Evolution of the Optical Spectra of the Acene Homologous Series: Neutrals and Dications up to Undecacene

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Table of Contents

Abbreviations

PAH	Polycyclic aromatic hydrocarbons
OFETs	Organic field-effect transistors
OLEDs	Organic light-emitting diodes
OPVs	Organic photovoltaics
HOMO	Highest occupied molecular orbital
LUMO	Lowest unoccupied molecular orbital
E_a	Activation energy
E_0	Sum of electronic and zero-point Energies
NICS	Nucleus-independent chemical shifts
PMMA	Polymethyl methacrylate
DFT	Density functional theory
MRCI	Multireference configuration interaction
UV-Vis	Ultraviolet–visible spectroscopy
PEN	Pentacene
PFP	Perfluoropentacene
F4PEN	2,3,9,10-tetrafluoropentacene
n-BuLi	*n*-Butyllithium
MeLi	Methyllithium
TEMPO	2,2,6,6-Tetramethylpiperidine-1-oxyl
NMO	*N*-methyl-morpholine *N*-oxide
HRMS	High resolution mass spectrometry
NMR	Nuclear magnetic resonance
TMS	Trimethylsilyl
OTf	Trifluoromethanesulfonate

TBAF	tetrabutylammonium fluoride
DCM	Dichloromethane
THF	Tetrahydrofuran
MeCN	Methyl cyanide
PS	Polystyrene
NIR	Near Infrared
eV	Electron volt
APPI	Atmospheric pressure photoionization
ESI	Electron spray ionization
TS	Transition state
DA reaction	Diels-Alder reaction
DMSO	Dimethyl sulfoxide

Abstract

Acenes are a series of polycyclic aromatic hydrocarbons built up from linearly fused benzene rings. Undecacene, the largest member of the acene family to date, was generated in polystyrene matrix under cryogenic conditions from a photoprecursor with two α-diketone bridges. The electronic absorption spectrum of undecacene contains two strong absorptions in the UV-Vis range. The optical gap of undecacene follows the trends that were observed earlier for the shorter members of acenes. The optical gap of polyacene obtained from an exponential extrapolation is 1.23 eV.

In addition, the dications of nonacene and undecacene were generated and investigated by dissolving the products of photodecarbonylation of α-diketone precursors in concentrated sulfuric acid. The exponential extrapolation of the optical gap to the limit of infinite chain length of the acene dication series (from tetracene dication to heptacene dication) arrives at 0.99 eV, in accord with the value obtained from data up to nonacene dication (0.98 eV) and undecacene dication (0.93 eV) respectively.

Moreover, the tetrazine induced synthesis of 2,3,9,10-tetrasubstituted pentacenes from 6,13-etheno bridged precursors was studied computationally. The computational investigation of the mechanism and energies for formation of 2,3,9,10-tetrasubstituted pentacenes revealed a linear correlation between barrier height and substituent constant (σ_p), indicating an electronic effect that could diminish the yield of electron poor 2,3,9,10-tetrasubstituted pentacenes in this reaction.

Kurzzusammenfassung

Acene sind eine Reihe polycyclischer aromatischer Kohlenwasserstoffe, die aus linear kondensierten Benzolringen aufgebaut sind. Undecacen, das bisher größte Mitglied der Acenfamilie, wurde unter kryogenen Bedingungen aus einem Photopräkursor mit zwei α-Diketonbrücken in einer Polystyrolmatrix erzeugt. Das elektronische Absorptionsspektrum von Undecacen enthält zwei starke Absorptionen im UV-Vis-Bereich. Die optische Lücke von Undecacen folgt den Trends, welche früher für die kürzeren Acene beobachtet wurden. Die optische Bandlücke von Polyacen, die aus einer exponentiellen Extrapolation erhalten wird, beträgt 1.23 eV.

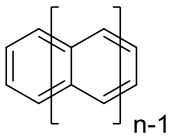
Zusätzlich wurden die Dikationen von Nonacen und Undecacen erzeugt und untersucht, indem die Produkte der Photodecarbonylierung von α-Diketon-Vorstufen in konzentrierter Schwefelsäure gelöst wurden. Die exponentielle Extrapolation der optischen Lücke bis zur Grenze der unendlichen Kettenlänge der Acendikation-Reihe (von Tetracendikation bis Heptacendikation) liegt bei 0,99 eV, was mit den Werten aus Daten bis zum Nonacendikation (0,98 eV) und Undecacendikation (0.93 eV) übereinstimmt.

Darüber hinaus wurde die Tetrazin-induzierte Synthese von 2,3,9,10-tetrasubstituierten Pentacenen aus 6,13-Etheno-verbrückten Vorstufen mit Hilfe von computerchemischen Verfahren untersucht. Die rechnerische Untersuchung des Mechanismus und der Energien für die Bildung von 2,3,9,10-tetrasubstituierten Pentacenen ergab eine lineare Korrelation zwischen Barrierenhöhe und Substituentenkonstante (σ_p), was auf einen elektronischen Effekt hindeutet, der die Ausbeute an elektronenarmen 2,3,9,10-tetrasubstituierten Pentacenen in dieser Reaktion verringern könnte.

1. Introduction

1.1 Introduction

Acenes, polycyclic aromatic hydrocarbons (PAH) consisting of linearly fused benzene rings,[1] have been extensively studied due to their high charge carrier mobility, relatively low processing costs, light weight and mechanical flexibility, which make them receive considerable attention for use in molecular electronic devices, such as organic field-effect transistors (OFETs), organic light-emitting diodes (OLEDs), and organic photovoltaics (OPVs).[2-7]



The smaller members of the acene series that can be isolated out of coal tar, while acenes higher than tetracene are not found in nature and need to be synthesized.[3] As the encouraging semiconducting properties of pentacene,[8] together with the enhanced electronic properties estimated by computational techniques on larger homologues,[9] significant efforts have been devoted to develop appropriate synthetic methodology for the preparation of higher acenes.[2-4] However, the synthesis of extended acenes is a challenging task because of their poor solubility, and high reactivity leading to decomposition and dimerization or oligomerization in the presence of light and oxygen.[10-12] Therefore, there is limited information available for acenes longer than pentacene. Meanwhile, with the broad use of smaller acene members including anthracene, tetracene, pentacene, and their derivatives in organic semiconductors, significant progress has been made in the synthesis of larger acenes over the last few decades.[2,13]

1.2 Structure and Reactivity

There are at least three series of fused benzenoid compounds, including acenes, phenacenes and helicenes. Phenacenes, with a zigzag type of condensation, are planar angular fused analogues of acenes, while helicenes are a set of C_2- symmetric helical polycyclic benzenoids (Figure 1).[14] Experimental evidence and calculation results reveal that a phenacene is always more stable than its isomeric acene and helicene, and acene is the most unstable structure.[14,15] Meanwhile, with the number of rings in acenes increasing, not only the band gap decreases, but also the proton and electron affinities increase, and the ionization potential reduces,[16,17] which reduce the stability of this kind of compounds.

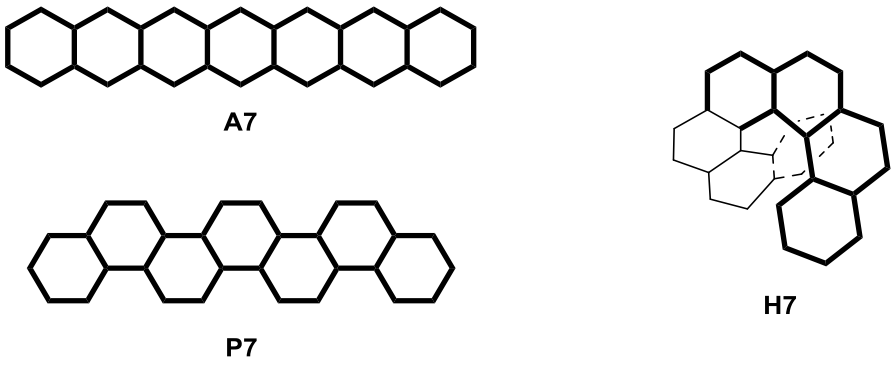


Figure 1 Three series of fused benzenoid compounds.

The acenes can be characterized by several limiting valence bond structures, such as the symmetrical, *cis*-distorted and *trans*-distorted forms (Figure 2a, 2b and 2c).[9]

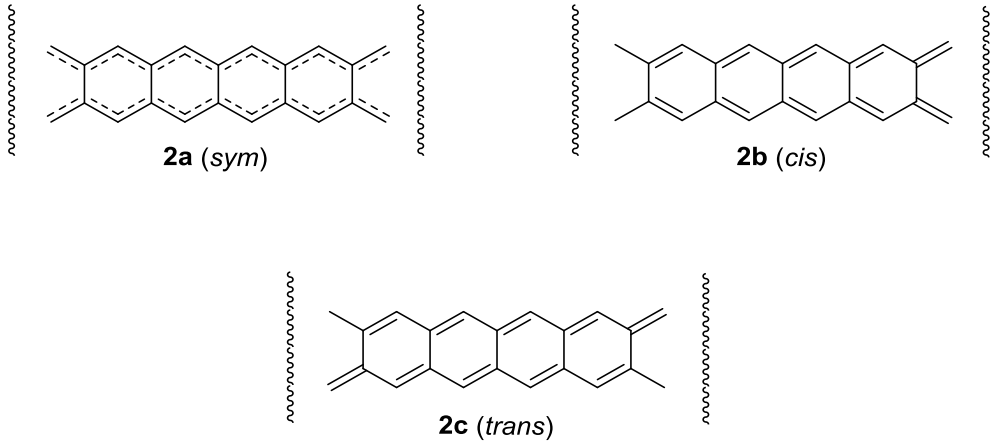


Figure 2 Structure of Acene.

Electronic properties depend on the preferred structure. The stability of acenes depends on amount of factors and the stability of all three structures are different in different computational studies.[2-4] Valence-bond theory indicates these three structures are energetically similar, while **2a** has the lowest energy.[18] The *trans*-distorted form is less stable than the *cis*-distorted form, while long range Coulomb interactions were considered. Non interacting models suggest the *trans*-distorted form is the most stable structure, however, the symmetrical form is favored according to MP2/6-311G**.[18,19] As reported by Houk et al., larger acenes are composed of two fully delocalized non-alternating ribbons joined by relatively longer bonds.[9] The energy levels are discrete in case of a particular finite acene and the HOMO-LUMO gap decrease dramatically with each additional fused ring.

From the sextet concept of Clar, we can see the qualitative explanation about the unstable nature of large acenes.[1] In a series of acenes, whether its benzene or pentacene or one of the larger analogs, there is only one π-electron sextet (Figure 3). Therefore, one sextet is shared over a larger number of rings in lager acenes and larger acenes become increasingly less stable, which can be explained by the sequential loss of benzenoid character according to molecular orbital theory.[20]

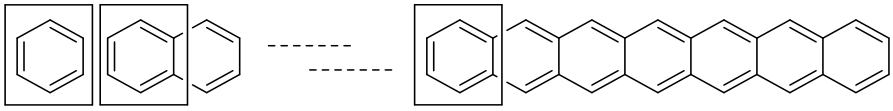


Figure 3 Clar's Sextet concept.

Initial calculations from Houk et al. show that, with number of rings more than eight, acenes are predicted to have triplet state.[9] Wirz et al. concluded from experimental data available through hexacene that nonacene should be the first acene with a triplet ground state.[21] However, later it was concluded by the Houk group that the ground states will maintain singlets with an open shell because of their disjointed biradical nature.[22] According to a computational analysis by Evers and coworkers, the optical gap (Δ_g), which is approximated as the energy difference between the LUMO and the HOMO, first decreases significantly with increasing chain length until decacene, subsequently, but it rises up and drops again repeatedly with periodicity of 11 rings (Figure 4).[23,24] The optical gap in Figure 4b reveals that an orbital crossing appears at the extremal points of the gap function in longer acenes. For a given N, the blue symbol represents the HOMO, while the red symbol means the LUMO (Figure 4c). When the LUMO and HOMO interchange at certain crossings, the gap has a minimum.[24]

To study the reactivity of acenes, Diels-Alder addition reactions were investigated by Stahl et al.[25] These reactions are likely to appear at the central rings of acenes which are the most reactive ones in acenes (Figure 5). From the Diels-Alder addition between pentacene and acetylene, we can see that the activation energy (E_a) for the inner rings of pentacene is 24.0 kcal/mol, while the E_a for outside rings of pentacene is 32.7 kcal/mol.[25]

The computational study about the reactivity of acenes toward nucleophilic and electrophilic additions as well as Diels-Alder addition with oxygen has been reported.[11,26] As the number of benzene rings increases, the reactivity of acenes with water and HCl increase

from benzene to hexacene and then remain almost constant from hexacene to nonacene due to the biradical feature of the ground state of longer acenes. The activation barrier (E_a) for HCl addition is calculated to be lower (~27 kcal/mol) than that for the addition of water. The addition of HCl to benzene has E_a of 44 kcal/mol, while it is only 16-18 kcal/mol for pentacene-nonacene. The barrier for singlet oxygen addition to acenes is in the similar region as that of HCl addition, which are about 48, 29 and 20 kcal/mol for benzene, anthracene and pentacene respectively.[26] Both triplet and singlet oxygen reacting with acenes give the same primary products, endoperoxides.[11]

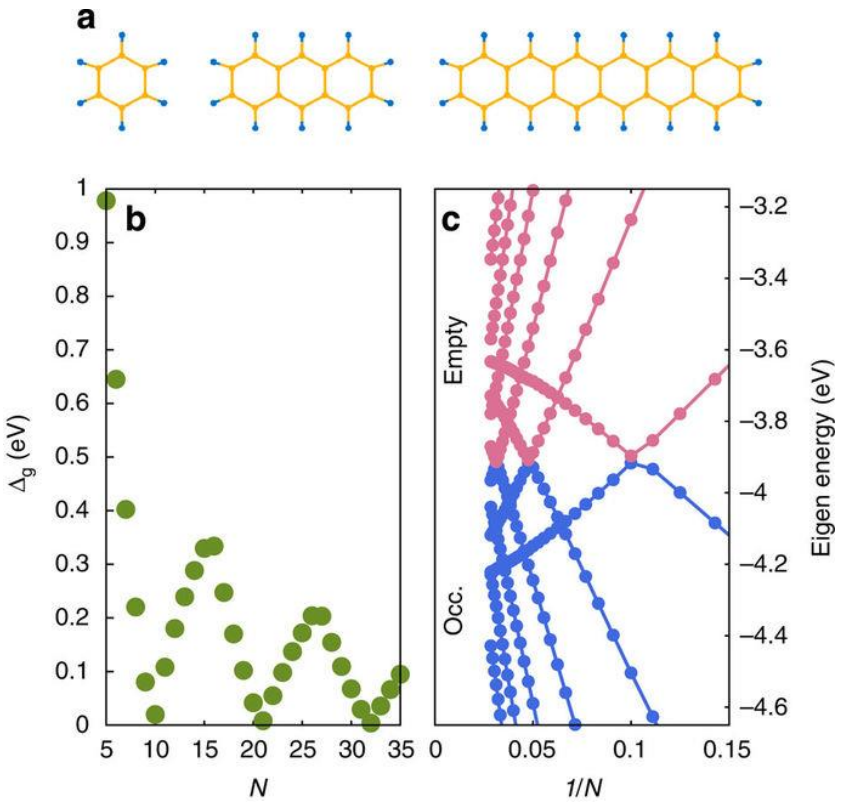


Figure 4 Electronic structure of oligoacenes. (a) Ball-and-stick representation of benzene, anthracene and hexacene with N=1, 3, 6 rings (blue: hydrogen, orange: carbon). (b) optical gap of oligoacenes as a function of the number of rings N calculated in DFT. (c) Flow of orbital energies as a function of 1/N, showing that a repeating interchange of orbitals occurs as the number of rings grows. Blue symbols are occupied orbitals and red are unoccupied. Close to N=10, N=21 and N=32, there is an interchange of frontier orbitals. The data points are connected by straight lines for visual guidance. Reprinted with permission from reference 24.

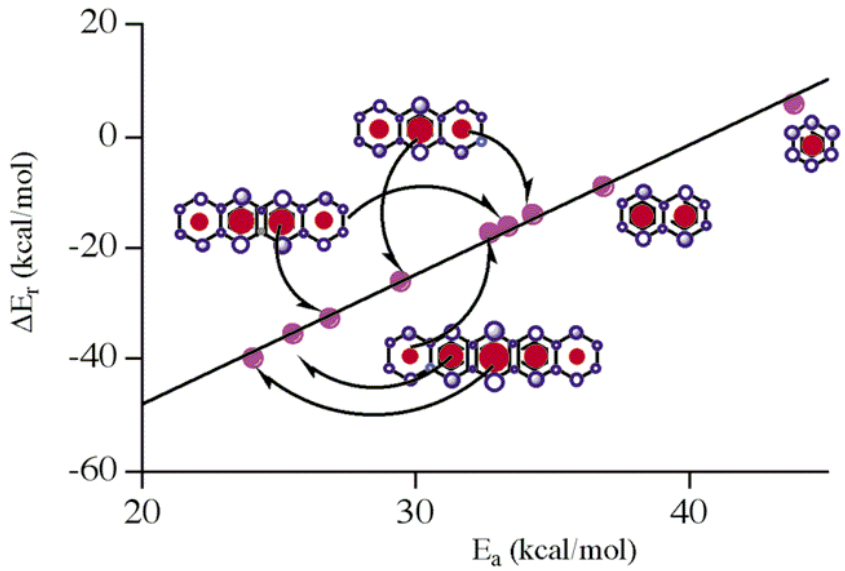


Figure 5 Correlation (R^2 = 0.997) of the activation (Ea) versus the reaction (ΔE) energies (B3LYP/6-31G* + ZPE data) of acetylene addition to acene rings. The red dots are based on NICS(0) values. The HOMO coefficients are indicated in blue. Reprinted with permission from reference 25. Copyright © 2001, American Chemical Society.

Generally, acenes adopt two common packing motifs in the solid state that produce strong intermolecular overlap: (I) The "herringbone" arrangement in which the aromatic edge-to-face interaction dominates yields two-dimensional electronic interactions in the solid (Figure 6, left). (II) The coplanar arrangement with π-stacked arrays results in strong electronic coupling, even two-dimensional electronic coupling along with adjacent stacks in the solid (Figure 6, right).[2]

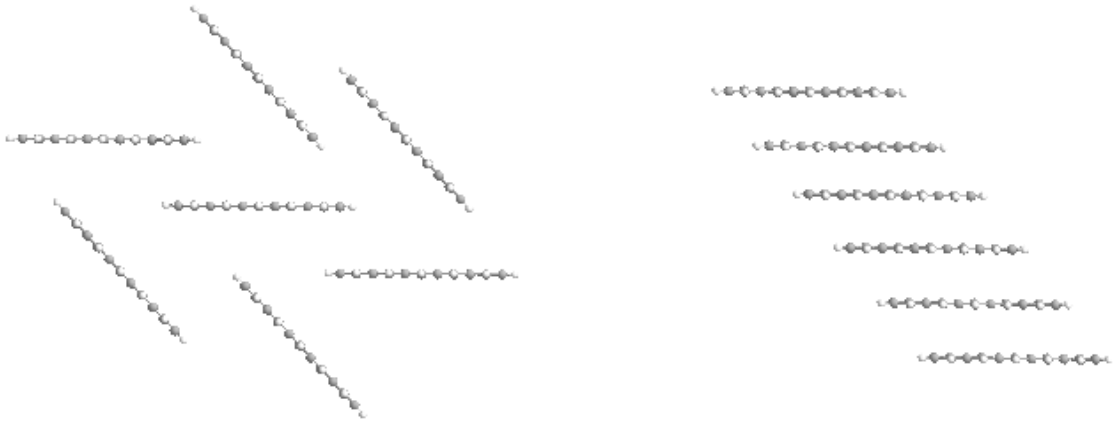
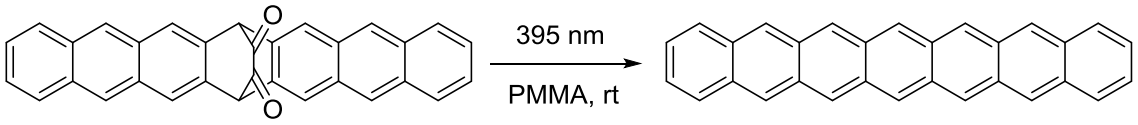


Figure 6 Herringbone (left) and π -stacking (right) arrangements of acenes.

1.3 Acenes larger than Pentacene

The small acenes are widely used in molecular electronic devices,[2-4,27] while the acenes that are larger than pentacene are generally not employed in devices. This is due to their instability and their poor solubility in common organic solvents. These properties make synthesis, purification and handling of the compounds quite challenging.

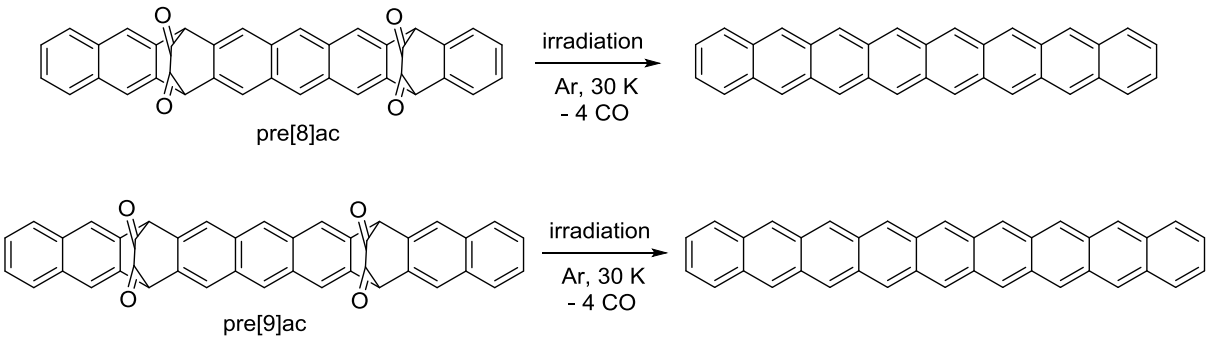
There are several reviews available on the higher acenes,[28-30] and hence it suffices to briefly summarize the state of the art and point our recent developments. Hexacene was frist prepared in 1939 by Clar,[31] and is a stable compound at rt in the absence of light and oxygen.[32] The synthesis of heptacene was first attempted in 1942 by Clar,[33] but definitive proof for the existence of heptacene was first provided by Neckers et al. in 2006 by photolysis of an α-diketone precursor (pre[7]acene) in a poly(methyl methacrylate) (PMMA) matrix at room temperature (Scheme 1).[34]



pre[7]ac **1-1**

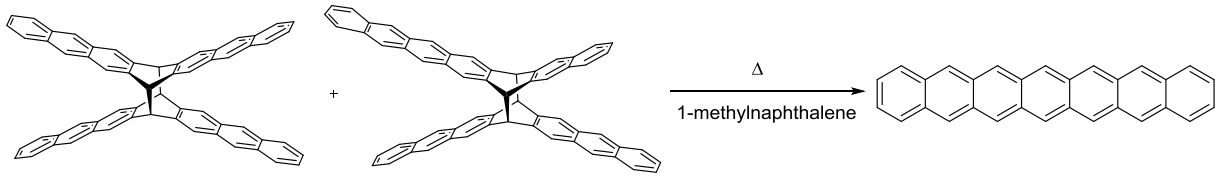
Scheme 1 Photochemical synthesis of heptacene from α-diketone precursor, according to Mondal et al.[34]

Since then, parent heptacene, octacene, and nonacene were photogenerated in argon matrices and their optical properties, infrared spectra, and photoionization to the radical cations and radical anions was investigated (Scheme 2).[35-37]



Scheme 2 Photogeneration of octacene and nonacene, according to Tönshoff et al.[37]

It was recently shown by the Bettinger group that parent heptacene can exist in the solid state according to solid state NMR spectroscopy, in optically transparent thin films under vaccum, and even in solution at high temperatures (Scheme 3).[38] The key to successful isolation of heptacene in a pure state is the thermal cycloreversion of diheptacenes.



Scheme 3 Synthesis of heptacene by heating a solution of diheptacenes in 1-methylnaphthalene, according to Einholz et al.[38]

The most important result of the matrix isolation studies on the acenes up to nonacene is the finding that the optical gap, the energy difference between the ground state and the first electric-dipole moment allowed excited state (using λ_{max}), can be fit to an exponential. A limiting value of (1.18 ± 0.06) eV for the transition energy and an effective conjugation length of 24-25 rings was derived from an extrapolation of the data.[37] Such an evolution of the optical band gap is supported by sophisticated density functional theory/multireference configuration interaction (DFT/MRCI) computations,[39] but contradicts the prediction of Evers et al.[24,40]

As the high concentration of π-electon density at central rings of acenes,[25,41] the stability of acenes can be improved by introducing substituents at inner rings. The strategy of introducing silylethynyl groups that turned out to be so beneficial for stabilization and handling of pentacene, with great π-overlap and tight crystal packing,[42-45] which was also successfully employed for the stabilization of hexacene, heptacene, and even nonacene.[46-53] The nonacene derivatives could be crystallized from solution and structurally characterized by single crystal x-ray crystallography and optical spectroscopy, but the compounds are too reactive for further detailed analysis (Figure 7).[48]

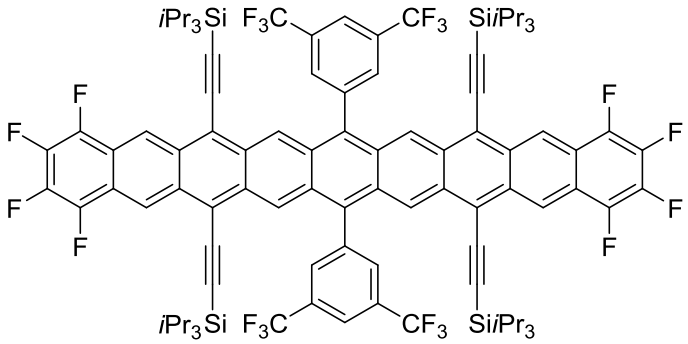
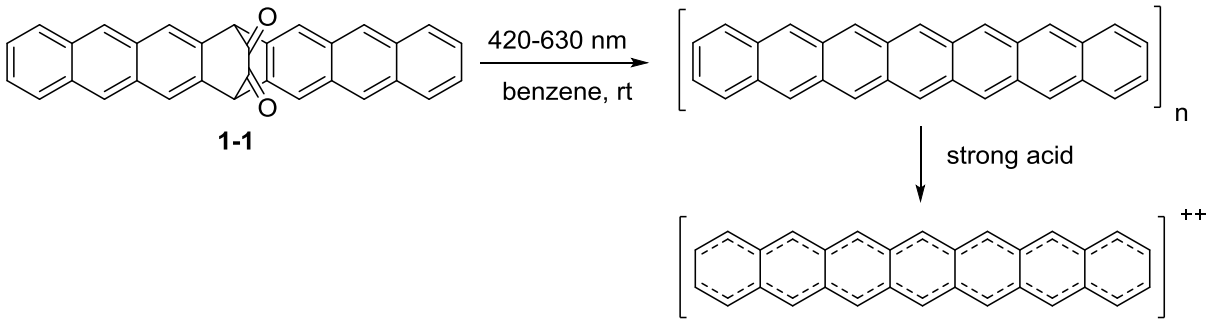


Figure 7 Substituted nonacene from John Anthony.

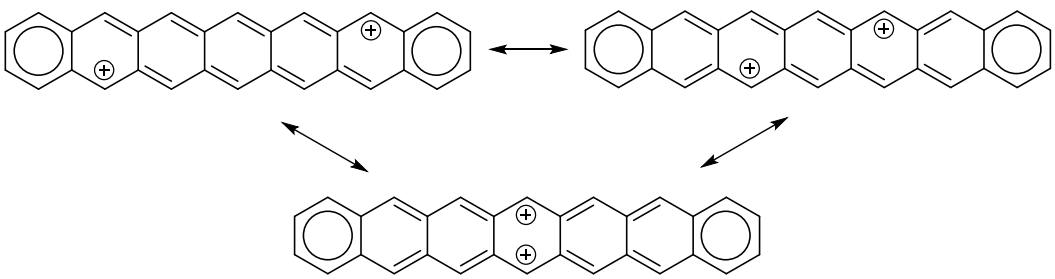
A quite unexpected observation was the finding that the heptacene dication is persistent in sulfuric acid solution at rt for a very long time (Scheme 4).[54] It is known[21,55-57] that polycyclic aromatic hydrocarbons can dissolve in concentrated sulfuric acid as dication. Einholz et al. observed that dissolution of the diheptacenes obtained from photolysis of its photoprecursor pre[7]ac yields the heptacene dication.[54]



Scheme 4 Generation of heptacene dication.

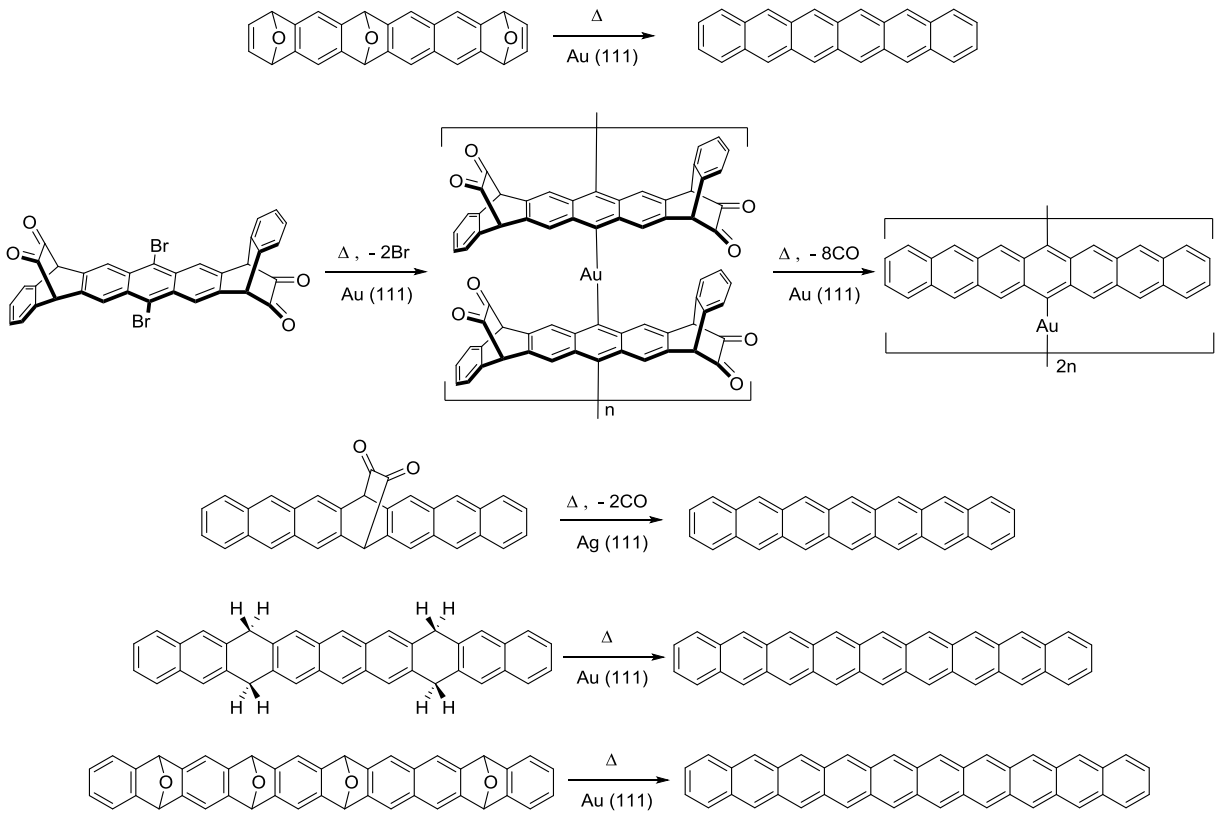
The number of π electrons in neutral acenes is always in accord with the Hückel rule due to the stoichiometry of $4n + 2$ where n is a non-negative integer. This is the reason why acenes are considered polycyclic aromatic hydrocarbons. Acene dications always contain a number of π electrons $4n$ that formally corresponds to an antiaromatic system. Hence, the observation by Einholz et al.[54] that the heptacene dication has a much higher persistence in solution at room temperature than the neutral compound is quite remarkable.

One explanation given for this observation is that oxidation to a dicaionic state allows the π system the formation of two Clar sextets (Scheme 5). This would increase the aromatic stabilization of the system.[54,58] Another important factor was suggested to be associated with the charge of the system. As dimerization is the most facile way of decomposition of neutral acenes in the absence of oxygen, this pathway is strongly opposed by the Coulomb repulsion that is associated with two positive ions. Indeed, that the oxidation of diheptacene is resulting in monomeric dications is most likely due to Coulomb repulsion between oxidized heptacene derived subunits.



Scheme 5 Heptacene dication resonances.

More recently, the larger acenes hexacene,[59] heptacene,[60,61] nonacene[62], decacene[63] were generated on-surface from various precursors (Scheme 6). Heating of the precursor molecules on a metal surface under ultrahigh vacuum provides the otherwise highly reactive acenes as monolayers on the metal and hence provides access to an acene-metal interface. The acene molecules on metal surfaces can be studied e.g. by high resolution scanning tunneling microscopy/spectroscopy (STM/STS), noncontact atomic force microscopy (NC-AFM), X-ray photoelectron spectroscopy (XPS), near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and density functional theory (DFT) calculations.



Scheme 6 On-surface generation of these acenes from various precursors.

The on-surface approach allows access to very unstable acenes, e.g. decacene, that could not be investigated previously. The approach, however, does not allow studying the molecular optical gap and hence it is not possible to probe the existence of potential band gap oscillations suggested by Evers et al.[24,40]

2. Objectives of this Thesis

One objective of this thesis is to synthesize and study even higher acene, undecacene, consisting of 11 linearly fused benzene rings, which would be the largest acene molecule experimentally investigated to date. The synthesis and characterization of such a large acene is supposed to give us more understanding of the aromaticity and photophysics, in particular it allows probing the theoretically predicted band gap oscillations that are expected to result in particularly small band gaps in the decacene/undecacene length regime. Undecacene is photogenerated in a polystryrene matrix under cryogenic conditions from a photoprecursor with two α-diketone bridges, although there are many tough issues in the way of generation compared to smaller acenes. The electronic absorption spectrum of undecacene includes two strong absorptions in the UV and optical range, but does not indicate the presence of band gap oscillations.

A second objective of the thesis is the preparation and investigation of acene dications of nonacene and undecacene. It was found previously by Einholz et al.[54] that heptacene in the dicationic state (obtained in sulfuric acid solution) shows higher persistence than in its neutral state. This behavior is surprising in view of the electron count of the system: while neutral heptacene is formally an aromatic compound with 30 π electrons (4n +2, n = 7), the dication is formally and an antiaromatic compound with 28 π electrons. Thus, research about nonacene dication and undecacene dication have been done in this thesis in order to learn if these acene dications can be observed in sulfuric acid as well and to study the evolution of optical gap in dicationic acene series.

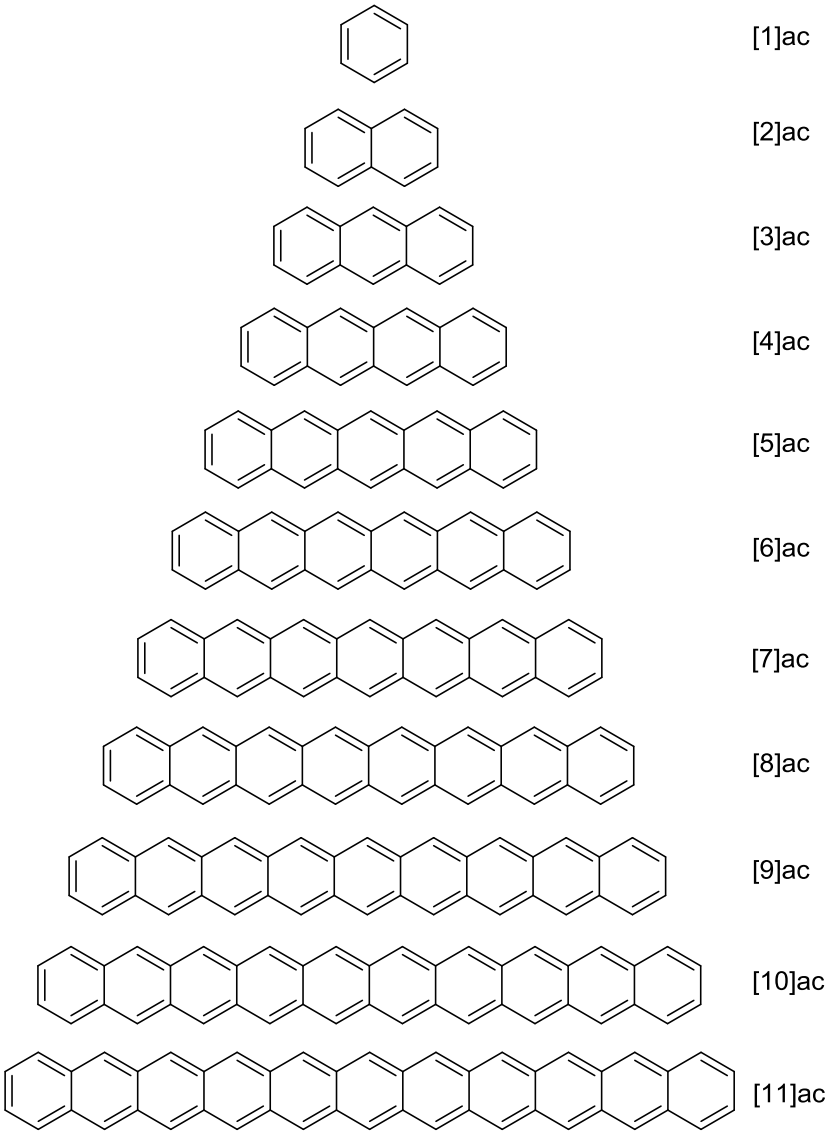
The third part of the thesis focuses on the partially fluorinated pentacene 2,3,9,10-tetrafluoropentacene. It has been shown previously for perfluoropentacene (PFP) that fluorination can turn pentacene (a typical *p* channel semiconductor)[64] into an *n* channel semiconductor.[65,66] In a sense, 2,3,9,10-tetrafluoropentacene (F4PEN) is bridging the gap

between pentacene and PFP, although the charge transport properties of F4PEN are not yet known. In this thesis, we investigated by computational means the mechanism and energy barriers for formation of F4PEN and other 2,3,9,10-tetrasubstituted pentacenes in order to explain trends observed in a previous experimental study and provide another way to improve the yield of synthetizing F4PEN that was used by the group of Professor Schreiber in a collaborative study of the molecular distortion upon absorption on a Cu(111) surface.[67]

3. Synthesis of Undecacene Photoprecursor

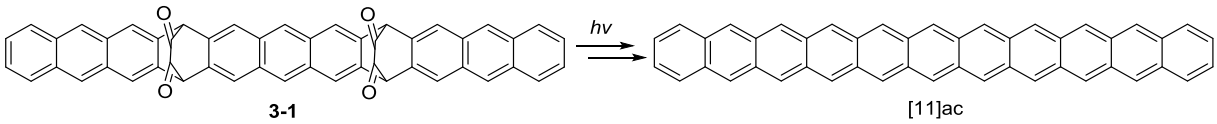
3.1 Introduction

Benzene, the smallest member of acene family, was first discovered in 1825.[68] Recently, the degree of aromaticity and stability of the oligoacenes (Scheme 7) have been discussed widely.[4]



Scheme 7 Structures of acenes.

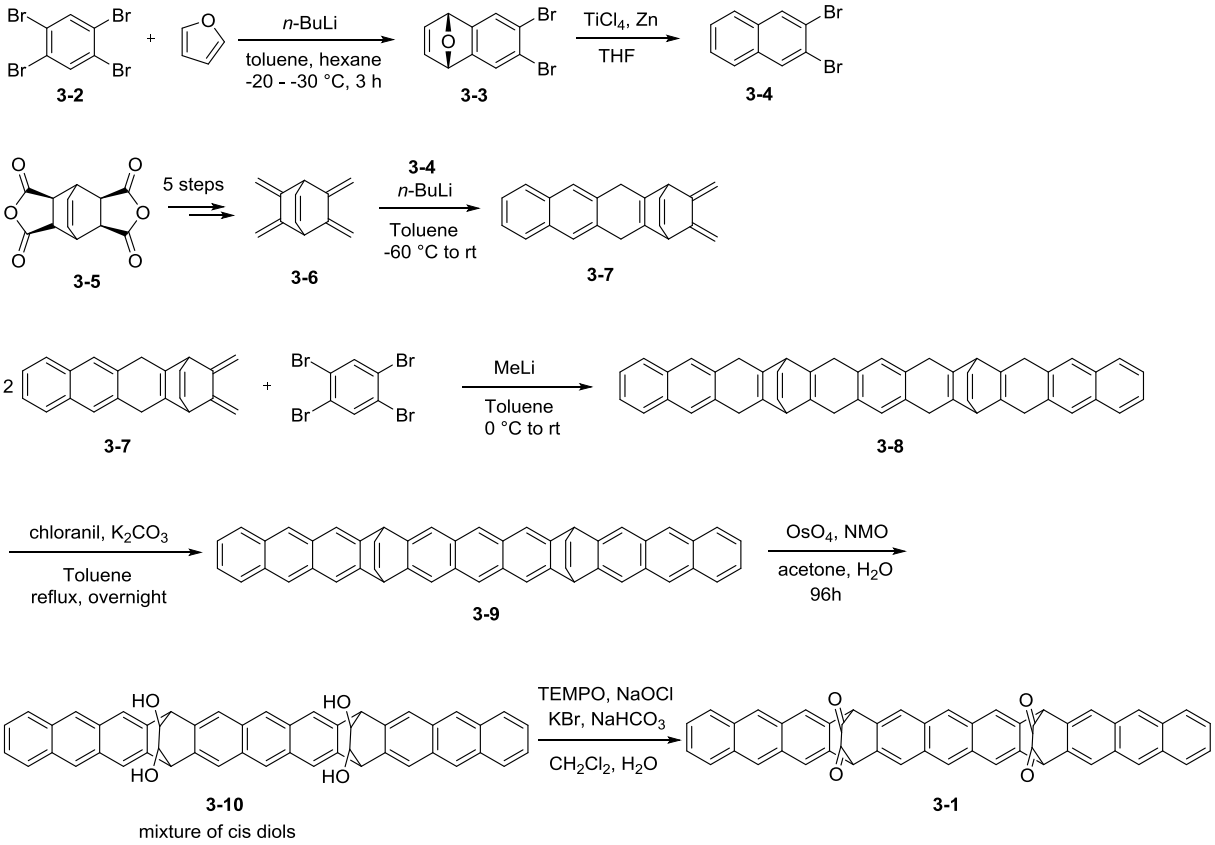
Undecacene ([11]ac) was unknown at the beginning of the thesis work and its successful synthesis would make it the largest member of the acene series known to date. It is supposed to be photogenerated in a stabilizing matrix under cryogenic conditions from a photoprecursor **3-1** with two α-diketone bridges (Scheme 8). A similar approach was previously employed successfully for the photogeneration of octacene and nonacene under matrix isolation conditions.[37] The photoinduced bis-decarbonylation of bridged percursors of aromatic compounds is occasionally called the Strating-Zwanenburg reaction,[69-71] and this reaction has been employed for the in-situ synthesis of acenes for electronic applications.[72,73] Thus, in order to obtain undecacene, we have to produce undecacene photoprecursor **3-1** with the protecting-group α-diketones. In this chapter, general synthetic approaches to undecacene photoprecursor **3-1** will be discussed.



Scheme 8 Undecacene photoprecursor to undecacene.

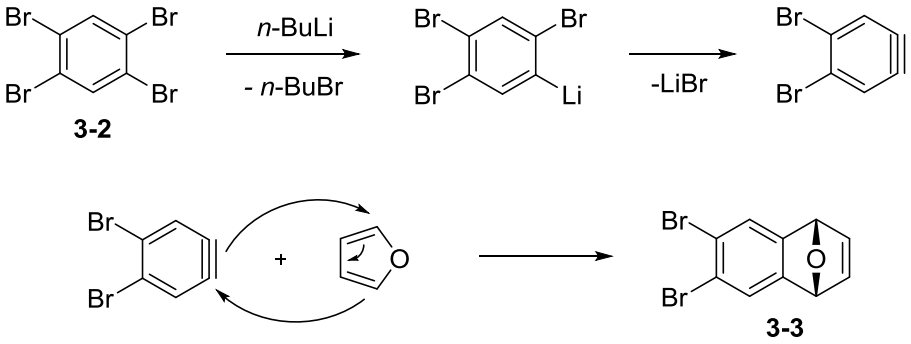
3.2 General Synthetic Approaches to undecacene photoprecursor

The following is the general synthetic procedure from starting materials to undecacene photoprecursor **3-1** (Scheme 9). We introduced two photolabile bridging α-diketone units as protection groups for the reactive fully conjugated π system of undecacene resulting in photoprecursor **3-1**.



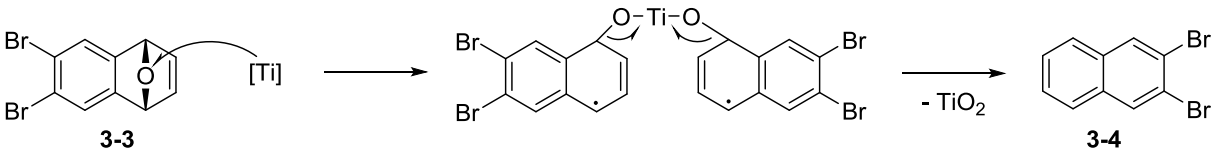
Scheme 9 Synthesis of photoprecursor **3-1** of undecacene.

Starting from tetrabromobenzene **3-2**, a naphthalene building block **3-3** is created in a Diels-Alder reaction with furan (Scheme 10). The dienophile is created in situ with the help of *n*-BuLi leading to a halogen-metal exchange at compound **3-2** followed by the elimination of lithium bromide. The intermediate aryne reacts with furan giving 6,7-dibromo-1,4-dihydro-1,4-epoxynaphthalene **3-3**.[74]



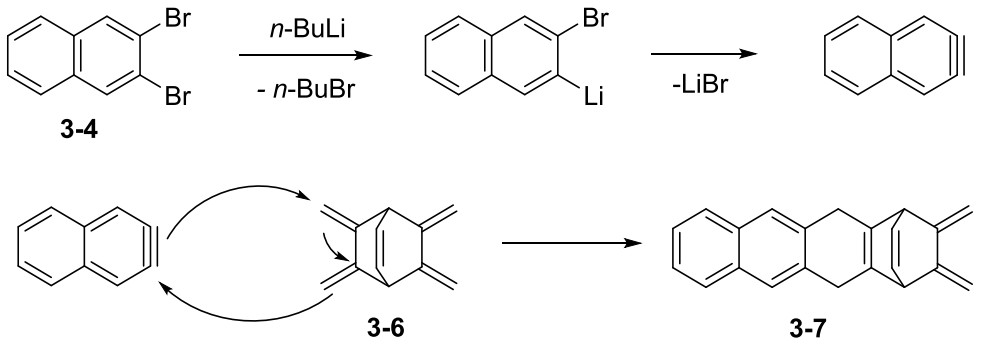
Scheme 10 Mechanism of synthesis of **3-3**.

The next step is the reduction of **3-3** with a mixture of zinc and titanium tetrachloride, conditions is similar to those McMurry reaction, leading to 2,3-dibromonaphthalene **3-4** (Scheme 11).[74] The mechanism of the McMurry reaction is not well understood, since neither the active species of titanium nor the exact mechanism of reduction are known. It is ensured, that zinc is reducing titanium to subvalent, reactive titanium of an oxidation state lower than four and that the organic compound is reduced giving Ti(IV) back again. The driving force of this reaction is the formation of strong Ti-O bonding.[75,76]



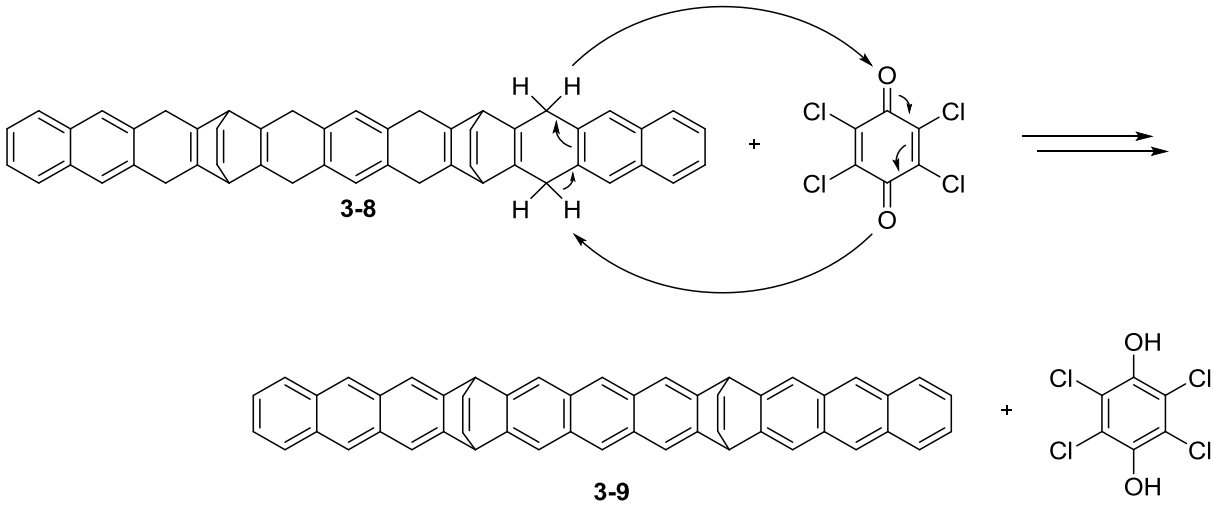
Scheme 11 Mechanism of synthesis of **3-4**.

The synthesis of **3-1** (Scheme 9) started from commercially available dianhydride **3-5** that was transformed in five steps into 2,3,5,6-tetramethylene-bicyclo[2.2.2]octene **3-6** as described previously.[77] The bisdiene **3-6** is used for Diels-Alder reaction with 2,3-didehydronaphthalene that is generated in situ from 2,3-dibromonaphthalene **3-4** and *n*-BuLi to give **3-7** (Scheme 12).[78] The mechanism of this reaction is based on the same principle as the first reaction of **3-2** with furan. *n*-Butyllithium is added to generate the aryne which then reacts with **3-6**.



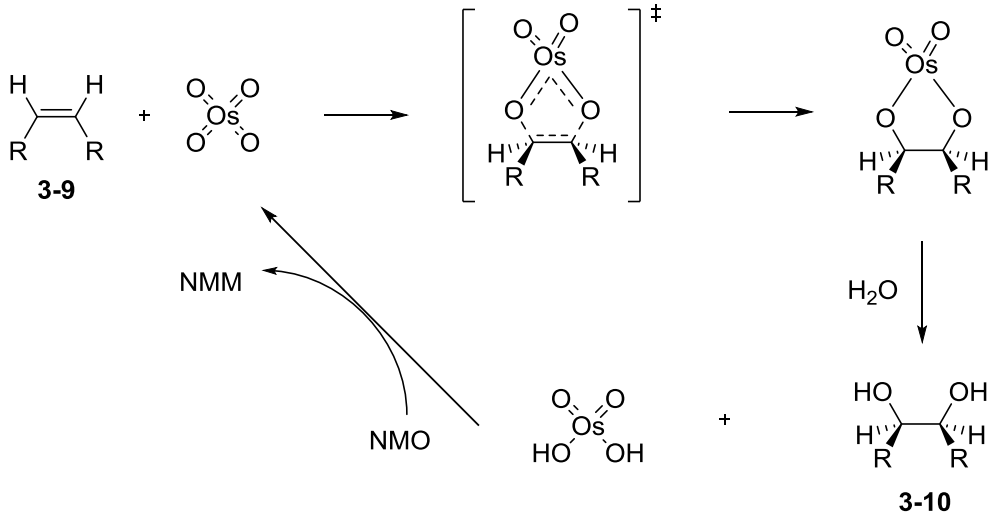
Scheme 12 Mechanism of synthesis of **3-7**.

Subsequently, two molecules of **3-7** are coupled with the bisaryne equivalent that is available from 1,2,4,5-tetrabromobenzene to give the undecacene backbone **3-8**. The mechanism of synthesis of **3-7** is similar as that in Scheme 12. This reaction turned out to be challenging, as yields were quite low. The best results were obtained by running the reaction with the more reactive MeLi than n-BuLi. The kinking of the backbone results in diastereomeric products. As the photoprecursors are ultimately planarized by photobisdecarbonylation, no attempts were made to separate these stereoisomers and mixtures were used in the following steps. The next step is the aromatization of **3-8** with chloranil leading to **3-9** (Scheme 13).



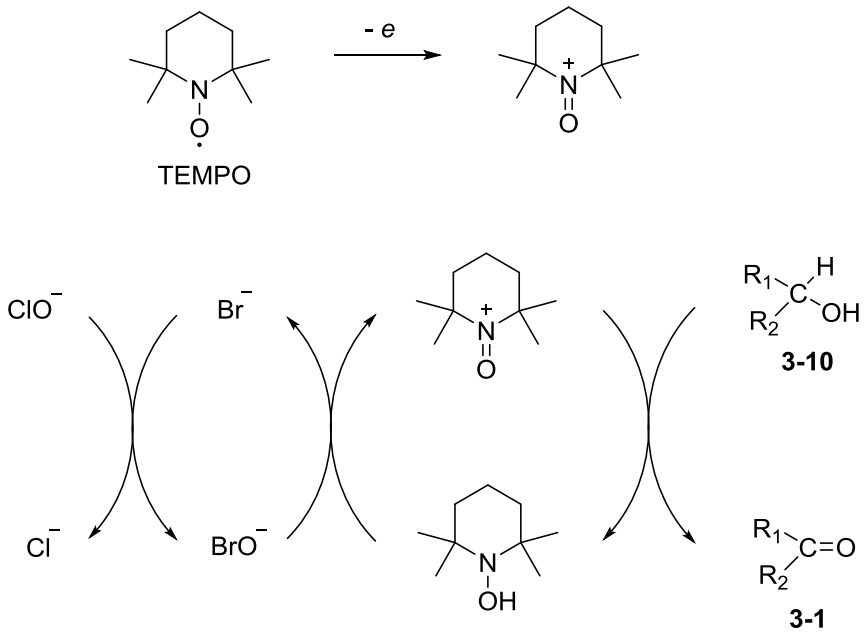
Scheme 13 Mechanism of synthesis of **3-9**.

The following step is twofold dihydroxylation of the etheno bridges of **3-9** with catalytic amounts of OsO_4 in the presence of N-methyl-morpholine-N-oxide (Scheme 14),[79] which produced a mixture of diastereomeric tetraols **3-10**.



Scheme 14 Mechanism of synthesis of **3-10**.

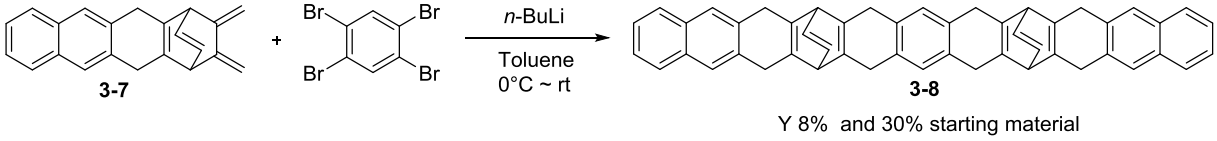
In order to obtain the final photoprecursor product **3-1** of this part, the mixture of diastereomeric tetraols **3-10** were oxidized using the Anneli protocol (NaOCl, TEMPO) (Scheme 15).[80] The tetraketone **3-1** could be isolated by chromatography and was obtained as a bench-stable yellow compound that could be fully characterized by spectroscopic techniques (multidimensional NMR, HRMS).



Scheme 15 Mechanism of synthesis of **3-1**.

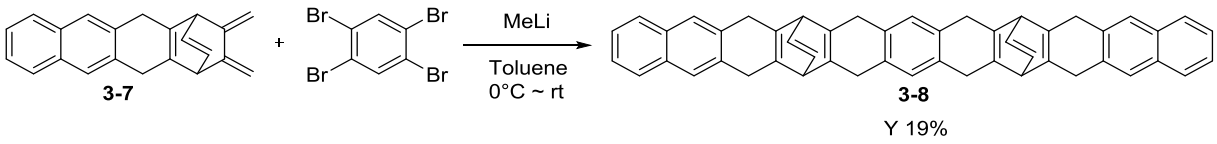
3.3 Attempted improvement

The step to build the framework of undecacene through a Diels-Alder reaction between **3-7** and 1,2,4,5-tetrabromobenzene is the key step for the synthesis of undecacene photoprecursor **3-1** (Scheme 16). Based on previous experience gained in the synthesis of the photoprecursor of nonacene, this reaction was run at 0 °C in toluene by dropping the required amount of diluted *n*-BuLi in the solution of **3-7** and 1,2,4,5-tetrabromobenzene.[37] However, the yield was lower than 10% under that condition. In order to get sufficient amount of **3-8**, optimization of the reaction conditions was necessary.



Scheme 16 Original way to synthesize **3-8**.

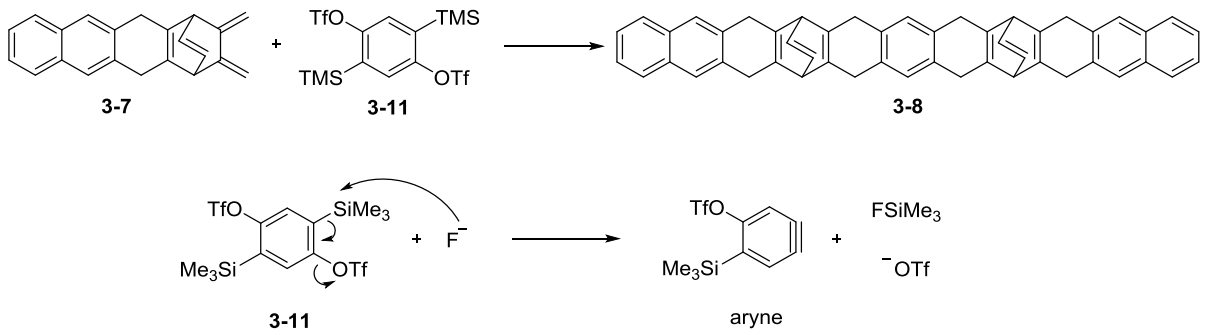
There are many ways conceivable to obtain a higher yield of the requested product **3-8**. We have applied different solvents (toluene, THF, diethyl ether and mixtures of them), different bases (*n*-BuLi, MeLi), different temperatures during adding base solution and the process of reaction, different proportions of starting materials (it will be explained in the following part), and even different starting materials in this reaction. Finally, when we use MeLi instead of *n*-BuLi under otherwise the same condition, we can obtain **3-8** with the best yield of 19% (Scheme 17).



Scheme 17 Using MeLi instead of *n*-BuLi to synthesize **3-8**.

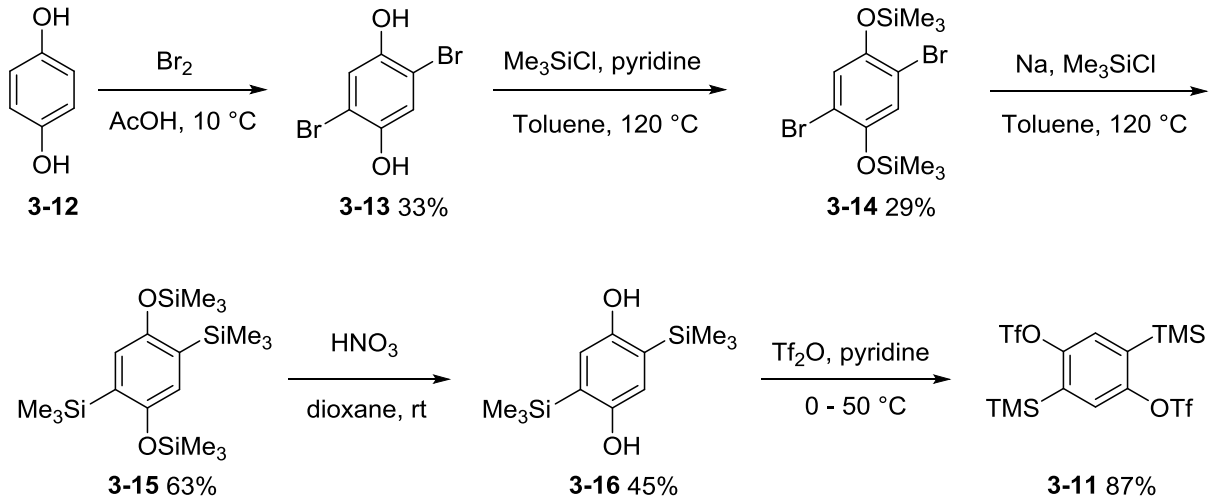
Using different starting material to replace 1,2,4,5-tetrabromobenzene

As *n*-BuLi is a strong base, it forces constraints on the temperature used for this reaction. There was much starting material left due to the poor solubility of **3-7** with a lower reaction temperature (Scheme 16). However, too many byproducts were come out at increased temperature, because *n*-BuLi is too reactive at a higher temperatures, and this caused difficulty in separation and purification of the product. Thus, we decided to use 2,5-bis(trimethylsilyl)-1,4-phenylene-bis(trifluoromethanesulfonate) **3-11** to replace 1,2,4,5-tetrabromobenzene (Scheme 18), since the triflate group (OTf) and trimethylsilyl substituent (TMS) both are excellent leaving groups used for aryne generation in the presence of a fluoride source. Furthermore, **3-11** is expected to generate less byproducts even at a higher reaction temperature, because aryne formation from **3-11** is more selective as it avoids participation of the strong-base *n*-BuLi.



Scheme 18 Use of **3-11** to replace 1,2,4,5-tetrabromobenzene.

As shown in the following synthetic process, bis-aryne precursor **3-11** can be produced in five steps (Scheme 19).[81,82] The starting material benzene-1,4-diol **3-12** was brominated in 99% acetic acid to yield **3-13**. The following formation of the corresponding silyl ether **3-14** could be effected in refluxing toluene with a reasonable yield. The introduction of two additional trimethylsilyl groups to produce **3-15** took place by a reaction similar to the Wurtz-Fittig reaction which actually describes an alkylation of aryl halides, rather than a silylation. In the next step, **3-16** was the product of deprotection of the silyl ether groups of **3-15**. With the help of pyridine as base, the prominent leaving group triflate (OTf) was successfully introduced by reaction with triflic anhydride to form **3-11** as colorless crystals.



Scheme 19 Synthesis of the substitution **3-11**.

However, the reaction in Scheme 18 did not work as well as we had hoped. There was still much starting material **3-7** as shown by thin layer chromatography. We have used different reactants and catalysts, including tetrabutylammonium fluoride (TBAF) and $Pd_2(dba)_3$ (dba: dibenzylideneacetone) with CsF, and different solvents (such as DCM, toluene and THF mixed with MeCN) at different temperatures. Among them, the best yield was 15% with the participation of $Pd_2(dba)_3$ and CsF in THF at 50 °C after 24 h. Compared with 1,2,4,5-tetrabromobenzene producing compound **3-8** in 19% yield, **3-11** gave a lower yield. As the synthesis of **3-11** takes much longer time than that of 1,2,4,5-tetrabromobenzene, the latter was preferentially employed in the syntheses.

4. Photodecomposition of Acene Precursor in Polymers

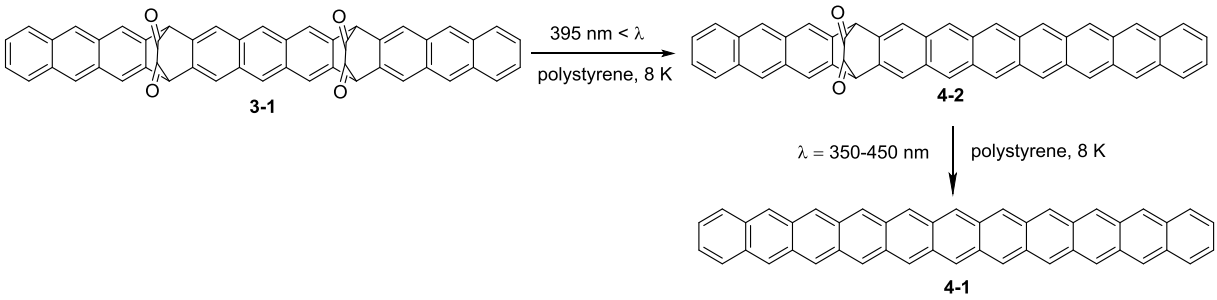
4.1 Introduction

Initial sublimation experiments indicated, not unexpectedly, that the undecacene photoprecursor **3-1** is difficult to sublime without decomposition in sufficient amounts for cryogenic inert gas matrix isolation that was employed in previous acene studies by the Bettinger group.[35-37] Inspired by the work of Neckers and co-workers,[34,78] who used a polymer matrix for photogeneration of heptacene and hexacene, we investigated the photoconversion of **3-1** in polystyrene and poly(methyl methacrylate) (PMMA) matrix under cryogenic conditions (8 K). The use of cryogenic conditions, not employed by Neckers et al. in their study of heptacene,[34] is expected to stabilize the undecacene molecules towards possible thermal reactions. The disadvantage of this approach is the limited optical transparency in the NIR and UV range and the increased bandwidths in the optical spectra.

In initial experiments the quality of the spectra proved to be superior in polystyrene (PS) compared to PMMA matrix, and hence the semirigid PS matrix was employed to generate the highly reactive undecacene under high-vacuum conditions. As smaller acenes were never measured in PS before, pentacene, heptacene, and nonacene were produced in PS to provide data for comparison will be discussed in this chapter. The acene precursors, pentacene diketone[83] and heptacene diketone[34] were provided by the group members Florian Reicherter and Ralf Einholz respectively, while the nonacene precursor was synthesized as described previously.[37]

4.2 Photochemical synthesis of undecacene 4-1

Scheme 20 shows the general process of photochemical synthesis of undecacene **4-1**. The procedure and results will be explained briefly below.



Scheme 20 Stepwise photochemical synthesis of undecacene **4-1** from photoprecursor **3-1**.

A solution of **3-1** in CH_2Cl_2 was dropped onto an optically transparent sapphire substrate in a glove box and the solvent was removed by slow evaporation. Once a dry film was obtained, the sapphire substrate was mounted onto the cold finger of the cryostat and the system was evacuated. The photoprecursor **3-1** shows absorptions around 450–510 nm that are the typical for α-diketone bridged acenes and arise from n → π* transitions of the diketone moieties.[34] Irradiation (λ > 395 nm) resulted in a quick decrease of this band while concomitantly the growth of a strong signal at 354 nm and weak signals in the 600–800 nm range (Figure 8a) was observed. These absorptions are in agreement with the *β* band and a *p* band, respectively, of a heptacene unit that is expected to result from cleavage of the first *α*-diketone bridge to give **4-2** (Scheme 20). A similar stepwise photodecarbonylation was observed previously in the photogeneration of octacene and nonacene under matrix isolation conditions.[37]

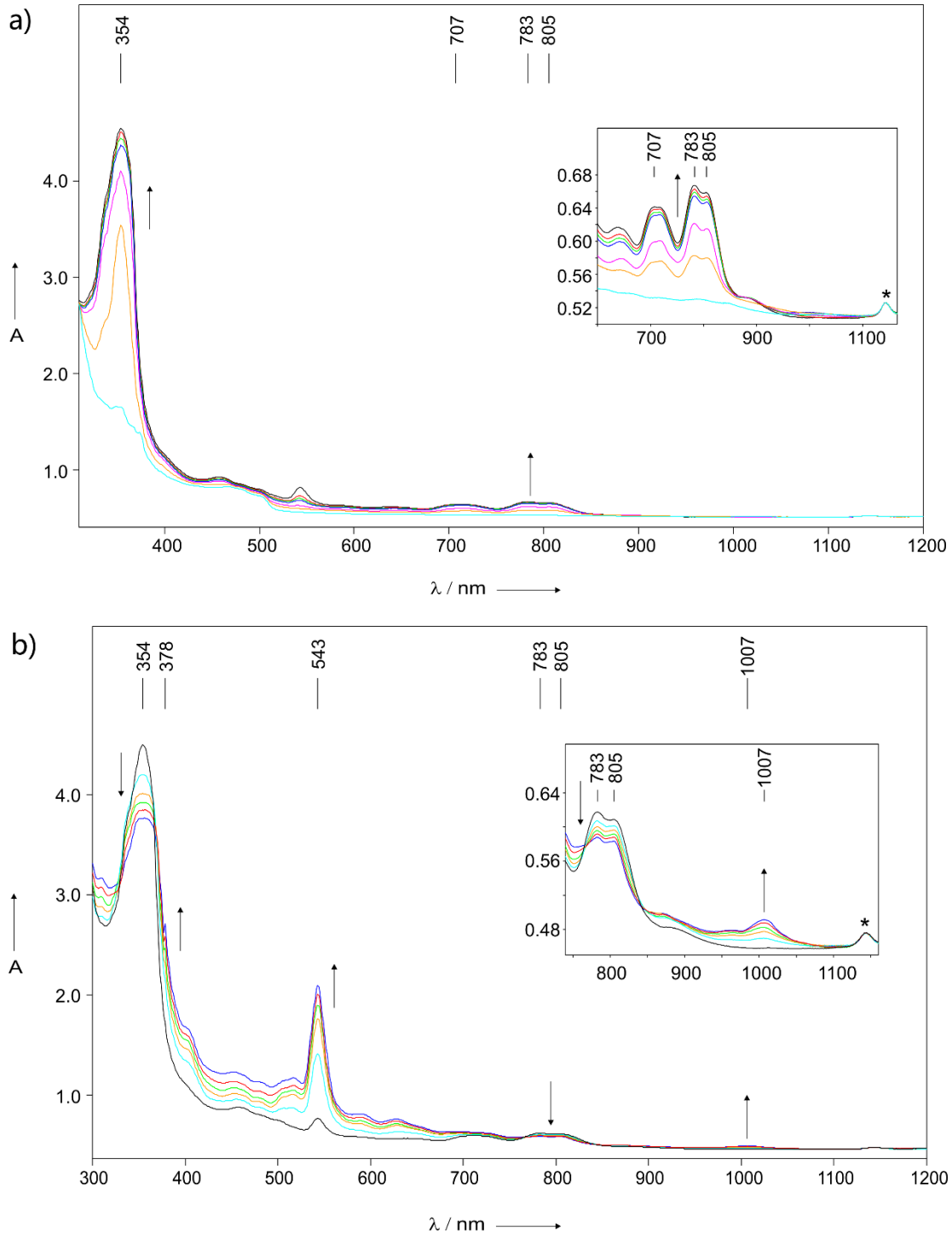


Figure 8 Spectra obtained after irradiation of **3-1** isolated in polystyrene at 8 K. Arrows pointing upwards indicate increasing, arrows pointing downwards indicate decreasing bands during irradiation. a) Irradiation with λ > 395 nm. b) Irradiation with 450 nm > λ > 350 nm. The * marks a PS absorption.

In order to cleave the second α-diketone bridge shorter wavelength irradiation was required, again as seen before.[37] However, the limited photostability of the undecacene in PS matrix did not allow using wavelengths shorter than 350 nm, and hence quite long reaction times were required for conversion of **4**-**2** to **4**-**1**. Under these irradiation conditions bands with maxima at 543 nm and 1007 nm grow (Figure 8b). These bands are compatible with formation of undecacene based on the comparison with the available data for the smaller acenes. For octacene and nonacene a new strong band in addition to the strong β band was observed.[37] A computational analysis of DFT/ MRCI of the excited electronic states of the acenens up and including to nonacene interpreted this new strong band to be associated with a formally doubly excited state and labelled it D2.[39] A DFT/ MRCI investigation of the electronic state of decacene and undecacene was performed by Dr. Jörg Tatchen of the group of Prof. Elsa Sanchez-Garcia at the University Duisburg-Essen with whom we collaborated.

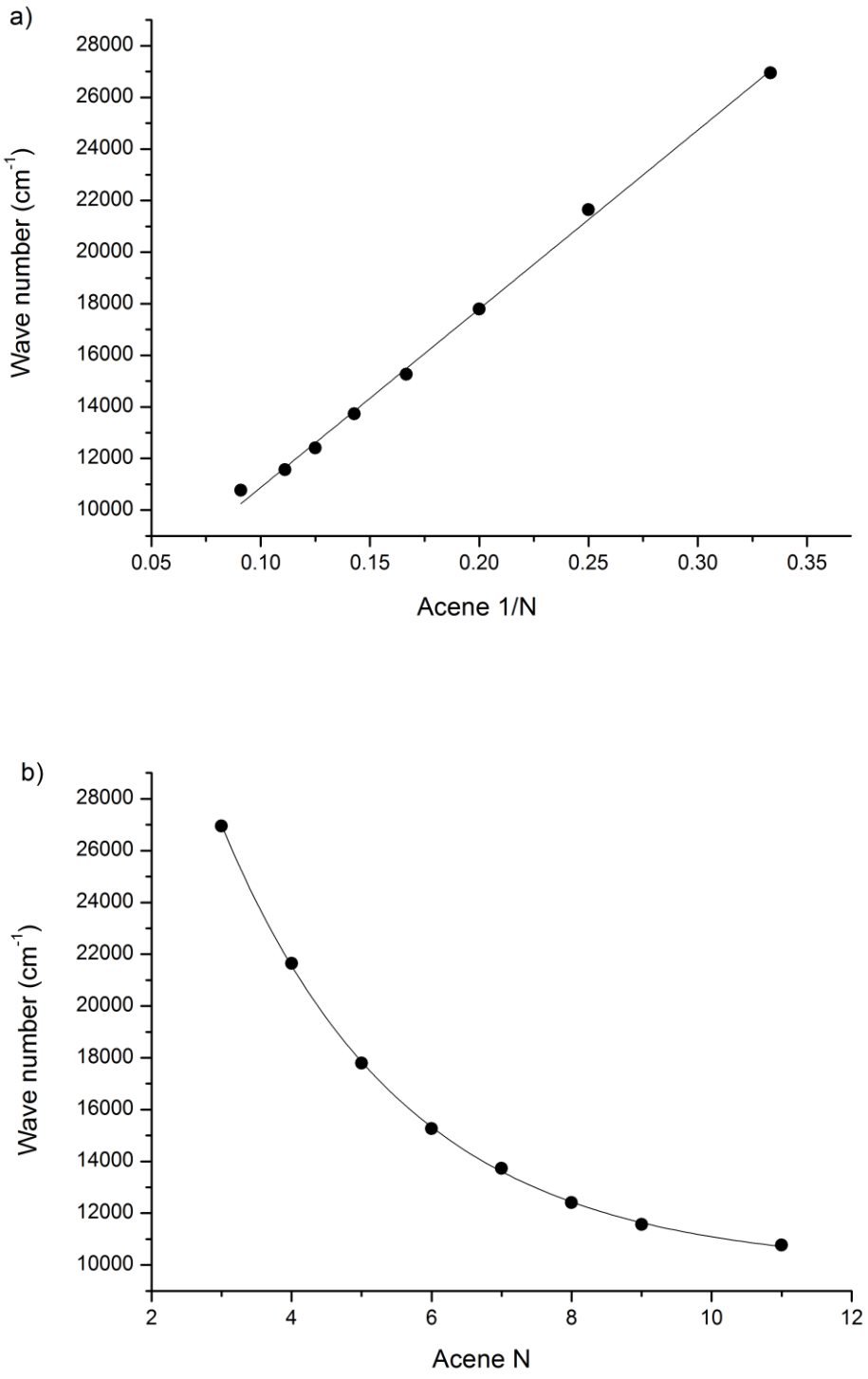


Figure 9 a) Plot of the energy maximum of the p band (H → L) transition energy in the acene series (N: number of condensed benzene rings), $R^2 = 0.9976$. b) Exponential fit of the transition energies. $E_g(N) = 9923\ cm^{-1} + 53873\ cm^{-1} \exp(-N/2.609)$, $R^2 = 0.9998$.

The comparison of the computed data with the measurements suggests that the strong band observed at 543 nm should be assigned to the D2 state (calc. 521 nm). Likewise, the very weak band at 1007 nm is assigned to the ^1L_b state (calc. 968 nm). The more polar PS matrix results in a bathchromic shift of roughly 750 cm^{-1} of the transition energies compared to argon matrix based on the data of pentacene, heptacene, and nonacene. Taking this matrix shift into account when plotting the ^1L_b state energies in argon over 1/N (N number of benzene rings) gives a straight line as expected for a particle in a box model (Figure 9a). The exponential extrapolation of the optical gap to the limit of infinite chain length of the acene series arrives at 1.23 eV, very similar to the value obtained from data up to nonacene (1.18 eV) previously.[37]

4.3 Conclusion

We have photogenerated the largest acene molecule to date, undecacene, in a polystyrene matrix under cryogenic conditions and recorded its optical absorption spectrum. The optical spectrum of undecacene follows the trends that were observed earlier for the shorter members of the series in as much as all observed optical transitions shift bathochromically. The large acenes have, however, electronic states at lower energies than the HOMO → LUMO transition that are associated with very low oscillator strengths are were not observed. The HOMO → LUMO transition energy that may be associated with the optical gap still follows the linear 1/N relationship observed for the shorter members, and exponential extrapolation results in a limiting value of 1.23 eV. Thus, indications for oscillations of the optical band gap are absent. If electron-electron interaction in the acene series is strong, and our investigation supports this, band gap oscillations may not be observable for gas phase molecules, but as suggested by Evers et al. only in screening environments such as on substrates and in electrolyte solutions.[40]

5. Generation of Dications of Nonacene and Undecacene

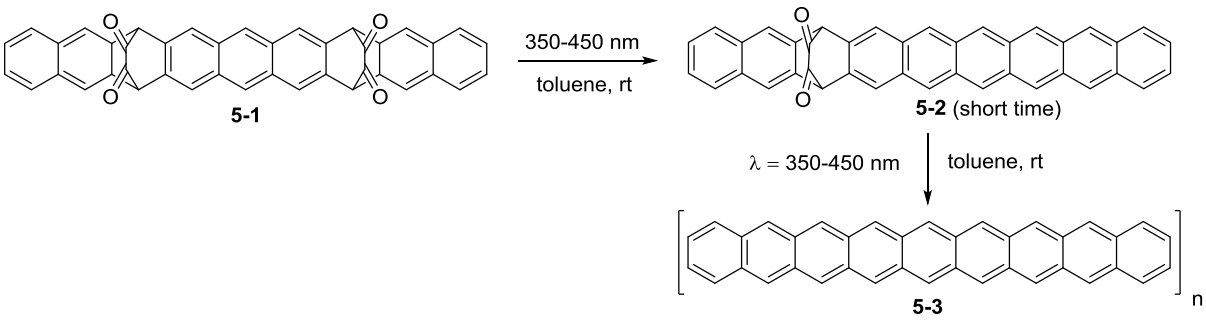
5.1 Introduction

It has been established that dissolution of acenes in concentrated sulfuric acid at room temperature results in formation of dications that have distinctive colors which differ from those of the neutral acenes.[54] Our research group has demonstrated previously that the photodecomposition of the heptacene diketone (**1-1**) in solution produces a mixture of covalently bound dimers of heptacenes, called diheptacenes.[38,54] Unexpectedly, dissolution of these dimers in concentrated sulfuric acid resulted in formation of heptacene dication that is persistent under these conditions for a long period of time.[54] The particularly interesting aspect of this observation was that the formally antiaromatic dication (28 π electrons) enjoys higher stability or persistence than the neutral aromatic (30 π electrons). This was explained by the presence of two aromatic Clar sextet[84,85] in the dication rather than one in the neutral compound. In addition, the most important decomposition channel of higher acenes, dimerization, is very unfavorable for dications due to the Coulomb repulsion.

Having investigated the optical gap of neutral acenes upto undecacene, we wanted to study if dications of even larger acenes can be generated in sulfuric acid solution and how the optical gap of the dication species evolves with system length. In this chapter, we will look into the evolution of the optical gap of dicationic acenes by photodecomposition of nonacene and undecacene photoprecursors in solution followed by dissolution of the photoproducts in 96% sulfuric acid, producing the corresponding dications.

5.2 General approach to photodecomposition of acene photoprecursors in solution

5.2.1 Photodecomposition of pre[9]acene



Scheme 21 Photodecomposition of pre[9]acene **5-1**.

Photolysis (λ = 350 – 450 nm) of the photoprecursor of nonacene **5-1** (Scheme 21) in toluene solution at room temperature was monitored by optical spectroscopy. After 0.5 minutes of photolysis of the solution a new structured absorption band in the region of 550-750 nm with maxima at 587, 622 and 681 nm (Figure 10) was detected. This band is indicative of a hexacene moiety. Upon extended periods of irradiation, these features disappeared and no intensive signals in the visible range were observed.

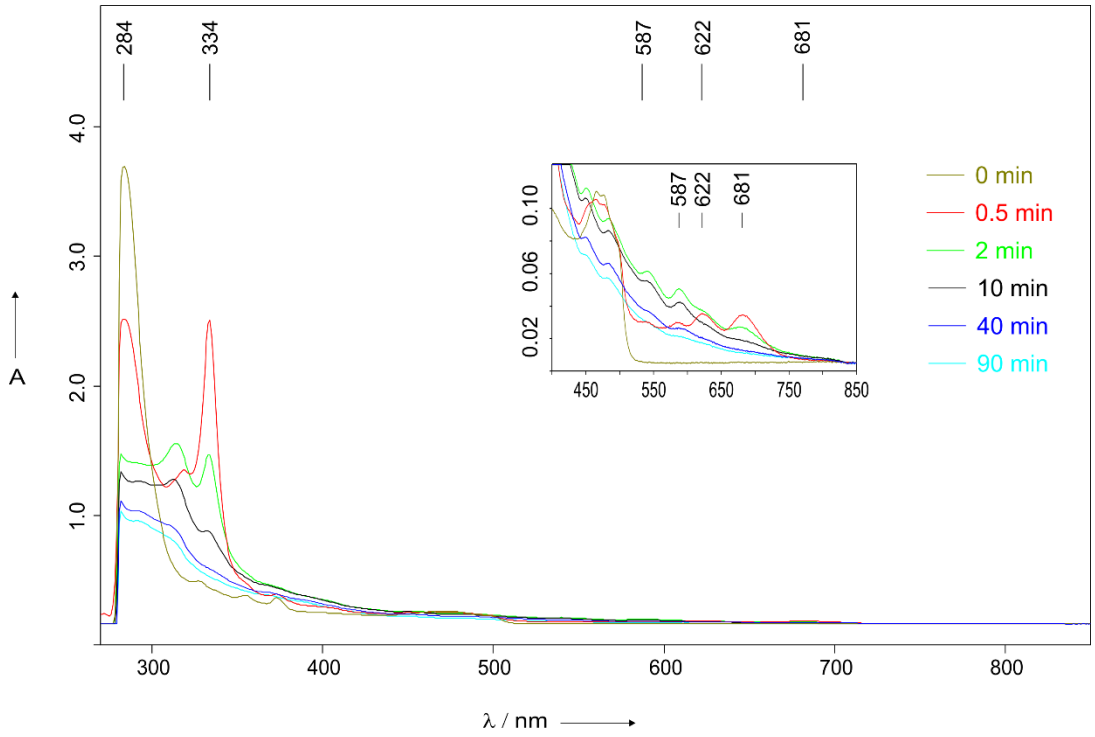


Figure 10 Absorption spectra measured during irradiation (450 > λ > 350 nm) of **5-1** in degassed toluene at rt

This behavior is similar to the photolysis of pre[6]acene that only gives hexacene in the early stages of irradiation.[36,78] After 1.5 h irradiation, a colorless to pale yellow solid **5-3** was obtained after removal of the solvent. The poor solubility of the photoproducts precludes characterization by solution phase NMR spectroscopy. Mass spectrometry using atmospheric pressure photoionization (APPI) and electrospray ionization (ESI) was performed at the Lehrstuhl II for Organic Chemistry at Friedrich-Alexander University Erlangen-Nuremberg. The mass spectra showed formation of nonacene under the ionization conditions as the only identifiable product. It is clear that the almost colorless photoproduct cannot be nonacene itself due to its high reactivity and pale olive color, but most likely is a dimer or oligomer of nonacene that splits under ionization conditions. It is not possible to derive the degree of polymerization from the available data. The cleavage of covalent acene dimers under mass spectrometry

conditions were observed previously by Anthony et al.[86] for silylethynyl substituted dihexacenes as well as in our group for diheptacenes,[38,54] and it is thus quite likely that also oligomers or polymers of nonacene would similarly undergo cleavage under ionization conditions. Such dimers or oligomers could form from either nonacene or from the hexacene subunits by photochemically allowed [π4s + π4s] cycloaddition (Figure 11). The computational analysis of Bendikov et al. has revealed that the formation of dimers, oligomers, or polymers of acenes is increasingly more favorable as the length of the acenes increases.[12,87] The observations made here are thus in agreement with the computed thermochemical values.

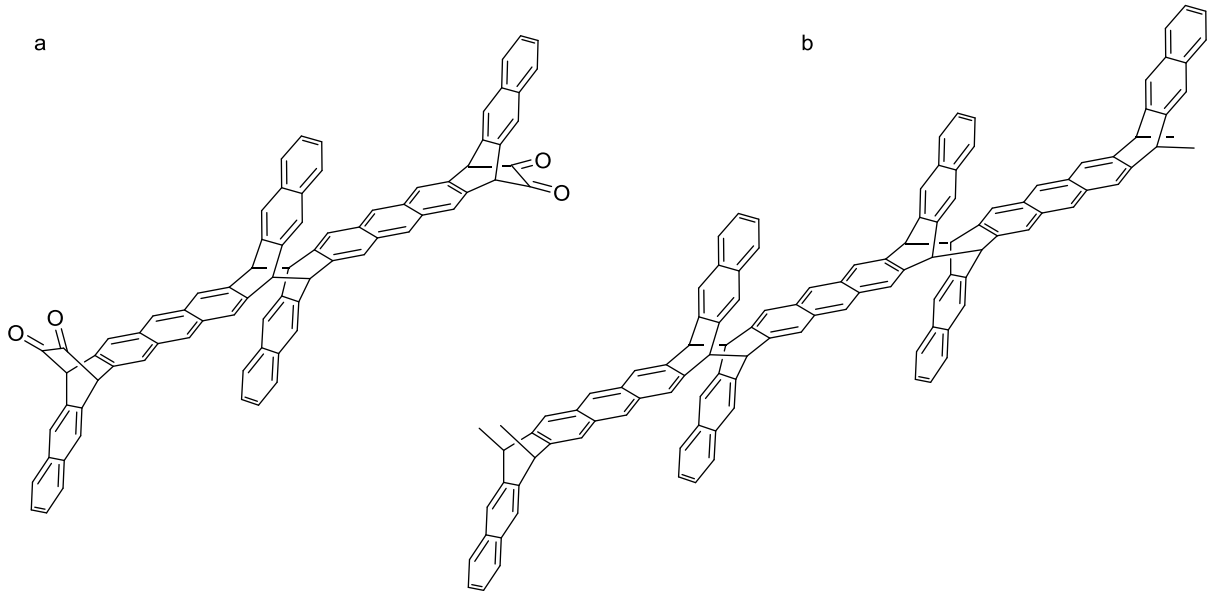
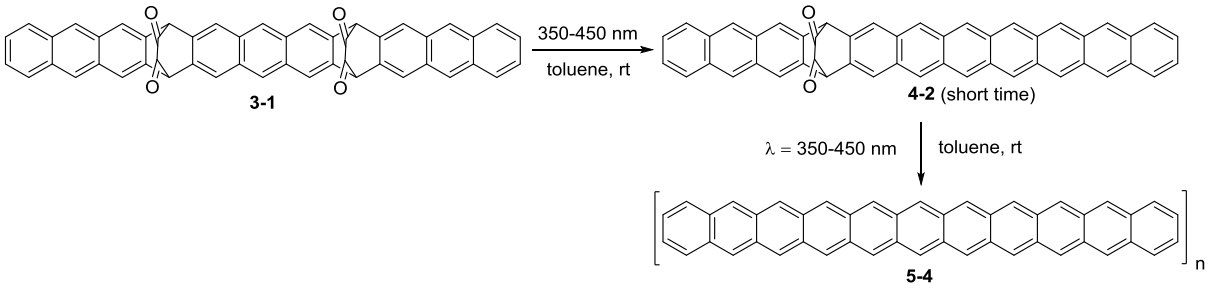


Figure 11 a) Dimer of diketone with a hexacene subunit. b) Oligomer of nonacene.

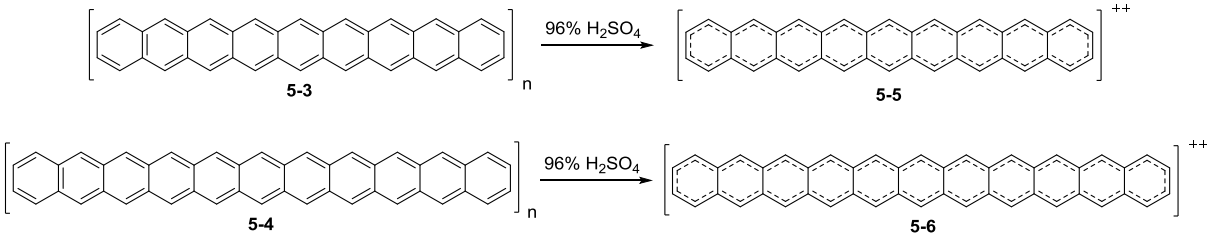
5.2.2 Photodecomposition of pre[11]acene

The pre[11]acene was similarly photolyzed (λ = 350 – 450 nm) in degassed toluene at room temperature. A colorless to pale yellow solid **5-4** was obtained after 1.5 h of irradiation. This solid could not be characterized by NMR spectroscopy due to poor solubility, and in contrast to the photoproduct obtained from the pre[9]acene was not characterized by mass spectrometry.



Scheme 22 Photodecomposition of pre[11]acene.

5.3 Generation of nonacene dication and undecacene dication in 96% H_2SO_4



Scheme 23 Generation of nonacene dication and undecacene dication in 96% H_2SO_4.

After photolysis of the photoprecursors, the toluene solvent was completely removed and the dried photoproducts **5-3** and **5-4** were dissolved within a UV/vis cuvette with 2.5 mL of 96% sulfuric acid. This produced a yellowish brown solution in the case of pre[9]acene and a brown solution in case of pre[11]acene. In the electronic excitation spectra (Figure 12) obtained from 96% H_2SO_4 solutions, the longest wavelength bands at 1074 nm and 1196 nm, respectively, are expected to belong to nonacene dication and undecacene dication, respectively. In particular the very strong absorption at 1074 nm is compatible with the available data for the smaller acenes.[54]

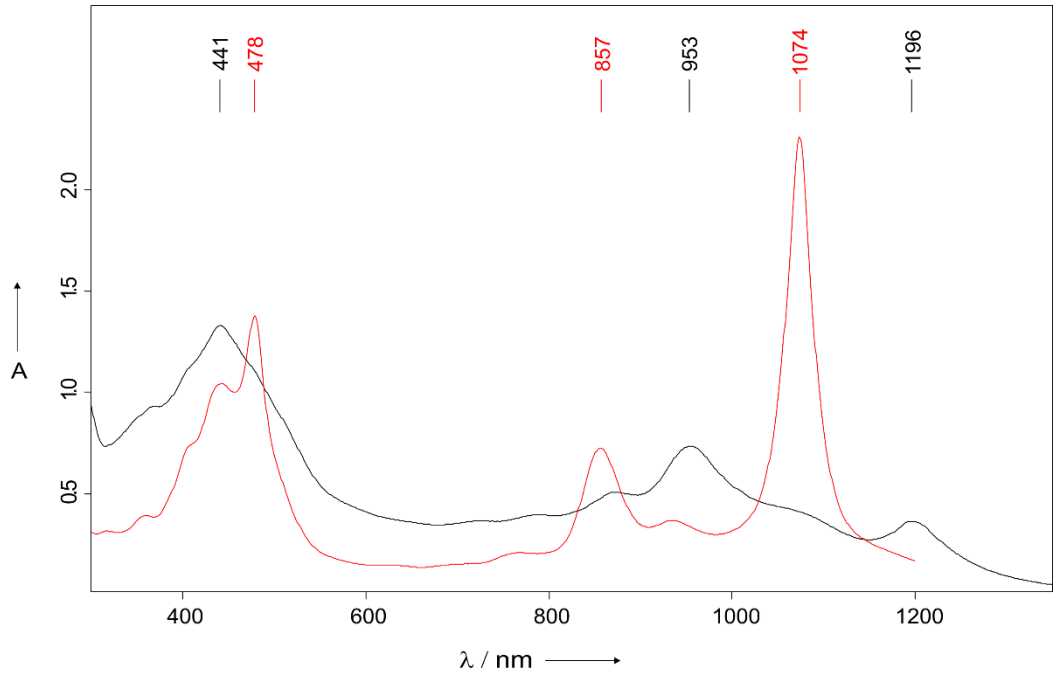
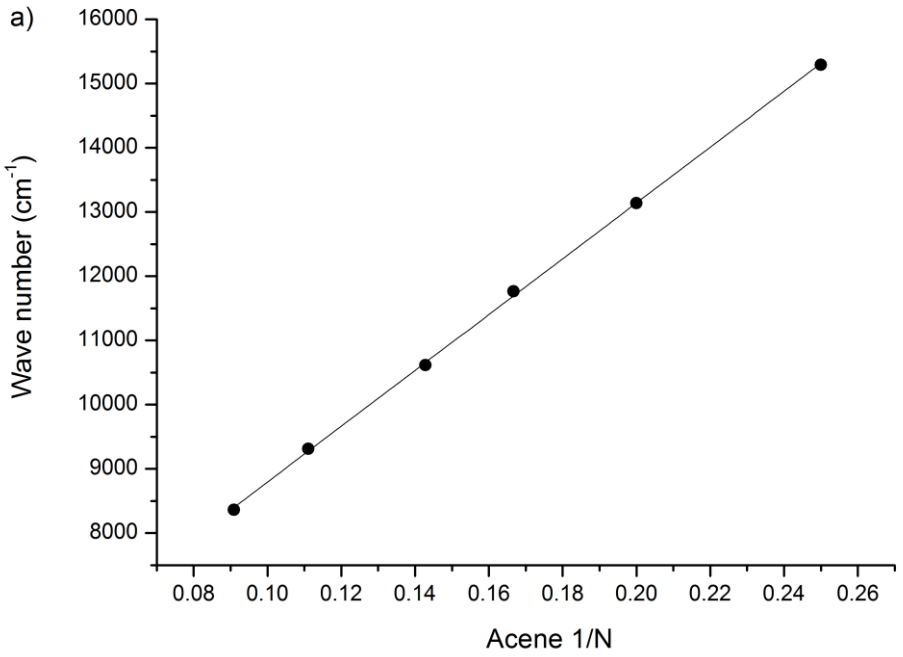


Figure 12 The spectra of nonacene dication (red) and undecacene dication (black) were measured after 1.5 h irradiations (450 > λ > 350 nm) of both tetraketone photoprecursors in degassed toluene after removing the organic solvent and dissolving the photoproducts in 96% H_2SO_4, respectively.

When plotting the transition energy of the largest wavelength absorption of the acene dication series in 96% sulfuric acid over 1/N (N: number of condensed benzene rings), a straight line is obtained as expected for a particle in a box model (Figure 13a). This correlation is strong indication that the data point assumed to be due to the undecacene dication is indeed arising from this species, even though its intensity is only small (see discussion below). The exponential extrapolation of the optical gap of the acene dication series (from tetracene dication to heptacene dication)[54] reaches at 0.99 eV, which is in a good agreement with the value obtained from data up to nonacene dication (0.98 eV) and undecacene dication (0.93 eV) respectively (Figure 13b). Electron paramagnetic resonance (EPR) measurements of the

sulfuric acid solutions at room temperature give no indication for a triplet state, indicating that the dications prefer a singlet electronic ground state.



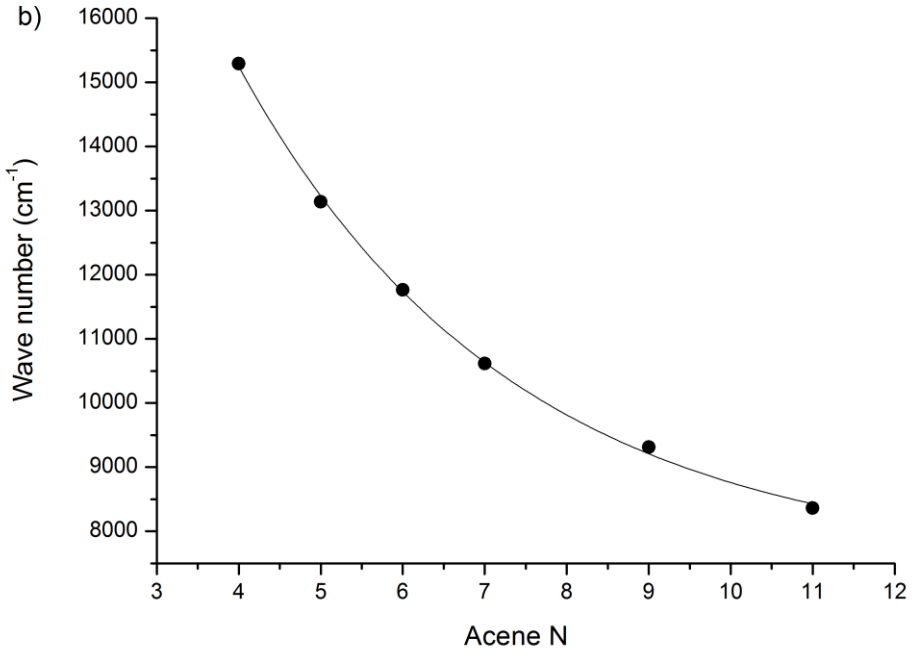


Figure 13 a) Plot of the energy maximum of the largest wavelength bands transition energy of acene dication series in 96% sulfuric acid (N: number of condensed benzene rings), $R^2 = 0.9996$. b) Exponential fit of the transition energies, $R^2 = 0.9987$.

However, based on the appearance of the electronic absorption spectra of the smaller acenes up to heptacene (Figure 14), the bands at 857 nm and 953 nm are most likely not arising from the nonacene dication and undecacene dication, respectively. The energies of these bands are similar to the strong bands of hexacene and heptacene dications, and thus they more likely belong to hexacene dication and heptacene dication moieties, respectively. In order to form nonacene and undecacene, the two α-diketone bridges on each photoprecursor should be removed totally. Thus, we speculated that the bands at 857 nm and 953 nm could be belong to the hexacene and heptacene derivatives obtained after only one of the α-diketone bridges are cleaved. The APPI-MS obtained from the photoproduct at Erlangen University gave no indication for the presence of such monobridged compounds.

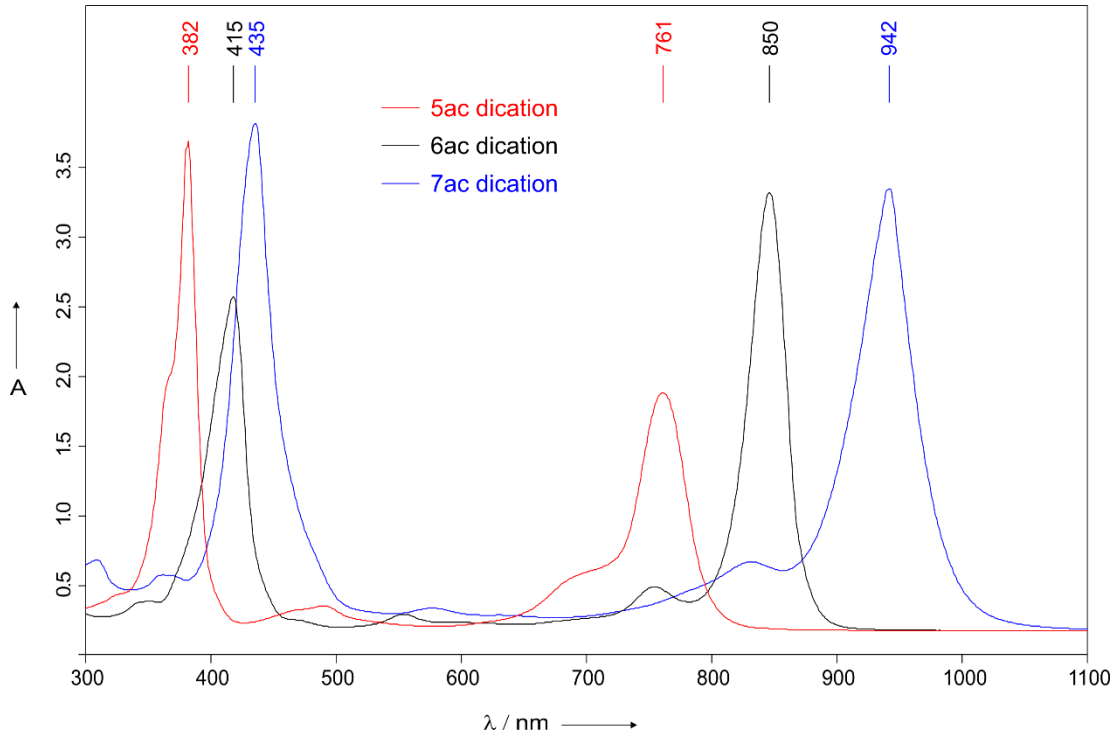


Figure 14 The spectra of small acene dications in 96% H_2SO_4.

For further investigations, we focused on the nonacene photoprecursor. Variation of the irradiation time of nonacene tetraketone **5-1** in toluene attracted our attention (Figure 15). When the irradiation time was significantly extended, around 24 h, the results did not show much difference according to the black curve and red curve in Figure 15. When the irradiation time was only 30 seconds, a light yellow solid was obtained after immediate removal of the solvent toluene with an oil pump. After adding 96% H_2SO_4 the excitation spectrum (blue curve in Figure 15) showed a new band at 849 nm. This is shifted hypsochromically from 857 nm observed after longer irradiation times. After short irradiation time, the band observed at 849 nm most likely belongs to the dication of hexacene derivative with an α-diketone bridge. The band at 857 nm observed after longer irradiation times (1.5 h and 24 h) most likely belongs to a different species. One reasonable postulate is that there is still a small amount of oxygen present in degassed toluene, which is reacting with the highly reactive nonacene and

undecacene during irradiation in solution giving rise to formation of endoperoxides. The formation of quinones, the final photoproducts of oxidation of acenes, is not supported by the APPI-MS data.

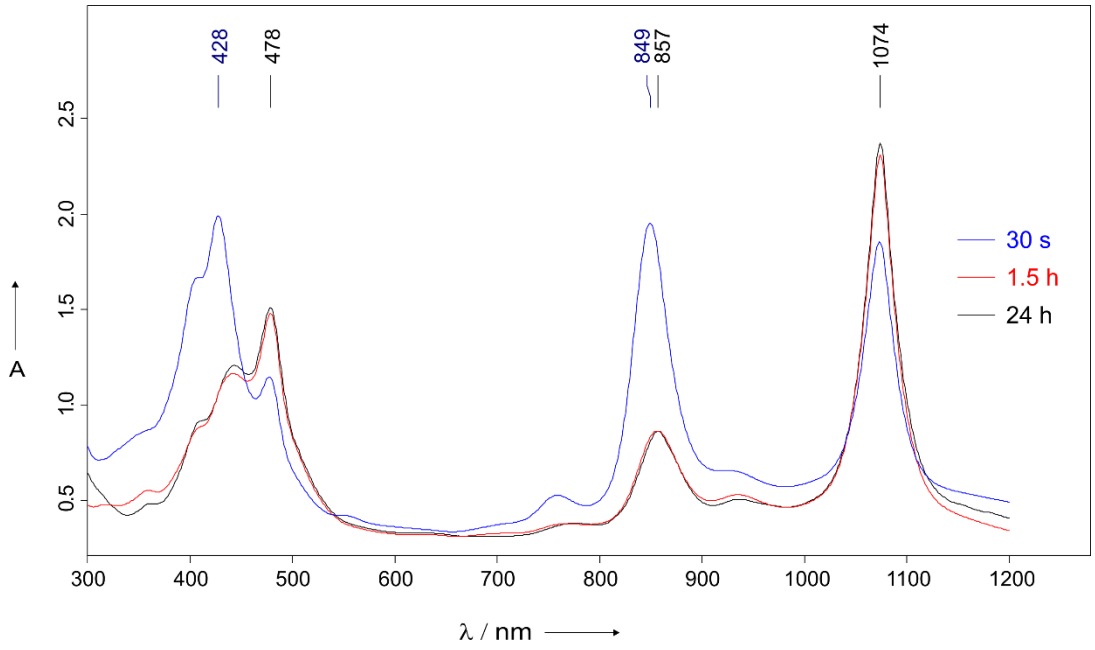


Figure 15 The spectra of nonacene dication in 96% H_2SO_4 after different irradiation times (450 > λ > 350 nm) in degassed toluene.

Therefore, the solvent toluene was extensively degassed by seven freeze-pump-thaw cycles, while it was three freeze-pump-thaw cycles before. However, there was almost no improvement. It is not clear if there is still oxygen or water left even after more cycles of degassing with a conventional oil pump. That degassing of toluene is essential, on the other hand, was shown by the following experiment: when dry toluene without any degassing was employed for an experiment no band shifts were observed, but only small amounts of nonacene dication (1074 nm) were obtained (black curve, Figure 16) as the band at 857 nm now has a higher intensity. Thus, we can conclude that the bands at 857 nm and 953 nm observed in the sulfuric acid solutions are not due to nonacene dication and undecacene dication, respectively,

but more likely belong to oxidation products that are formed during the irradiation of the photoprecursors in the presence of trace amounts of oxygen.

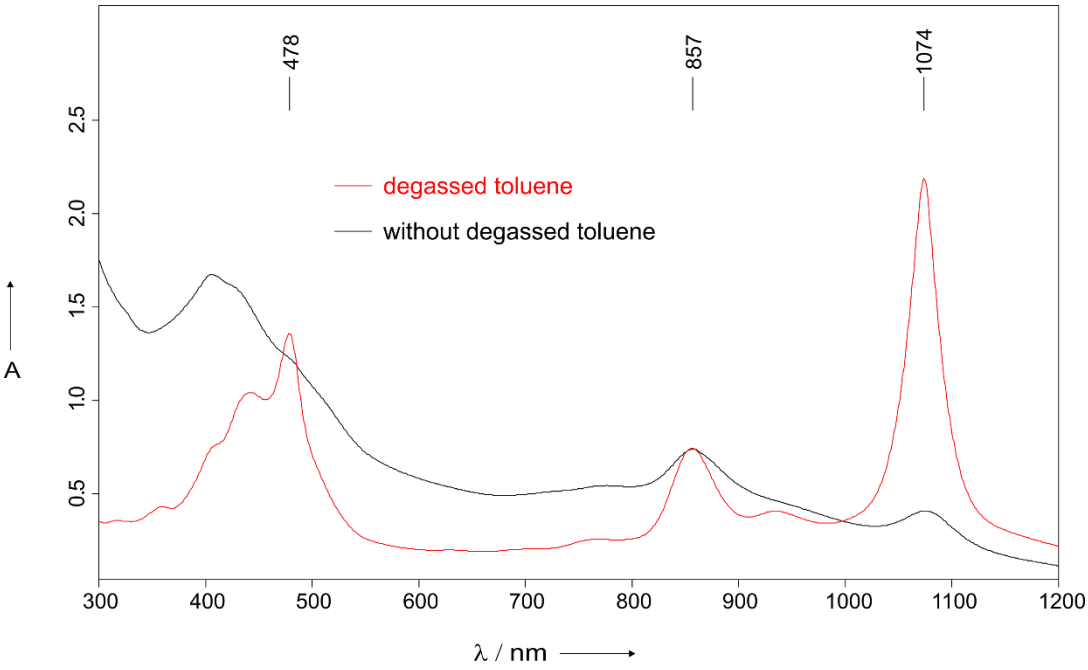


Figure 16 The spectra of nonacene dication in 96% H_2SO_4 after 1.5 h irradiations (450 > λ > 350 nm) in degassed and without degassed toluene respectively.

6. Investigation of 2,3,9,10-Tetrafluoropentacene

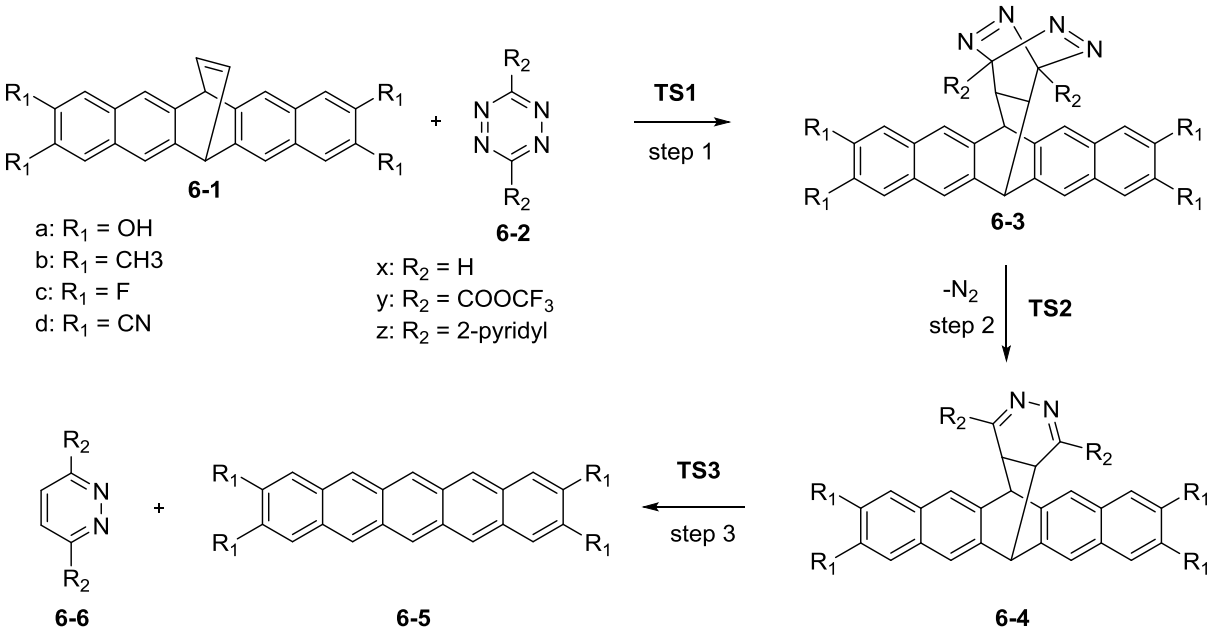
6.1 Introduction

The most important member of the acene family, pentacene (PEN), is a typical *p* channel semiconductor.[64] Introduction of inductively electron withdrawing fluorine atoms can modify the electronic structure to such an extend as to turn perfluoropentacene[88] (PFP) into an *n* channel semiconductor.[65,66] The availability of *n* channel interfaces is important for construction of complementary integrated circuits.

Besides providing a way for electronic modification of an organic semiconductor, full or partial fluorination was recently introduced as a means for crystal engineering of rubrene (5,6,11,12-tetraphenyltetracene).[89,90] Partially fluorinated (hetero)acenes were shown to interact with fluorinated self-assembled monolayers, resulting in improved crystallinity and charge transport in OFETs.[91-93] In addition, partially fluorinated 6,13-di(triorganylsilylethynyl)-substituted pentacenes[94] were studied in the context of singlet fission,[95,96] and were employed in blends for investigation of charge-transfer processes that are relevant for photophysical applications.[97-102] The recent study by Leo *et al*. reveals that blends of organic semiconductors, phthalocyanines and partially fluorinated phthalocyanines, allow smooth tuning of the band gap over a wide energy range.[103,104] This finding also makes partially fluorinated pentacene interesting objects of research. Other fluorinated acenes, e.g. octafluoro-diphenylanthracene,[105] were investigated with respect to the tuning of the HOMO-LUMO gap.

Only two partially fluorinated pentacenes are known. These are 1,2,3,4-tetrafluoropentacene[106] and 2,3,9,10-tetrafluoropentacene (F4PEN) that was prepared in the Bettinger research group.[107] The syntheses of both known tetrafluoropentacene isomers employ a protection group strategy that avoids the common problems associated with low solubility and air sensitivity of pentacenes. While 1,2,3,4-tetrafluoropentacene was obtained by retro-chelotropic extrusion of CO from a bridged ketone,[108,109] Bula et al.[107] obtained F4PEN (**6-5c**)

from a sequence of Diels-Alder and retro-Diels-Alder reactions employing 2,3,9,10-tetrafluoro-6,13-dihydro-6,13-ethenopentacene (**6-1**) and 3,6-disubstituted 1,2,4,5-tetrazines (**6-2**) (Scheme 24).[107,110,111] The yield, however, is rather low for the electron poor tetrafluoro derivative.[107] It was significantly larger for parent pentacene and even more so for the electron rich 2,3,9,10-tetrakis(benzyloxy)pentacene.[107]



Scheme 24 Stepwise formation of pentacenes **6-5** from reaction of 6,13-dihydro-6,13-ethenopentacenes **6-1** upon reaction with 3,6-disubstituted 1,2,4,5-tetrazines **6-2**.

In his Ph.D. thesis, Bula suggests that an electronic effect might be operating that results in the poor yield of F4PEN.[112] As this hypothesis was never investigated, the substituent effects on the formation of 2,3,9,10-tetrasubstituted pentacenes **6-5** was explored using quantum chemical methods. In addition, the photochemical synthesis of F4PEN from an α-diketone bridged precursor was explored.

6.2 Computational Investigation of the Removal of an Etheno Bridge

The generation of pentacenes **6-5** from 2,3,9,10-tetrasubstituted-6,13-dihydro-6,13-ethenopentacene precursors **6-1** with 3,6-disubstituted 1,2,4,5-tetrazines **6-2**, involves one inverse-electron-demand Diels-Alder reaction[113-117] via **TS1** followed by two retro-Diels-Alder reactions via **TS2** and **TS3** (Scheme 24). In order to investigate possible electronic effects on reaction barriers, we have applied computational chemistry methods (M06-2X/6-31G*).

As the barrier for loss of nitrogen from **6-3** to **6-4** is very low or almost nonexistent,[118] we only studied the transition states of the first inverse electron demand DA reaction (**TS1**) and the third (**TS3**) step, *i.e.*, the retro-DA reaction giving pentacenes **6-5** and pyridazines **6-6** (Scheme 24). The structure of **TS1** is characterized by carbon-carbon distances of the forming bonds of 2.224 Å (Figure 17a), which is typical for DA reactions of 1,2,4,5-tetrazines.[119] In **TS3** the breaking bonds are stretched to 2.169 Å (Figure 17b). Although pentacene is well-known to act as a diene in Diels-Alder reactions,[120] and the retro-Diels-Alder reaction was employed for obtaining pentacene for device applications,[121,122] little is known on the structure of transition states involved in the (retro-)DA reaction.[25,123] Hence, comparison of **TS3** with transition state structures of related pentacene DA reactions is not possible.

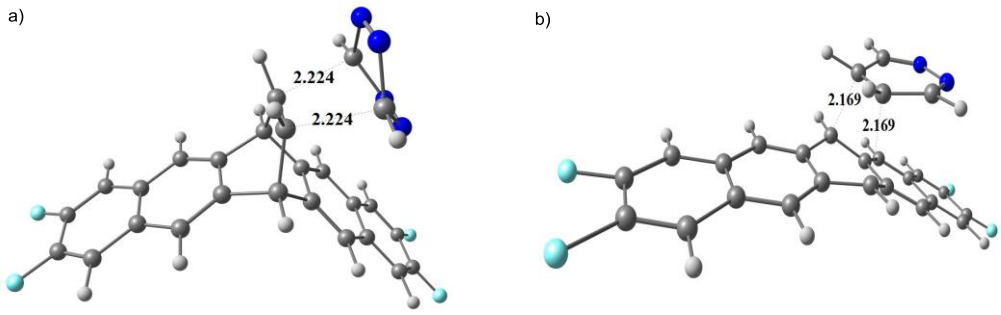


Figure 17 The structures of **TS1** (a) and **TS3** (b) as computed at the M06-2X/6-31G* level of theory.

It is well-know that tetrazines are electron-deficient dienes that can quickly undergo inverse-electron-demand Diels-Alder reactions with alkenes or alkynes.[118,124-126] The

observation that the energy barriers involving **TS1** are more than 20 kcal mol^{-1} lower than those of the retro-Diels-Alder reaction through **TS3** (Table 1) therefore is in line with expectations, and confirm that this last step is rate determining in the reaction sequence. Hence, we focused our analysis on this final step.

Table 1. The energy barriers including zero point vibrational energy corrections (ΔE_0, kcal/mol) involving **TS1** and **TS3** calculated at the M06-2X/6-31G(d) level of theory. The substituent R_2 on tetrazine is H.

	R_1 = OH	R_1 = CH_3	R_1 = F	R_1 = CN
ΔE_0(**TS1**)	11.0	11.4	11.8	13.1
ΔE_0(**TS3**)	35.4	35.9	36.1	36.3

The reactivity of 1,2,4,5-tetrazines can be increased by introduction of electron withdrawing groups at the 3,6-positions, and hence we have investigated the often-used 2-pyridyl (2-py) and trifluoromethylcarboxyl (CO_2CF_3) substituents. For all substituted pentacenes investigated, the barriers for retro-DA reactions via **TS3** are lowest with CO_2CF_3-substituted and highest with parent tetrazine (Table 2). The differences range between 5-8 kcal mol^{-1}. Most interestingly, substituents on the pentacene backbone have a significant impact on the barrier heights (Table 2). These decrease in the series CN > F > CH_3 > OH, which is in line with the electron-withdrawing ability of these groups as expressed by the substituent constants σ_p (0.660, 0.062, -0.170, -0.37, respectively).[127] For R_2 = CO_2CF_3, a linear correlation between σ_p and the computed barrier height (R^2 = 0.987) is obtained. In summary, electron withdrawing groups on the 1,2,4,5-tetrazine and electron-donating groups on the pentacene backbone enhance the thermal extrusion of the pyridazine molecule. This is in good overall agreement to the observations that we made experimentally.[107]

Table 2. Energy barriers (ΔE_0, kcal mol^{-1}) involving **TS3** as computed at the M06-2X/6-31G(d) + ZPVE level of theory.

	ΔE_0(**TS3**)		
R_1	R_2 = H	R_2 = 2-pyridyl	R_2 = CO_2CF_3
OH	35.4	31.0	27.8
CH_3	35.9	31.7	28.8
F	36.1	32.1	29.7
CN	36.3	32.4	31.5

Reaction rates computed from Gibbs free energies of activation for CO_2CF_3-substituted 1,2,4,5-tetrazine （Table 3) show that the electron-donor substituent OH results in an almost 50-fold increase in rate compared to F, and a more than 150-fold increase compared to CN.

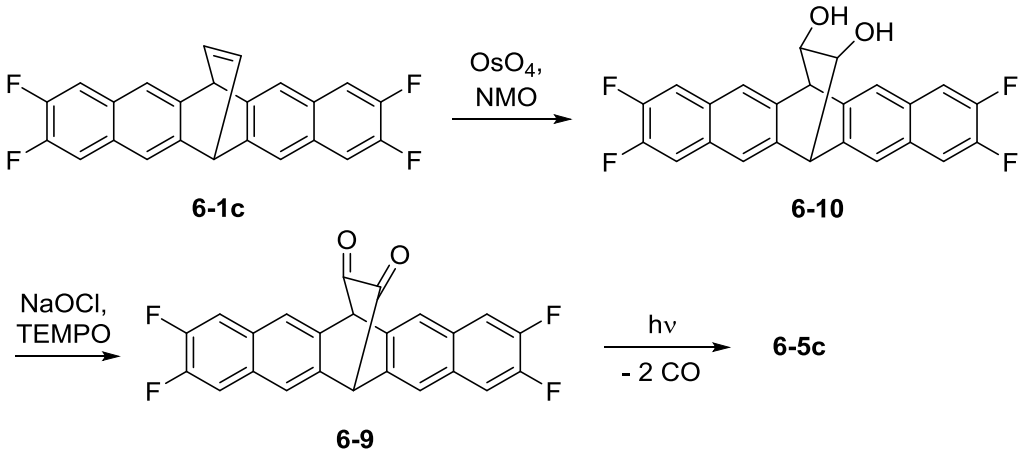
Table 3. The free energy of activation ($\Delta G^{‡}$, kcal/mol, T = 298.15 K) and the reaction rates (k, s^{-1}) associated with **TS3** were calculated at M06-2X/6-31G(d) (R_2 = CO_2CF_3).

	R_1 = OH	R_1 = CH_3	R_1 = F	R_1 = CN
$\Delta G^{‡}$	28.7	29.6	31.0	31.7
k (10^{-11})	567.4	124.2	11.7	3.6

6.3 Photochemical Synthesis of F4PEN

An alternative to the thermal tetrazine induced synthesis of F4PEN can be the photochemical extrusion of carbon monoxide from a bridged α-diketone precursor, in analogy to the work on undecacene described above. Indeed, such α-diketones are well-known precursors to various acenes under photochemical conditions (Scheme 25).[73] In order to

transform **6-1c** into the corresponding α-diketone, 2,3,9,10-tetrafluoro-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**6-9**), the olefinic double bond was dihydroxylated with catalytic amounts of OsO_4 and *N*-methyl-morpholine *N*-oxide (NMO) to furnish the corresponding diol **6-10** in 89 % yield following the previously reported procedures for closely related compounds.[128] The final oxidation step employed the Annelli protocol (NaOCl) that our research group has earlier found to be advantageous.[37] This step only proceeds with a yield of 40 %, while the final photobisdecarbonylation again runs with high yield (90 %). Overall, the three-step photochemical synthesis thus provides F4PEN in 32 % from **6-1c**, an almost three-fold increase over the reported procedure.[107] The photoirradiation ($\lambda \geq 395$ nm) of the α-diketone **6-9** can conveniently be run in DMSO solution at room temperature and results in precipitation of F4PEN in the form of a blue solid. Its spectral properties are identical to those of samples obtained previously by tetrazine induced elimination.[107]



Scheme 25 Photochemical synthesis of F4PEN (**6-5c**) starting from **6-1c**.

The F4PEN samples thus obtained were employed in a collaborative research project with the group of Professor Frank Schreiber that focused on the structural distortion of the F4PEN molecule on a Cu(111) surface.[67]

7. Experimental Section

7.1 Instrument and Reagents

^{1}H NMR spectra were recorded from Bruker Avance III HD 400 or Bruker Avance III HDX 600 MHz instruments. Chemical shifts for ^{1}H NMR were reported as δ relative to the signal of $CHCl_3$ at 7.26(s) ppm. Chemical shifts for ^{13}C NMR were reported as δ relative to the signal of $CHCl_3$ at 77.16 ppm. The following abbreviations were used to describe splitting patterns: s = singlet, d = doublet, m = multiplet.

Unless otherwise stated, all chemical were either used as received from their respective commercial suppliers or purified according to *Purification of Common Laboratory Chemicals*.[129] Solvents for flash column and thin layer chromatography, including dichloromethane, *n*-hexane, ethyl acetate, toluene, and methanol, are all of HPLC grade quality. 1,2,4-Trichlorobenzene was dried over 3 Å molecular sieves and degassed by the freeze-pump-thaw method. Dichloromethane used in the UV-Vis and fluorescence experiments was taken from a MBRAUN SPS-800 solvent purification system and degassed by three consecutive freeze-pump-thaw cycles.

Absorption spectra were measured on a PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer. Thin layer chromatography was performed on a fluorescence indicator marked precoated silica gel 60 plates and visualized by UV light (254 nm/366 nm). Flash column chromatography was performed on silica gel (0.040 – 0.063 mm).

7.2 Computational Methods

All DFT computations were performed with Gaussian 09.[130] Geometry optimizations of all the minima and transition states were carried out at the M06-2X level of theory and the 6-31G(d) basis set,[131,132] which has been shown to give reliably energetics for

cycloadditions.[133,134] The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K, using the rigid rotor, harmonic oscillator model of an ideal gas. Intrinsic reaction coordinate (IRC) calculations were carried out to verify the connectivity of each transition state with the corresponding product and reactant.[135]

7.3 Synthesis of the undecacene photoprecursor

6,7,10,11-Tetrahydro-7,10-dietheno-8,9-dimethylenetetracene 3-7[78]

Under argon protection, 2,3-dibromonaphthalene **3-4**[74] (7.38 g, 25.8 mmol) and 2,3,5,6-tetramethylidenbicyclo[2.2.2]oct-7-ene **3-6**[136] (4.04 g, 25.8 mmol) were dissolved in toluene (350 mL) and cooled down to -50 – -60 °C. Then *n*-butyllithium (16.1 mL, 25.8 mmol) diluted with *n*-hexane (20 mL) was added dropwise over three hours. After complete addition, the mixture was stirred for an additional hour and then was allowed to slowly warm up overnight. The mixture was quenched with methanol, washed with water and the solvent was removed. The solid was purified by column chromatography over silica gel with hexane and dichloromethane as eluent. During elution, the percentage of dichloromethane was rised from 1% to 25%. Compound **3-7** was obtained as a colorless solid. Yield: 3.42g (47%).

^{1}H-NMR (400 MHz, CDCl3): δ 3.69-3.79 (m, 4H), 3.99-4.05 (m, 2H), 4.90 (s, 2H), 5.11 (s, 2H), 6.49-6.55 (m, 2H), 7.35-7.40 (m, 2H), 7.62 (s, 2H), 7.70-7.75 (m, 2H)

6,7,8,10,11,12,19,20,21,23,24,25-Dodecahydro-7,24:11,20-bisethenoundecacene 3-8

1,2,4,5-tetrabromobenzene (0.14 g, 0.4 mmol) and **3-7** (0.20 g, 0.7 mmol) were added into toluene (60 mL) was added under argon atmosphere. The solution was cooled down with an ice bath. Methyllithium (0.7 mL, 1.6 M in diethyl ether) diluted with diethyl ether (2 mL) was added dropwise within two hours. After complete addition, the ice bath was removed and the reaction mixture was allowed to slowly warm up to room temperature. Stirring was continued overnight. After quenching with methanol and removal of the solvent, the remaining solid was purified by column chromatography over silica gel with hexane and dichloromethane as eluent. The product **3-8** was obtained as a slightly yellowish solid. Yield: 44mg (19%).

^{1}H-NMR (400 MHz, CDCl3): δ 3.54 (s, 8H), 3.77 (s, 8H), 4.30-4.34 (m, 4H), 6.84-6.89 (m, 6H), 7.31-7.35 (m, 4H), 7.58 (s, 4H), 7.56-7.59 (m, 4H). **^{13}C-NMR** (100 MHz, CDCl3): δ 32.92, 33.32, 54.54, 125.16, 126.88, 127.18, 128.73, 131.97, 132.34, 133.44, 139.52, 140.42, 140.52. **HRMS** (ESI) m/z calcd for $C_{50}H_{38}$ $[M + Na]^+$: 661.2866; found: 661.2870. **Mp**: decomposed at 138 °C.

7,11,20,24-Tetrahydro-7,24:11,20-bisethenoundecacene 3-9

Under inert conditions, **3-8** (0.18 g, 0.3 mmol), chloranil (0.42 g, 1.7 mmol) and potassium carbonate (0.81 g) were mixed in toluene (75 mL). The reaction mixture was refluxed overnight. After cooling down to room temperature, the mixture was filtered, washed with water and dried over magnesium sulfate. The solvent was removed and the residue was purified by column chromatography over silica gel with hexane and dichloromethane as eluent. The compound **3-9** was obtained as a slightly yellowish solid. Yield: 126 mg (68%).

^{1}H-NMR (400 MHz, CDCl3): δ 5.28-5.31 (m, 4H), 7.01-7.05 (m, 4H), 7.34-7.40 (m, 4H), 7.81 (s, 4H), 7.83 (s, 4H), 7.88-7.93 (m, 4H), 8.14 (s, 2H), 8.24 (s, 4H). **^{13}C-NMR** (150 MHz, CDCl3): δ 49.98, 121.06, 121.09, 125.03, 125.27, 125.73, 128.10, 130.65, 130.69, 131.78,

137.73, 140.60, 141.07. **HRMS** (ESI) m/z calcd for $C_{50}H_{30}$ $[M + Na]^+$: 653.2240; found: 653.2243. **Mp**: decomposed at 239 °C.

7,11,20,24-Tetrahydro-7,24:11,20-bisethenoundecacene-27,28,29,30-tetraol 3-10

To a solution of N-methylmorpholine-N-oxide monohydrate (135 mg, 1.0 mmol) and OsO_4 (0.25 Ml, 2.5% in *t*-BuOH) in acetone (20 mL) and water (0.6 mL), a suspension of **3-9** (52 mg, 0.08 mmol) was added under argon. After stirring for 72 h at rt, a solution of sodiumdithionite (200mg) in water (2 mL) was added into the light yellow suspension. The mixture was filtered over celite after 10 min of stirring, and the solid residue was washed with acetone. The combined acetone solution was evaporated to dryness and the brown solid was dissolved in EtOAc (80 mL) and water (40 mL). The aqueous phase was separated and extracted with EtOAc three times. The combined EtOAc phase was washed with water and dried over $MgSO_4$, then the solvent was removed and light yellow solid (42 mg) was obtained.

Attempts to get completely pure product by column chromatography were not successful. The ^{1}H NMR spectrum of the crude product shows that no alkene moieties (chemical shift at 5.29-5.30) are present. Without further purification, the product was used in the next oxidation step.

^{1}H-NMR (400 MHz, CDCl3): δ 4.32 (s, 4H), 4.67 (s, 4H), 7.40-7.44 (m, 4H), 7.90-8.00 (m, 16 H), 8.38 (s, 2H). **HRMS** (ESI) m/z calcd for $C_{50}H_{34}O_4$ $[M + Na]^+$: 721.2349; found: 721.2357.

7,11,20,24-Tetrahydro-7,24:11,20-bisethenoundecacene-27,28,29,30-tetraketone 3-1

To a suspension of **3-10** (63 mg) in CH_2Cl_2 (40 mL) and water (8 mL), TEMPO (14 mg), KBr (36 mg) and $NaCO_3$ (90 mg) were added. After cooling to 0 °C, a solution of NaOCl (1.1 mL, 5% active chlorine) in water (1.2 mL) cooled to 0 °C as well, was added dropwise within 2 min.

The mixture was poured into water (9 mL) after stirring for another 2 min. The aqueous phase was separated and extracted with CH_2Cl_2. The combined organic phase was washed with brine and dried over $MgSO_4$, and then the solvent was removed on a rotary evaporator. The residue was purified by column chromatorgraphy (silica, toluene/EtOAc = 1:1). The product was obtained as a yellow solid. Yield: 5 mg (8%).

^{1}H-NMR (400 MHz, CDCl3): δ 5.39 (s, 4H), 7.44-7.51 (m, 4H), 7.96-8.00 (m, 4H), 8.10 (s, 4H), 8.12 (s, 4H), 8.41 (s, 4H), 8.45 (s, 2H). **^{13}C-NMR** (150 MHz, CDCl3): δ 61.25, 125.64, 125.66, 125.76, 126.27, 126.72, 126.97, 128.30, 131.45, 132.05, 132.20, 132.38, 185.65. **HRMS** (ESI) m/z calcd for $C_{50}H_{26}O_4$ $[M + Na]^+$: 713.1723; found: 713.1728. **MS** (APCI): m/z: 691 ($M^+ + H$), 663 ($M^+ + H - CO$).

7.4 Synthesis of the substitution 3-11[81,82]

2,5-dibromobenzene-1,4-diol 3-13

99% acetic acid (100 mL) was added into a three-necked flask with reflux condenser. The hydroquinone **3-12** (10 g) was added and the resulting colorless suspension kept stirring. Using an ice bath for cooling, the bromine (9.3 mL) was added via a dropping funnel over the course of one hour, so that the temperature could be kept below 14 °C always – the crystallisation warmth of the acetic acid adding to the resulting temperature was noticable during this step. The solution was kept stirring for 18h, after which excess bromine was treated using a saturated solution of sodium thiosulfate. The colorless crude product was filtered, washed with H_2O and dried under reduced pressure. Recrystallization using methanol (12 mL) would yield a colorless, crystalline product **3-13**. Yield: 7.980g (33%).

^{1}H–NMR (400MHz; $CDCl_3$): δ 7.16 (s, 2H) , 3.49 (s, 2H).

((2,5-dibromo-1,4-phenylene)bis(oxy))bis(trimethylsilane) 3-14

The educt **3-13** (7.98 g) was charged in a 250mL three-necked Schlenk flask with dropping funnel and reflux condenser under argon atmosphere. Me_3SiCl (23.2 mL) was mixed added to pyridine (10 mL) in the dropping funnel. Adding dry toluene (120 mL) resulted in a colorless suspension. The reaction mixture was heated at 120 °C, in the course of which the educt dissolved, yielding a colorless solution. The solution of Me_3SiCl was added dropwise over the course of one hour and a colorless precipitate of pyridinium chloride was immediately formed. The reaction mixture was kept stirring for an additional 5h and afterwards allowed to cool to room temperature. Half of the solvent was removed under reduced pressure and the pyridinium chloride removed by filtration under ambient conditions. Since even after repeated filtrations there would still be insoluble residue left, solvents were completely removed under vacuum and the solids dissolved in pentane (300 mL). The product was then extracted using saturated solution of $NaHCO_3$ (3 × 100 mL) and brine (100 mL). Removing the pentane under reduced pressure resulted in a brown oil, from which colorless crystals readily formed when cooled using a water bath. Acetone (0.1 mL) was added to no visible effect and the crude product stored for 60h under -18 °C. Leftover solvents were removed under reduced pressure, the corse grained crystals crushed using a spatula and the product **3-14** again dried under vacuum. Yield: 3.561 g (29%).

^{1}H–NMR (400MHz; $CDCl_3$): δ 7.03 (s, 2H), 0.29 (s, 18H).

(2,5-bis((trimethylsilyl)oxy)-1,4-phenylene)bis(trimethylsilane) 3-15

In a 100 mL three-necked Schlenk flask with reflux condenser and dropping flask under argon atmosphere the educt **3-14** (3.56 g) was charged and dry toluene (35 mL) subsequently added.

Me_3SiCl (2.3 mL) and dry toluene (3.5 mL) were placed into the dropping funnel and the sodium (0.894 g) added to the colorless suspension of the product in the Schlenk flask, which resulted in a greenish color. The reaction mixture was heated to 120 °C, followed by dropwise addi-tion of the MeSiCl. A colorless, coarse grained precipitate of sodium bromide was formed. After the addition, the reaction mixture consisted of a colorless solution and a deep-blue precipitate, which was removed by filtration using a Schlenk frit. The solvent was removed under vacuum and the colorless crude product recrystallized in a 250mL Schlenk flask using methanol (108 mL). The product **3-15** of colorless crystals. Yield: 2.155g (63%).

^{1}H–NMR (400MHz; $CDCl_3$): δ 6.76 (s, 2H), 0.29 (s, 18H), 0.24 (s, 18H).

2,5-bis(trimethylsilyl)benzene-1,4-diol 3-16

The educt **3-15** was dissolved in 1,4-dioxane (100 mL) in a 500mL round-bottom flask. To the resulting colorless solution HNO_3 (6M, 5.3 mL) was slowly added, after which the reaction mixture was kept stirring for 30min. H2O (170 mL) was subsequently added and a colorless precipitatewas formed. From this suspension, the crude product was extracted using chloroform (3 × 200 mL) and the organic phase dried using anhydrous sodium sulfate. Removal of the solvent under reduced pressure was followed by recrystalisation using hexane (106 mL), yielding a product **3-16** of colorless crystals. Yield: 609mg (45%).

^{1}H–NMR (400MHz; $CDCl_3$): δ 6.67 (s, 2H), 4.43 (s, 2H), 0.29 (s, 18H).

2,5-[Bis(trimethylsilyl)]phenyl-1,4-trifluoromethanesulfonate 3-11

In a 50 mL three-necked Schlenk flask, triflic anhydride (0.5 mL) was added dropwise into a solution of the educt **3-16** (300 mg) in dry pyridine (9 mL) with ice bath under argon atmosphere.

The mixture was warmed to room temperature slowly, and then heated up to 50 °C for one hour. A yellow residue was obtained after removing pyridine under reduced pressure. The residue was extractd using hot hexane (3 × 40 mL). Removal of combined hexane under reduced pressure was followed by recrystalisation using hexane, yielding a product **3-11** of colorless solid. Yield: 532 mg (87%).

^{1}H–NMR (400MHz; $CDCl_3$): δ 7.44 (s, 2H), 0.38 (s, 18H).

7.5 Photogeneration of undecacene 4-1

20 mg polystyrene was dissolved in 0.2 mL of 0.1 mg/mL solution which was made from 7,11,20,24-Tetrahydro-7,24:11,20-bisethenoundecacene-27,28,29,30-tetraketone **3-1** and dichloromethane. After polystyrene completely dissolved, the mixture was dropped slowly on the quartz disc of matrix and dried for 2 h in a glove box. Attempt was made to avoid light as much as possible while preparing the polystyrene film. Then the quartz disc equipment was fixed back into the matrix. After the vacuum of the matrix was below 4.5×10^{-6} mbar , the matrix was cooled to 8 K. The polystyrene film was irradiated by the ligh of 395 nm < λ for 3 h to generate photoproduct **4-2**, then the ligh of λ = 350-450 nm to generate undecacene **4-1**.

7.6 Synthesis of the dications of nonacene and undecacene

Synthesis of nonacene dication 5-5

2.5 mL of 0.04 mg/mL light yellow solution, made from 6,10,17,21-Tetrahydro-6,21:10,17-bisethanononacene-23,24,25,26-tetraketone **5-1**[37] and degassed toluene, was transferred to a small cuvette in glovebox. The cuvette was sealed and exposed to ligh of λ = 350-450 nm for 1.5 hours at rt. The α-diketone of **5-1** was disappeared by optical spectroscopy and the light

yellow solution became colorless after irradiation. A colorless to pale yellow solid of photoproduct **5-3** was obtained after removing the solvent. The nonacene dication **5-5** was generated by dissolving the photoproduct **5-3** in the cuvette with 2.5 mL 96% sulfuric acid, yellowish brown solution.

Synthesis of undecacene dication 5-6

2.5 mL of 0.04 mg/mL light yellow solution, made from 7,11,20,24-Tetrahydro-7,24:11,20-bisethenoundecacene-27,28,29,30-tetraketone **3-1** and degassed toluene, was transferred to a small cuvette in glovebox. The cuvette was sealed and exposed to the ligh of λ = 350-450 nm for 1.5 hours at rt. The α-diketone of **3-1** was disappeared by optical spectroscopy and the light yellow solution became colorless after irradiation. A colorless to pale yellow solid of photoproduct **5-4** was obtained after removing the solvent. The undecacene dication **5-6** was generated by dissolving the photoproduct **5-4** in the cuvette with 2.5 mL 96% sulfuric acid, brown solution.

7.7 Synthesis of the F4PEN photoprecursor

2,3,9,10-Tetrafluoro-6,13-dihydro-6,13-ethanopentacene-15,16-diol 6-10

A solution of **6-1c** (407 mg, 1.08 mmol) dissolved in 80 mL acetone was added to a solution of *N*-methylmorpholine-*N*-oxide monohydrate (585 mg, 5.00 mmol) and OsO_4 (1.35 mL, 2.5% in *t*BuOH) in 180 mL acetone and 3 mL water under argon. The mixture was stirred for 48 h at RT. The reaction was quenched by adding a solution of sodium dithionite (1.35 g) in 13 mL water, and after 15 minutes of stirring the mixture was filtered and the solid residue washed thoroughly with acetone. The filtrate was evaporated and the brown residue was dissolved in 200 mL CH_2Cl_2 and 200 mL water. The aqueous phase was separated and extracted with

CH_2Cl_2. The combined organic phase was washed with brine and dried over $MgSO_4$, then the solvent was removed. The brown residue was purified by column chromatography (silica, CH_2Cl_2/methanol = 100:1). The product **6-10** was obtained as a white solid (394 mg, 0.96 mmol, 89%).

^{1}H NMR (400 MHz, d_6-DMSO): δ 4.03 (s, 2H), 4.59 (s, 2H), 4.83 (s, 2H), 5.75 (s, 1H), 7.84 (s, 2H), 7.86-7.92 (m, 6H). **^{13}C-NMR** (100 MHz, d_6-DMSO): δ 50.8, 67.0, 113.4 (dd, J = 6.0, 26.0 Hz), 113.5 (dd, J = 6.0, 26.2 Hz), 122.5, 123.9, 128.9 (dd, J = 4.4, 12.0 Hz), 129.0 (dd, J = 4.4, 12.1 Hz), 138.1, 138.8, 148.5 (dd, J = 17.5, 246.1 Hz), 148.7 (dd, J = 17.6, 247.0 Hz). **^{19}F NMR** (376 MHz, d_6-DMSO): δ -139.3 (appt, J = 10.2 Hz), -138.6 (appt, J = 10.0 Hz). **MS** (FAB): m/z (%): 433 (10, M^++Na). **HRMS** (ESI): *m/z* $[M+Na]^{+\cdot}$ calcd. for $C_{24}H_{14}F_4O_2$: 433.0822; found: 433.0831. **Mp**: 149 °C.

2,3,9,10-Tetrafluoro-6,13-dihydro-6,13-ethanopentacene-15,16-dione 6-9

To a solution of **6-10** (50 mg, 0.12 mmol) dissolved in 30 mL CH_2Cl_2 and 9 mL water, TEMPO (19 mg), KBr (75 mg), and $NaHCO_3$ (125 mg) were added. Then a solution of NaOCl (0.40 mL, 5 % active chlorine) diluted with 1.3 mL water was added dropwise within 10 minutes at 0°C. After stirring for another 5 minutes, the mixture was poured into 20 mL water. The aqueous phase was separated and extracted with CH_2Cl_2. The combined organic phases were washed with brine and dried over $MgSO_4$, and then the solvent was removed on a rotary evaporator. The residue was purified by column chromatography (silica, CH_2Cl_2/*n*-hexane = 80:20). The product was obtained as a yellow solid (20 mg, 0.049 mmol, 40%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 5.29 (s, 2H), 7.59 (dd, J = 9.2, 9.2 Hz, 4H), 7.89 (s, 4H). **^{13}C-NMR** (100 MHz, $CDCl_3$): δ 60.5, 114.0 (dd, J = 6.0, 12.0 Hz), 124.9, 130.6 (dd, J = 4.6, 4.6 Hz), 132.4, 150.9 (dd, J = 16.0, 251.6 Hz), 184.4. **^{19}F NMR** ($CDCl_3$, 376 MHz): δ -134.3 (appt, J = 9.2 Hz). MS (FAB): m/z (%): 407 (8, M^++ H). **HRMS** (ESI): *m/z* $[M+MeOH+Na]^{+\cdot}$ calcd. for $C_{24}H_{10}F_4O_2$: 461.0771; found: 461.0775.

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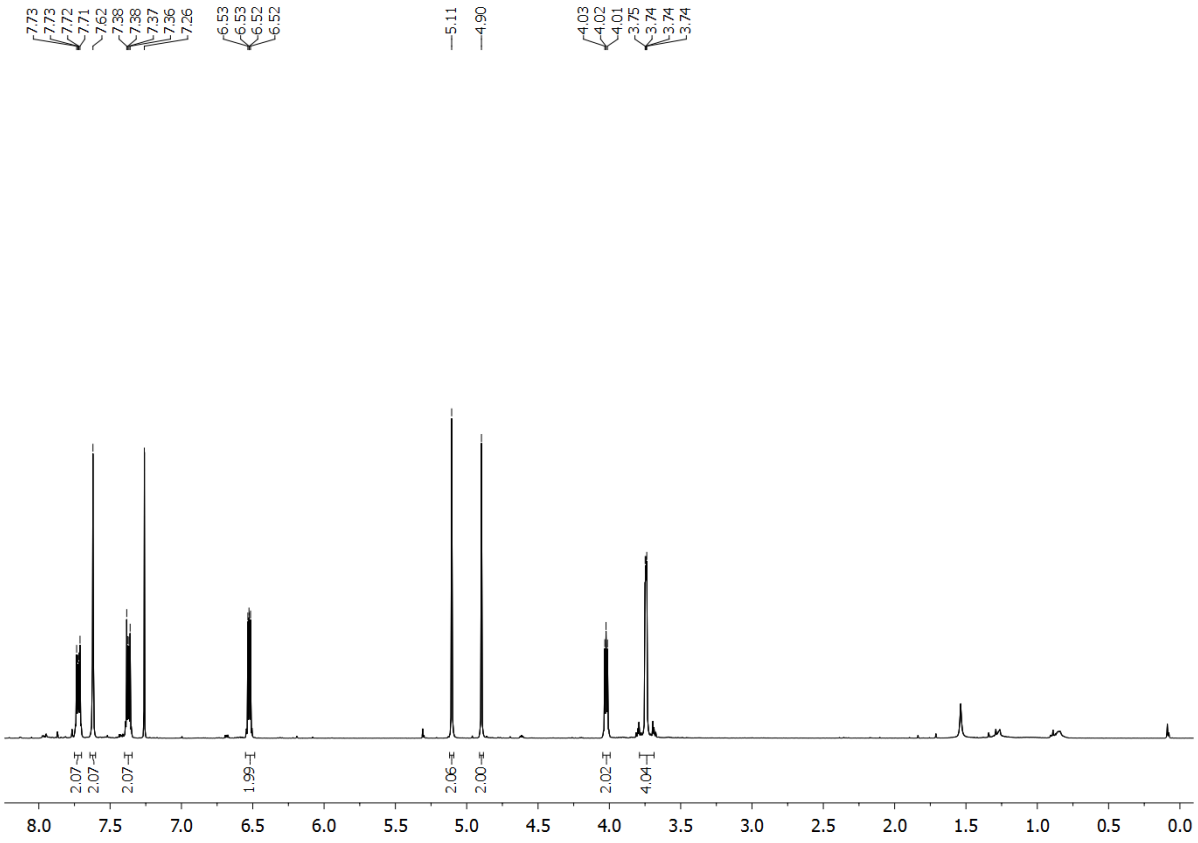
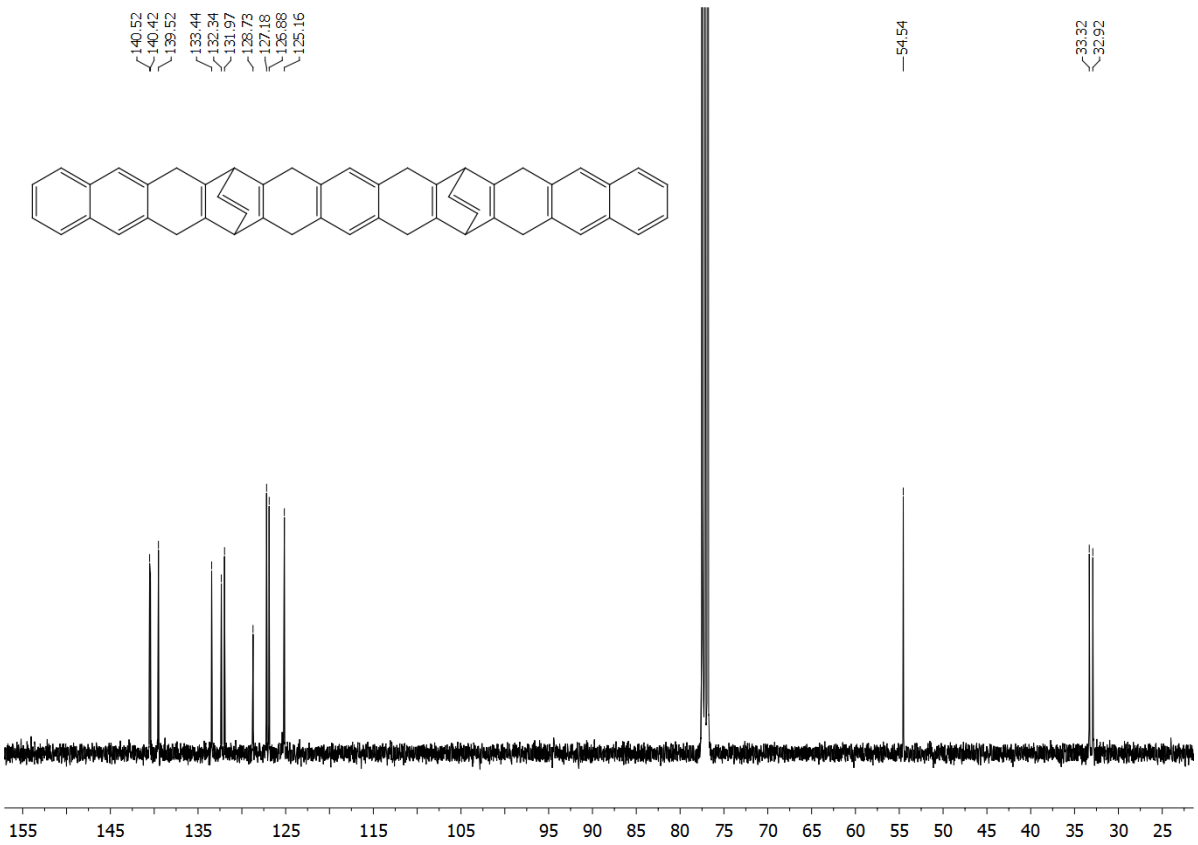
9. Appendix



^{1}H-NMR (400 MHz) spectrum of **3-7** in $CDCl_3$

^{1}H-NMR (400 MHz) spectrum of **3**-**8** in $CDCl_3$



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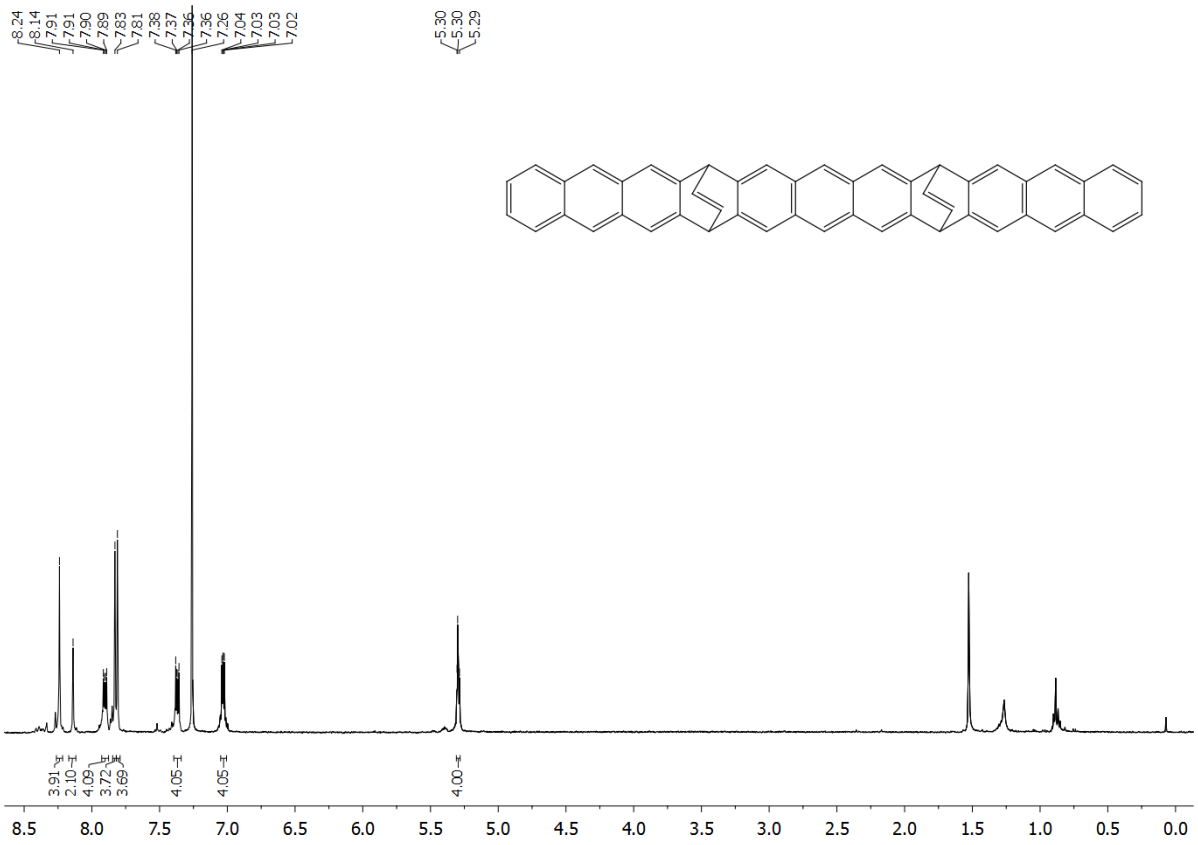
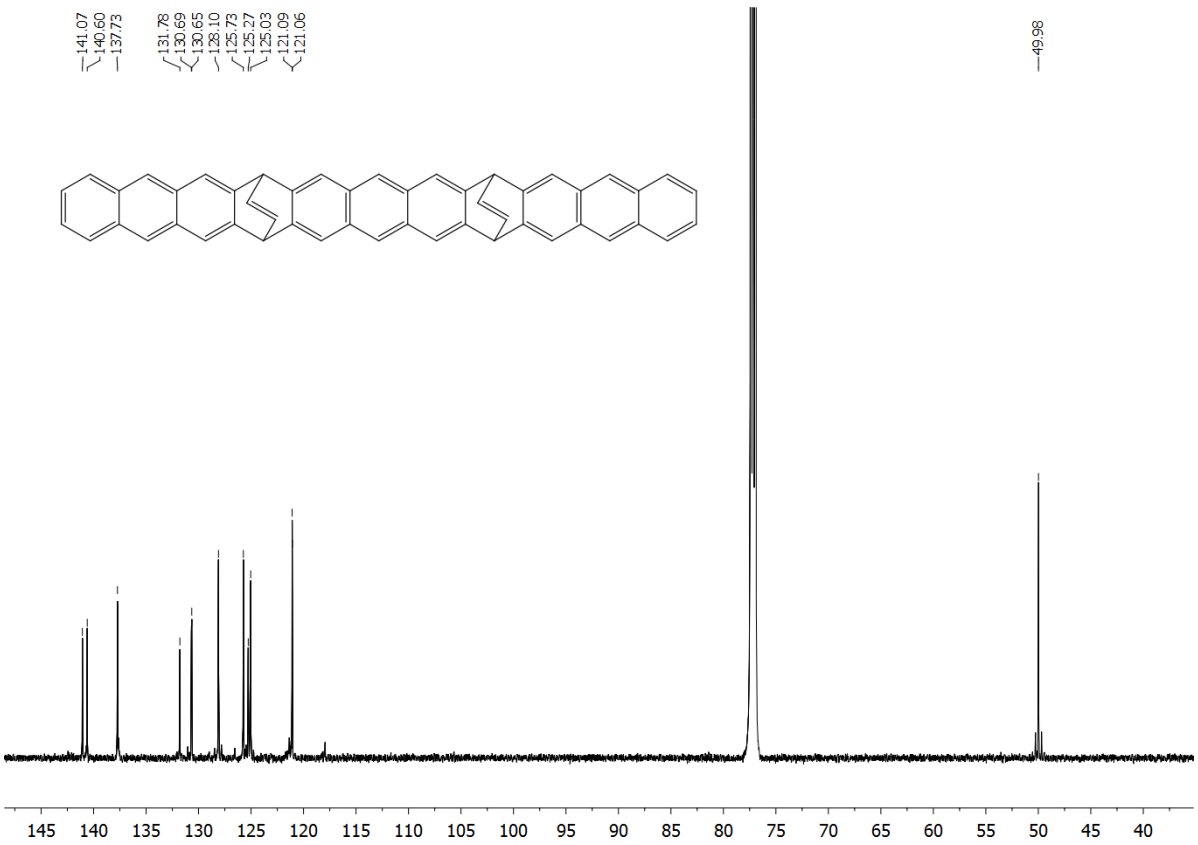


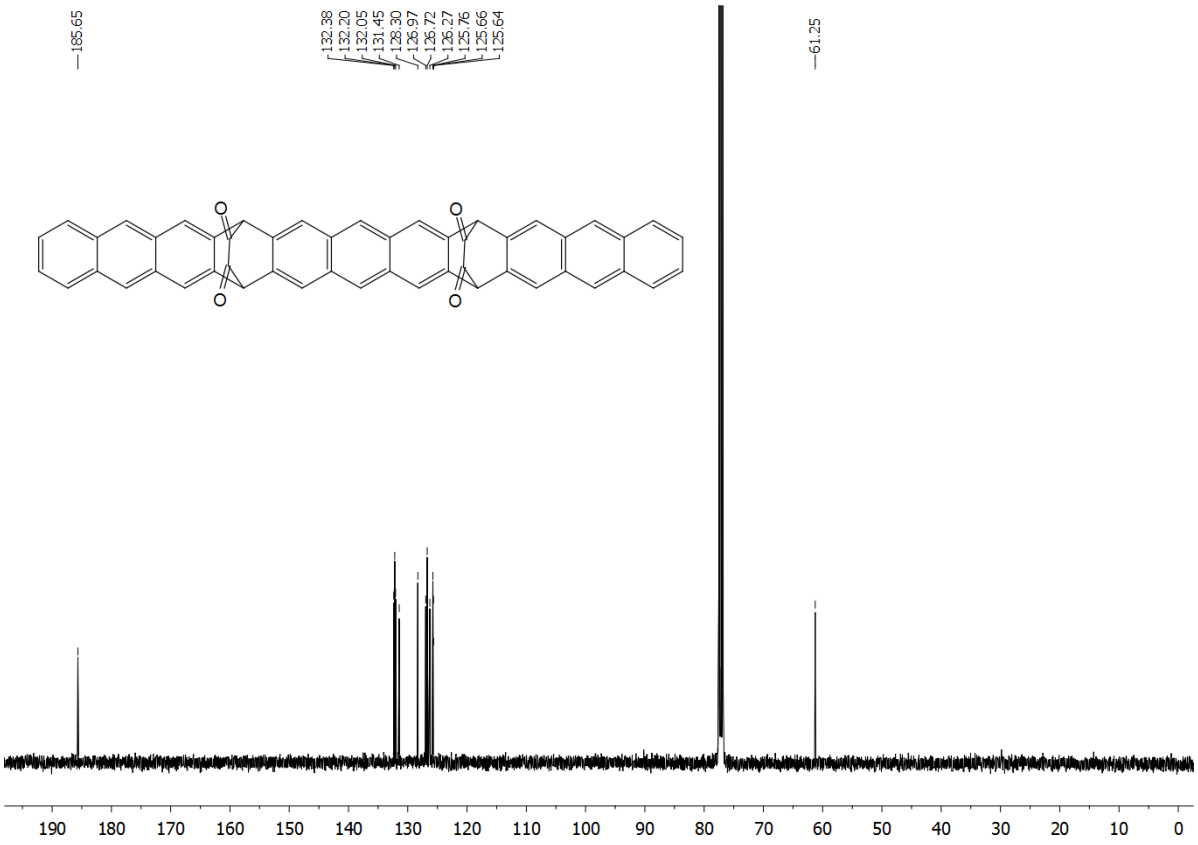
^{1}H-NMR (400 MHz) spectrum of **3**-**9** in $CDCl_3$



^{13}C-NMR (150 MHz) spectrum of **3**-**9** in $CDCl_3$

^{1}H-NMR (400 MHz) spectrum of **3-10** in $CDCl_3$

^{1}H-NMR (400 MHz) spectrum of **3-1** in $CDCl_3$



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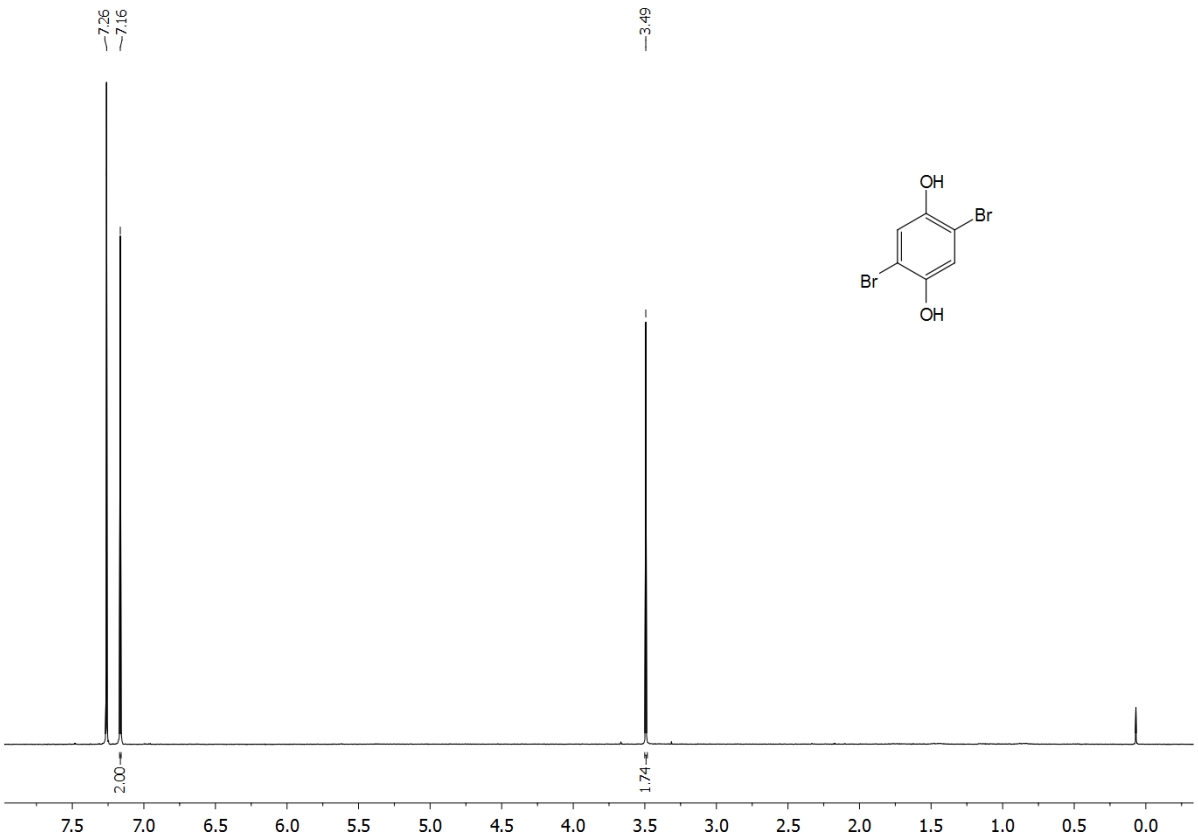

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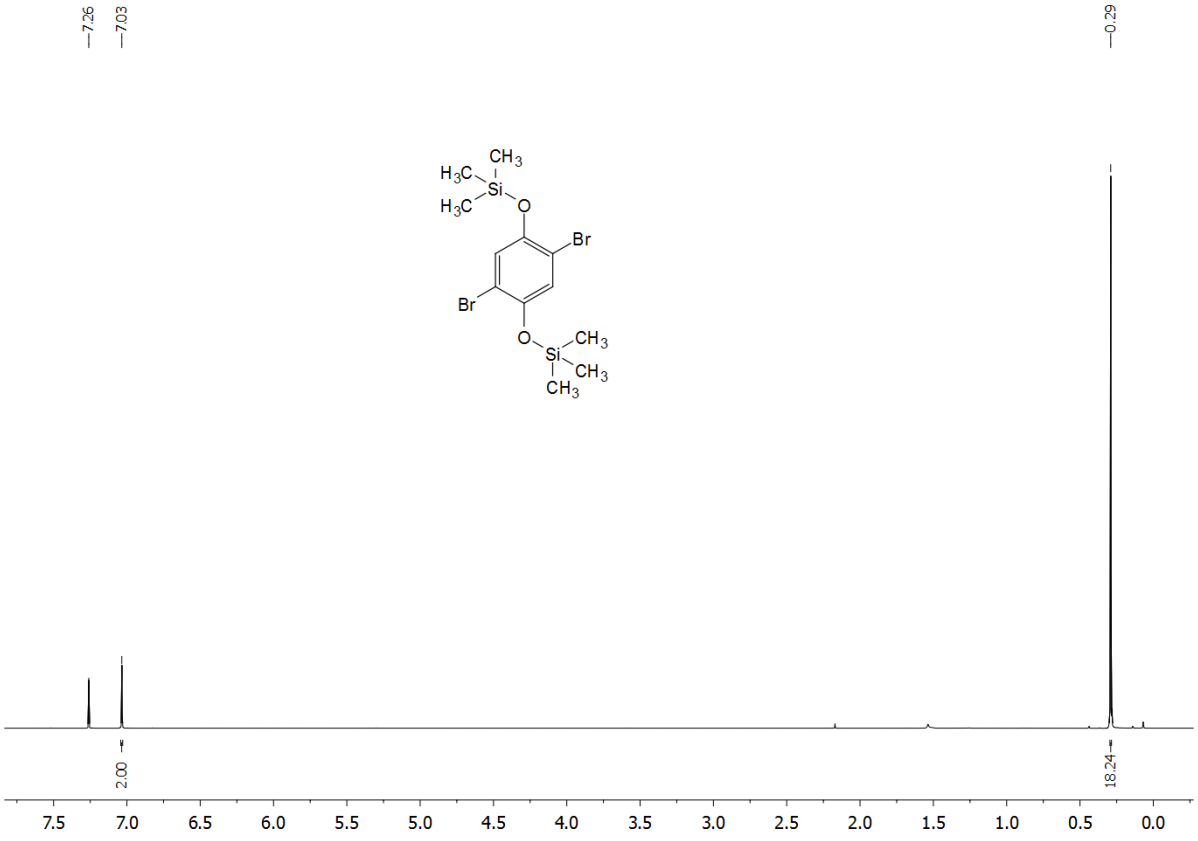

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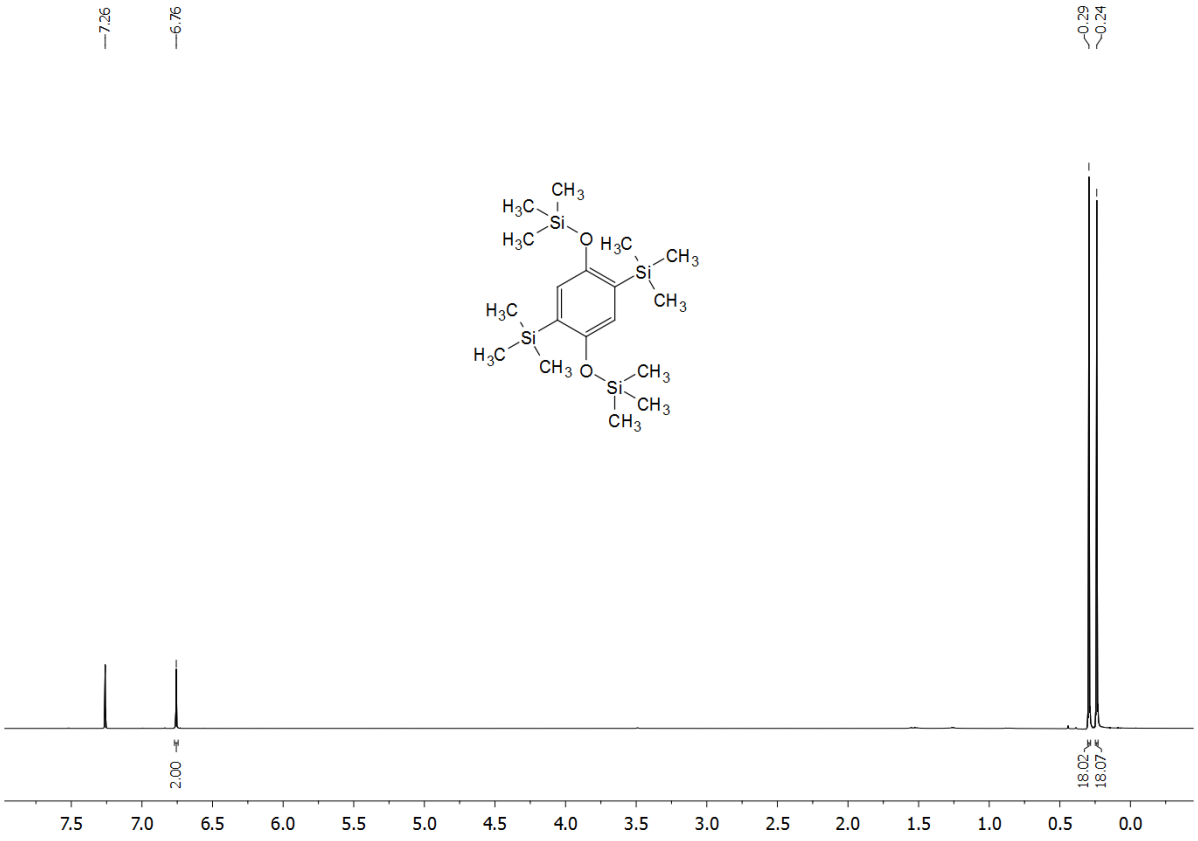

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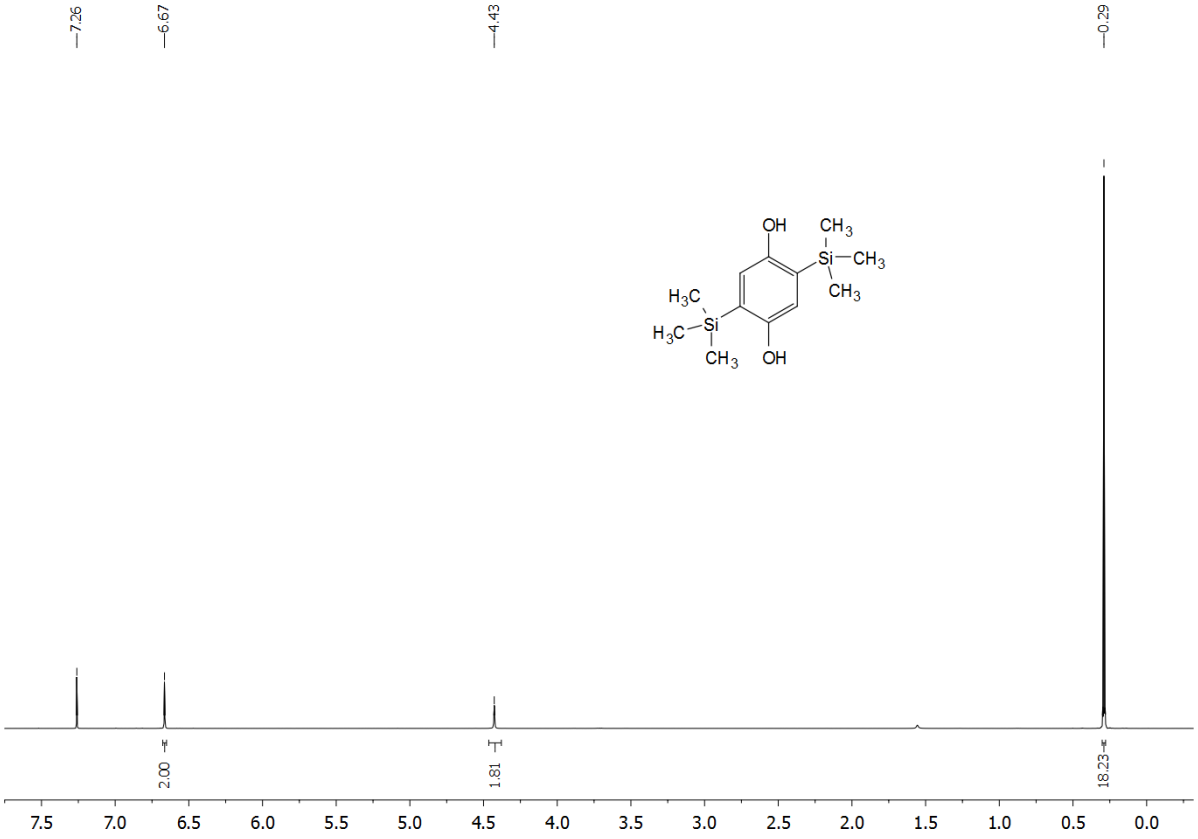

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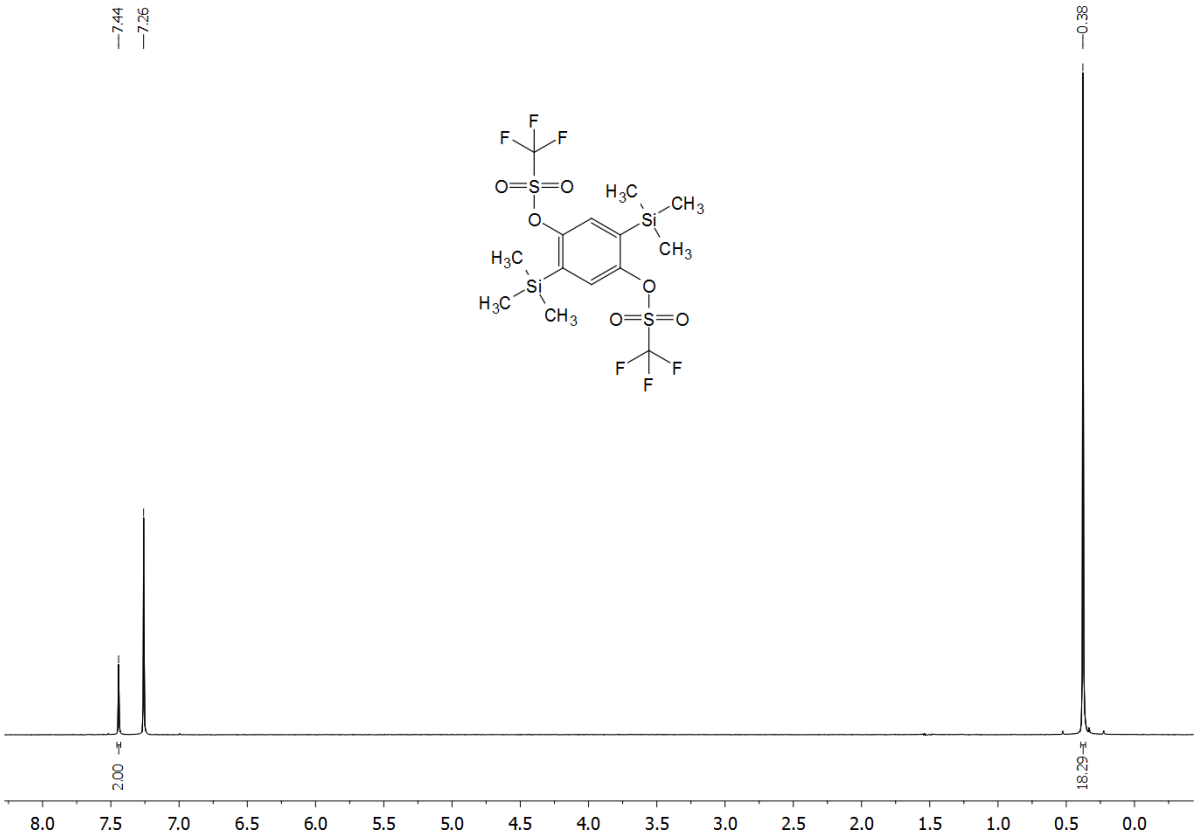
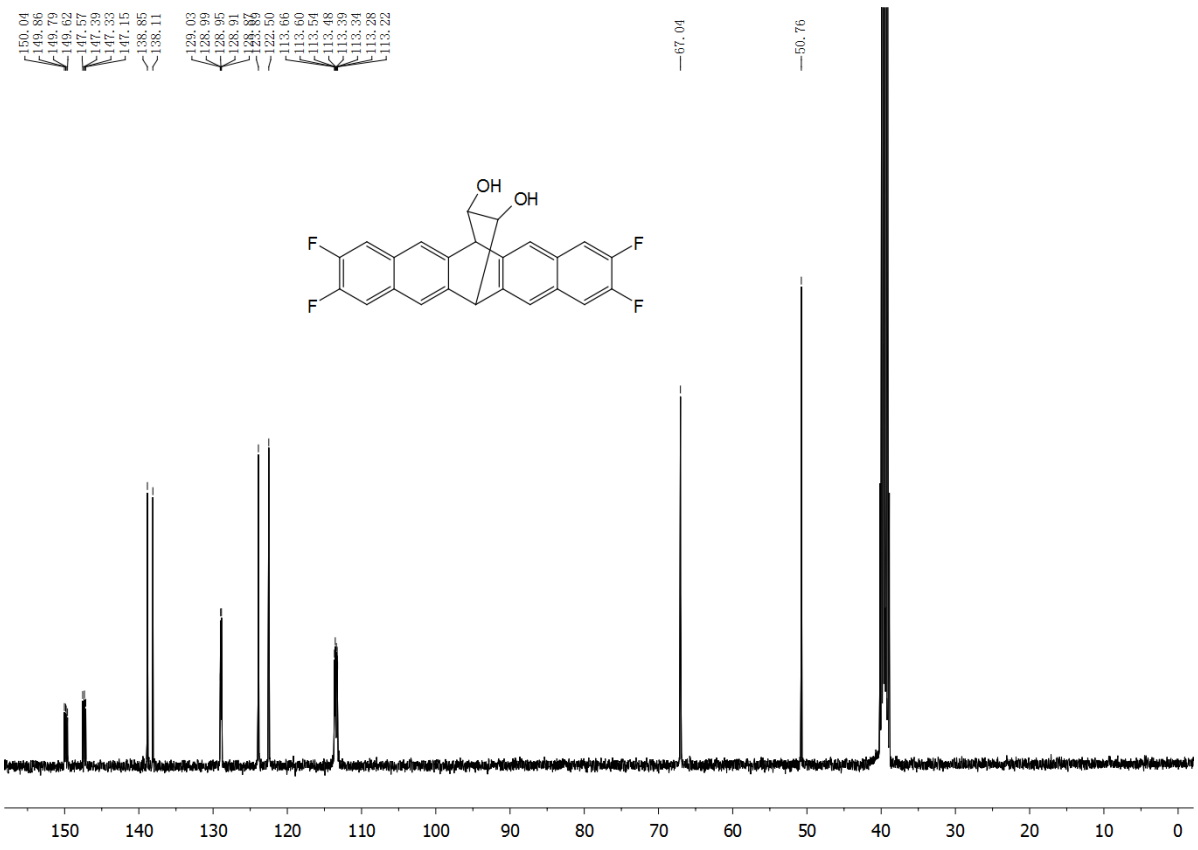
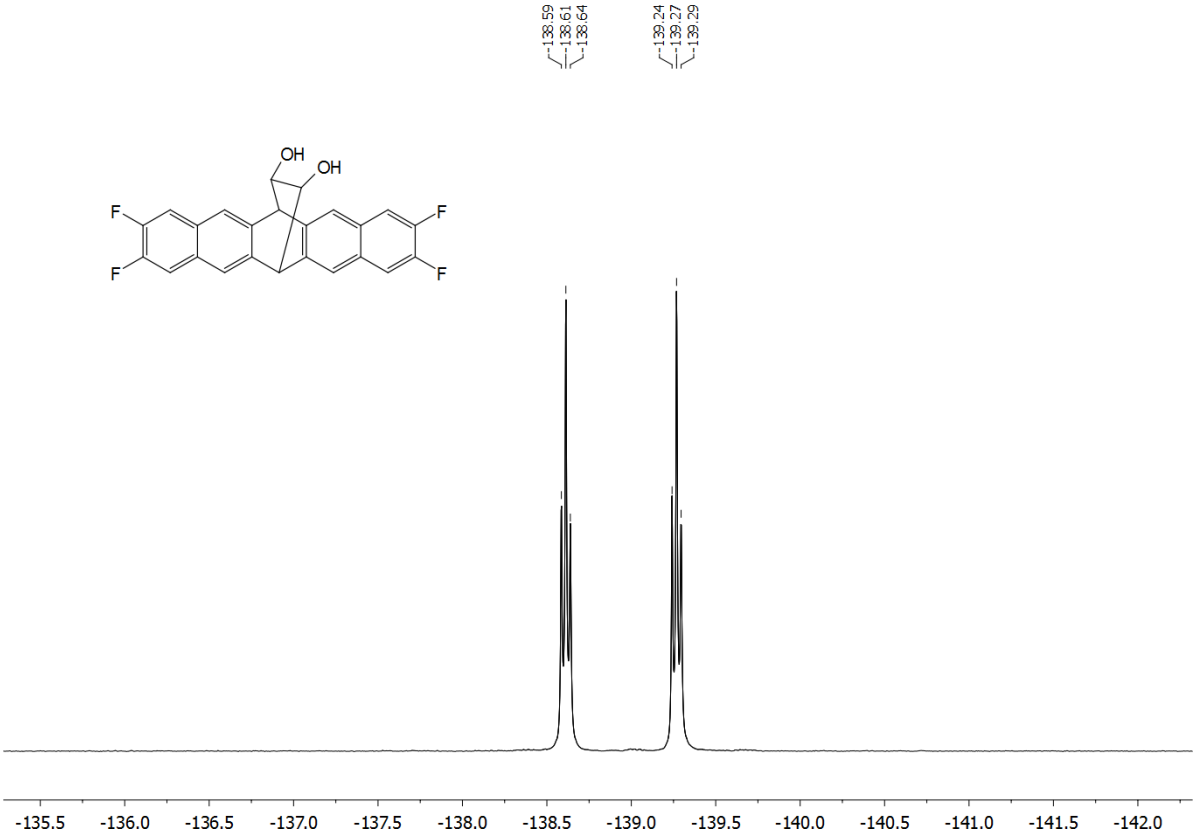


^{1}H-NMR (400 MHz) spectrum of **3-11** in $CDCl_3$

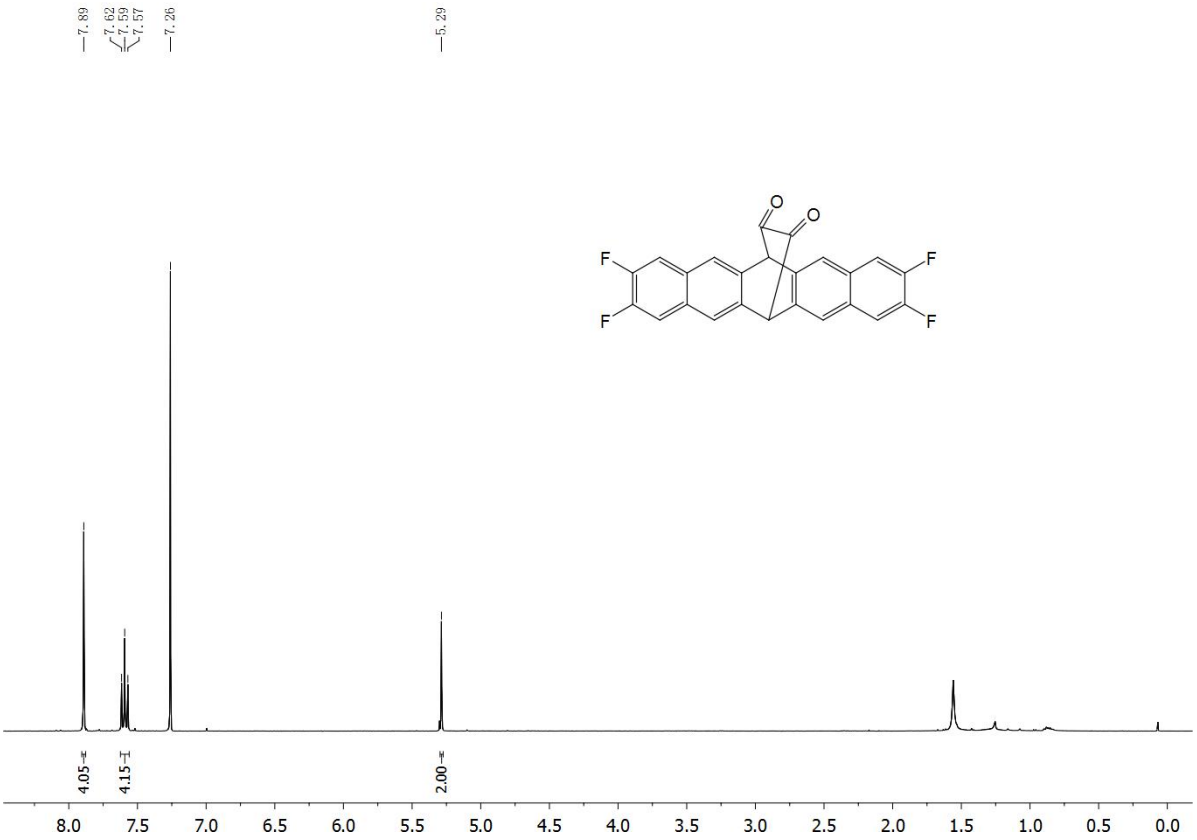
^{1}H-NMR (400 MHz) spectrum of **6**-**10** in DMSO-d_6



^{13}C-NMR (100 MHz) spectrum of **6**-**10** in DMSO-d_6



^{19}F-NMR (376 MHz) spectrum of **6-10** in DMSO-d_6



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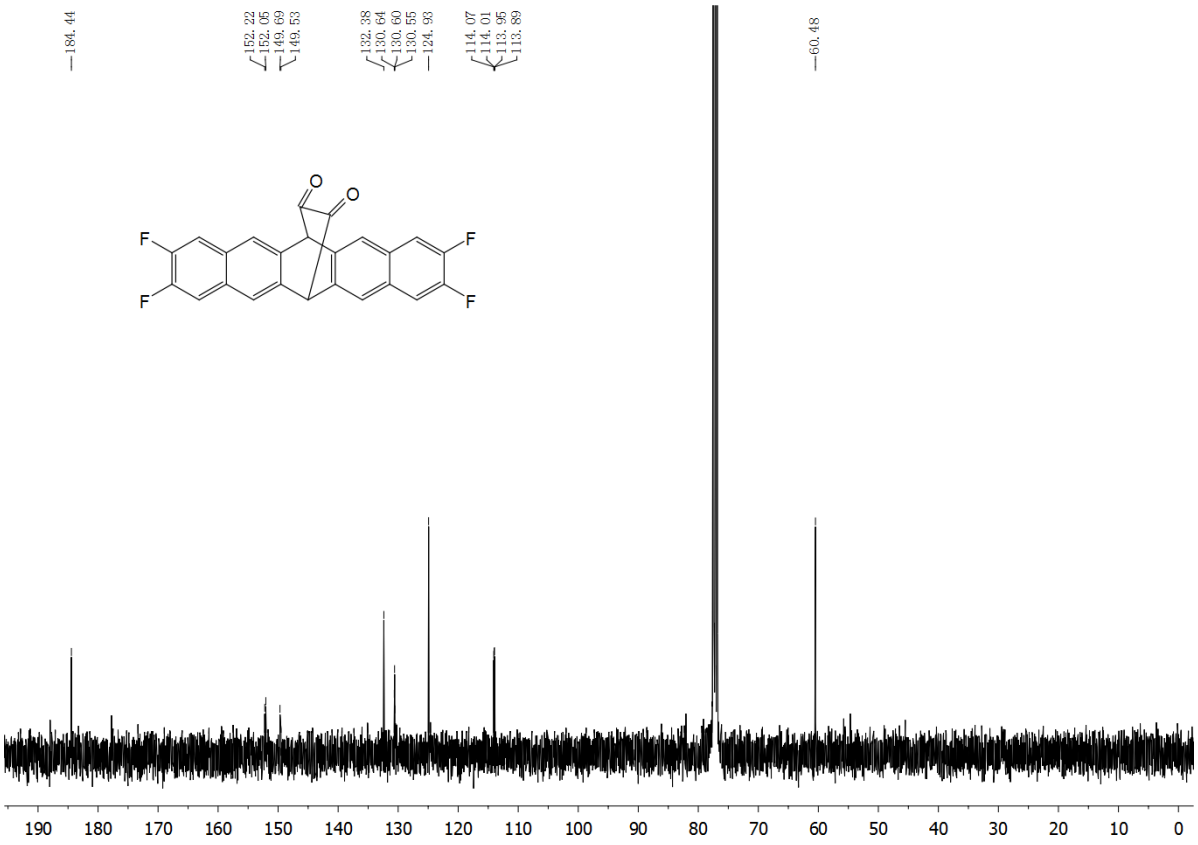

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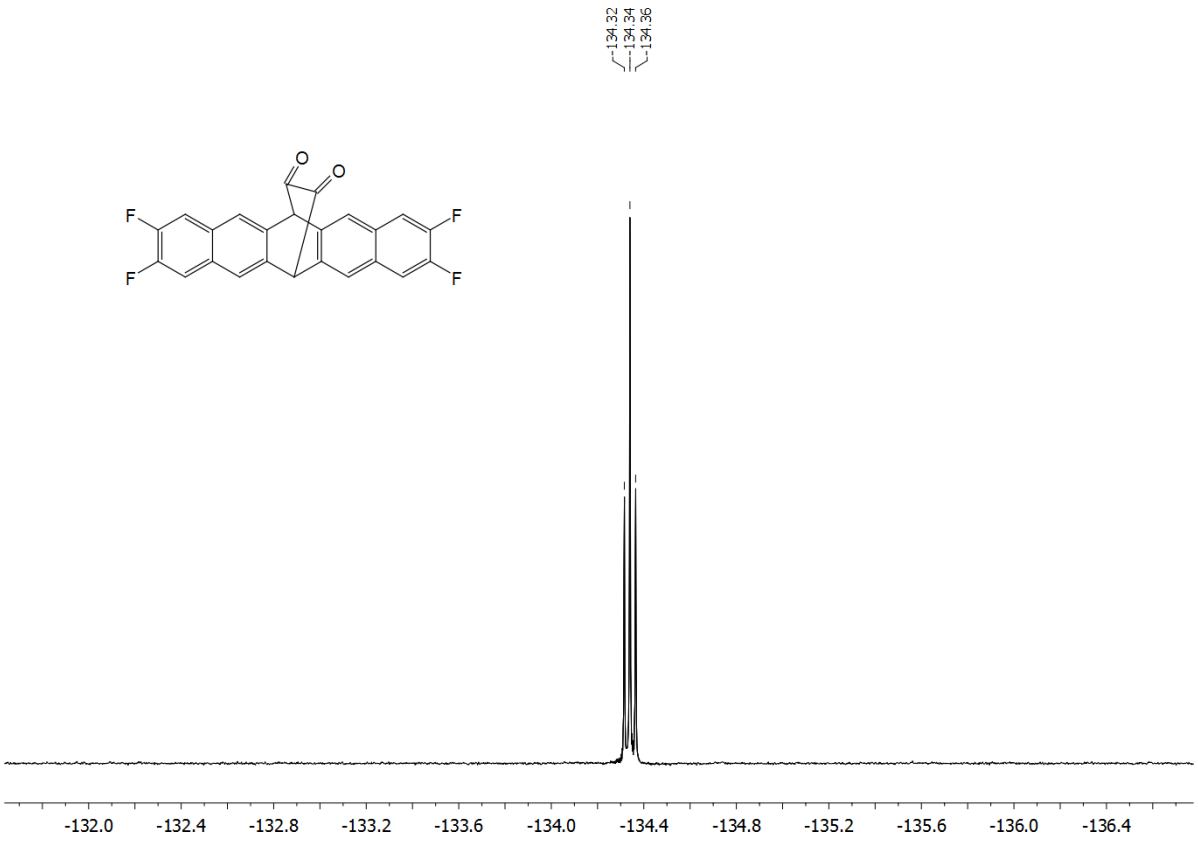

^{19}F-NMR (376 MHz) spectrum of **6-9** in $CDCl_3$

10. Cartesian Coordinates

M062X/6-31G*							
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O	-6.397525000	-1.961415000	1.250512000	H	6.576583000	-3.006036000	-1.219379000
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H	-0.000017000	1.903780000	2.383889000
F	6.396607000	-1.860488000	1.326446000
F	6.396814000	-1.860352000	-1.326154000
F	-6.396606000	-1.860704000	-1.326153000
F	-6.396794000	-1.860256000	1.326316000

1d

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C	-4.331020000	-0.463014000	-1.399689000
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H	-4.337806000	-0.467761000	2.485416000
C	-2.207567000	0.810207000	1.412602000
C	-2.207581000	0.810301000	-1.412539000
H	-4.337819000	-0.467611000	-2.485429000
C	-1.207995000	1.420834000	-0.713187000
C	-1.207986000	1.420798000	0.713302000
H	-2.209798000	0.803763000	-2.499718000
C	1.208040000	1.420879000	0.713249000
C	2.207622000	0.810327000	1.412573000
C	3.271002000	0.172646000	0.711748000
C	3.270981000	0.172626000	-0.711761000
C	2.207566000	0.810256000	-1.412575000
C	1.208004000	1.420835000	-0.713252000
H	4.337832000	-0.467695000	2.485407000
H	2.209881000	0.803787000	2.499751000
C	4.331027000	-0.463045000	1.399668000
C	4.331015000	-0.463036000	-1.399696000
H	2.209780000	0.803662000	-2.499752000
C	5.354773000	-1.076073000	-0.713849000
C	5.354775000	-1.076086000	0.713811000
H	4.337835000	-0.467659000	-2.485435000
C	-0.000016000	2.146602000	-1.293700000
C	0.000031000	2.146595000	1.293772000
C	-0.000025000	3.538508000	0.665830000
C	-0.000011000	3.538520000	-0.665724000
H	-0.000058000	4.428543000	1.284386000
H	-0.000036000	4.428576000	-1.284241000
H	-0.000078000	2.155238000	-2.384948000
H	0.000096000	2.155220000	2.385022000
C	6.418993000	-1.715502000	1.438441000
N	7.267280000	-2.225644000	2.036938000
C	6.419012000	-1.715435000	-1.438497000
N	7.267489000	-2.225290000	-2.036969000
C	-6.419001000	-1.715508000	1.438428000
N	-7.267463000	-2.225443000	2.036852000
C	-6.419022000	-1.715416000	-1.438494000
N	-7.267438000	-2.225389000	-2.036951000

2x

E(SCF) = -296.202948495

N	-0.657295000	-1.189766000	0.000195000
C	-1.260658000	-0.000259000	0.000086000
C	1.260658000	-0.000259000	-0.000086000
N	0.657295000	-1.189766000	0.000105000
H	-2.345305000	-0.000233000	0.000162000
H	2.345305000	-0.000233000	-0.000160000
N	0.656805000	1.190021000	-0.000195000
N	-0.656805000	1.190021000	-0.000105000

2y

E(SCF) = -1347.05398232

N	0.902376000	-1.014530000	-0.033262000
C	1.226923000	0.280376000	-0.024341000
C	-1.226922000	-0.280480000	-0.024363000
N	-0.374194000	-1.307539000	-0.031000000
N	-0.902343000	1.014502000	-0.033165000
N	0.374136000	1.307490000	-0.030883000
C	-2.689744000	-0.659581000	0.000272000
O	-3.086595000	-1.779908000	0.062726000

				O	-3.467518000	0.454340000	-0.054089000
				C	-4.837221000	0.262338000	0.001287000
				F	-5.386189000	1.459732000	-0.049023000
				F	-5.186802000	-0.333620000	1.129649000
				F	-5.260479000	-0.458898000	-1.023185000
				C	2.689728000	0.659538000	0.000212000
				O	3.086533000	1.779885000	0.062619000
				O	3.467546000	-0.454351000	-0.054135000
				C	4.837238000	-0.262300000	0.001309000
				F	5.386256000	-1.459668000	-0.049064000
				F	5.186757000	0.333602000	1.129722000
				F	5.260505000	0.459015000	-1.023105000
2z							
E(SCF) = -790.201597226							
N	0.663452000	1.170592000	0.000173000				
C	1.280173000	-0.019442000	0.000102000				
C	-1.280196000	0.020158000	-0.000060000				
N	-0.642495000	1.199212000	0.000090000				
N	-0.663113000	-1.170239000	-0.000142000				
N	0.642091000	-1.198820000	-0.000060000				
C	-2.768730000	0.010201000	-0.000176000				
C	-3.455263000	-1.206765000	-0.000355000				
N	-3.376311000	1.199454000	-0.000091000				
C	-4.844713000	-1.176223000	-0.000451000				
H	-2.901897000	-2.137948000	-0.000413000				
C	-4.705503000	1.209574000	-0.000184000				
C	-5.488442000	0.055058000	-0.000365000				
H	-5.413123000	-2.100987000	-0.000589000				
H	-5.172828000	2.191784000	-0.000108000				
H	-6.570682000	0.127754000	-0.000434000				
C	2.768724000	-0.009884000	0.000185000				
C	3.455731000	1.206833000	0.000361000				
N	3.375872000	-1.199352000	0.000080000				
C	4.845139000	1.175712000	0.000431000				
H	2.902764000	2.138245000	0.000438000				
C	4.705095000	-1.210018000	0.000149000				
C	5.488441000	-0.055824000	0.000324000				
H	5.413920000	2.100248000	0.000566000				
H	5.171993000	-2.192427000	0.000057000				
H	6.570658000	-0.128871000	0.000373000				
TS1-ax				**TS1-bx**			
E(SCF) = -1520.78097299				E(SCF) = -1377.19431276			
C	4.721219000	-2.729186000	-0.728904000	C	4.713022000	-2.740999000	-0.715419000
C	3.782369000	-2.006525000	-1.412893000	C	3.777841000	-1.993135000	-1.388139000
C	2.808071000	-1.243585000	-0.718787000	C	2.804143000	-1.217841000	-0.710428000
C	2.810645000	-1.235219000	0.704889000	C	2.804130000	-1.218016000	0.710197000
C	3.794777000	-1.993315000	1.393051000	C	3.777824000	-1.993462000	1.387739000
C	4.721079000	-2.716473000	0.696108000	C	4.713017000	-2.741164000	0.714856000
H	1.831568000	-0.483728000	-2.499844000	H	1.839764000	-0.446370000	-2.496105000
H	3.797166000	-2.022353000	-2.498103000	H	3.776014000	-1.988707000	-2.476460000
C	1.825865000	-0.486885000	-1.412145000	C	1.830952000	-0.452285000	-1.408171000
C	1.832944000	-0.477121000	1.401030000	C	1.830914000	-0.452647000	1.408111000
H	3.806938000	-1.991098000	2.481200000	H	3.775985000	-1.989286000	2.476061000
C	0.901230000	0.240071000	0.704621000	C	0.907303000	0.272392000	0.710548000
C	0.899728000	0.235796000	-0.714199000	C	0.907330000	0.272584000	-0.710447000

H	1.845501000	-0.465358000	2.488926000	H	1.839692000	-0.447016000	2.496047000
C	-1.501865000	0.562947000	-0.716859000	C	-1.493575000	0.593584000	-0.713641000
C	-2.580010000	0.099197000	-1.412151000	C	-2.568491000	0.124664000	-1.409326000
C	-3.726625000	-0.384085000	-0.716541000	C	-3.709965000	-0.366989000	-0.709906000
C	-3.724707000	-0.380853000	0.705795000	C	-3.709991000	-0.367193000	0.709650000
C	-2.580879000	0.103081000	1.403283000	C	-2.568543000	0.124256000	1.409253000
C	-1.501385000	0.564754000	0.708323000	C	-1.493602000	0.593373000	0.713740000
H	-4.886067000	-0.872122000	-2.495670000	H	-4.848567000	-0.856028000	-2.475939000
H	-2.581842000	0.091760000	-2.499903000	H	-2.570693000	0.117907000	-2.497365000
C	-4.866681000	-0.861802000	-1.410333000	C	-4.852206000	-0.857328000	-1.387531000
C	-4.870006000	-0.857810000	1.394081000	C	-4.852257000	-0.857721000	1.387095000
H	-2.583136000	0.098888000	2.491412000	H	-2.570783000	0.117186000	2.497290000
C	-5.955189000	-1.313382000	0.697391000	C	-5.953032000	-1.332662000	0.713923000
C	-5.961309000	-1.318894000	-0.726049000	C	-5.953005000	-1.332460000	-0.714534000
H	-4.878402000	-0.858817000	2.482356000	H	-4.848657000	-0.856731000	2.475503000
C	-0.194750000	1.108826000	1.290650000	C	-0.188582000	1.141079000	1.296309000
C	-0.195010000	1.104621000	-1.300943000	C	-0.188524000	1.141446000	-1.296007000
N	2.786411000	2.498702000	-0.613794000	N	2.779777000	2.550320000	-0.644150000
C	1.920968000	3.354249000	-1.222821000	C	1.904314000	3.414122000	-1.226650000
C	-0.077835000	2.507362000	-0.697738000	C	-0.078249000	2.543464000	-0.690761000
C	-0.083410000	2.510821000	0.684418000	C	-0.078299000	2.543269000	0.691462000
C	1.889007000	3.396346000	1.230930000	C	1.904228000	3.413777000	1.227669000
N	2.770884000	2.521602000	0.675136000	N	2.779732000	2.550132000	0.644984000
H	-0.489163000	3.342983000	-1.254094000	H	-0.499705000	3.376653000	-1.243140000
H	-0.509915000	3.344036000	1.232873000	H	-0.499785000	3.376330000	1.244012000
H	-0.190886000	1.114283000	2.383341000	H	-0.185156000	1.145337000	2.388843000
H	-0.192012000	1.107977000	-2.393433000	H	-0.185055000	1.146015000	-2.388539000
N	1.644468000	4.598935000	0.621422000	N	1.650189000	4.626462000	0.642231000
N	1.662436000	4.577316000	-0.661404000	N	1.650209000	4.626645000	-0.640868000
H	1.854224000	3.290153000	-2.303430000	H	1.824146000	3.369453000	-2.307302000
H	1.794991000	3.371266000	2.311083000	H	1.823996000	3.368778000	2.308303000
O	-7.054976000	-1.776914000	-1.381512000	C	-7.151371000	-1.850242000	-1.465516000
H	-7.709734000	-2.046289000	-0.717511000	H	-7.355112000	-2.898896000	-1.220299000
O	-7.108779000	-1.792235000	1.256707000	H	-8.055428000	-1.283057000	-1.216039000
H	-7.041674000	-1.768617000	2.221158000	H	-6.996295000	-1.780367000	-2.544764000
O	5.656809000	-3.459546000	-1.382963000	C	-7.151430000	-1.850643000	1.464718000
H	6.228708000	-3.875853000	-0.718447000	H	-8.055440000	-1.283274000	1.215486000
O	5.712309000	-3.477722000	1.254675000	H	-7.355272000	-2.899178000	1.219079000
H	5.681993000	-3.399285000	2.218070000	H	-6.996328000	-1.781218000	2.543990000
				C	5.733269000	-3.555730000	-1.466081000
				H	6.754930000	-3.251774000	-1.211136000
				H	5.648751000	-4.622184000	-1.226837000
				H	5.606665000	-3.441056000	-2.545290000
				C	5.733270000	-3.556050000	1.465341000
				H	5.648664000	-4.622475000	1.225995000
				H	6.754929000	-3.252135000	1.210331000
				H	5.606776000	-3.441479000	2.544572000

TS1-cx				**TS1-dx**			
E(SCF) = -1616.81408949				E(SCF) = -1588.85280900			
C	4.667133000	-2.762102000	-0.706754000	C	-4.856805000	-2.350527000	0.714743000
C	3.754735000	-2.029472000	-1.406241000	C	-3.891572000	-1.651188000	1.400681000
C	2.788909000	-1.254835000	-0.712207000	C	-2.889332000	-0.926682000	0.712066000
C	2.788925000	-1.254785000	0.712196000	C	-2.889440000	-0.926622000	-0.711707000
C	3.754777000	-2.029362000	1.406264000	C	-3.891783000	-1.651075000	-1.400228000
C	4.667156000	-2.762043000	0.706807000	C	-4.856912000	-2.350471000	-0.714201000
H	1.828252000	-0.478720000	-2.496105000	H	-1.897217000	-0.196150000	2.499138000
H	3.778897000	-2.047351000	-2.490918000	H	-3.899499000	-1.653960000	2.486296000
C	1.818563000	-0.485280000	-1.408700000	C	-1.886438000	-0.203596000	1.412090000

C	1.818591000	-0.485188000	1.408661000	C	-1.886650000	-0.203479000	-1.411824000
H	3.778972000	-2.047150000	2.490941000	H	-3.899873000	-1.653761000	-2.485842000
C	0.899886000	0.244574000	0.710153000	C	-0.939100000	0.485793000	-0.710972000
C	0.899875000	0.244528000	-0.710215000	C	-0.938996000	0.485733000	0.711148000
H	1.828317000	-0.478546000	2.496065000	H	-1.897600000	-0.195939000	-2.498869000
C	-1.495769000	0.585528000	-0.713404000	C	1.466064000	0.734993000	0.714376000
C	-2.572095000	0.121653000	-1.409802000	C	2.527390000	0.240757000	1.412918000
C	-3.715851000	-0.365468000	-0.711632000	C	3.656704000	-0.273522000	0.711158000
C	-3.715848000	-0.365434000	0.711635000	C	3.656607000	-0.273471000	-0.711673000
C	-2.572088000	0.121718000	1.409780000	C	2.527198000	0.240856000	-1.413245000
C	-1.495762000	0.585561000	0.713357000	C	1.465965000	0.735044000	-0.714526000
H	-4.880201000	-0.864516000	-2.490245000	H	4.790441000	-0.783993000	2.485090000
H	-2.574201000	0.113974000	-2.497332000	H	2.530877000	0.233988000	2.500126000
C	-4.852909000	-0.851457000	-1.405476000	C	4.782550000	-0.780827000	1.399368000
C	-4.852904000	-0.851392000	1.405505000	C	4.782363000	-0.780724000	-1.400069000
H	-2.574190000	0.114086000	2.497310000	H	2.530538000	0.234163000	-2.500453000
C	-5.929149000	-1.314789000	0.705987000	C	5.870707000	-1.270856000	-0.713918000
C	-5.929152000	-1.314822000	-0.705934000	C	5.870802000	-1.270910000	0.713038000
H	-4.880194000	-0.864402000	2.490275000	H	4.790111000	-0.783809000	-2.485792000
C	-0.187433000	1.123443000	1.296391000	C	0.180251000	1.322720000	-1.297340000
C	-0.187448000	1.123377000	-1.296473000	C	0.180432000	1.322622000	1.297413000
N	2.788028000	2.498169000	-0.644311000	N	-2.725350000	2.810836000	0.644852000
C	1.922513000	3.371622000	-1.227373000	C	-1.828325000	3.651337000	1.228254000
C	-0.062709000	2.525057000	-0.691470000	C	0.110050000	2.728637000	0.691865000
C	-0.062771000	2.525107000	0.691322000	C	0.109982000	2.728694000	-0.691682000
C	1.922178000	3.372108000	1.227383000	C	-1.828322000	3.651653000	-1.227854000
N	2.787886000	2.498434000	0.644933000	N	-2.725347000	2.811002000	-0.644664000
H	-0.479250000	3.360425000	-1.244162000	H	0.566449000	3.542500000	1.244877000
H	-0.479510000	3.360400000	1.243977000	H	0.566396000	3.542573000	-1.244656000
H	-0.184011000	1.127165000	2.388769000	H	0.176838000	1.325813000	-2.389387000
H	-0.184056000	1.127049000	-2.388852000	H	0.177175000	1.325640000	2.389461000
N	1.681350000	4.588056000	0.640702000	N	-1.539479000	4.858391000	-0.639714000
N	1.681575000	4.587807000	-0.641285000	N	-1.539491000	4.858231000	0.640422000
H	1.844176000	3.329487000	-2.308286000	H	-1.754976000	3.609962000	2.309592000
H	1.843553000	3.330486000	2.308295000	H	-1.754980000	3.610556000	-2.309203000
F	-7.013395000	-1.784227000	-1.326669000	C	7.003434000	-1.778119000	1.438584000
F	-7.013390000	-1.784166000	1.326748000	N	7.906148000	-2.180083000	2.039755000
F	5.587504000	-3.504445000	1.326551000	C	7.003250000	-1.777998000	-1.439650000
F	5.587442000	-3.504575000	-1.326469000	N	7.905896000	-2.179900000	-2.040964000
				C	-5.863055000	-3.078049000	1.439169000
				N	-6.664410000	-3.658896000	2.037814000
				C	-5.863266000	-3.077947000	-1.438529000
				N	-6.664710000	-3.658760000	-2.037087000

TS1-ay				**TS1-by**			
E(SCF) = -2571.65701000				E(SCF) = -2428.06972869			
C	-3.772813000	-0.835357000	4.130334000	C	-3.799172000	-0.869454000	4.130649000
C	-2.823889000	0.047812000	3.699556000	C	-2.833107000	0.000537000	3.688091000
C	-2.011108000	-0.265839000	2.578212000	C	-2.021212000	-0.287594000	2.562839000
C	-2.201776000	-1.511661000	1.915913000	C	-2.217478000	-1.517270000	1.879084000
C	-3.193808000	-2.408558000	2.389829000	C	-3.219480000	-2.402733000	2.349207000
C	-3.966278000	-2.085087000	3.471723000	C	-3.999033000	-2.106671000	3.440449000
H	-0.897950000	1.598280000	2.595334000	H	-0.899898000	1.573325000	2.607984000
H	-2.688360000	1.000959000	4.206207000	H	-2.681211000	0.945668000	4.205229000
C	-1.022809000	0.636098000	2.105555000	C	-1.028378000	0.619281000	2.103333000
C	-1.395911000	-1.827154000	0.789108000	C	-1.413616000	-1.824253000	0.747667000
H	-3.355637000	-3.360802000	1.894716000	H	-3.370391000	-3.341238000	1.819367000
C	-0.450388000	-0.938840000	0.356363000	C	-0.462710000	-0.935224000	0.330615000
C	-0.261550000	0.301422000	1.020192000	C	-0.270037000	0.296435000	1.013456000

H	-1.561434000	-2.767967000	0.269713000	H	-1.583860000	-2.756514000	0.214125000
C	2.072860000	0.317450000	0.340143000	C	2.066130000	0.310261000	0.343780000
C	3.280320000	0.642887000	0.885653000	C	3.271148000	0.622214000	0.900720000
C	4.371919000	-0.267664000	0.795908000	C	4.356682000	-0.295582000	0.801800000
C	4.181724000	-1.513949000	0.135845000	C	4.167592000	-1.529170000	0.124181000
C	2.909790000	-1.823159000	-0.424690000	C	2.895657000	-1.826034000	-0.447888000
C	1.884650000	-0.927426000	-0.324955000	C	1.875627000	-0.926689000	-0.339737000
H	5.802764000	0.989352000	1.853924000	H	5.767121000	0.931610000	1.878059000
H	3.424937000	1.593264000	1.394311000	H	3.417664000	1.564577000	1.424075000
C	5.639819000	0.042903000	1.347993000	C	5.627169000	-0.015254000	1.360136000
C	5.272444000	-2.417600000	0.050243000	C	5.258909000	-2.427262000	0.036034000
H	2.768984000	-2.777730000	-0.927102000	H	2.754078000	-2.773023000	-0.964203000
C	6.483839000	-2.091554000	0.594843000	C	6.486229000	-2.140478000	0.585158000
C	6.678748000	-0.844060000	1.254577000	C	6.675904000	-0.898953000	1.267031000
H	5.136693000	-3.374166000	-0.450337000	H	5.111150000	-3.372361000	-0.482861000
C	0.456818000	-1.104094000	-0.849681000	C	0.449098000	-1.088578000	-0.873575000
C	0.801368000	1.166474000	0.370283000	C	0.798838000	1.164789000	0.377776000
N	-2.444537000	1.399959000	-0.616153000	N	-2.437331000	1.429432000	-0.620233000
C	-1.610436000	2.293748000	-1.215882000	C	-1.595076000	2.324775000	-1.206428000
C	0.440833000	1.318558000	-1.106895000	C	0.446419000	1.337320000	-1.099038000
C	0.259463000	0.111303000	-1.758775000	C	0.262255000	0.139352000	-1.767553000
C	-1.914076000	0.194221000	-2.420311000	C	-1.907238000	0.241484000	-2.436305000
N	-2.605125000	0.295279000	-1.251759000	N	-2.602211000	0.333291000	-1.269109000
H	0.788091000	2.190708000	-1.653849000	H	0.802918000	2.213900000	-1.632877000
H	0.463712000	0.019220000	-2.822046000	H	0.471796000	0.059934000	-2.830813000
H	0.312533000	-2.054117000	-1.369625000	H	0.303063000	-2.031142000	-1.406362000
H	0.941971000	2.125723000	0.874101000	H	0.941646000	2.116710000	0.894643000
N	-1.755723000	1.300111000	-3.213615000	N	-1.739577000	1.355578000	-3.216158000
N	-1.598751000	2.401903000	-2.581155000	N	-1.578349000	2.448914000	-2.570401000
C	-1.861788000	-1.127667000	-3.116909000	C	-1.860947000	-1.072333000	-3.148448000
O	-1.387303000	-1.316832000	-4.194857000	O	-1.386091000	-1.251717000	-4.227804000
O	-2.349212000	-2.112829000	-2.298805000	O	-2.355247000	-2.064727000	-2.342628000
C	-2.208786000	-3.411791000	-2.725408000	C	-2.219964000	-3.359302000	-2.783328000
F	-2.693781000	-4.179763000	-1.763103000	F	-2.709342000	-4.135479000	-1.829102000
F	-0.927367000	-3.720532000	-2.909752000	F	-0.940351000	-3.672131000	-2.970252000
F	-2.872434000	-3.641723000	-3.844156000	F	-2.884724000	-3.574698000	-3.904350000
C	-1.217969000	3.464934000	-0.375507000	C	-1.198681000	3.484013000	-0.350959000
O	-1.420429000	3.567572000	0.795953000	O	-1.401058000	3.571994000	0.821424000
O	-0.493605000	4.364644000	-1.115649000	O	-0.469730000	4.389789000	-1.079502000
C	0.092515000	5.401544000	-0.424458000	C	0.124558000	5.412557000	-0.374546000
F	0.754659000	6.124296000	-1.308185000	F	0.790868000	6.142629000	-1.249320000
F	0.947920000	4.940582000	0.484134000	F	0.978198000	4.932438000	0.525986000
F	-0.804652000	6.163344000	0.177333000	F	-0.765722000	6.172445000	0.239246000
O	-4.917324000	-2.932495000	3.931161000	C	-5.058941000	-3.066288000	3.913159000
H	-5.350883000	-2.512293000	4.691304000	H	-4.872749000	-3.392749000	4.942877000
O	-4.611555000	-0.638763000	5.193015000	H	-6.051868000	-2.602449000	3.899942000
H	-4.452263000	0.233036000	5.580502000	H	-5.092515000	-3.954761000	3.278163000
O	7.892085000	-0.556183000	1.781262000	C	-4.649175000	-0.533902000	5.327698000
H	8.480414000	-1.308805000	1.609251000	H	-5.712579000	-0.497783000	5.064692000
O	7.598443000	-2.883101000	0.572305000	H	-4.541047000	-1.285775000	6.117803000
H	7.405122000	-3.714748000	0.118047000	H	-4.371124000	0.437108000	5.743910000
				C	8.014343000	-0.572912000	1.875042000
				H	8.305289000	-1.318525000	2.623824000
				H	8.805185000	-0.557220000	1.116318000
				H	7.994511000	0.404679000	2.362390000
				C	7.626632000	-3.117957000	0.474933000
				H	8.484788000	-2.673530000	-0.042086000
				H	7.978636000	-3.434872000	1.463259000
				H	7.324683000	-4.010375000	-0.078147000
TS1-cy				**TS1-dy**			

E(SCF) = -2667.68857203			
C	-3.753531000	-0.794013000	4.147768000
C	-2.801302000	0.081502000	3.718347000
C	-1.997300000	-0.246701000	2.595494000
C	-2.196871000	-1.492476000	1.934480000
C	-3.197046000	-2.379868000	2.411381000
C	-3.952646000	-2.030545000	3.490827000
H	-0.874876000	1.612272000	2.600401000
H	-2.673575000	1.026800000	4.235206000
C	-1.004996000	0.649095000	2.115015000
C	-1.397753000	-1.819855000	0.805916000
H	-3.373751000	-3.332756000	1.923295000
C	-0.450768000	-0.937538000	0.367410000
C	-0.253930000	0.305540000	1.026784000
H	-1.572106000	-2.760524000	0.289673000
C	2.073685000	0.311409000	0.333661000
C	3.282987000	0.635152000	0.873676000
C	4.368827000	-0.282699000	0.782618000
C	4.173588000	-1.532650000	0.129472000
C	2.896690000	-1.839138000	-0.425434000
C	1.878331000	-0.937391000	-0.325471000
H	5.816802000	0.970372000	1.831676000
H	3.433640000	1.586610000	1.378037000
C	5.640198000	0.024573000	1.329877000
C	5.255082000	-2.446002000	0.042696000
H	2.751080000	-2.795467000	-0.922036000
C	6.464639000	-2.119542000	0.583745000
C	6.658428000	-0.877966000	1.229447000
H	5.135209000	-3.407059000	-0.446742000
C	0.448079000	-1.110408000	-0.843613000
C	0.806227000	1.165222000	0.365338000
N	-2.433188000	1.399715000	-0.608818000
C	-1.597751000	2.288269000	-1.215517000
C	0.436710000	1.312162000	-1.110942000
C	0.248770000	0.101917000	-1.757531000
C	-1.911481000	0.183909000	-2.408832000
N	-2.599629000	0.293049000	-1.238767000
H	0.791375000	2.178806000	-1.661904000
H	0.456791000	0.002993000	-2.819431000
H	0.298410000	-2.062505000	-1.357847000
H	0.952447000	2.125824000	0.864428000
N	-1.756474000	1.287200000	-3.208821000
N	-1.594677000	2.390572000	-2.582648000
C	-1.870223000	-1.141179000	-3.101389000
O	-1.402064000	-1.336070000	-4.180588000
O	-2.355949000	-2.120651000	-2.275301000
C	-2.222242000	-3.423010000	-2.697256000
F	-2.704742000	-4.183454000	-1.727221000
F	-0.942370000	-3.735477000	-2.884607000
F	-2.891770000	-3.655513000	-3.810462000
C	-1.200043000	3.463345000	-0.381663000
O	-1.384838000	3.560614000	0.793222000
O	-0.491746000	4.365373000	-1.131265000
C	0.105424000	5.402211000	-0.446329000
F	0.753220000	6.126220000	-1.338474000
F	0.975559000	4.936023000	0.446078000
F	-0.782098000	6.160039000	0.172039000
F	-4.905801000	-2.835624000	3.964299000
F	-4.531588000	-0.519655000	5.196445000

E(SCF) = -2639.72503858			
C	4.157382000	1.332511000	3.515772000
C	3.172118000	0.398442000	3.295434000
C	2.265099000	0.538286000	2.217200000
C	2.386173000	1.663870000	1.353998000
C	3.405567000	2.615295000	1.596447000
C	4.275639000	2.463836000	2.650168000
H	1.171222000	-1.296800000	2.620361000
H	3.092121000	-0.460993000	3.953899000
C	1.246034000	-0.423735000	1.978276000
C	1.495866000	1.806929000	0.257379000
H	3.503806000	3.472289000	0.937029000
C	0.536283000	0.859178000	0.044564000
C	0.402044000	-0.256197000	0.916425000
H	1.612191000	2.653515000	-0.413801000
C	-1.973056000	-0.349034000	0.408311000
C	-3.142115000	-0.556692000	1.079664000
C	-4.233560000	0.340966000	0.888598000
C	-4.087222000	1.444731000	0.002814000
C	-2.850929000	1.639356000	-0.677792000
C	-1.827713000	0.761429000	-0.477085000
H	-5.587539000	-0.684735000	2.234378000
H	-3.258693000	-1.397493000	1.758913000
C	-5.466106000	0.154741000	1.556579000
C	-5.175596000	2.326950000	-0.187172000
H	-2.741465000	2.486023000	-1.350893000
C	-6.368064000	2.130623000	0.471566000
C	-6.516166000	1.023283000	1.359658000
H	-5.069950000	3.171124000	-0.861772000
C	-0.440680000	0.827915000	-1.113217000
C	-0.705809000	-1.203514000	0.492792000
N	2.421854000	-1.685493000	-0.649529000
C	1.536619000	-2.630317000	-1.074898000
C	-0.448984000	-1.605814000	-0.962631000
C	-0.301327000	-0.524820000	-1.817123000
C	1.797324000	-0.717251000	-2.565113000
N	2.558585000	-0.679539000	-1.436599000
H	-0.865167000	-2.540070000	-1.329234000
H	-0.586251000	-0.599533000	-2.862914000
H	-0.326800000	1.675647000	-1.792617000
H	-0.813751000	-2.061258000	1.159706000
N	1.584564000	-1.919305000	-3.195759000
N	1.450624000	-2.920264000	-2.414088000
C	1.731198000	0.502449000	-3.431436000
O	1.163726000	0.565469000	-4.477898000
O	2.322762000	1.562646000	-2.799190000
C	2.186802000	2.802385000	-3.383871000
F	2.784169000	3.663034000	-2.575822000
F	0.902707000	3.137812000	-3.487265000
F	2.745880000	2.853455000	-4.575950000
C	1.171493000	-3.674706000	-0.067718000
O	1.375914000	-3.586415000	1.105448000
O	0.463200000	-4.680424000	-0.661317000
C	-0.152992000	-5.588378000	0.178401000
F	-0.815194000	-6.428158000	-0.590834000
F	-1.011414000	-4.965379000	0.982266000
F	0.721237000	-6.252915000	0.909359000
C	5.302706000	3.444001000	2.876177000
N	6.121179000	4.243606000	3.044924000

F	7.502092000	-2.955830000	0.523456000	C	5.066712000	1.164805000	4.616555000
F	7.865767000	-0.622642000	1.735138000	N	5.787868000	1.013438000	5.508060000
				C	-7.759571000	0.808233000	2.048305000
				N	-8.753129000	0.617884000	2.608861000
				C	-7.457633000	3.044520000	0.261110000
				N	-8.321006000	3.791929000	0.077845000

TS1-az				**TS1-bz**			
E(SCF) = -2014.79132675				E(SCF) = -1871.20374502			
C	3.861385000	-1.956467000	-3.560192000	C	3.853124000	-2.155616000	-3.488443000
C	3.010967000	-0.908179000	-3.350998000	C	2.999649000	-1.096876000	-3.297502000
C	2.105547000	-0.924309000	-2.256796000	C	2.105452000	-1.036724000	-2.199464000
C	2.101112000	-2.051474000	-1.386576000	C	2.100087000	-2.111552000	-1.269527000
C	2.992455000	-3.127807000	-1.635355000	C	2.985712000	-3.197717000	-1.484099000
C	3.857096000	-3.088415000	-2.694939000	C	3.845673000	-3.238695000	-2.554490000
H	1.244937000	1.030392000	-2.658111000	H	1.253663000	0.901076000	-2.698922000
H	3.026313000	-0.047235000	-4.016206000	H	3.004406000	-0.268447000	-4.003216000
C	1.215540000	0.154557000	-2.015446000	C	1.223969000	0.061346000	-2.009559000
C	1.211709000	-2.062650000	-0.278982000	C	1.220043000	-2.061983000	-0.154214000
H	3.001199000	-3.996358000	-0.983909000	H	2.977047000	-4.020674000	-0.771187000
C	0.377958000	-1.000193000	-0.062623000	C	0.391628000	-0.986557000	0.008555000
C	0.366602000	0.110413000	-0.945606000	C	0.381957000	0.076424000	-0.934734000
H	1.216925000	-2.912250000	0.400712000	H	1.225962000	-2.874780000	0.569703000
C	-1.971738000	0.501923000	-0.410895000	C	-1.957238000	0.489748000	-0.432332000
C	-3.119646000	0.843013000	-1.064784000	C	-3.100650000	0.788802000	-1.112660000
C	-4.314744000	0.097759000	-0.849961000	C	-4.293619000	0.050886000	-0.859647000
C	-4.289828000	-1.005113000	0.048355000	C	-4.275405000	-0.994818000	0.100566000
C	-3.075665000	-1.338228000	0.714617000	C	-3.062939000	-1.288725000	0.791740000
C	-1.949302000	-0.600400000	0.492370000	C	-1.937857000	-0.562592000	0.532249000
H	-5.561840000	1.272011000	-2.196172000	H	-5.515101000	1.132589000	-2.270928000
H	-3.138952000	1.683988000	-1.754477000	H	-3.118346000	1.588599000	-1.850324000
C	-5.524771000	0.433052000	-1.508161000	C	-5.506141000	0.330336000	-1.535123000
C	-5.483254000	-1.742900000	0.259898000	C	-5.472491000	-1.711486000	0.342819000
H	-3.061674000	-2.183651000	1.399376000	H	-3.052064000	-2.093666000	1.523862000
C	-6.635287000	-1.396435000	-0.390738000	C	-6.642179000	-1.427295000	-0.321894000
C	-6.664805000	-0.292955000	-1.289453000	C	-6.659216000	-0.376769000	-1.289773000
H	-5.474478000	-2.589532000	0.943691000	H	-5.455770000	-2.512201000	1.080105000
C	-0.566494000	-0.820630000	1.108239000	C	-0.557024000	-0.744747000	1.164983000
C	-0.612976000	1.191467000	-0.531186000	C	-0.599511000	1.176335000	-0.580684000
N	2.504106000	1.506376000	0.518494000	N	2.511326000	1.546323000	0.475696000
C	1.712975000	2.511834000	1.010674000	C	1.718120000	2.579050000	0.904186000
C	-0.295950000	1.598797000	0.909263000	C	-0.291821000	1.660964000	0.836861000
C	-0.240866000	0.519670000	1.778219000	C	-0.241082000	0.631056000	1.763653000
C	1.851520000	0.467237000	2.411314000	C	1.843132000	0.615709000	2.418655000
N	2.571618000	0.455616000	1.247325000	N	2.572479000	0.538736000	1.262728000
H	-0.644647000	2.566549000	1.255255000	H	-0.641835000	2.646331000	1.127454000
H	-0.479966000	0.626424000	2.831854000	H	-0.490524000	0.794830000	2.807486000
H	-0.539339000	-1.655786000	1.813032000	H	-0.531330000	-1.540487000	1.913999000
H	-0.622407000	2.036353000	-1.220526000	H	-0.607849000	1.982682000	-1.314733000
N	1.770915000	1.660893000	3.102319000	N	1.756889000	1.846048000	3.040607000
N	1.697351000	2.706168000	2.374698000	N	1.690035000	2.849092000	2.254748000
C	1.827454000	-0.796415000	3.196094000	C	1.813822000	-0.604661000	3.268976000
C	2.605461000	-1.887073000	2.800404000	C	2.591444000	-1.714863000	2.929810000
N	1.002587000	-0.821087000	4.247420000	N	0.985396000	-0.576981000	4.317231000
C	2.528752000	-3.052789000	3.553630000	C	2.509499000	-2.842683000	3.737633000
H	3.243312000	-1.800521000	1.927859000	H	3.231353000	-1.671549000	2.055777000
C	0.948217000	-1.943759000	4.961403000	C	0.926089000	-1.664172000	5.084025000
C	1.687970000	-3.085967000	4.660939000	C	1.664200000	-2.821049000	4.841907000
H	3.121526000	-3.920791000	3.281194000	H	3.100785000	-3.724188000	3.508572000

H	0.272860000	-1.932599000	5.814045000	H	0.246635000	-1.611118000	5.931826000
H	1.600422000	-3.973481000	5.278396000	H	1.570866000	-3.677585000	5.500857000
C	1.520595000	3.715892000	0.156630000	C	1.535385000	3.732004000	-0.019404000
C	1.334895000	4.972401000	0.739201000	C	1.364669000	5.023330000	0.485955000
N	1.516196000	3.513170000	-1.164945000	N	1.526941000	3.449103000	-1.326102000
C	1.154897000	6.066863000	-0.097362000	C	1.196567000	6.066807000	-0.416103000
H	1.348088000	5.068613000	1.818345000	H	1.379800000	5.184073000	1.557394000
C	1.345655000	4.574933000	-1.950861000	C	1.367800000	4.462461000	-2.175514000
C	1.164043000	5.870915000	-1.474015000	C	1.201982000	5.786966000	-1.778284000
H	1.015274000	7.058787000	0.321389000	H	1.069040000	7.084076000	-0.058748000
H	1.350066000	4.378585000	-3.021123000	H	1.369296000	4.200927000	-3.231683000
H	1.030660000	6.695317000	-2.166060000	H	1.077437000	6.569435000	-2.518903000
O	-7.825809000	0.020876000	-1.914919000	C	-7.931784000	-0.055724000	-2.028860000
H	-8.500026000	-0.616135000	-1.629128000	H	-8.736506000	0.223769000	-1.339231000
O	-7.838102000	-2.037979000	-0.262381000	H	-7.780777000	0.772654000	-2.725100000
H	-7.751160000	-2.777562000	0.354504000	H	-8.289287000	-0.918219000	-2.603260000
O	4.716858000	-4.108844000	-2.937951000	C	-7.898778000	-2.208453000	-0.040619000
H	5.238813000	-3.875597000	-3.722383000	H	-8.704024000	-1.556082000	0.316572000
O	4.776766000	-2.042419000	-4.575952000	H	-8.270100000	-2.707763000	-0.942962000
H	4.762118000	-1.227947000	-5.097036000	H	-7.722382000	-2.973195000	0.719472000
				C	4.778247000	-4.404833000	-2.751043000
				H	4.611035000	-4.893572000	-3.717758000
				H	5.826944000	-4.086129000	-2.732910000
				H	4.639877000	-5.153032000	-1.966687000
				C	4.793337000	-2.186075000	-4.665040000
				H	5.838218000	-2.254268000	-4.340966000
				H	4.601652000	-3.051989000	-5.309486000
				H	4.687291000	-1.283692000	-5.271793000

TS1-cz				**TS1-dz**			
E(SCF) = -2110.82525058				E(SCF) = -2082.86690259			
C	3.821366000	-1.913986000	-3.616831000	C	4.167382000	-2.516869000	-2.641325000
C	2.979147000	-0.866137000	-3.392230000	C	3.264776000	-1.484487000	-2.747592000
C	2.086525000	-0.898511000	-2.288688000	C	2.307015000	-1.243994000	-1.733204000
C	2.084801000	-2.034873000	-1.429051000	C	2.288442000	-2.088474000	-0.586063000
C	2.973852000	-3.109150000	-1.696533000	C	3.222065000	-3.148410000	-0.496220000
C	3.818650000	-3.041617000	-2.764526000	C	4.144386000	-3.367225000	-1.492731000
H	1.228766000	1.063820000	-2.658022000	H	1.414293000	0.491801000	-2.692015000
H	3.005027000	-0.010158000	-4.058388000	H	3.289036000	-0.840327000	-3.620940000
C	1.200576000	0.180524000	-2.026501000	C	1.374839000	-0.177644000	-1.837751000
C	1.202934000	-2.061591000	-0.315409000	C	1.349294000	-1.840006000	0.449531000
H	2.992318000	-3.987823000	-1.059713000	H	3.212056000	-3.797157000	0.374438000
C	0.372792000	-1.001046000	-0.082762000	C	0.476708000	-0.795281000	0.327347000
C	0.360658000	0.122512000	-0.951535000	C	0.476589000	0.030529000	-0.830302000
H	1.211813000	-2.919122000	0.353728000	H	1.352528000	-2.464926000	1.339409000
C	-1.971140000	0.512886000	-0.401748000	C	-1.890428000	0.454365000	-0.509562000
C	-3.118707000	0.866354000	-1.047813000	C	-3.016260000	0.553488000	-1.273208000
C	-4.313793000	0.119500000	-0.837110000	C	-4.193515000	-0.154163000	-0.892820000
C	-4.291667000	-0.996976000	0.045928000	C	-4.177573000	-0.961689000	0.279225000
C	-3.074498000	-1.343242000	0.702831000	C	-2.984478000	-1.050229000	1.052995000
C	-1.949174000	-0.603964000	0.486030000	C	-1.876315000	-0.355952000	0.666956000
H	-5.570279000	1.313448000	-2.164151000	H	-5.402953000	0.543328000	-2.548678000
H	-3.138355000	1.716485000	-1.725730000	H	-3.032130000	1.166381000	-2.170960000
C	-5.525535000	0.467134000	-1.486362000	C	-5.382716000	-0.070176000	-1.653193000
C	-5.482859000	-1.737025000	0.256713000	C	-5.350295000	-1.658228000	0.651542000
H	-3.061316000	-2.198241000	1.374720000	H	-2.975614000	-1.670071000	1.946009000
C	-6.631538000	-1.374803000	-0.385026000	C	-6.499331000	-1.565115000	-0.100830000
C	-6.652969000	-0.267494000	-1.260892000	C	-6.515861000	-0.755190000	-1.276060000
H	-5.495834000	-2.593184000	0.923330000	H	-5.345270000	-2.276429000	1.543984000

C	-0.565642000	-0.835581000	1.094700000	C	-0.521347000	-0.339269000	1.369098000
C	-0.612059000	1.201189000	-0.515886000	C	-0.550719000	1.143600000	-0.765094000
N	2.504428000	1.481198000	0.529156000	N	2.493749000	1.834311000	0.284048000
C	1.720873000	2.484851000	1.037765000	C	1.660498000	2.911134000	0.448405000
C	-0.286541000	1.586104000	0.929615000	C	-0.307534000	1.943042000	0.519500000
C	-0.232961000	0.493851000	1.782998000	C	-0.263931000	1.145570000	1.655272000
C	1.851400000	0.418889000	2.409013000	C	1.771607000	1.327661000	2.360669000
N	2.568190000	0.419713000	1.242830000	N	2.547698000	1.023944000	1.274253000
H	-0.633212000	2.549520000	1.289205000	H	-0.702762000	2.952469000	0.567482000
H	-0.472575000	0.583438000	2.838077000	H	-0.566250000	1.519927000	2.628276000
H	-0.538946000	-1.681290000	1.786451000	H	-0.501639000	-0.948348000	2.275707000
H	-0.620459000	2.055867000	-1.192532000	H	-0.551651000	1.764727000	-1.660435000
N	1.779938000	1.604212000	3.117352000	N	1.633935000	2.664800000	2.694435000
N	1.710660000	2.659432000	2.405489000	N	1.574349000	3.468103000	1.708447000
C	1.825389000	-0.853665000	3.180034000	C	1.746914000	0.332017000	3.467798000
C	2.616509000	-1.935127000	2.786252000	C	2.630275000	-0.749143000	3.469176000
N	0.986832000	-0.892616000	4.219900000	N	0.820603000	0.529941000	4.410863000
C	2.539060000	-3.107145000	3.530099000	C	2.550870000	-1.657075000	4.519677000
H	3.266964000	-1.836123000	1.924326000	H	3.354438000	-0.851273000	2.668680000
C	0.931344000	-2.020812000	4.925109000	C	0.762725000	-0.346092000	5.412474000
C	1.684203000	-3.154933000	4.625830000	C	1.602376000	-1.453764000	5.515549000
H	3.142907000	-3.968378000	3.260608000	H	3.225645000	-2.506606000	4.562351000
H	0.244758000	-2.021060000	5.768668000	H	0.002625000	-0.157595000	6.166921000
H	1.596004000	-4.047506000	5.235733000	H	1.508442000	-2.135765000	6.353505000
C	1.539460000	3.703267000	0.201348000	C	1.492117000	3.832272000	-0.709550000
C	1.396973000	4.957103000	0.800472000	C	1.321162000	5.202610000	-0.504517000
N	1.506248000	3.514003000	-1.121924000	N	1.497147000	3.264361000	-1.920552000
C	1.231422000	6.064786000	-0.021999000	C	1.167563000	6.019806000	-1.618334000
H	1.431895000	5.041904000	1.880104000	H	1.325066000	5.598307000	0.504162000
C	1.351455000	4.588183000	-1.894332000	C	1.353762000	4.064478000	-2.976318000
C	1.212800000	5.883256000	-1.400317000	C	1.188689000	5.444433000	-2.883486000
H	1.124748000	7.055580000	0.408766000	H	1.040063000	7.091157000	-1.497811000
H	1.333714000	4.403640000	-2.966429000	H	1.368261000	3.576635000	-3.948661000
H	1.091224000	6.718542000	-2.081353000	H	1.078633000	6.043650000	-3.780739000
F	-7.810170000	0.031738000	-1.856426000	C	-7.710447000	-0.653642000	-2.069209000
F	-7.770097000	-2.049915000	-0.208387000	N	-8.662824000	-0.561152000	-2.719208000
F	4.671380000	-4.031859000	-3.043038000	C	-7.675617000	-2.287431000	0.300618000
F	4.676459000	-1.916323000	-4.643497000	N	-8.611052000	-2.877305000	0.639805000
				C	5.083722000	-4.448322000	-1.370450000
				N	5.831548000	-5.323036000	-1.252912000
				C	5.132009000	-2.734867000	-3.684504000
				N	5.902083000	-2.897321000	-4.532283000

4ax				**4bx**			
E(SCF) = -1411.41180578				E(SCF) = -1267.82497739			
C	-5.203853000	-2.036814000	0.698700000	C	-5.225844000	-2.033154000	0.715688000
C	-4.200405000	-1.424917000	1.394952000	C	-4.197678000	-1.420050000	1.388536000
C	-3.133180000	-0.789292000	0.705591000	C	-3.129552000	-0.780193000	0.710472000
C	-3.129427000	-0.802851000	-0.718021000	C	-3.129551000	-0.780474000	-0.710144000
C	-4.186275000	-1.448457000	-1.411581000	C	-4.197672000	-1.420607000	-1.387957000
C	-5.203998000	-2.053579000	-0.726624000	C	-5.225837000	-2.033446000	-0.714867000
H	-2.085974000	-0.131109000	2.488103000	H	-2.075471000	-0.134458000	2.495288000
H	-4.212538000	-1.418943000	2.483057000	H	-4.194838000	-1.416418000	2.476846000
C	-2.075496000	-0.144431000	1.399998000	C	-2.068180000	-0.140034000	1.407105000
C	-2.064835000	-0.165502000	-1.411003000	C	-2.068187000	-0.140578000	-1.407029000
H	-4.201155000	-1.466894000	-2.496784000	H	-4.194826000	-1.417414000	-2.476269000
C	-1.053294000	0.439367000	-0.717013000	C	-1.054524000	0.458884000	-0.712717000
C	-1.057183000	0.449443000	0.706102000	C	-1.054517000	0.459154000	0.712557000
H	-2.067858000	-0.167308000	-2.498974000	H	-2.075486000	-0.135417000	-2.495214000

C	1.387058000	0.604463000	0.710172000	C	1.389172000	0.617531000	0.712808000
C	2.467277000	0.137818000	1.408106000	C	2.470048000	0.148569000	1.406924000
C	3.605597000	-0.363281000	0.719955000	C	3.604565000	-0.351296000	0.710397000
C	3.606663000	-0.365429000	-0.703774000	C	3.604559000	-0.351536000	-0.710348000
C	2.474314000	0.131074000	-1.402728000	C	2.470034000	0.148089000	-1.407035000
C	1.389895000	0.601466000	-0.713534000	C	1.389163000	0.617285000	-0.713067000
H	4.755177000	-0.863925000	2.503584000	H	4.740749000	-0.850628000	2.476689000
H	2.468869000	0.141435000	2.496109000	H	2.474571000	0.149008000	2.495178000
C	4.738295000	-0.857317000	1.418188000	C	4.744752000	-0.851639000	1.388289000
C	4.747207000	-0.864306000	-1.388241000	C	4.744741000	-0.852104000	-1.388082000
H	2.480646000	0.128804000	-2.491000000	H	2.474545000	0.148154000	-2.495289000
C	5.822740000	-1.332325000	-0.687534000	C	5.841389000	-1.332481000	-0.715118000
C	5.826144000	-1.332242000	0.737924000	C	5.841395000	-1.332241000	0.715478000
H	4.757333000	-0.870206000	-2.476439000	H	4.740730000	-0.851458000	-2.476481000
C	0.126038000	1.180950000	-1.305990000	C	0.124843000	1.201383000	-1.300179000
C	0.122240000	1.192023000	1.293257000	C	0.124867000	1.201852000	1.299733000
N	-2.146268000	3.884179000	0.712544000	N	-2.155693000	3.885820000	0.714813000
C	-1.170002000	3.352060000	1.328598000	C	-1.185292000	3.348493000	1.335491000
C	0.041266000	2.664152000	0.760393000	C	0.037257000	2.675632000	0.772639000
C	0.031256000	2.657246000	-0.785842000	C	0.037207000	2.675353000	-0.773605000
C	-1.203429000	3.313220000	-1.342799000	C	-1.185435000	3.347910000	-1.336619000
N	-2.169374000	3.853622000	-0.717830000	N	-2.155794000	3.885461000	-0.716071000
H	-1.230390000	3.399373000	2.418844000	H	-1.262931000	3.373857000	2.425355000
H	-1.298250000	3.316367000	-2.431631000	H	-1.263218000	3.372743000	-2.426485000
H	0.927003000	3.191833000	1.133041000	H	0.916013000	3.209019000	1.153694000
H	0.902377000	3.196802000	-1.175763000	H	0.915911000	3.208642000	-1.154918000
H	0.127829000	1.155726000	-2.400614000	H	0.124974000	1.180750000	-2.394847000
H	0.120868000	1.176040000	2.388067000	H	0.125016000	1.181609000	2.394408000
O	-6.216770000	-2.673022000	-1.379278000	C	-6.348762000	-2.700562000	-1.464671000
H	-6.830637000	-3.022957000	-0.713866000	H	-6.419131000	-3.765914000	-1.216634000
O	-6.275754000	-2.678614000	1.257089000	H	-7.317141000	-2.250571000	-1.217428000
H	-6.234304000	-2.609642000	2.220866000	H	-6.202764000	-2.614074000	-2.543988000
O	6.971100000	-1.829869000	-1.240799000	C	-6.348777000	-2.699962000	1.465750000
H	6.906178000	-1.812908000	-2.205595000	H	-7.317161000	-2.250121000	1.218253000
O	6.912982000	-1.803251000	1.395451000	H	-6.419099000	-3.765431000	1.218205000
H	7.564165000	-2.084287000	0.732757000	H	-6.202831000	-2.612969000	2.545034000
				C	7.038044000	-1.856084000	-1.464715000
				H	7.944182000	-1.292081000	-1.215494000
				H	7.237607000	-2.905179000	-1.218090000
				H	6.883726000	-1.786849000	-2.544105000
				C	7.038058000	-1.855587000	1.465240000
				H	7.237675000	-2.904739000	1.218902000
				H	7.944176000	-1.291610000	1.215885000
				H	6.883717000	-1.786066000	2.544608000

4cx				**4dx**			
E(SCF) = -1507.44446877				E(SCF) = -1479.48258462			
C	-5.185024000	-2.050036000	0.707357000	C	-5.249505000	-1.767489000	0.714882000
C	-4.181143000	-1.450060000	1.407216000	C	-4.221931000	-1.164038000	1.401039000
C	-3.119431000	-0.812461000	0.712428000	C	-3.154721000	-0.538910000	0.711925000
C	-3.119466000	-0.812669000	-0.712041000	C	-3.154740000	-0.539134000	-0.711689000
C	-4.181213000	-1.450471000	-1.406591000	C	-4.221970000	-1.164482000	-1.400575000
C	-5.185059000	-2.050244000	-0.706507000	C	-5.249525000	-1.767714000	-0.714196000
H	-2.067405000	-0.162824000	2.495299000	H	-2.095678000	0.093029000	2.498169000
H	-4.208486000	-1.462599000	2.491893000	H	-4.229414000	-1.166994000	2.486678000
C	-2.059428000	-0.169206000	1.407647000	C	-2.086905000	0.086873000	1.410852000
C	-2.059500000	-0.169611000	-1.407499000	C	-2.086944000	0.086429000	-1.410841000
H	-4.208609000	-1.463328000	-2.491264000	H	-4.229488000	-1.167780000	-2.486213000
C	-1.048644000	0.432963000	-0.712308000	C	-1.067158000	0.670913000	-0.713295000

C	-1.048606000	0.433167000	0.712232000	C	-1.067139000	0.671139000	0.713094000
H	-2.067534000	-0.163539000	-2.495152000	H	-2.095747000	0.092244000	-2.498160000
C	1.392051000	0.606750000	0.712473000	C	1.372862000	0.799342000	0.713397000
C	2.473523000	0.141158000	1.407402000	C	2.443835000	0.313372000	1.410719000
C	3.609415000	-0.356463000	0.712214000	C	3.568710000	-0.203314000	0.711930000
C	3.609379000	-0.356653000	-0.712325000	C	3.568692000	-0.203549000	-0.711948000
C	2.473453000	0.140782000	-1.407590000	C	2.443802000	0.312913000	-1.410880000
C	1.392014000	0.606559000	-0.712730000	C	1.372845000	0.799111000	-0.713692000
H	4.770416000	-0.867674000	2.491321000	H	4.700989000	-0.720978000	2.486371000
H	2.477946000	0.141136000	2.495139000	H	2.449187000	0.313247000	2.498120000
C	4.743395000	-0.854512000	1.406570000	C	4.693665000	-0.717367000	1.400640000
C	4.743326000	-0.854887000	-1.406603000	C	4.693626000	-0.717837000	-1.400516000
H	2.477820000	0.140468000	-2.495327000	H	2.449128000	0.312433000	-2.498281000
C	5.814212000	-1.326134000	-0.706933000	C	5.778520000	-1.211469000	-0.714367000
C	5.814247000	-1.325944000	0.706974000	C	5.778542000	-1.211224000	0.714628000
H	4.770294000	-0.868339000	-2.491351000	H	4.700921000	-0.721818000	-2.486245000
C	0.125124000	1.183543000	-1.300561000	C	0.118660000	1.401362000	-1.301858000
C	0.125197000	1.183902000	1.300215000	C	0.118690000	1.401778000	1.301400000
N	-2.182271000	3.838059000	0.714880000	N	-2.150434000	4.078734000	0.714413000
C	-1.204003000	3.316549000	1.336345000	C	-1.176575000	3.551980000	1.337586000
C	0.026100000	2.657061000	0.772710000	C	0.045373000	2.876555000	0.772478000
C	0.026034000	2.656848000	-0.773448000	C	0.045356000	2.876309000	-0.773394000
C	-1.204154000	3.316114000	-1.337157000	C	-1.176610000	3.551540000	-1.338691000
N	-2.182368000	3.837795000	-0.715752000	N	-2.150459000	4.078486000	-0.715666000
H	-1.280482000	3.343855000	2.426127000	H	-1.250402000	3.584780000	2.427145000
H	-1.280775000	3.343027000	-2.426939000	H	-1.250471000	3.583970000	-2.428259000
H	0.899925000	3.197702000	1.154460000	H	0.927489000	3.402214000	1.155254000
H	0.899807000	3.197410000	-1.155429000	H	0.927466000	3.401842000	-1.156360000
H	0.125355000	1.162255000	-2.395003000	H	0.118469000	1.379147000	-2.395821000
H	0.125487000	1.162910000	2.394663000	H	0.118521000	1.379906000	2.395369000
F	-6.202403000	-2.654830000	-1.323915000	C	-6.318484000	-2.401041000	-1.437439000
F	-6.202341000	-2.654436000	1.324992000	N	-7.169119000	-2.909392000	-2.033961000
F	6.896112000	-1.803749000	-1.325390000	C	-6.318439000	-2.400599000	1.438351000
F	6.896176000	-1.803396000	1.325505000	N	-7.169090000	-2.908690000	2.035070000
				C	6.909679000	-1.723506000	-1.438862000
				N	7.811464000	-2.129580000	-2.038662000
				C	6.909729000	-1.722991000	1.439271000
				N	7.811551000	-2.128836000	2.039171000

4ay				**4by**			
E(SCF) = -2462.28598492				E(SCF) = -2318.69858960			
C	4.038032000	-1.712264000	-3.851208000	C	4.110270000	-1.654891000	-3.819724000
C	3.319746000	-0.623411000	-3.438573000	C	3.379367000	-0.578082000	-3.381195000
C	2.299725000	-0.758070000	-2.461270000	C	2.339549000	-0.713713000	-2.427575000
C	2.022841000	-2.042386000	-1.911614000	C	2.050318000	-2.007620000	-1.916357000
C	2.784675000	-3.157091000	-2.351461000	C	2.815570000	-3.107084000	-2.379015000
C	3.762652000	-2.994736000	-3.291275000	C	3.820634000	-2.957235000	-3.302938000
H	1.772210000	1.345841000	-2.422524000	H	1.817078000	1.393221000	-2.357956000
H	3.543542000	0.347207000	-3.869950000	H	3.597933000	0.414376000	-3.770638000
C	1.550758000	0.363143000	-2.011102000	C	1.587581000	0.402895000	-1.969141000
C	0.999584000	-2.179487000	-0.936666000	C	1.013059000	-2.162817000	-0.956096000
H	2.586217000	-4.139776000	-1.928863000	H	2.594827000	-4.094855000	-1.979571000
C	0.281405000	-1.084161000	-0.540762000	C	0.295577000	-1.073325000	-0.545907000
C	0.564809000	0.203235000	-1.075962000	C	0.586782000	0.225682000	-1.054179000
H	0.803588000	-3.158437000	-0.502202000	H	0.806310000	-3.151548000	-0.550108000
C	-1.742854000	0.893640000	-0.601670000	C	-1.729615000	0.906663000	-0.603481000
C	-2.751142000	1.641770000	-1.145849000	C	-2.729693000	1.664410000	-1.147748000
C	-4.080875000	1.143674000	-1.159146000	C	-4.060746000	1.165358000	-1.184933000
C	-4.356942000	-0.132560000	-0.590152000	C	-4.339993000	-0.118074000	-0.642178000

C	-3.290301000	-0.880349000	-0.022802000	C	-3.282677000	-0.879856000	-0.074669000
C	-2.016740000	-0.379777000	-0.033033000	C	-2.010195000	-0.378833000	-0.060386000
H	-4.950148000	2.864729000	-2.161824000	H	-4.912572000	2.894367000	-2.158020000
H	-2.546014000	2.621090000	-1.573121000	H	-2.520574000	2.651414000	-1.554988000
C	-5.150354000	1.888548000	-1.724679000	C	-5.129096000	1.911573000	-1.743695000
C	-5.686887000	-0.628305000	-0.601891000	C	-5.673786000	-0.597058000	-0.683494000
H	-3.500579000	-1.854968000	0.412526000	H	-3.498656000	-1.862041000	0.341144000
C	-6.701151000	0.106867000	-1.151600000	C	-6.696702000	0.140478000	-1.226940000
C	-6.420107000	1.384126000	-1.720404000	C	-6.416057000	1.432729000	-1.773411000
H	-5.915325000	-1.599088000	-0.173186000	H	-5.882466000	-1.580838000	-0.267325000
C	-0.787533000	-1.051863000	0.528443000	C	-0.788595000	-1.058235000	0.508319000
C	-0.291631000	1.294007000	-0.474679000	C	-0.280267000	1.305110000	-0.448112000
N	2.347599000	1.225068000	1.912315000	N	2.327210000	1.186703000	1.970139000
C	1.358633000	1.838608000	1.392556000	C	1.348907000	1.811333000	1.443744000
C	-0.012254000	1.309837000	1.073432000	C	-0.021947000	1.295641000	1.103170000
C	-0.221659000	-0.110642000	1.660061000	C	-0.244868000	-0.133353000	1.663701000
C	1.082048000	-0.696036000	2.141948000	C	1.045323000	-0.727706000	2.169294000
N	2.231359000	-0.150249000	2.203692000	N	2.195967000	-0.188449000	2.257140000
H	-0.728343000	2.012244000	1.510597000	H	-0.739649000	1.995124000	1.542468000
H	-0.936858000	-0.096205000	2.488813000	H	-0.978738000	-0.129971000	2.476039000
H	-1.010637000	-2.046730000	0.923536000	H	-1.016080000	-2.059502000	0.884648000
H	-0.094053000	2.277968000	-0.905811000	H	-0.077708000	2.296091000	-0.860348000
O	4.555711000	-3.992252000	-3.786649000	C	4.619266000	-4.144156000	-3.772717000
H	4.344292000	-4.829581000	-3.351077000	H	4.542171000	-4.273308000	-4.858357000
O	5.011846000	-1.595725000	-4.784018000	H	5.683753000	-4.026037000	-3.539976000
H	5.399385000	-2.474645000	-4.924625000	H	4.269864000	-5.063291000	-3.296776000
O	-7.973247000	-0.356026000	-1.165685000	C	5.209964000	-1.478581000	-4.833214000
H	-8.530533000	0.310662000	-1.598349000	H	6.172715000	-1.825495000	-4.441460000
O	-7.521395000	2.011658000	-2.233381000	H	5.009589000	-2.054261000	-5.744174000
H	-7.270966000	2.869566000	-2.603389000	H	5.317894000	-0.428376000	-5.114305000
C	1.090286000	-2.158316000	2.511889000	C	-8.104134000	-0.394555000	-1.251611000
O	1.922069000	-2.966006000	2.248658000	H	-8.789227000	0.258976000	-0.699446000
O	-0.071786000	-2.449324000	3.208086000	H	-8.487445000	-0.466120000	-2.275810000
C	-0.363877000	-3.776670000	3.413126000	H	-8.152085000	-1.389469000	-0.802877000
F	-1.537119000	-3.822792000	4.021276000	C	-7.529439000	2.252345000	-2.370088000
F	0.539117000	-4.378486000	4.166852000	H	-8.008306000	1.729012000	-3.205493000
F	-0.456488000	-4.419427000	2.250895000	H	-8.312995000	2.458522000	-1.631976000
C	1.554673000	3.306069000	1.117435000	H	-7.154573000	3.209000000	-2.741225000
O	0.683839000	4.024322000	0.713304000	C	1.036523000	-2.190447000	2.537968000
O	2.823248000	3.722476000	1.384553000	O	1.872379000	-3.001190000	2.299500000
C	3.106640000	5.052134000	1.167558000	O	-0.147133000	-2.476440000	3.199895000
F	4.370492000	5.230525000	1.504649000	C	1.560383000	3.278656000	1.179140000
F	2.345102000	5.841880000	1.911473000	O	0.697042000	4.008913000	0.780714000
F	2.948455000	5.378990000	-0.107974000	O	2.833901000	3.679756000	1.447339000
				C	3.130729000	5.007684000	1.238055000
				C	-0.450072000	-3.802696000	3.396904000
				F	4.397696000	5.170474000	1.571913000
				F	2.972335000	5.344285000	-0.035082000
				F	2.380336000	5.800838000	1.989289000
				F	-0.516317000	-4.443887000	2.232477000
				F	0.430678000	-4.408768000	4.172973000
				F	-1.638544000	-3.843443000	3.975878000

4cy				**4dy**			
E(SCF) = -2558.31694217				E(SCF) = -2530.35324048			
C	3.983363000	-1.721606000	-3.867111000	C	4.415197000	-1.494719000	-3.374348000
C	3.304350000	-0.619091000	-3.441116000	C	3.549343000	-0.465205000	-3.088620000
C	2.282133000	-0.754159000	-2.465303000	C	2.520553000	-0.625697000	-2.129496000
C	1.980280000	-2.046040000	-1.946192000	C	2.387477000	-1.874282000	-1.458784000

C	2.711861000	-3.170515000	-2.410151000	C	3.291237000	-2.920558000	-1.761901000
C	3.687347000	-3.003320000	-3.347481000	C	4.284999000	-2.746144000	-2.696502000
H	1.797301000	1.359885000	-2.386116000	H	1.737023000	1.389685000	-2.330553000
H	3.555231000	0.352250000	-3.854612000	H	3.657068000	0.483860000	-3.604757000
C	1.557009000	0.374225000	-1.993574000	C	1.624634000	0.434817000	-1.822402000
C	0.956062000	-2.182182000	-0.969596000	C	1.357725000	-2.044412000	-0.493569000
H	2.508429000	-4.164113000	-2.024553000	H	3.199683000	-3.872280000	-1.247781000
C	0.263873000	-1.080210000	-0.550157000	C	0.501707000	-1.011387000	-0.230732000
C	0.569666000	0.213330000	-1.061737000	C	0.636842000	0.242493000	-0.897005000
H	0.739775000	-3.166543000	-0.559126000	H	1.274033000	-2.990021000	0.037847000
C	-1.725951000	0.931801000	-0.580872000	C	-1.751257000	0.661924000	-0.557260000
C	-2.719034000	1.704432000	-1.116319000	C	-2.821563000	1.204022000	-1.212399000
C	-4.057529000	1.225662000	-1.141743000	C	-4.072763000	0.529628000	-1.196861000
C	-4.351000000	-0.057019000	-0.594930000	C	-4.198380000	-0.700328000	-0.490254000
C	-3.299156000	-0.831741000	-0.035913000	C	-3.069775000	-1.235897000	0.188002000
C	-2.020170000	-0.348127000	-0.033605000	C	-1.876699000	-0.569018000	0.150541000
H	-4.916732000	2.981550000	-2.118962000	H	-5.115406000	1.996141000	-2.405598000
H	-2.499160000	2.687717000	-1.525534000	H	-2.731342000	2.148285000	-1.743728000
C	-5.109847000	2.000283000	-1.697605000	C	-5.202993000	1.057876000	-1.866255000
C	-5.687874000	-0.535182000	-0.621259000	C	-5.449329000	-1.363093000	-0.477279000
H	-3.525940000	-1.810099000	0.381797000	H	-3.169742000	-2.175537000	0.726126000
C	-6.672143000	0.235184000	-1.164896000	C	-6.536610000	-0.833892000	-1.132303000
C	-6.381777000	1.509867000	-1.704479000	C	-6.411057000	0.401252000	-1.840232000
H	-5.939389000	-1.509637000	-0.215301000	H	-5.552297000	-2.302523000	0.057306000
C	-0.803362000	-1.047696000	0.521106000	C	-0.592018000	-1.002706000	0.814583000
C	-0.269207000	1.307833000	-0.442161000	C	-0.373422000	1.268633000	-0.438601000
N	2.366753000	1.158089000	1.940211000	N	2.152993000	1.846618000	1.984133000
C	1.388702000	1.794789000	1.428617000	C	1.102266000	2.252073000	1.389443000
C	0.008251000	1.293027000	1.104846000	C	-0.162226000	1.488681000	1.102655000
C	-0.224767000	-0.133267000	1.667832000	C	-0.185742000	0.125354000	1.839116000
C	1.068960000	-0.746090000	2.144614000	C	1.181675000	-0.214954000	2.383809000
N	2.225911000	-0.218492000	2.215106000	N	2.234974000	0.499525000	2.395698000
H	-0.695383000	2.000791000	1.553532000	H	-0.990235000	2.119214000	1.440079000
H	-0.941931000	-0.120904000	2.494668000	H	-0.911241000	0.126643000	2.658919000
H	-1.043030000	-2.045206000	0.899306000	H	-0.696725000	-1.969040000	1.314910000
H	-0.056044000	2.295236000	-0.857288000	H	-0.291404000	2.217094000	-0.973060000
C	1.053678000	-2.213378000	2.493915000	C	5.188362000	-3.825448000	-2.989256000
O	1.875616000	-3.027830000	2.221926000	N	5.904233000	-4.705432000	-3.214624000
O	-0.117958000	-2.496399000	3.174966000	C	5.447388000	-1.307251000	-4.357391000
C	1.607214000	3.261904000	1.165592000	N	6.268895000	-1.139085000	-5.153928000
O	0.739704000	3.997122000	0.784757000	C	-7.796245000	-1.525783000	-1.098923000
O	2.887879000	3.650861000	1.406036000	N	-8.801480000	-2.096354000	-1.059020000
C	3.190368000	4.979696000	1.196524000	C	-7.543739000	0.962573000	-2.524782000
C	-0.425468000	-3.824145000	3.367284000	N	-8.443305000	1.431013000	-3.080708000
F	4.466564000	5.129056000	1.496449000	C	1.075553000	3.697069000	0.963611000
F	2.998845000	5.323528000	-0.069737000	O	0.115207000	4.208081000	0.457712000
F	2.466681000	5.771883000	1.973532000	O	2.245170000	4.337179000	1.211164000
F	-0.514259000	-4.454367000	2.198249000	C	2.322189000	5.668170000	0.846693000
F	0.465117000	-4.438880000	4.123176000	F	3.529711000	6.079805000	1.177010000
F	-1.604485000	-3.862291000	3.963872000	F	1.420613000	6.395709000	1.486710000
F	4.396339000	-4.034571000	-3.808083000	F	2.152165000	5.815278000	-0.459420000
F	4.947403000	-1.633666000	-4.784522000	C	1.396527000	-1.625485000	2.872019000
F	-7.395693000	2.209376000	-2.215760000	O	2.318308000	-2.334256000	2.622846000
F	-7.938589000	-0.180928000	-1.210652000	O	0.308615000	-2.004967000	3.633725000
				C	0.204129000	-3.341967000	3.955240000
				F	-0.914334000	-3.484544000	4.642032000
				F	1.221318000	-3.762544000	4.680246000
				F	0.125427000	-4.073910000	2.844814000

4az	**4bz**

E(SCF) = -1905.41451171				E(SCF) = -1761.82739336			
C	4.495115000	-1.526018000	3.172851000	C	4.527779000	-1.816837000	3.024915000
C	3.593109000	-2.017908000	2.272817000	C	3.627454000	-2.194508000	2.059277000
C	2.561868000	-1.185508000	1.762549000	C	2.590394000	-1.334553000	1.618043000
C	2.488363000	0.166525000	2.201966000	C	2.490238000	-0.040120000	2.195403000
C	3.438982000	0.646032000	3.140826000	C	3.427685000	0.332500000	3.191058000
C	4.422389000	-0.175007000	3.620621000	C	4.423917000	-0.515337000	3.609277000
H	1.687103000	-2.695140000	0.471399000	H	1.749065000	-2.711874000	0.164905000
H	3.660831000	-3.050134000	1.935029000	H	3.705544000	-3.182504000	1.609526000
C	1.612197000	-1.668725000	0.824326000	C	1.656533000	-1.728407000	0.621117000
C	1.468040000	1.007404000	1.681223000	C	1.461748000	0.839903000	1.760720000
H	3.398685000	1.674060000	3.487151000	H	3.346007000	1.324597000	3.631283000
C	0.559174000	0.514492000	0.785032000	C	0.568611000	0.432843000	0.808988000
C	0.628307000	-0.840915000	0.357386000	C	0.664440000	-0.869087000	0.237392000
H	1.423539000	2.046473000	2.001236000	H	1.393923000	1.835509000	2.195061000
C	-1.772975000	-0.808060000	-0.147947000	C	-1.738579000	-0.831978000	-0.257112000
C	-2.871034000	-1.621862000	-0.079962000	C	-2.818626000	-1.671236000	-0.279899000
C	-4.096428000	-1.130024000	0.446099000	C	-4.049234000	-1.266795000	0.307040000
C	-4.163992000	0.220755000	0.891399000	C	-4.144284000	0.017113000	0.909242000
C	-3.011287000	1.045455000	0.798230000	C	-3.009017000	0.872983000	0.908663000
C	-1.842808000	0.541002000	0.296079000	C	-1.835786000	0.455591000	0.344089000
H	-5.215921000	-2.985911000	0.206973000	H	-5.116954000	-3.087285000	-0.146910000
H	-2.819071000	-2.654533000	-0.419020000	H	-2.747677000	-2.656087000	-0.737851000
C	-5.249483000	-1.953191000	0.539994000	C	-5.193589000	-2.104378000	0.314551000
C	-5.389722000	0.707270000	1.420705000	C	-5.377541000	0.402351000	1.493162000
H	-3.068475000	2.079560000	1.131753000	H	-3.086920000	1.859890000	1.360090000
C	-6.480883000	-0.110932000	1.500478000	C	-6.475294000	-0.422723000	1.492594000
C	-6.418355000	-1.463034000	1.054338000	C	-6.380907000	-1.713957000	0.883840000
H	-5.450959000	1.737853000	1.765102000	H	-5.445794000	1.385732000	1.954745000
C	-0.545854000	1.289918000	0.106847000	C	-0.559212000	1.252845000	0.228812000
C	-0.412944000	-1.179559000	-0.685482000	C	-0.372490000	-1.109079000	-0.837299000
N	2.248933000	0.262037000	-2.538025000	N	2.242590000	0.648238000	-2.506818000
C	1.264150000	-0.543927000	-2.429780000	C	1.303812000	-0.217589000	-2.474165000
C	-0.118441000	-0.225015000	-1.902325000	C	-0.098936000	-0.016383000	-1.937778000
C	-0.250775000	1.248981000	-1.437231000	C	-0.292573000	1.391073000	-1.313271000
C	0.975092000	2.062480000	-1.761410000	C	0.878362000	2.300667000	-1.575249000
N	2.076177000	1.627201000	-2.244647000	N	1.993989000	1.973168000	-2.108090000
H	-0.861449000	-0.436811000	-2.679745000	H	-0.822898000	-0.166160000	-2.747303000
H	-1.098369000	1.735628000	-1.927313000	H	-1.175734000	1.879967000	-1.733326000
H	-0.611933000	2.324029000	0.449239000	H	-0.646492000	2.239851000	0.685901000
H	-0.364572000	-2.227238000	-0.994019000	H	-0.302438000	-2.114026000	-1.261287000
O	5.335041000	0.273039000	4.517934000	C	5.405338000	-0.090131000	4.669415000
H	5.944141000	-0.457192000	4.712139000	H	5.367665000	-0.754891000	5.540219000
O	5.526843000	-2.236740000	3.726769000	H	6.434868000	-0.115380000	4.294037000
H	5.544193000	-3.129198000	3.355003000	H	5.195559000	0.926278000	5.011085000
O	-7.705490000	0.250936000	1.994801000	C	5.619555000	-2.753964000	3.470461000
H	-7.677479000	1.168350000	2.299554000	H	6.612676000	-2.328188000	3.285937000
O	-7.523975000	-2.241851000	1.150061000	H	5.556433000	-2.961689000	4.544949000
H	-8.232030000	-1.706844000	1.542930000	H	5.557309000	-3.706369000	2.938425000
C	0.911741000	3.535734000	-1.525585000	C	-7.770300000	0.017436000	2.123339000
C	2.079435000	4.306856000	-1.546054000	H	-8.585121000	0.043297000	1.390458000
N	-0.301908000	4.059150000	-1.313994000	H	-8.080950000	-0.667276000	2.920897000
C	1.971413000	5.674629000	-1.344293000	H	-7.673410000	1.016358000	2.555287000
H	3.029107000	3.816407000	-1.722613000	C	-7.579125000	-2.626324000	0.876038000
C	-0.388736000	5.376381000	-1.127404000	H	-7.909218000	-2.861465000	1.894520000
C	0.711124000	6.228124000	-1.132377000	H	-8.430746000	-2.163591000	0.364120000
H	2.857577000	6.301928000	-1.350712000	H	-7.351240000	-3.567303000	0.369736000
H	-1.389942000	5.769451000	-0.964710000	C	0.732319000	3.742723000	-1.215371000
H	0.579800000	7.292633000	-0.970447000	C	1.843982000	4.592714000	-1.233894000
C	1.545386000	-1.962733000	-2.817588000	N	-0.497684000	4.161834000	-0.895806000

C	0.613387000	-2.690012000	-3.565223000	C	1.659160000	5.929412000	-0.914352000
N	2.714296000	-2.479137000	-2.422244000	H	2.811306000	4.184698000	-1.501416000
C	0.917901000	-3.995643000	-3.932230000	C	-0.659000000	5.450539000	-0.594178000
H	-0.326243000	-2.236917000	-3.866091000	C	0.380449000	6.374807000	-0.587993000
C	2.988194000	-3.732922000	-2.775981000	H	2.500509000	6.615789000	-0.918435000
C	2.133350000	-4.535093000	-3.529785000	H	-1.672131000	5.757041000	-0.343498000
H	0.218261000	-4.578690000	-4.523449000	H	0.189680000	7.411403000	-0.331612000
H	3.945777000	-4.121061000	-2.434770000	C	1.670651000	-1.580801000	-2.973264000
H	2.415604000	-5.550232000	-3.787422000	C	0.778047000	-2.310657000	-3.765122000
				N	2.878126000	-2.043714000	-2.632544000
				C	1.164349000	-3.560968000	-4.234510000
				H	-0.195297000	-1.901134000	-4.018268000
				C	3.230724000	-3.245166000	-3.083230000
				C	2.419525000	-4.044603000	-3.887389000
				H	0.496574000	-4.144597000	-4.860969000
				H	4.217304000	-3.591554000	-2.782246000
				H	2.765974000	-5.015233000	-4.225413000

4cz				**4dz**			
E(SCF) = -2001.44841788				E(SCF) = -1973.48936943			
C	4.494108000	-1.598429000	3.127560000	C	-4.681322000	-1.539139000	-2.795713000
C	3.598245000	-2.073289000	2.216857000	C	-3.715697000	-2.006109000	-1.934934000
C	2.565262000	-1.227605000	1.734220000	C	-2.682443000	-1.158361000	-1.468176000
C	2.483966000	0.113279000	2.207600000	C	-2.654996000	0.199294000	-1.897292000
C	3.433215000	0.571751000	3.158848000	C	-3.657850000	0.662361000	-2.782437000
C	4.409620000	-0.269613000	3.602764000	C	-4.651013000	-0.177429000	-3.229285000
H	1.696619000	-2.705699000	0.403594000	H	-1.725390000	-2.660418000	-0.225119000
H	3.688109000	-3.095418000	1.863946000	H	-3.746408000	-3.040241000	-1.606028000
C	1.616010000	-1.690075000	0.783372000	C	-1.680729000	-1.634346000	-0.580081000
C	1.460822000	0.965892000	1.711341000	C	-1.629926000	1.061448000	-1.424333000
H	3.394250000	1.587761000	3.538074000	H	-3.642396000	1.696262000	-3.113590000
C	0.555773000	0.492440000	0.802288000	C	-0.671039000	0.574863000	-0.579800000
C	0.630910000	-0.852484000	0.339787000	C	-0.693458000	-0.787121000	-0.158961000
H	1.412336000	1.995551000	2.058978000	H	-1.623033000	2.103799000	-1.734430000
C	-1.768107000	-0.815146000	-0.166357000	C	1.725694000	-0.704844000	0.215590000
C	-2.860879000	-1.635987000	-0.122308000	C	2.832648000	-1.495181000	0.071706000
C	-4.087830000	-1.161211000	0.415943000	C	4.015397000	-0.956567000	-0.503212000
C	-4.164955000	0.176636000	0.899867000	C	4.035759000	0.407230000	-0.914559000
C	-3.014032000	1.008749000	0.831585000	C	2.871811000	1.205155000	-0.748599000
C	-1.844972000	0.521843000	0.315960000	C	1.743716000	0.657900000	-0.202611000
H	-5.207129000	-3.014935000	0.123150000	H	5.170481000	-2.785483000	-0.366357000
H	-2.804499000	-2.658225000	-0.490077000	H	2.822073000	-2.535567000	0.388214000
C	-5.237920000	-1.991630000	0.483151000	C	5.178822000	-1.744598000	-0.675400000
C	-5.391006000	0.648903000	1.439890000	C	5.220099000	0.937223000	-1.481213000
H	-3.077081000	2.032421000	1.193291000	H	2.890814000	2.246799000	-1.059611000
C	-6.474293000	-0.177217000	1.489507000	C	6.341533000	0.156857000	-1.638419000
C	-6.397506000	-1.504037000	1.007780000	C	6.320250000	-1.212077000	-1.227821000
H	-5.478496000	1.662375000	1.817884000	H	5.243248000	1.976112000	-1.796061000
C	-0.551901000	1.281685000	0.145290000	C	0.441352000	1.372426000	0.056481000
C	-0.407228000	-1.166574000	-0.713673000	C	0.407861000	-1.112358000	0.824579000
N	2.254387000	0.343871000	-2.506380000	N	-2.185692000	0.170133000	2.814413000
C	1.276720000	-0.473390000	-2.425360000	C	-1.150664000	-0.564473000	2.686587000
C	-0.113534000	-0.177727000	-1.903340000	C	0.171177000	-0.171970000	2.066922000
C	-0.259484000	1.282225000	-1.399603000	C	0.205763000	1.308326000	1.610305000
C	0.957133000	2.117476000	-1.706027000	C	-1.062246000	2.045280000	1.970176000
N	2.063776000	1.702155000	-2.193588000	N	-2.119398000	1.537933000	2.479568000
H	-0.848945000	-0.376925000	-2.691236000	H	0.977725000	-0.370736000	2.781605000
H	-1.113324000	1.772736000	-1.874689000	H	1.038965000	1.843557000	2.073480000
H	-0.622227000	2.306020000	0.514399000	H	0.466003000	2.410502000	-0.275777000

H	-0.354182000	-2.205082000	-1.050288000	H	0.397247000	-2.162618000	1.126918000
F	5.319023000	0.127115000	4.497090000	C	-5.652454000	0.319870000	-4.132770000
F	5.480576000	-2.364474000	3.601697000	N	-6.446284000	0.739058000	-4.862278000
F	-7.642056000	0.231716000	1.992168000	C	-5.715742000	-2.424289000	-3.256992000
F	-7.497973000	-2.256526000	1.086296000	N	-6.538055000	-3.152336000	-3.620121000
C	0.872882000	3.585807000	-1.447659000	C	7.531288000	0.722552000	-2.213569000
C	2.024059000	4.379968000	-1.494041000	N	8.480032000	1.194853000	-2.677044000
N	-0.343576000	4.081519000	-1.190895000	C	7.488069000	-2.035309000	-1.385460000
C	1.895289000	5.742693000	-1.270661000	N	8.418059000	-2.713370000	-1.501462000
H	2.977303000	3.911150000	-1.706776000	C	-1.093839000	3.519700000	1.734171000
C	-0.450752000	5.394290000	-0.983276000	C	-2.289913000	4.233715000	1.860142000
C	0.631725000	6.267669000	-1.011513000	N	0.072393000	4.099903000	1.425703000
H	2.768134000	6.387830000	-1.296922000	C	-2.262116000	5.606472000	1.661005000
H	-1.453754000	5.764673000	-0.783276000	H	-3.197580000	3.700367000	2.115523000
H	0.484606000	7.327118000	-0.831531000	C	0.083268000	5.420692000	1.243027000
C	1.575946000	-1.882829000	-2.832494000	C	-1.051341000	6.219071000	1.348269000
C	0.678027000	-2.593471000	-3.634895000	H	-3.172194000	6.191961000	1.748837000
N	2.727409000	-2.405311000	-2.396436000	H	1.047951000	5.860588000	1.000533000
C	1.001826000	-3.890497000	-4.016735000	H	-0.983876000	7.289346000	1.186286000
H	-0.247573000	-2.133470000	-3.967672000	C	-1.283415000	-1.985705000	3.137563000
C	3.020304000	-3.650729000	-2.765426000	C	-0.371667000	-2.510519000	4.057745000
C	2.200223000	-4.436424000	-3.573731000	N	-2.286775000	-2.699533000	2.617277000
H	0.330741000	-4.462080000	-4.650633000	C	-0.526095000	-3.827663000	4.474166000
H	3.963046000	-4.044647000	-2.391801000	H	0.425624000	-1.890893000	4.457261000
H	2.495978000	-5.444934000	-3.841661000	C	-2.417892000	-3.962653000	3.023455000
				C	-1.572916000	-4.574377000	3.947019000
				H	0.156384000	-4.259019000	5.199908000
				H	-3.244438000	-4.516646000	2.583845000
				H	-1.735572000	-5.606242000	4.238531000

TS3-ax				**TS3-bx**			
E(SCF) = -1411.35118974				E(SCF) = -1267.76320415			
C	-5.747481000	-1.200750000	0.759292000	C	-5.766153000	-1.255801000	0.721368000
C	-4.616191000	-0.882710000	1.443039000	C	-4.609595000	-0.979967000	1.393915000
C	-3.393843000	-0.644655000	0.742274000	C	-3.389135000	-0.686506000	0.715642000
C	-3.388860000	-0.748060000	-0.689059000	C	-3.389142000	-0.686783000	-0.715314000
C	-4.596289000	-1.091816000	-1.368262000	C	-4.609599000	-0.980532000	-1.393467000
C	-5.745674000	-1.312761000	-0.672728000	C	-5.766153000	-1.256102000	-0.720807000
H	-2.225994000	-0.203399000	2.495506000	H	-2.214827000	-0.359089000	2.490874000
H	-4.632018000	-0.800408000	2.527679000	H	-4.605740000	-0.974936000	2.481989000
C	-2.213674000	-0.306573000	1.412435000	C	-2.206552000	-0.389420000	1.403275000
C	-2.201198000	-0.495095000	-1.384927000	C	-2.206573000	-0.389936000	-1.403070000
H	-4.610579000	-1.172433000	-2.450364000	H	-4.605743000	-0.975944000	-2.481543000
C	-1.021302000	-0.202404000	-0.709753000	C	-1.022468000	-0.146430000	-0.715532000
C	-1.024158000	-0.113692000	0.716689000	C	-1.022452000	-0.146180000	0.715633000
H	-2.203664000	-0.537569000	-2.471840000	H	-2.214860000	-0.360008000	-2.490680000
C	1.447681000	-0.006100000	0.710454000	C	1.449151000	-0.031187000	0.715157000
C	2.648024000	-0.132513000	1.405360000	C	2.648096000	-0.194746000	1.403633000
C	3.849822000	-0.370152000	0.731082000	C	3.849745000	-0.400456000	0.716426000
C	3.853024000	-0.443446000	-0.703846000	C	3.849718000	-0.400731000	-0.716390000
C	2.648381000	-0.275380000	-1.395592000	C	2.648046000	-0.195261000	-1.403628000
C	1.448926000	-0.079705000	-0.716055000	C	1.449129000	-0.031438000	-0.715167000
H	5.094726000	-0.489171000	2.515884000	H	5.084666000	-0.610333000	2.482142000
H	2.650307000	-0.063184000	2.491396000	H	2.650941000	-0.181695000	2.491777000
C	5.086548000	-0.540084000	1.429082000	C	5.089356000	-0.609034000	1.393895000
C	5.084996000	-0.681794000	-1.386886000	C	5.089297000	-0.609588000	-1.393832000
H	2.650273000	-0.318007000	-2.482658000	H	2.650850000	-0.182608000	-2.491777000
C	6.246602000	-0.836011000	-0.693952000	C	6.262166000	-0.804447000	-0.721506000
C	6.238200000	-0.762081000	0.741426000	C	6.262198000	-0.804153000	0.721596000

H	5.105617000	-0.742497000	-2.470339000	H	5.084558000	-0.611320000	-2.482077000
C	0.194297000	0.187433000	-1.367417000	C	0.195154000	0.270231000	-1.352116000
C	0.194501000	0.335958000	1.328994000	C	0.195192000	0.270701000	1.352039000
N	-2.162711000	3.007430000	0.580137000	N	-2.183286000	2.970274000	0.692676000
C	-1.035573000	2.823618000	1.191428000	C	-1.071181000	2.753136000	1.320607000
C	0.186250000	2.366111000	0.582426000	C	0.169480000	2.342135000	0.715856000
C	0.154532000	2.282735000	-0.848493000	C	0.169464000	2.341885000	-0.716639000
C	-1.102836000	2.656943000	-1.444507000	C	-1.071211000	2.752670000	-1.321507000
N	-2.197930000	2.916652000	-0.803122000	N	-2.183302000	2.970029000	-0.693627000
H	-1.061271000	2.979380000	2.270163000	H	-1.126802000	2.839334000	2.405847000
H	-1.187781000	2.673408000	-2.531120000	H	-1.126855000	2.838491000	-2.406775000
H	1.120660000	2.574703000	1.092013000	H	1.090192000	2.528686000	1.257882000
H	1.061378000	2.448096000	-1.420311000	H	1.090165000	2.528244000	-1.258749000
H	0.190482000	0.211837000	-2.456819000	H	0.191914000	0.354806000	-2.438487000
H	0.191548000	0.480452000	2.409189000	H	0.191986000	0.355651000	2.438381000
O	-6.899214000	-1.639845000	-1.300713000	C	-7.040711000	-1.554558000	-1.464568000
H	-7.595031000	-1.720056000	-0.628812000	H	-7.428892000	-2.548133000	-1.212630000
O	-6.970610000	-1.444187000	1.318975000	H	-7.826239000	-0.831905000	-1.215558000
H	-6.929649000	-1.298692000	2.274357000	H	-6.879122000	-1.518113000	-2.544410000
O	7.421789000	-1.058891000	-1.326774000	C	-7.040703000	-1.553978000	1.465255000
H	8.116915000	-1.138545000	-0.654066000	H	-7.826394000	-0.831726000	1.215608000
O	7.474063000	-0.935367000	1.297765000	H	-7.428613000	-2.547856000	1.214088000
H	7.412116000	-0.888248000	2.261992000	H	-6.879214000	-1.516639000	2.545082000
				C	7.553064000	-1.021033000	-1.465433000
				H	8.293621000	-0.252802000	-1.214902000
				H	8.001257000	-1.989527000	-1.215629000
				H	7.389838000	-0.993254000	-2.545269000
				C	7.553123000	-1.020457000	1.465556000
				H	8.001103000	-1.989222000	1.216413000
				H	8.293811000	-0.252553000	1.214409000
				H	7.390003000	-0.991879000	2.545388000

TS3-cx				**TS3-dx**			
E(SCF) = -1507.38265930				E(SCF) = -1479.42035929			
C	-5.723548000	-1.265236000	0.712345000	C	-5.762162000	-1.110071000	0.719889000
C	-4.594847000	-0.994775000	1.413155000	C	-4.610204000	-0.836125000	1.405424000
C	-3.381534000	-0.701017000	0.717530000	C	-3.396436000	-0.550113000	0.716335000
C	-3.381538000	-0.700903000	-0.717594000	C	-3.396437000	-0.549997000	-0.716436000
C	-4.594855000	-0.994547000	-1.413261000	C	-4.610209000	-0.835899000	-1.405566000
C	-5.723553000	-1.265121000	-0.712489000	C	-5.762165000	-1.109956000	-0.720070000
H	-2.207124000	-0.371985000	2.490470000	H	-2.222818000	-0.230470000	2.493192000
H	-4.624360000	-0.998362000	2.497548000	H	-4.618205000	-0.835030000	2.490980000
C	-2.198778000	-0.402431000	1.403392000	C	-2.213576000	-0.260579000	1.406327000
C	-2.198786000	-0.402212000	-1.403415000	C	-2.213577000	-0.260356000	-1.406384000
H	-4.624373000	-0.997956000	-2.497654000	H	-4.618215000	-0.834632000	-2.491121000
C	-1.016113000	-0.154993000	-0.715153000	C	-1.030699000	-0.020200000	-0.715957000
C	-1.016109000	-0.155101000	0.715162000	C	-1.030700000	-0.020310000	0.715938000
H	-2.207138000	-0.371598000	-2.490488000	H	-2.222820000	-0.230074000	-2.493244000
C	1.452816000	-0.025822000	0.714807000	C	1.437062000	0.093078000	0.715781000
C	2.651138000	-0.188495000	1.404034000	C	2.631674000	-0.086895000	1.407161000
C	3.853263000	-0.394472000	0.718529000	C	3.828595000	-0.308968000	0.717552000
C	3.853258000	-0.394395000	-0.718566000	C	3.828601000	-0.308832000	-0.717605000
C	2.651130000	-0.188336000	-1.404041000	C	2.631682000	-0.086643000	-1.407183000
C	1.452814000	-0.025737000	-0.714788000	C	1.437064000	0.093199000	-0.715779000
H	5.114682000	-0.614609000	2.497829000	H	5.063792000	-0.540458000	2.491564000
H	2.653679000	-0.176645000	2.491659000	H	2.635314000	-0.076031000	2.494575000
C	5.085431000	-0.605970000	1.413293000	C	5.056357000	-0.535882000	1.405827000
C	5.085420000	-0.605823000	-1.413363000	C	5.056371000	-0.535606000	-1.405912000
H	2.653664000	-0.176361000	-2.491665000	H	2.635330000	-0.075584000	-2.494595000

C	6.229740000	-0.800792000	-0.712866000	C	6.221079000	-0.748095000	-0.720520000
C	6.229746000	-0.800863000	0.712766000	C	6.221071000	-0.748242000	0.720406000
H	5.114663000	-0.614349000	-2.497901000	H	5.063819000	-0.539966000	-2.491649000
C	0.198145000	0.269151000	-1.352928000	C	0.185586000	0.394579000	-1.355615000
C	0.198147000	0.268972000	1.352989000	C	0.185585000	0.394360000	1.355664000
N	-2.207929000	2.928614000	0.693277000	N	-2.219706000	3.036533000	0.693406000
C	-1.092312000	2.733879000	1.322003000	C	-1.103161000	2.855382000	1.323908000
C	0.154325000	2.341673000	0.716213000	C	0.146053000	2.472097000	0.715776000
C	0.154372000	2.341762000	-0.715896000	C	0.146044000	2.472213000	-0.715393000
C	-1.092210000	2.734072000	-1.321730000	C	-1.103181000	2.855597000	-1.323442000
N	-2.207875000	2.928720000	-0.693065000	N	-2.219716000	3.036648000	-0.692893000
H	-1.148958000	2.821160000	2.406937000	H	-1.159969000	2.944932000	2.408308000
H	-1.148765000	2.821516000	-2.406654000	H	-1.160007000	2.945324000	-2.407826000
H	1.072854000	2.538804000	1.258257000	H	1.064738000	2.668834000	1.257778000
H	1.072944000	2.538940000	-1.257851000	H	1.064722000	2.669040000	-1.257375000
H	0.194385000	0.353544000	-2.439085000	H	0.182237000	0.478724000	-2.441383000
H	0.194391000	0.353224000	2.439157000	H	0.182234000	0.478331000	2.441446000
F	7.399934000	-1.003338000	1.320102000	C	-6.971129000	-1.401759000	-1.440301000
F	7.399922000	-1.003207000	-1.320232000	N	-7.933426000	-1.639504000	-2.036499000
F	-6.878448000	-1.543366000	-1.319651000	C	-6.971124000	-1.401977000	1.440084000
F	-6.878440000	-1.543585000	1.319468000	N	-7.933414000	-1.639801000	2.036260000
				C	7.444633000	-0.974118000	-1.439498000
				N	8.420716000	-1.154985000	-2.033254000
				C	7.444614000	-0.974420000	1.439354000
				N	8.420686000	-1.155421000	2.033088000

TS3-ay				**TS3-by**			
E(SCF) = -2462.23737970				E(RM062X) = -2318.64851278			
C	5.334152000	0.421775000	2.071269000	C	5.340694000	0.390787000	2.110507000
C	4.416513000	-0.528324000	1.730336000	C	4.390215000	-0.535023000	1.770263000
C	3.051251000	-0.169767000	1.558502000	C	3.028566000	-0.176241000	1.577219000
C	2.667759000	1.199902000	1.737698000	C	2.655707000	1.194502000	1.739212000
C	3.653752000	2.161841000	2.106363000	C	3.660839000	2.137521000	2.102034000
C	4.954425000	1.790351000	2.272990000	C	4.964416000	1.769156000	2.287420000
H	2.398547000	-2.143029000	0.975478000	H	2.362874000	-2.147096000	0.996295000
H	4.722391000	-1.558923000	1.565461000	H	4.674936000	-1.574317000	1.620594000
C	2.086820000	-1.118300000	1.167603000	C	2.059126000	-1.118249000	1.180738000
C	1.332750000	1.564013000	1.520184000	C	1.326682000	1.576332000	1.513667000
H	3.379368000	3.202713000	2.242388000	H	3.369563000	3.178875000	2.219572000
C	0.374330000	0.607542000	1.175179000	C	0.360472000	0.626380000	1.174330000
C	0.769921000	-0.753625000	0.975020000	C	0.746817000	-0.740281000	0.978670000
H	1.040281000	2.607137000	1.620384000	H	1.045604000	2.624208000	1.598046000
C	-1.591370000	-1.396539000	0.566058000	C	-1.620060000	-1.363775000	0.572066000
C	-2.547701000	-2.388772000	0.450528000	C	-2.583580000	-2.351655000	0.471672000
C	-3.911757000	-2.111276000	0.657038000	C	-3.942270000	-2.058752000	0.685994000
C	-4.317565000	-0.764208000	0.942713000	C	-4.339467000	-0.711452000	0.962274000
C	-3.349379000	0.242578000	1.018767000	C	-3.364593000	0.292157000	1.022282000
C	-1.998352000	-0.058917000	0.862371000	C	-2.017294000	-0.019553000	0.858115000
H	-4.615348000	-4.157147000	0.362470000	H	-4.646729000	-4.086463000	0.421801000
H	-2.246560000	-3.405038000	0.206471000	H	-2.290049000	-3.372845000	0.237819000
C	-4.900961000	-3.132506000	0.577426000	C	-4.951018000	-3.062838000	0.630105000
C	-5.706267000	-0.488477000	1.137181000	C	-5.725265000	-0.437902000	1.164056000
H	-3.652111000	1.271322000	1.205702000	H	-3.660392000	1.322937000	1.208312000
C	-6.621500000	-1.490977000	1.052455000	C	-6.674457000	-1.419268000	1.103867000
C	-6.219888000	-2.840161000	0.767936000	C	-6.273934000	-2.776093000	0.828693000
H	-6.020282000	0.529884000	1.355065000	H	-6.020331000	0.588127000	1.373853000
C	-0.974181000	0.941412000	0.869998000	C	-0.983631000	0.971954000	0.863172000
C	-0.178948000	-1.577813000	0.234692000	C	-0.210619000	-1.562415000	0.250990000
N	2.001556000	0.546722000	-1.794018000	N	2.031305000	0.466433000	-1.792817000

C	1.389165000	-0.598519000	-1.745990000	C	1.369036000	-0.649940000	-1.755169000
C	-0.038879000	-0.817527000	-1.459098000	C	-0.064644000	-0.805714000	-1.469041000
C	-0.749066000	0.450141000	-1.506522000	C	-0.726477000	0.485621000	-1.512742000
C	-0.000436000	1.629263000	-1.639957000	C	0.077141000	1.632918000	-1.624688000
N	1.315481000	1.711218000	-1.695881000	N	1.393640000	1.657929000	-1.672258000
H	-0.494053000	-1.647745000	-1.998878000	H	-0.553816000	-1.627445000	-1.989975000
H	-1.821639000	0.475641000	-1.638793000	H	-1.795373000	0.559490000	-1.660446000
H	-1.280031000	1.985389000	0.945402000	H	-1.280078000	2.018793000	0.935004000
H	0.131970000	-2.608321000	0.063977000	H	0.091159000	-2.594993000	0.077790000
O	5.903625000	2.687776000	2.620189000	C	-0.553834000	2.976525000	-1.432918000
H	6.759856000	2.231236000	2.645853000	O	-0.040624000	3.945080000	-0.966062000
O	6.665375000	0.198442000	2.250539000	O	-1.898920000	2.928609000	-1.780250000
H	6.880355000	-0.721710000	2.040800000	C	-2.698138000	3.945156000	-1.333000000
O	-7.969141000	-1.354101000	1.218519000	F	-3.933358000	3.668266000	-1.720061000
H	-8.191610000	-0.430214000	1.400531000	F	-2.349064000	5.122898000	-1.820971000
O	-7.167631000	-3.798857000	0.693855000	F	-2.678506000	4.010835000	0.001080000
H	-8.030972000	-3.387600000	0.862490000	C	2.161845000	-1.904412000	-1.819458000
C	-0.688403000	2.953299000	-1.507469000	O	1.682036000	-3.006139000	-1.775977000
O	-0.190022000	4.005883000	-1.262621000	O	3.514635000	-1.679071000	-1.864332000
O	-2.067884000	2.784096000	-1.623191000	C	4.329853000	-2.759051000	-1.670806000
C	-2.864005000	3.802280000	-1.182624000	F	5.574078000	-2.310636000	-1.664475000
F	-4.119510000	3.389254000	-1.291247000	F	4.205832000	-3.667426000	-2.627639000
F	-2.715061000	4.909883000	-1.887940000	F	4.088192000	-3.346853000	-0.495799000
F	-2.623788000	4.074856000	0.102549000	C	6.778158000	-0.015220000	2.290889000
C	2.234730000	-1.815533000	-1.801208000	H	7.431166000	0.519739000	1.592093000
O	1.806418000	-2.938565000	-1.768070000	H	7.133577000	0.215933000	3.301552000
O	3.580418000	-1.531515000	-1.824792000	H	6.906113000	-1.086555000	2.121532000
C	4.437382000	-2.575163000	-1.634027000	C	6.009011000	2.787017000	2.659506000
F	5.662483000	-2.072734000	-1.600868000	H	6.494560000	2.534665000	3.609059000
F	4.370462000	-3.477405000	-2.601064000	H	6.797735000	2.843461000	1.900871000
F	4.210479000	-3.190786000	-0.467365000	H	5.565525000	3.780238000	2.759246000
				C	-8.130036000	-1.103134000	1.321306000
				H	-8.732953000	-1.382161000	0.449970000
				H	-8.533805000	-1.653418000	2.178791000
				H	-8.274671000	-0.036243000	1.505618000
				C	-7.316069000	-3.860000000	0.764544000
				H	-7.868070000	-3.937309000	1.708138000
				H	-8.053668000	-3.659678000	-0.020870000
				H	-6.858233000	-4.830414000	0.560005000
TS3-cy				**TS3-dy**			
E(SCF) = -2558.26546344				E(SCF) = -2530.29886385			
C	-5.310575000	0.373151000	-2.123028000	C	5.379757000	-0.003556000	-1.983174000
C	-4.404375000	-0.574943000	-1.768687000	C	4.376306000	0.861850000	-1.638188000
C	-3.041744000	-0.205767000	-1.572738000	C	3.047291000	0.393081000	-1.438376000
C	-2.655446000	1.164667000	-1.744140000	C	2.772810000	-1.004681000	-1.586651000
C	-3.641233000	2.126149000	-2.122356000	C	3.835040000	-1.882694000	-1.945296000
C	-4.926798000	1.732072000	-2.304767000	C	5.102703000	-1.406289000	-2.144979000
H	-2.390270000	-2.177106000	-0.987383000	H	2.237588000	2.319197000	-0.896673000
H	-4.727956000	-1.600168000	-1.622368000	H	4.593517000	1.916985000	-1.501813000
C	-2.081388000	-1.150219000	-1.170674000	C	2.016003000	1.266631000	-1.059248000
C	-1.323919000	1.535771000	-1.514448000	C	1.475931000	-1.484364000	-1.353990000
H	-3.376091000	3.169627000	-2.254432000	H	3.634204000	-2.943680000	-2.056293000
C	-0.368361000	0.582813000	-1.160292000	C	0.447870000	-0.605036000	-1.020308000
C	-0.764657000	-0.778879000	-0.966125000	C	0.730856000	0.789586000	-0.855266000
H	-1.035359000	2.580257000	-1.610632000	H	1.277681000	-2.551489000	-1.425110000
C	1.593290000	-1.421791000	-0.556403000	C	-1.676777000	1.247954000	-0.501626000
C	2.547903000	-2.420730000	-0.446605000	C	-2.709884000	2.174104000	-0.452141000
C	3.908480000	-2.141977000	-0.649907000	C	-4.034817000	1.775873000	-0.679837000

C	4.319781000	-0.794502000	-0.930092000	C	-4.328786000	0.392881000	-0.922032000
C	3.353799000	0.216337000	-0.998865000	C	-3.288092000	-0.543143000	-0.926016000
C	2.003498000	-0.082750000	-0.840684000	C	-1.971761000	-0.130195000	-0.742573000
H	4.617511000	-4.195159000	-0.363425000	H	-4.891352000	3.763993000	-0.486618000
H	2.242589000	-3.437965000	-0.212854000	H	-2.492090000	3.220490000	-0.252422000
C	4.898292000	-3.168385000	-0.573219000	C	-5.105640000	2.715598000	-0.670094000
C	5.708532000	-0.515800000	-1.123947000	C	-5.681945000	0.004500000	-1.147637000
H	3.661359000	1.243837000	-1.181794000	H	-3.508304000	-1.596880000	-1.083003000
C	6.614374000	-1.521664000	-1.039510000	C	-6.691340000	0.927897000	-1.132370000
C	6.205981000	-2.858337000	-0.761804000	C	-6.396603000	2.315857000	-0.886116000
H	6.046203000	0.492722000	-1.338239000	H	-5.910937000	-1.039994000	-1.335614000
C	0.976933000	0.919257000	-0.819629000	C	-0.866924000	-1.043604000	-0.658262000
C	0.185496000	-1.610482000	-0.252352000	C	-0.297819000	1.566744000	-0.201092000
N	-2.009096000	0.562121000	1.784169000	N	2.070005000	-0.336070000	1.936562000
C	-1.374652000	-0.569383000	1.761218000	C	1.300011000	0.705639000	1.899043000
C	0.052635000	-0.761498000	1.504485000	C	-0.131854000	0.712362000	1.631934000
C	0.747492000	0.504962000	1.473619000	C	-0.673546000	-0.620080000	1.560342000
C	-0.024336000	1.682412000	1.617309000	C	0.243225000	-1.698780000	1.733229000
N	-1.331573000	1.740093000	1.686804000	N	1.537618000	-1.592243000	1.836506000
H	0.524974000	-1.592959000	2.022181000	H	-0.714545000	1.500631000	2.099352000
H	1.816641000	0.551262000	1.627165000	H	-1.726159000	-0.798953000	1.734860000
H	1.284594000	1.962021000	-0.900193000	H	-1.087820000	-2.108809000	-0.725109000
H	-0.129858000	-2.630365000	-0.038203000	H	-0.068278000	2.607767000	0.016584000
C	0.640408000	3.020237000	1.473218000	C	6.159245000	-2.307874000	-2.514661000
O	0.116783000	4.058906000	1.223048000	N	6.998951000	-3.043116000	-2.817940000
O	2.018056000	2.874673000	1.588515000	C	6.713915000	0.493725000	-2.181193000
C	2.798093000	3.912558000	1.151598000	N	7.779989000	0.913108000	-2.340239000
F	4.058320000	3.521254000	1.263201000	C	-8.047550000	0.511176000	-1.362562000
F	2.622383000	5.012180000	1.860640000	N	-9.133685000	0.160371000	-1.549698000
F	2.551296000	4.179806000	-0.131981000	C	-7.459309000	3.283091000	-0.865378000
C	-2.203638000	-1.806088000	1.828264000	N	-8.303503000	4.073496000	-0.843302000
O	-1.747612000	-2.917444000	1.801808000	C	-0.251687000	-3.102886000	1.536254000
O	-3.545860000	-1.543140000	1.857432000	O	0.372200000	-4.014645000	1.092792000
C	-4.392446000	-2.605732000	1.679254000	O	-1.599324000	-3.173149000	1.841364000
F	-5.621029000	-2.122455000	1.663561000	C	-2.290893000	-4.272306000	1.389440000
F	-4.290075000	-3.501198000	2.648365000	F	-3.553235000	-4.100871000	1.739795000
F	-4.161417000	-3.214305000	0.511979000	F	-1.842154000	-5.398980000	1.905729000
F	7.162331000	-3.783090000	-0.695395000	F	-2.223808000	-4.344868000	0.058418000
F	7.918779000	-1.309655000	-1.209333000	C	1.973964000	2.039735000	1.957721000
F	-6.594466000	0.075719000	-2.310269000	O	1.383735000	3.083051000	1.882210000
F	-5.882690000	2.591274000	-2.655790000	O	3.330378000	1.938166000	2.033666000
				C	4.055485000	3.092998000	1.852628000
				F	5.328681000	2.761543000	1.916291000
				F	3.790137000	4.000353000	2.775508000
				F	3.807473000	3.618354000	0.649729000

TS3-az				**TS3-bz**			
E(SCF) = -1905.35901813				E(SCF) = -1761.77035201			
C	-5.252909000	-0.628726000	-2.378466000	C	-5.273783000	-0.636796000	-2.413272000
C	-4.062847000	-1.265513000	-2.215400000	C	-4.070620000	-1.255289000	-2.221556000
C	-2.912292000	-0.541155000	-1.775754000	C	-2.916775000	-0.547784000	-1.770524000
C	-3.039470000	0.863847000	-1.516997000	C	-3.035275000	0.854947000	-1.516367000
C	-4.304578000	1.495975000	-1.706312000	C	-4.301596000	1.477104000	-1.724811000
C	-5.384464000	0.777929000	-2.123530000	C	-5.392923000	0.776434000	-2.156157000
H	-1.590294000	-2.241491000	-1.746945000	H	-1.604647000	-2.257147000	-1.723418000
H	-3.977284000	-2.333236000	-2.404972000	H	-3.976465000	-2.323211000	-2.407070000
C	-1.678916000	-1.170716000	-1.575919000	C	-1.687866000	-1.185113000	-1.557321000
C	-1.925091000	1.576492000	-1.053476000	C	-1.922904000	1.568523000	-1.049400000
H	-4.419078000	2.557233000	-1.509367000	H	-4.387589000	2.543559000	-1.524937000

C	-0.699173000	0.948998000	-0.876351000	C	-0.699790000	0.936763000	-0.867775000
C	-0.565675000	-0.445822000	-1.156304000	C	-0.573980000	-0.462687000	-1.137271000
H	-2.030807000	2.631814000	-0.809930000	H	-2.024689000	2.625972000	-0.812188000
C	1.890684000	-0.254292000	-0.869055000	C	1.884244000	-0.280953000	-0.859410000
C	3.161962000	-0.778333000	-1.089939000	C	3.151727000	-0.813181000	-1.081051000
C	4.302670000	0.027951000	-0.991277000	C	4.293329000	-0.006124000	-0.999046000
C	4.151496000	1.406179000	-0.616624000	C	4.153793000	1.374531000	-0.644076000
C	2.872965000	1.916345000	-0.365637000	C	2.878542000	1.894862000	-0.390276000
C	1.742017000	1.119016000	-0.507568000	C	1.744493000	1.099387000	-0.513879000
H	5.745488000	-1.522251000	-1.534400000	H	5.706905000	-1.559737000	-1.523787000
H	3.273307000	-1.826509000	-1.361507000	H	3.257709000	-1.865527000	-1.339517000
C	5.611630000	-0.484587000	-1.245677000	C	5.604907000	-0.511194000	-1.250564000
C	5.321947000	2.220267000	-0.507618000	C	5.332928000	2.174788000	-0.558134000
H	2.761464000	2.957225000	-0.069083000	H	2.774146000	2.940239000	-0.107208000
C	6.550745000	1.692747000	-0.752583000	C	6.577347000	1.665803000	-0.799530000
C	6.707392000	0.315396000	-1.129650000	C	6.717863000	0.275525000	-1.157537000
H	5.217069000	3.265691000	-0.224935000	H	5.221597000	3.223473000	-0.289416000
C	0.407306000	1.556488000	-0.184363000	C	0.413521000	1.548093000	-0.192210000
C	0.692862000	-1.049898000	-0.825241000	C	0.682928000	-1.069789000	-0.804928000
N	-1.717352000	-1.608832000	1.663146000	N	-1.732288000	-1.570482000	1.702485000
C	-0.448601000	-1.884850000	1.532468000	C	-0.468744000	-1.867457000	1.566614000
C	0.562413000	-0.874585000	1.356053000	C	0.556957000	-0.873903000	1.379069000
C	0.180497000	0.486267000	1.609805000	C	0.195693000	0.492858000	1.624625000
C	-1.228498000	0.652611000	1.893121000	C	-1.207295000	0.683825000	1.915314000
N	-2.105791000	-0.307111000	1.820078000	N	-2.100082000	-0.262605000	1.853332000
H	1.598124000	-1.145577000	1.523143000	H	1.589471000	-1.159100000	1.542170000
H	0.871061000	1.165197000	2.096779000	H	0.900888000	1.170408000	2.091750000
H	0.285661000	2.580891000	0.161163000	H	0.299157000	2.576316000	0.144143000
H	0.790642000	-2.121234000	-0.993866000	H	0.774208000	-2.143118000	-0.963834000
O	-6.593373000	1.360655000	-2.302390000	C	-6.718372000	1.460486000	-2.361173000
H	-7.219315000	0.671701000	-2.577863000	H	-7.064861000	1.361243000	-3.396298000
O	-6.419092000	-1.217261000	-2.784554000	H	-7.495324000	1.025508000	-1.721941000
H	-6.286894000	-2.170120000	-2.886093000	H	-6.647007000	2.525892000	-2.129534000
O	7.735733000	2.370135000	-0.676324000	C	-6.475851000	-1.412883000	-2.882110000
H	7.575077000	3.287086000	-0.413294000	H	-7.294244000	-1.359255000	-2.155004000
O	7.954499000	-0.156516000	-1.362858000	H	-6.863540000	-1.020284000	-3.829237000
H	8.581017000	0.572687000	-1.228758000	H	-6.225452000	-2.465959000	-3.030098000
C	-0.072160000	-3.332486000	1.499074000	C	7.802245000	2.535389000	-0.699972000
C	1.212945000	-3.740556000	1.115499000	H	8.508889000	2.149260000	0.043493000
N	-1.013209000	-4.212622000	1.864546000	H	8.338279000	2.581581000	-1.655038000
C	1.521972000	-5.096068000	1.114971000	H	7.534167000	3.555158000	-0.414137000
H	1.964690000	-3.018411000	0.813965000	C	8.088088000	-0.288009000	-1.424796000
C	-0.704011000	-5.504211000	1.856235000	H	8.584700000	0.239986000	-2.246832000
C	0.545258000	-6.006688000	1.493287000	H	8.737645000	-0.193382000	-0.546986000
H	2.512377000	-5.430478000	0.821075000	H	8.029956000	-1.346414000	-1.689486000
H	-1.498728000	-6.182044000	2.162577000	C	-1.722961000	2.048427000	2.206033000
H	0.738068000	-7.073916000	1.510958000	C	-3.100938000	2.282392000	2.293930000
C	-1.767761000	2.007666000	2.185909000	N	-0.811016000	3.017299000	2.354889000
C	-3.150177000	2.221848000	2.253370000	C	-3.536952000	3.572991000	2.550640000
N	-0.872024000	2.988696000	2.352350000	H	-3.781602000	1.451240000	2.152560000
C	-3.608755000	3.505335000	2.505802000	C	-1.247993000	4.251563000	2.610851000
H	-3.817165000	1.382198000	2.097968000	C	-2.593529000	4.585236000	2.717984000
C	-1.330830000	4.215825000	2.605308000	H	-4.598811000	3.789613000	2.620857000
C	-2.682454000	4.530294000	2.691033000	H	-0.480012000	5.012293000	2.733307000
H	-4.674582000	3.706845000	2.557270000	H	-2.889371000	5.608433000	2.923512000
H	-0.575681000	4.986941000	2.742045000	C	-0.116622000	-3.321369000	1.541930000
H	-2.996324000	5.548799000	2.893083000	C	1.159881000	-3.754512000	1.157400000
				N	-1.071814000	-4.182079000	1.916239000
				C	1.444053000	-5.115530000	1.163595000
				H	1.923921000	-3.048055000	0.849787000
				C	-0.786640000	-5.479049000	1.913971000

C	0.452023000	-6.006170000	1.549480000
H	2.427162000	-5.469726000	0.868311000
H	-1.592878000	-6.140326000	2.226048000
H	0.625174000	-7.076666000	1.571667000

TS3-cz

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C	-5.217259000	-0.646247000	-2.415509000
C	-4.047662000	-1.301063000	-2.209324000
C	-2.896828000	-0.577215000	-1.769164000
C	-3.002153000	0.837423000	-1.553603000
C	-4.254722000	1.484582000	-1.783770000
C	-5.321271000	0.757773000	-2.201016000
H	-1.604835000	-2.297053000	-1.662885000
H	-3.997788000	-2.372331000	-2.372744000
C	-1.675954000	-1.219939000	-1.530064000
C	-1.884308000	1.549541000	-1.100042000
H	-4.362483000	2.552618000	-1.625426000
C	-0.669182000	0.909196000	-0.895134000
C	-0.557331000	-0.498021000	-1.123541000
H	-1.975337000	2.613333000	-0.890652000
C	1.897738000	-0.338823000	-0.826009000
C	3.159830000	-0.893627000	-1.020163000
C	4.310584000	-0.098087000	-0.964057000
C	4.184479000	1.300711000	-0.661782000
C	2.913990000	1.842067000	-0.432912000
C	1.772425000	1.053868000	-0.531998000
H	5.738535000	-1.695678000	-1.428520000
H	3.255248000	-1.955654000	-1.237345000
C	5.612483000	-0.643652000	-1.194806000
C	5.363532000	2.107608000	-0.599180000
H	2.819467000	2.897843000	-0.189762000
C	6.577457000	1.546589000	-0.821611000
C	6.702888000	0.159150000	-1.121777000
H	5.297166000	3.167053000	-0.374450000
C	0.446644000	1.531343000	-0.236082000
C	0.686940000	-1.111757000	-0.755827000
N	-1.794249000	-1.454949000	1.721284000
C	-0.543713000	-1.806935000	1.602253000
C	0.523741000	-0.856278000	1.410319000
C	0.209643000	0.526845000	1.623055000
C	-1.184812000	0.780571000	1.900763000
N	-2.112829000	-0.132141000	1.848670000
H	1.542310000	-1.174627000	1.597026000
H	0.939482000	1.194578000	2.065443000
H	0.343190000	2.570180000	0.068898000
H	0.766787000	-2.190441000	-0.880043000
C	-1.648064000	2.169641000	2.163073000
C	-3.015020000	2.453482000	2.267661000
N	-0.700102000	3.109033000	2.273374000
C	-3.401713000	3.764891000	2.499196000
H	-3.726940000	1.643537000	2.161590000
C	-1.089399000	4.363628000	2.505627000
C	-2.420965000	4.746569000	2.625936000
H	-4.453954000	4.020003000	2.582406000
H	-0.293916000	5.099923000	2.597982000
H	-2.677471000	5.783980000	2.811645000
C	-0.257624000	-3.275947000	1.588508000

TS3-dz

E(SCF) = -1973.43382496

C	5.343909000	0.682625000	-2.068952000
C	4.162118000	1.337488000	-1.848206000
C	2.979407000	0.623343000	-1.503140000
C	3.041476000	-0.803085000	-1.381697000
C	4.283024000	-1.460280000	-1.615907000
C	5.404934000	-0.750624000	-1.949754000
H	1.736700000	2.376176000	-1.281548000
H	4.121904000	2.419144000	-1.930380000
C	1.772190000	1.290229000	-1.257791000
C	1.896181000	-1.515577000	-1.002705000
H	4.337687000	-2.540782000	-1.522697000
C	0.695372000	-0.852192000	-0.785336000
C	0.625246000	0.570072000	-0.935466000
H	1.954608000	-2.592078000	-0.858110000
C	-1.836467000	0.461003000	-0.702064000
C	-3.075833000	1.059834000	-0.907062000
C	-4.243123000	0.287886000	-0.939090000
C	-4.161019000	-1.127565000	-0.718966000
C	-2.914736000	-1.717638000	-0.476804000
C	-1.753991000	-0.951244000	-0.486701000
H	-5.590585000	1.944495000	-1.344725000
H	-3.140078000	2.135013000	-1.057012000
C	-5.520565000	0.874070000	-1.176421000
C	-5.359172000	-1.898811000	-0.747534000
H	-2.854437000	-2.788079000	-0.295772000
C	-6.573558000	-1.310349000	-0.974558000
C	-6.656251000	0.111005000	-1.193426000
H	-5.304321000	-2.970913000	-0.584405000
C	-0.449851000	-1.481169000	-0.185586000
C	-0.609756000	1.198505000	-0.559861000
N	1.852878000	1.329927000	1.915347000
C	0.617000000	1.716534000	1.799954000
C	-0.490518000	0.820949000	1.585938000
C	-0.226891000	-0.580314000	1.735718000
C	1.160230000	-0.891322000	2.015320000
N	2.121117000	-0.013803000	2.006902000
H	-1.491950000	1.203630000	1.755031000
H	-0.981299000	-1.250140000	2.131423000
H	-0.379887000	-2.537284000	0.063714000
H	-0.655443000	2.284820000	-0.612777000
C	1.567200000	-2.308558000	2.223061000
C	2.917791000	-2.645946000	2.361896000
N	0.583009000	-3.215859000	2.249407000
C	3.249577000	-3.981268000	2.539083000
H	3.661944000	-1.858958000	2.325109000
C	0.918362000	-4.494406000	2.430207000
C	2.231097000	-4.930671000	2.578798000
H	4.288075000	-4.278965000	2.647483000
H	0.094681000	-5.204344000	2.454529000
H	2.444550000	-5.984684000	2.719291000
C	0.367349000	3.188984000	1.786516000
C	-0.471964000	3.763220000	2.742501000

C	1.020821000	-3.768893000	1.294375000	N	0.964672000	3.895030000	0.819215000
N	-1.280204000	-4.091447000	1.875935000	C	-0.678142000	5.137697000	2.710000000
C	1.235359000	-5.143015000	1.301796000	H	-0.930641000	3.142163000	3.505963000
H	1.842119000	-3.100593000	1.057534000	C	0.753249000	5.211997000	0.799168000
C	-1.061409000	-5.400929000	1.876511000	C	-0.049592000	5.882337000	1.718773000
C	0.173791000	-5.986188000	1.598124000	H	-1.312946000	5.617642000	3.448453000
H	2.219605000	-5.543930000	1.078753000	H	1.252294000	5.759718000	0.003173000
H	-1.921177000	-6.023132000	2.117138000	H	-0.176899000	6.957258000	1.652094000
H	0.291495000	-7.064186000	1.617248000	C	-7.766212000	-2.111759000	-0.991903000
F	7.703256000	2.261063000	-0.770987000	N	-8.717099000	-2.770485000	-1.001295000
F	7.935675000	-0.307777000	-1.327757000	C	-7.931619000	0.730673000	-1.427292000
F	-6.509396000	1.322002000	-2.428810000	N	-8.950821000	1.244989000	-1.614183000
F	-6.317041000	-1.281071000	-2.826629000	C	6.644220000	-1.442096000	-2.177622000
				N	7.631346000	-2.017894000	-2.357588000
				C	6.522539000	1.426916000	-2.417984000
				N	7.461579000	2.039983000	-2.702015000

Curriculum Vitae

12.2013-04.2018	Department of Chemistry, Tubingen University Major: Organic Chemistry. PhD candidate Academic supervisor: Prof. Dr. Holger Bettinger
09.2010-07.2013	Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences Major: Organic Chemistry. Master's Degree Academic supervisor: Prof. Dr. Ling Song
09.2005-07.2009	College of Chemistry and environmental Engineering, Yangtze University Major: Applied Chemistry. Bachelor's Degree

Publications

1. **Shen, B.**; Geiger, T.; Einholz, R.; Reicherter, F.; Schundelmeier, S.; Maichle-Mössmer, C.; Speiser, B.; Bettinger, H. F., Bridging the Gap between Pentacene and Perfluoropentacene: Synthesis and Characterization of 2,3,9,10-Tetrafluoropentacene in the Neutral, Cationic and Dicationic State. ***J. Org. Chem.*** 2018, 83, 3149–3158.

2. **Shen, B.**; Tatchen, J.; Sanchez-Garcia, E.; Bettinger, H. F., Evolution of the Optical Gap in the Acene Series: Undecacene. ***Angew. Chem. Int. Ed.*** Accepted

3. Franco-Cañellas, A.; Wang, Q.; Broch, K.; **Shen, B.**; Gerlach, A.; Bettinger, H. F.; Duhm, S.; Schreiber F. Resolving intramolecular-distortion changes induced by the partial fluorination of pentacene adsorbed on Cu(111). ***Phys. Rev. Materials*** 2018, 2, 044002.