0	5.979425	-1.453245	-3.395952
93	6	0	4.857223	-2.644075	2.312111	84	1	0	6.589943	-1.161944	-4.245529
94	1	0	4.737003	-3.724963	2.314913	85	6	0	5.339896	-2.691928	-3.393301
95	6	0	5.450103	-1.993513	3.396900	86	1	0	5.453921	-3.362293	-4.240161
96	1	0	5.801714	-2.571988	4.246178	87	6	0	4.546558	-3.073399	-2.308749
97	6	0	5.584797	-0.605807	3.397821	88	1	0	4.033855	-4.032623	-2.309099
98	1	0	6.042655	-0.107483	4.247255	89	6	0	4.414391	-2.210908	-1.227998
99	6	0	5.128251	0.148192	2.314167	90	6	0	3.568344	-2.439257	0.000043
100	1	0	5.217901	1.232108	2.317603	91	1	0	3.081621	-3.420057	0.000065
101	6	0	4.552652	-0.501324	1.229401	92	6	0	4.414415	-2.210846	1.228045
						93	6	0	4.546607	-3.073280	2.308840
						94	1	0	4.033896	-4.032498	2.309277
						95	6	0	5.339980	-2.691751	3.393345
						96	1	0	5.454016	-3.362066	4.240245
						97	6	0	5.979528	-1.453077	3.395913
						98	1	0	6.590067	-1.161755	4.245468
						99	6	0	5.834220	-0.580901	2.314135
						100	1	0	6.321205	0.391578	2.319845
						101	6	0	5.056507	-0.967813	1.229670

AICBA e-face *b*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-2.917031	-3.663538	-1.130800
2	1	0	-2.734488	-3.974945	-2.161705
3	6	0	-4.363231	-3.575728	-0.700819
4	6	0	-5.542732	-3.432951	-1.414822
5	1	0	-5.543292	-3.412314	-2.501821
6	6	0	-6.739084	-3.317174	-0.697553
7	1	0	-7.679504	-3.221802	-1.232724
8	6	0	-6.739031	-3.317177	0.697797

AICBA e-edge

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z

1	6	0	-4.162296	2.699186	1.254098
2	1	0	-5.116274	2.299363	1.604683
3	6	0	-4.222608	3.651862	0.083697
4	6	0	-5.171595	3.850387	-0.906672
5	1	0	-6.108063	3.298170	-0.906270
6	6	0	-4.892880	4.784852	-1.910513
7	1	0	-5.627376	4.972031	-2.688483
8	6	0	-3.680187	5.474626	-1.926833
9	1	0	-3.483931	6.193239	-2.717345
10	6	0	-2.712388	5.249413	-0.940542
11	1	0	-1.760445	5.773940	-0.968031
12	6	0	-3.003370	4.343179	0.068064
13	6	0	-2.194959	3.815437	1.231538
14	1	0	-1.356380	4.433036	1.560273
15	6	0	-3.313332	3.515136	2.248485
16	1	0	-3.824956	4.420326	2.586645
17	1	0	-2.974704	2.934789	3.113312
18	6	0	-1.320544	-2.418985	-3.258359
19	6	0	-0.277142	-3.326277	-2.822681
20	6	0	-0.538907	-4.255968	-1.821888
21	6	0	-1.854143	-4.321512	-1.220336
22	6	0	-2.855762	-3.453780	-1.640256
23	6	0	-2.583416	-2.479574	-2.681208
24	6	0	-0.706120	-1.130474	-3.523295
25	6	0	0.720135	-1.254456	-3.260154
26	6	0	0.981040	-2.601624	-2.829654
27	6	0	1.919410	-2.824058	-1.823457
28	6	0	0.442485	-4.494588	-0.779203
29	6	0	-1.687756	-4.608241	0.195865
30	6	0	-2.529766	-4.012930	1.128577
31	6	0	-3.567654	-3.100858	0.687116
32	6	0	-3.727597	-2.828622	-0.663788
33	6	0	-3.988349	-1.469684	-1.108326
34	6	0	-3.289150	-1.256397	-2.347945
35	6	0	-2.691157	-0.019789	-2.587227
36	6	0	-1.373395	0.037456	-3.189392
37	6	0	1.411219	-0.201864	-2.667252
38	6	0	0.713894	1.024692	-2.327117
39	6	0	-0.653597	1.146352	-2.585911
40	6	0	-1.506019	1.777645	-1.624036
41	6	0	-2.793567	1.048090	-1.618999
42	6	0	-3.473076	0.847316	-0.441557
43	6	0	-4.053193	-0.436431	-0.175803
44	6	0	-3.885280	-0.721782	1.238239
45	6	0	-3.659351	-2.028776	1.663733
46	6	0	-0.269611	-4.717970	0.466301
47	6	0	-0.581541	-1.319879	3.524012
48	6	0	0.090402	-2.495451	3.227429
49	6	0	1.413930	-2.443851	2.623567
50	6	0	2.002227	-1.214355	2.341739
51	6	0	1.301103	0.015371	2.661878
52	6	0	-0.982319	0.879217	2.815388
53	6	0	-2.269033	0.148469	2.820146
54	6	0	-2.001621	-1.202793	3.257495
55	6	0	-2.692265	-2.277304	2.700682
56	6	0	-1.987239	-3.502291	2.374018
57	6	0	-0.625563	-3.609826	2.632791
58	6	0	1.510663	-3.509053	1.662263
59	6	0	2.188712	-3.286316	0.465373
60	6	0	2.816121	-2.013156	0.203356
61	6	0	2.733095	-1.000247	1.123182
62	6	0	2.751942	0.489293	0.777284
63	6	0	1.598246	0.976613	1.654187
64	6	0	0.599233	1.826782	1.236093
65	6	0	-0.703819	1.796213	1.825874
66	6	0	-3.198802	0.386489	1.838157
67	6	0	-3.141687	1.558673	0.863202
68	6	0	-1.743364	2.348510	0.854572
69	6	0	-0.967348	2.257803	-0.450337
70	6	0	0.432422	2.118383	-0.200268
71	6	0	1.274066	1.538456	-1.123923
72	6	0	2.570878	0.803826	-0.780891
73	6	0	2.406766	-0.438347	-1.658080
74	6	0	2.646856	-1.721495	-1.240369
75	6	0	0.251363	-4.231071	1.659945
76	6	0	1.639855	-3.790337	-0.778601
77	6	0	0.034426	-0.033184	3.246603
78	6	0	4.113639	1.145496	1.256354
79	1	0	4.252275	0.941094	2.322956
80	6	0	4.006901	2.621073	0.957818
81	6	0	4.000039	3.652701	1.887979
82	1	0	4.106988	3.434566	2.948126
83	6	0	3.852050	4.969646	1.445800
84	1	0	3.853466	5.783788	2.164795
85	6	0	3.699398	5.243110	0.087110
86	1	0	3.583357	6.269535	-0.248620
87	6	0	3.691517	4.203134	-0.845758
88	1	0	3.558568	4.411742	-1.904823
89	6	0	3.852094	2.895121	-0.405927
90	6	0	3.823906	1.650168	-1.260282
91	1	0	3.715643	1.873566	-2.326569
92	6	0	5.048473	0.819386	-0.960185
93	6	0	5.938586	0.293274	-1.888370
94	1	0	5.805793	0.494192	-2.948921
95	6	0	6.999348	-0.499465	-1.443561
96	1	0	7.703357	-0.910289	-2.161167
97	6	0	7.155013	-0.770704	-0.084935
98	1	0	7.979816	-1.392073	0.251274
99	6	0	6.251403	-0.252237	0.845984
100	1	0	6.361389	-0.473277	1.905176

101 6 0 5.205159 0.546878 0.403397

AICBA *cis*-2 a

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.348223	-4.038419	-1.698251
2	1	0	0.707548	-4.885643	-1.952258
3	6	0	2.463975	-4.312430	-0.728715
4	6	0	2.654270	-5.323068	0.199604
5	1	0	1.934085	-6.130774	0.303367
6	6	0	3.803600	-5.280920	0.996214
7	1	0	3.985675	-6.067387	1.722820
8	6	0	4.718471	-4.238095	0.861170
9	1	0	5.609862	-4.220633	1.481654
10	6	0	4.504463	-3.209581	-0.063929
11	1	0	5.223133	-2.406249	-0.152597
12	6	0	3.369736	-3.251367	-0.858295
13	6	0	2.803957	-2.322928	-1.920931
14	1	0	3.513273	-1.639595	-2.391098
15	6	0	2.113114	-3.346914	-2.842379
16	1	0	2.826687	-4.017075	-3.329292
17	1	0	1.460561	-2.889973	-3.593746
18	6	0	-3.774103	2.740571	1.209121
19	6	0	-3.408521	3.187096	-0.123901
20	6	0	-3.893362	2.511534	-1.237883
21	6	0	-4.770392	1.368412	-1.070259
22	6	0	-5.125390	0.944968	0.205750
23	6	0	-4.611751	1.643561	1.368541
24	6	0	-2.613800	2.897635	2.065787
25	6	0	-1.538092	3.443627	1.255763
26	6	0	-2.027798	3.624673	-0.087705
27	6	0	-1.183425	3.353384	-1.162254
28	6	0	-3.016735	2.240647	-2.361090
29	6	0	-4.445114	0.393732	-2.095130
30	6	0	-4.492021	-0.964604	-1.804084
31	6	0	-4.856871	-1.406048	-0.468502
32	6	0	-5.164499	-0.472259	0.513457
33	6	0	-4.669103	-0.650261	1.866485
34	6	0	-4.328231	0.655458	2.394112
35	6	0	-3.213186	0.803890	3.211482
36	6	0	-2.335948	1.949903	3.041309
37	6	0	-0.232162	3.001588	1.451070
38	6	0	0.060369	2.012589	2.471389
39	6	0	-0.972466	1.502512	3.256679
40	6	0	-1.001134	0.094869	3.547953
41	6	0	-2.387265	-0.343654	3.528649
42	6	0	-2.713225	-1.594428	3.022321
43	6	0	-3.880177	-1.752859	2.178181
44	6	0	-3.557963	-2.726546	1.149656
45	6	0	-4.039542	-2.558705	-0.141942
46	6	0	-3.358579	0.928474	-2.891737
47	6	0	-0.789490	-2.713066	-1.873103
48	6	0	-1.051926	-1.783237	-2.840285
49	6	0	-0.151068	-0.618798	-2.991209
50	6	0	0.961291	-0.470867	-2.176411
51	6	0	1.545139	-1.581991	-1.302603
52	6	0	0.019659	-3.012775	0.291742
53	6	0	-1.357255	-3.408567	0.279588
54	6	0	-1.861249	-3.230659	-1.069080
55	6	0	-3.175165	-2.823908	-1.279178
56	6	0	-3.455442	-1.846056	-2.301627
57	6	0	-2.405870	-1.330012	-3.058623
58	6	0	-0.967893	0.508379	-3.314812
59	6	0	-0.642681	1.766770	-2.806936
60	6	0	0.502051	1.912430	-1.968207
61	6	0	1.279337	0.812687	-1.654752
62	6	0	2.140370	0.709630	-0.398793
63	6	0	1.837451	-0.759391	-0.042981
64	6	0	1.416267	-1.150145	1.174496
65	6	0	0.507428	-2.306924	1.362063
66	6	0	-2.193175	-3.167149	1.368292
67	6	0	-1.669872	-2.467933	2.510386
68	6	0	-0.347075	-2.030765	2.489498
69	6	0	-0.005730	-0.725066	3.021419
70	6	0	1.066440	-0.174208	2.232303
71	6	0	1.114327	1.171594	1.984581
72	6	0	1.741668	1.776467	0.736762
73	6	0	0.638300	2.752930	0.338621
74	6	0	0.173985	2.918969	-0.936309
75	6	0	-2.358365	0.086605	-3.356572
76	6	0	-1.691913	2.647367	-2.321646
77	6	0	0.528005	-2.823373	-1.122406
78	6	0	3.664866	0.981599	-0.773888
79	1	0	3.975234	0.306842	-1.576368
80	6	0	4.505528	0.820147	0.470380
81	6	0	5.614075	-0.000539	0.620143
82	1	0	5.975870	-0.581742	-0.223297
83	6	0	6.284821	-0.038476	1.844813
84	1	0	7.151829	-0.681767	1.966285
85	6	0	5.851576	0.753837	2.906060
86	1	0	6.371193	0.714379	3.858875
87	6	0	4.772651	1.625718	2.737960
88	1	0	4.458477	2.278440	3.549043
89	6	0	4.119337	1.668885	1.513104
90	6	0	3.022961	2.621351	1.113774
91	1	0	2.763859	3.323504	1.912799

Kinetics and Thermodynamics of the Diels-Alder Addition to Fullerenes

92	6	0	3.438935	3.321772	-0.160507
93	6	0	3.450873	4.692080	-0.383656
94	1	0	3.185994	5.379580	0.416385
95	6	0	3.797980	5.174509	-1.648201
96	1	0	3.816426	6.244891	-1.830823
97	6	0	4.112642	4.289158	-2.677742
98	1	0	4.375390	4.672018	-3.659535
99	6	0	4.087336	2.910002	-2.454799
100	1	0	4.320423	2.216600	-3.259834
101	6	0	3.756962	2.432414	-1.193100

AICBA *cis*-2 *b*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.226033	4.048653	1.656274
2	1	0	0.685065	4.597261	2.430257
3	6	0	1.617530	4.829554	0.424676
4	6	0	1.125449	5.998655	-0.133308
5	1	0	0.343074	6.570625	0.359365
6	6	0	1.662205	6.424733	-1.353651
7	1	0	1.306351	7.346852	-1.804119
8	6	0	2.643970	5.675308	-2.002693
9	1	0	3.041730	6.022351	-2.951958
10	6	0	3.118844	4.481023	-1.447852
11	1	0	3.870641	3.890669	-1.966586
12	6	0	2.606434	4.077712	-0.223743
13	6	0	2.834779	2.847175	0.623500
14	1	0	3.784968	2.338290	0.469399
15	6	0	2.570542	3.403821	2.034718
16	1	0	3.317607	4.142257	2.339103
17	1	0	2.482913	2.623186	2.798334
18	6	0	-3.415312	-2.776585	1.773392
19	6	0	-2.779146	-2.038152	2.845562
20	6	0	-3.179091	-0.738239	3.125753
21	6	0	-4.232191	-0.119825	2.346922
22	6	0	-4.839262	-0.825038	1.313014
23	6	0	-4.421644	-2.181757	1.020192
24	6	0	-2.395308	-3.578098	1.118477
25	6	0	-1.134812	-3.330242	1.792130
26	6	0	-1.366533	-2.381652	2.847957
27	6	0	-0.413195	-1.395867	3.092409
28	6	0	-2.185848	0.281794	3.420555
29	6	0	-3.890496	1.280669	2.165945
30	6	0	-4.171281	1.915599	0.963793
31	6	0	-4.798903	1.178939	-0.116348
32	6	0	-5.124967	-0.161460	0.053542
33	6	0	-4.880480	-1.109858	-1.016160
34	6	0	-4.448104	-2.359739	-0.420333
35	6	0	-3.473242	-3.128684	-1.045039
36	6	0	-2.426147	-3.751740	-0.258375
37	6	0	0.045313	-3.252669	1.052855
38	6	0	0.014375	-3.437806	-0.386222
39	6	0	-1.195641	-3.689365	-1.028953
40	6	0	-1.478947	-3.035290	-2.281507
41	6	0	-2.884999	-2.681271	-2.295649
42	6	0	-3.292765	-1.478374	-2.860067
43	6	0	-4.311972	-0.677138	-2.209086
44	6	0	-3.969519	0.721836	-2.386003
45	6	0	-4.211761	1.633239	-1.364919
46	6	0	-2.627693	1.520315	2.837332
47	6	0	-0.781691	2.959544	-1.090458
48	6	0	-0.759051	3.138343	0.268400
49	6	0	0.426808	2.782816	1.153129
50	6	0	1.575763	1.905225	0.436735
51	6	0	1.252696	1.528688	-0.998938
52	6	0	-0.372964	1.409289	-2.807218
53	6	0	-1.783607	1.752246	-2.832178
54	6	0	-2.031916	2.706014	-1.768154
55	6	0	-3.227166	2.651475	-1.054409
56	6	0	-3.200841	2.823469	0.376389
57	6	0	-1.982574	3.044228	1.013764
58	6	0	-0.288711	2.070660	2.288188
59	6	0	0.126104	0.872379	2.808162
60	6	0	1.174885	0.073512	2.132968
61	6	0	1.780167	0.499339	1.010005
62	6	0	2.304372	-0.454100	-0.075388
63	6	0	1.650497	0.196018	-1.286311
64	6	0	1.062609	-0.506373	-2.319025
65	6	0	0.028055	0.101601	-3.091806
66	6	0	-2.731443	0.787150	-3.138555
67	6	0	-2.312600	-0.576001	-3.432172
68	6	0	-0.966694	-0.908361	-3.407432
69	6	0	-0.536178	-2.162597	-2.819371
70	6	0	0.721878	-1.935390	-2.148180
71	6	0	1.000531	-2.567274	-0.965239
72	6	0	1.907640	-1.997105	0.126973
73	6	0	1.043256	-2.269343	1.348716
74	6	0	0.808828	-1.346984	2.332334
75	6	0	-1.688436	2.380109	2.269926
76	6	0	-0.831211	-0.037861	3.384115
77	6	0	0.255172	2.130043	-1.745078
78	6	0	3.887452	-0.391267	-0.201925
79	1	0	4.203509	0.633454	-0.404427
80	6	0	4.290167	-1.313981	-1.326003
81	6	0	4.896172	-0.940607	-2.519395
82	1	0	5.138678	0.102904	-2.708185

83	6	0	5.187189	-1.919126	-3.472689
84	1	0	5.666203	-1.637679	-4.405869
85	6	0	4.861466	-3.253773	-3.234040
86	1	0	5.086847	-4.008029	-3.982269
87	6	0	4.236911	-3.625182	-2.041140
88	1	0	3.965850	-4.662468	-1.858395
89	6	0	3.960344	-2.651774	-1.089992
90	6	0	3.241521	-2.851996	0.219822
91	1	0	2.981013	-3.899492	0.402467
92	6	0	4.066126	-2.256585	1.335545
93	6	0	4.422664	-2.882337	2.523536
94	1	0	4.129315	-3.913005	2.709311
95	6	0	5.156840	-2.172022	3.476567
96	1	0	5.443469	-2.655053	4.406120
97	6	0	5.517858	-0.846052	3.243064
98	1	0	6.085508	-0.300224	3.991002
99	6	0	5.148183	-0.213988	2.053098
100	1	0	5.420441	0.824162	1.873690
101	6	0	4.427848	-0.924923	1.101608

AICBA *cis*-3 *a*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	-1.950938	3.760230	1.228133
2	1	0	-2.245362	3.717996	2.279023
3	6	0	-3.074528	3.744204	0.220285
4	6	0	-4.401160	3.360516	0.310555
5	1	0	-4.814371	2.987557	1.244067
6	6	0	-5.198562	3.469364	-0.835766
7	1	0	-6.251467	3.202532	-0.785142
8	6	0	-4.661191	3.917563	-2.041935
9	1	0	-5.298405	3.990707	-2.918729
10	6	0	-3.311707	4.282644	-2.134045
11	1	0	-2.894375	4.629113	-3.076198
12	6	0	-2.535828	4.209223	-0.988504
13	6	0	-1.084244	4.526035	-0.716865
14	1	0	-0.590508	5.181677	-1.437559
15	6	0	-1.165967	4.998697	0.749313
16	1	0	-1.741117	5.922156	0.857513
17	1	0	-0.187999	5.113402	1.228026
18	6	0	3.775375	-2.390903	1.741172
19	6	0	3.502481	-3.101628	0.504218
20	6	0	4.028479	-2.636846	-0.694216
21	6	0	4.853702	-1.446324	-0.713450
22	6	0	5.112529	-0.761595	0.468176
23	6	0	4.560932	-1.242881	1.723174
24	6	0	2.578172	-2.434495	2.555473
25	6	0	1.565448	-3.170258	1.814124
26	6	0	2.134415	-3.583289	0.558551
27	6	0	1.342083	-3.558116	-0.586956
28	6	0	3.209927	-2.630254	-1.895557
29	6	0	4.554387	-0.710437	-1.930455
30	6	0	4.528452	0.680215	-1.911866
31	6	0	4.792059	1.392567	-0.673960
32	6	0	5.076364	0.686735	0.487722
33	6	0	4.492098	1.099851	1.752985
34	6	0	4.182978	-0.093515	2.519323
35	6	0	3.033964	-0.136804	3.303259
36	6	0	2.214783	-1.334156	3.319522
37	6	0	0.236448	-2.757355	1.857795
38	6	0	-0.143051	-1.606072	2.655075
39	6	0	0.823688	-0.917179	3.381083
40	6	0	0.790155	0.521260	3.394423
41	6	0	2.146059	1.008319	3.352948
42	6	0	2.434441	2.144793	2.602923
43	6	0	3.634768	2.191268	1.793494
44	6	0	3.335322	2.930668	0.580227
45	6	0	3.912637	2.546310	-0.626738
46	6	0	3.542796	-1.444104	-2.662667
47	6	0	0.760857	2.196686	-2.481028
48	6	0	1.127773	1.106883	-3.263950
49	6	0	0.310071	-0.077412	-3.237240
50	6	0	-0.825481	-0.106687	-2.422255
51	6	0	-1.205741	1.049681	-1.649367
52	6	0	-0.320128	3.159744	-0.533428
53	6	0	1.191596	3.366530	-0.507143
54	6	0	1.773637	2.932136	-1.746343
55	6	0	3.108592	2.544673	-1.820901
56	6	0	3.487664	1.393450	-2.624765
57	6	0	2.518668	0.691449	-3.328239
58	6	0	1.174599	-1.228366	-3.297447
59	6	0	0.854214	-2.355837	-2.546170
60	6	0	-0.346308	-2.386759	-1.744171
61	6	0	-1.165766	-1.290492	-1.681734
62	6	0	-2.064501	-0.941871	-0.498562
63	6	0	-1.806715	0.564576	-0.390587
64	6	0	-1.564909	1.219902	0.760061
65	6	0	-0.938767	2.607729	0.842945
66	6	0	1.955858	3.350442	0.631893
67	6	0	1.384265	2.848968	1.902995
68	6	0	0.093657	2.386584	1.941728
69	6	0	-0.207721	1.189528	2.680405
70	6	0	-1.222970	0.451272	1.972509
71	6	0	-1.205030	-0.920872	1.972955
72	6	0	-1.737686	-1.776536	0.828513
73	6	0	-0.584940	-2.768559	0.681986

74	6	0	-0.039741	-3.152747	-0.514718
75	6	0	2.545581	-0.758986	-3.349833
76	6	0	1.895407	-3.073484	-1.838843
77	6	0	-0.442103	2.191242	-1.695967
78	6	0	-3.580650	-1.218999	-0.886957
79	1	0	-3.827297	-0.656669	-1.793468
80	6	0	-4.433329	-0.817864	0.291077
81	6	0	-5.429564	0.147739	0.294486
82	1	0	-5.657480	0.696848	-0.615271
83	6	0	-6.127780	0.404957	1.477408
84	1	0	-6.917670	1.152125	1.487045
85	6	0	-5.815393	-0.288795	2.645378
86	1	0	-6.358153	-0.078146	3.562294
87	6	0	-4.812044	-1.262010	2.639982
88	1	0	-4.568041	-1.809318	3.547460
89	6	0	-4.136059	-1.532479	1.457350
90	6	0	-3.047355	-2.556857	1.258886
91	1	0	-2.837587	-3.130685	2.167367
92	6	0	-3.419353	-3.437225	0.088085
93	6	0	-3.436759	-4.825977	0.072905
94	1	0	-3.197488	-5.386244	0.973768
95	6	0	-3.758451	-5.491871	-1.112414
96	1	0	-3.780237	-6.577503	-1.132299
97	6	0	-4.044803	-4.770229	-2.270368
98	1	0	-4.288725	-5.296017	-3.188767
99	6	0	-4.012096	-3.373606	-2.257602
100	1	0	-4.220361	-2.807941	-3.162829
101	6	0	-3.705285	-2.712500	-1.075205

AICBA *cis*-3 *b*

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms)		
			X	Y	Z
1	6	0	1.766194	3.789650	-1.963270
2	1	0	1.993240	3.773925	-3.031496
3	6	0	2.783293	4.462797	-1.070592
4	6	0	4.131700	4.739920	-1.233870
5	1	0	4.645706	4.506225	-2.162922
6	6	0	4.818124	5.335676	-0.169021
7	1	0	5.870746	5.580171	-0.278694
8	6	0	4.168046	5.616100	1.033205
9	1	0	4.720806	6.076693	1.846959
10	6	0	2.813421	5.308330	1.204245
11	1	0	2.313718	5.509686	2.148579
12	6	0	2.130483	4.744637	0.137887
13	6	0	0.714466	4.240816	-0.011538
14	1	0	-0.020585	4.630575	0.696480
15	6	0	0.472521	4.495462	-1.511313
16	1	0	0.470136	5.560631	-1.758233
17	1	0	-0.440174	4.022908	-1.890332
18	6	0	1.005831	-3.816664	2.431957
19	6	0	0.250611	-4.426092	1.351497
20	6	0	0.875410	-4.716739	0.145774
21	6	0	2.280684	-4.414944	-0.036645
22	6	0	3.004274	-3.825291	0.993458
23	6	0	2.353083	-3.518555	2.255713
24	6	0	0.138519	-2.870639	3.104071
25	6	0	-1.152614	-2.897400	2.433335
26	6	0	-1.083752	-3.854173	1.360487
27	6	0	-1.729507	-3.575137	0.158590
28	6	0	0.195376	-4.445463	-1.110201
29	6	0	2.471933	-3.968661	-1.406073
30	6	0	3.380637	-2.952553	-1.684687
31	6	0	4.129215	-2.333380	-0.605219
32	6	0	3.943567	-2.761335	0.702442
33	6	0	3.864344	-1.790129	1.781235
34	6	0	2.888580	-2.265258	2.744835
35	6	0	2.057309	-1.359176	3.394858
36	6	0	0.651299	-1.670790	3.575948
37	6	0	-1.864190	-1.714633	2.247561
38	6	0	-1.325116	-0.459876	2.739151
39	6	0	-0.100627	-0.440313	3.400389
40	6	0	0.834255	0.614291	3.109161
41	6	0	2.163407	0.058274	3.107024
42	6	0	3.085637	0.510389	2.166806
43	6	0	3.957622	-0.433767	1.498993
44	6	0	4.150750	0.017589	0.131925
45	6	0	4.248076	-0.915852	-0.897093
46	6	0	1.185127	-3.991900	-2.070993
47	6	0	1.559105	0.491937	-2.958969
48	6	0	1.054294	-0.708174	-3.449361
49	6	0	-0.341479	-1.010378	-3.262690
50	6	0	-1.153474	-0.097355	-2.587062
51	6	0	-0.612735	1.154103	-2.119866
52	6	0	1.525358	2.341741	-1.381912
53	6	0	2.787660	1.500709	-1.249072
54	6	0	2.849936	0.519004	-2.295985
55	6	0	3.576445	-0.659437	-2.143274
56	6	0	3.038352	-1.916706	-2.639159
57	6	0	1.806281	-1.939175	-3.277350
58	6	0	-0.470294	-2.418197	-2.984745
59	6	0	-1.412300	-2.840787	-2.050753
60	6	0	-2.277229	-1.887902	-1.393996
61	6	0	-2.149526	-0.549196	-1.653738
62	6	0	-2.501675	0.563077	-0.672274
63	6	0	-1.297221	1.483840	-0.856187
64	6	0	-0.607861	2.053916	0.146173

65	6	0	0.782936	2.661949	0.006685
66	6	0	3.412465	1.244177	-0.053389
67	6	0	2.732676	1.550779	1.227667
68	6	0	1.468201	2.082490	1.232332
69	6	0	0.494505	1.590064	2.169485
70	6	0	-0.794598	1.567912	1.526187
71	6	0	-1.695073	0.575240	1.815899
72	6	0	-2.737797	0.059982	0.829341
73	6	0	-2.562185	-1.447260	1.021437
74	6	0	-2.483389	-2.355023	-0.003417
75	6	0	0.858053	-2.999126	-2.988558
76	6	0	-1.072833	-3.880109	-1.100751
77	6	0	0.710647	1.460164	-2.319628
78	6	0	-3.816448	1.312943	-1.152915
79	1	0	-3.673944	1.660799	-2.181518
80	6	0	-4.039074	2.446752	-0.182883
81	6	0	-3.997841	3.803893	-0.476680
82	1	0	-3.831971	4.137708	-1.498766
83	6	0	-4.169610	4.731613	0.553647
84	1	0	-4.148400	5.794798	0.332219
85	6	0	-4.365297	4.298938	1.864701
86	1	0	-4.494507	5.026595	2.660490
87	6	0	-4.393600	2.933792	2.160431
88	1	0	-4.532972	2.593058	3.183790
89	6	0	-4.238167	2.012247	1.132291
90	6	0	-4.192500	0.509269	1.273767
91	1	0	-4.369990	0.177681	2.301987
92	6	0	-5.154220	-0.109554	0.288569
93	6	0	-6.125191	-1.062413	0.570117
94	1	0	-6.271336	-1.410412	1.590094
95	6	0	-6.905365	-1.570635	-0.471193
96	1	0	-7.670845	-2.311734	-0.260573
97	6	0	-6.701658	-1.137075	-1.780448
98	1	0	-7.309012	-1.541455	-2.584896
99	6	0	-5.714875	-0.190047	-2.064358
100	1	0	-5.543154	0.139735	-3.086479
101	6	0	-4.949295	0.324873	-1

