MECHANISTIC STUDY OF PHOTO-BIS-DECARBONYLATION OF ALPHA-DIKETONES

Saswata Chakraborty

A Thesis

Submitted to the Graduate College of Bowling Green State University in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

August 2010

Committee:

Douglas C. Neckers, Advisor

Thomas H. Kinstle

John R. Cable

© 2010

Saswata Chakraborty

All Rights Reserved

ABSTRACT

Douglas C. Neckers, Advisor

The photo-*bis*-decarbonylation, the Strating-Zwanenberg reaction, of several α diketones has been used to synthesize polyacenes, including heptacene. An effort has been made in this thesis to study the mechanism involved in the photo-bisdecarbonylation process. A range of diketones has been studied. Among these it is believed that Bicyclo[2.2.2]octene-2,3-dione (3) goes through an alleged allylic rearrangement before the decarbonylation resulting from biradical intermediates. The allylic product is highly unstable, and may be characterized only by absorption and IR spectroscopy. Aside from 3, none of the other polyacene precursors have shown this property. 2,3,9,10-Tetrabromo-6,13-dihydro-6,13-ethanopentacene-15,16-dione (14) exhibited dimer formation upon irradiation, and trapping of the biradical of 2,3,9,10-Tetra(2-methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-dione (13) with an acrylate monomer has been shown using MALDI-TOF. Other α -diketones provided no mass spectroscopic evidence when the trapping experiments were performed, explained by the short lifetime of the biradicals produced. The observations and results discussed will give us an insight into the photo-bis-decarbonylation process.

This thesis is dedicated to my grandmother, Beetika Rani Sarkar, whom I lost last year on the 16^{th} of June, 2009.

ACKNOWLEDGMENTS

I would like to thank my advisor, Dr. Neckers, for his full support and guidance throughout my work. I would like to thank Dr. Kinstle for making himself available for help whenever needed, and I would like to thank Dr. Cable for being on my committee. I am grateful to Bowling Green State University for the financial support, and for being such a great academic institution.

I would like to thank Dmitriy Khon for being my lab mentor, Puran De and Dr. Xinchen Cai for their help with spectrometers, and all other group members for making this lab such a nice working environment. I would like to thank Leandro Estrada for donating 9,10-dihydro-9,10-ethanoanthracene-11,12-dione (**4**), and Dr. Yuewei Zhao for his help, and for providing 2,3,9,10-Tetra(2-methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**13**) and 2,3,9,10-tetrabromo-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**14**). I would like to thank Alita Frater, Nora Cassidy, and Mary Toth for making my experience at Bowling Green State University a positive one.

Finally, I would like to thank my mom (Rama Chakraborty) and dad (Subir Chakraborty), Brienna Larrick, and all of my family members and friends for their love and affection. It would not have been possible without their support.

TABLE OF CONTENTS

1. INTRODUCTION	1
1.1 Strating-Zwanenburg Reaction	2
1.2 Recent Theoretical Interpretation	4
1.3 Photochemistry of Bicyclo[2.2.2]octane-2,3dione	5
1.4 Trapping Experiment with 3 and 4	7
1.5 Trapping Experiment with 13 and 14	8
2. Results and Discussion	10
2.1 Synthetic Scheme	10
2.2 Photodecarbonylation of 3	12
2.3 Photophysics of 3	13
2.4 NMR and GC-MS Experiment for the Characteristics of the Allylic	
Rearranged Product	16
2.5 Trapping Experiment with 3	17
2.6 Trapping Experiments with 4 , 13 , 14	19
3. Conclusion	25

Page

4. Future Research	25
5. Experimental Section	27
5.1 General Remarks	27
5.2 Irradiation Experiment	27
5.3 Biradical Trapping Experiments	28
5.4 Synthetic Procedures	28
6. References	34
7. Appendix	38

LIST OF FIGURES

		Page
Figure 1.	Structures of Acenes	1
Figure 2.	Crystal structure of Graphite	1
Figure 3.	Carbon nanotubes	1
Figure 4.	α-Diketone photoprecursor of heptacene	2
Figure 5.	Compounds studied by Strating and Zwanenburg undergoing	
	Photodecarbonylation	3
Figure 6.	Bicyclo[2.2.2]octene-2,3-dione	5
Figure 7.	Absorption spectrum of 3 before and after irradiation	13
Figure 8.	Fluorescence emission of 3 before and after irradiation	14
Figure 9.	Structures of different α-Diketones used for reference studies	15
Figure 10.	NMR Spectra of Irradiated α -diketone 3 in the presence of anthracene	16
Figure 11.	Acrylates/monomers used for the trapping experiment	17
Figure 12.	MALDI-TOF of 14 with PEA monomer system after irradiation	22
Figure 13.	Formation of 1:1 and 1:2 adduct of α -dione 13 and monomer after irradiation.	23
Figure 14.	. Trapped biradical adduct with ethyl acrylate/monomer	26

LIST OF TABLES

Page

Table 1. Emission properties of several α-diketones					
Table 2.	Trapping experiment of the diketone 3 with acrylates upon irradiation	18			

LIST OF SCHEMES

Page

Scheme 1.	Preferred biradical formation of α-diketone						
Scheme 2.	Photochemistry of 3 upon irradiation						
Scheme 3.	Proposed biradical formation of 3 during photodecarbonylation						
Scheme 4.	Trapping reaction for 3 and 4 with acrylates after irradiation						
Scheme 5.	Formation of dimer from the irradiation of 14 in benzene	8					
Scheme 6.	Formation of adduct of 13 with ethyl acrylate	9					
Scheme 7.	Synthesis of Bicyclo[2.2.2]octene-2,3-dione	10					
Scheme 8.	Synthesis of 5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene						
Scheme 9.	Synthesis of 2,3,9,10-Tetra(2-methylphenyl)-6,13-dihydro-6,13-						
	ethanopentacene-15,16-dione	11					
Scheme 10.	Thermal instability of the rearranged product of 3	12					
Scheme 11.	Expected trapped adduct of biradicals (from 3) with acrylates	17					
Scheme 12.	2. Polymerization mechanism with PEA involving biradicals from 3						
Scheme 13.	α-Diketones used for the trapping experiment						
Scheme 14.	Expected 1:1 adduct of the α -diketones (4, 13, 14) with different acrylate						

		Page
Scheme 15.	Mechanism of the formation of the blue polymer by 14 with PEA	21
Scheme 16.	Biradical adduct photoformation of 13 with ethyl acrylate	24

Appendix

Appendix 1. GC-MS spectra of <i>cis</i> 2,3-Bicyclo[2.2.2]octyl carbonate	38
Appendix 2. ¹ H NMR spectra of <i>cis</i> 2,3-Bicyclo[2.2.2]octyl carbonate in CDCl ₃	38
Appendix 3. ¹ H NMR spectra of <i>cis-endo</i> -2,3-Bicyclo[2.2.2]oct-5-enediol in CDCl ₃	39
Appendix 4. GC-MS spectra of 3	39
Appendix 5. ¹ H NMR spectra of 3 in CDCl ₃	40
Appendix 6. ¹ H NMR Spectra of Anthracene in Benzene- D_6 before irradiation	40
Appendix 7 . ¹ H NMR Spectra of Anthracene with 3 in benzene- D_6 before irradiation	41
Appendix 8. ¹ H NMR Spectra of Anthracene after irradiation for 100 mins. in benzene- d_{6}	41
Appendix 9. ¹ H NMR Spectra of 1,3-Cyclohexadiene in Benzene-d ₆	42
Appendix 10. GC-MS spectra of Anthracene with 3 after irradiation	42
Appendix 11. GC-MS spectra of 3 with ethyl acrylate upon irradiation	43
Appendix 12. GC-MS spectra of 3 with hexyl acrylate upon irradiation	43
Appendix 13. MALDI-TOF spectra of 3 with Lauryl acrylate upon irradiation	44
Appendix 14. GC-MS spectra of 3 with 2-phenoxy ethyl acrylate upon irradiation	44
Appendix 15. ¹ H NMR Spectra of 14	45

Page

Page

Appendix 16	¹ H NMR Spectra of 5 in CDCl ₃	45
Appendix 17	¹ H NMR Spectra of 6 in D_2O	46
Appendix 18	¹ H NMR Spectra of 8 in CDCl ₃	46
Appendix 19	• DIP-MS spectra of 9	47
Appendix 20	• ¹ H NMR Spectra of 9 in CDCl ₃	47
Appendix 21	• DIP-MS spectra of 10	48
Appendix 22	• MALDI-TOF spectra of 2,3,9,10-tetrabromo-6,13-dihydro-6,13-	
	ethanopentacene-15,16-dione with ethyl acrylate upon irradiation	48

LIST OF ABBREVIATIONS

- CO Carbon Monoxide
- C-C Carbon- Carbon bond
- NMR- Nuclear Magnetic Resonance
- IR Infra-Red
- GC-MS Gas Chramatography- Mass Spectra
- MALDI-TOF Matrix Assisted Laser Desorption/Ionization- Time of Flight
- NaOH Sodium Hydroxide
- DMSO Dimethyl Sulfoxide
- TFAA Trifloroaceticanhydride
- CH_2Cl_2 Dichloromethane
- Et₃N Triethylamine
- p-TsOH Para Toluenesulfonic acid
- LiAlH₄ Lithiumaluminumhydride
- THF Tetrahydrofuran
- TsCl Tosylchloride
- tBuOK Potassium Tertiary Butoxide

n-Buli - n-Butyllithium

- Cs₂CO₃ Cesium Carbonate
- Pd(PPh₃)₄ Tetrakis(triphenylphosphine)Palladium(0)
- OsO₄ Osmium Tetroxide
- NMO N-methyl Morpholine
- Na₂SO₄ Sodium Sulfate
- PEA 2-Phenoxy Ethyl Acrylate
- FT-IR Fourier Transform- Infra Red
- UV- VIS Ultra Violet- Visible Spetra
- Mp Melting Point

1. Introduction

Because of their linear poly(benzenoid) structure, polyacenes, including pentacene, hexacene and heptacene, are of current interest in many electronic applications such as organic superconductors,¹ organic thin-film transistors,² and organic light emitting diodes.^{3, 4} They are also used as building blocks for making carbon⁵ and graphite nanotubes⁶ (Figures 2 and 3).



Figure 1. Structures of Acenes.⁷



Figure 2. Crystal structure of Graphite.⁵



Figure 3. Carbon nanotubes.⁶

The synthesis of higher polyacenes is a challenge because of their reactivity and poor stability.⁸ However, these compounds remain of interest because of their conductivity which increases with size (Figure 1).⁹ The synthesis of heptacene and octacene was reported by E. Clar in 1942,¹⁰ but this report was later withdrawn.¹¹ Similarly Marschalk¹² and Bailey¹³ failed in approaches to heptacene. It was not until later, in 2006, that the synthesis of unsubstituted heptacene was reported by using the Strating–Zwanenburg reaction.¹⁵ Pentacene¹⁶ and hexacene,¹⁷ have also been recently synthesized using the Strating-Zwanenburg reaction, which is a very clean reaction, of α -diketones for the formation of compounds like polyacenes.



Figure 4. α -Diketone photoprecursor of heptacene.¹⁴

1.1 Strating-Zwanenburg Reaction

The photodecarbonylation of aromatic diones was first reported by Strating and Zwanenburg¹⁵ in 1969. The Strating-Zwanenburg reaction reports that α -diketones, upon irradiation at 395 nm, undergo photodecarbonylation to give aromatic compounds. All four α -diketones discussed (Figure 5), when irradiated with 395 nm light in benzene, undergo clean photodecarbonylation to give their corresponding acenes,¹⁵ along with the evolution of carbon monoxide. However, it has also been observed that camphorquinone, which also has an α -diketone functionalization, does not undergo any transformations under similar conditions.¹⁸

This transformation involved the extrusion of C₂O₂ and/or 2 CO molecules, according to mass spectra reported by Strating and Zwanenburg.



Figure 5. α-Diketones studied by Strating and Zwanenburg.¹³

The mechanism of the decarbonylation has yet to be resolved. This photoprocess may generate the dimer of carbon monoxide in a concerted fashion, or two molecules of CO in a stepwise process.¹⁵ Whatever the reaction mechanism , the reaction has worked efficiently for the photo*bis*-decarbonylation of several α -diketones.

1.2 Recent Theoretical Interpretation

A recent computational study¹⁹ has given some insight into the pathway's mechanism for the mechanism. In the process, homolytic cleavage of a C-C bond resulting in the formation of biradicals was suggested to occur prior to the photodecarbonylation in an excited state of the diketone. Further theoretical calculations²⁰ showed that the homolytic cleavage of the C-C bond between the methylene carbon and carbonyl carbon, resulting in biradicals, was energetically more favorable than the homolysis of carbonyl-carbonyl bond as shown in Scheme 1. This suggests that the process does not expel the dimer of CO in a concerted way; a stepwise mechanism via a biradical is instead proposed. Moreover, low temperature matrix isolation analysis also suggests that the loss of C_2O_2 is not favored.²¹ However, no concrete evidence was found in these studies for the formed biradical. To explore the mechanism of the



Scheme 1. Preferred biradical formation of α -diketone.²⁰

reaction, we have considered the behaviors of the following α -diketones:

1.3 Photochemistry of Bicyclo[2.2.2]octene-2,3-dione (3)²²



Figure 6. Bicyclo[2.2.2]octene-2,3-dione.

The photochemistry of **3** (Figure 6) was first studied by the group of Rubin.²² The diketone undergoes a competitive alleged allylic rearrangement through the excited singlet manifold before photodecarbonylation, in addition to the formation of a biradical via triplet manifold (Scheme 2).



Scheme 2. Photochemistry of 3 upon irradiation at 425 nm.²²

The rearranged product was too unstable for characterization and no NMR spectra were reported.²³ Absorption and IR spectra^{23a} of **3** were the only reported evidences for the formation of the alleged rearranged product.^{22,24} Attempts have been made to characterize the isomer in the presence of a triplet quencher such as anthracene through ¹H NMR and GC-MS spectroscopy.



Scheme 3. Proposed biradical formation of 3 during photodecarbonylation.²²

The mechanism of photodecarbonylation is proposed to occur through biradical formation (Scheme 3). Biradical **2** was proposed to be energetically more favorable than **1** though the literature does not have any evidence for the formation of biradicals.^{21, 25}

The biradicals formed during the decarbonylation process should be quite reactive. Since radicals are well known to initiate acrylate polymerization²⁶ we tried to detect the existence of the biradicals, using acrylate monomers as scavengers.²⁷

1.4 Trapping Experiment with Bicyclo[2.2.2]octene-2,3-dione (3), and 9,10-Dihydro-9,10ethanoanthracene-11,12-dione (4)^{19,28}



Scheme 4. Trapping reaction for 3 and 4 with acrylates after irradiating at 395 nm.

Compounds **3** and **4** showed no evidence of biradical formation in that no monomer adduct was formed when the compounds were immersed in acrylate monomer and irradiated at 395 nm. The

lifetime of the formed biradical must be too short, so only the corresponding decarbonylated products are formed.





Dimer observed in MALDI-TOF

Scheme 5. Formation of dimer from the irradiation of 14 in benzene.³⁰

Irradiating a sample of **14** and acrylate at 395 nm resulted in a blue polymer,³⁰ the formation of which was attributed to the previously reported photochemistry of tetrabromopentacedione.³⁰ Formation of the tribromopentacene radical from tetrabromopentacene led to the formation of the dimer of the substituted pentacene (Scheme 5) detected in MALDI-TOF.³⁰

When **13** was immersed in ethyl acrylate (Scheme 6) and irradiated, evidence of biradical formation from the dione was observed in the MALDI-TOF spectra. This trapping of the biradical from **13**, gives insight into the lifetime of the biradicals generated during the photoprocess.²⁷



Scheme 6. Formation of adduct of 13 with ethyl acrylate.²⁷

This trapping experiment, as well as the possible existence of biradicals, compelled us to look into the mechanism in detail.

2 Results and Discussion

2.1 Synthetic Scheme

Scheme 7. Bicyclo[2.2.2]octene-2,3-dione³²⁻³⁵



Reagents and conditions: (i) Benzene, 180°C; (ii) NaOH, Dioxane, reflux 1hour; (iii) dry DMSO, dry TFAA; dry CH₂Cl₂, Et₃N.

Scheme 8. 5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene³⁶⁻³⁸



Reagents and conditions: (i) n—Butanol, p-TsOH, Toluene, reflux 22 hours; (ii) LiAlH₄, dry THF; (iii) Pyridine, TsCl; (iv) DMSO, tBuOK.

Scheme 9. 2,3,9,10-Tetra(2-methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16dione^{29,39-42}



Reagents and conditions: (i) n-BuLi, Toluene, -50 to -60°C; (ii) Chloranil, refluxing Toluene, 2 hours; (iii) O-Tolylboronicacid, Cs_2CO_3 , Pd(PPh₃)₄ (catalyst); (iv) OsO₄, NMO, Na₂SO₄; (v) Swern Oxidation, TFAA, -70°C.

Bicyclo[2.2.2]oct-5-ene-2,3-dione (**3**) was synthesized according to Scheme 7,³²⁻³⁵ and 5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene (**8**) (pentaene) using Scheme 8.³⁶⁻³⁸ 2,3,9,10-Tetra(2methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-dione $(13)^{20,39-42}$ was prepared using Scheme 9. A Diels-Alder reaction followed by basic hydrolysis and Swern oxidation³⁴ was effected (Scheme 7). **13** was synthesized with lithiation,³⁹ aromatization⁴⁰ followed by Suzuki coupling,^{41,42} hydroxylation, and Swern oxidation³⁴ steps. Each α -diketone was found highly sensitive to light, and needed protection from light both during and after synthesis.

2.2 Photodecarbonylation of 3

3, upon initial irradiation at 425 nm was observed to undergo a competition between allylic rearrangement and photodecarbonylation (Scheme 2).²²



Scheme 10. Thermal instability of the rearranged product of 3.²³

The allylic rearranged product, being highly sensitive to moisture and air,²³ (Scheme 10) could not be isolated. The assignment of the structure of the alleged allylic rearranged product on the basis of the absorption spectra ²² is described below.

2.3 Photophysics of 3.

In benzene, **3** was observed to absorb at 454 nm (\mathcal{E} =110) (Figure 8) resulting from its (n, π^*) transition. However, with passage of time, the absorption intensity decreased, and a small peak was observed in the spectrum in the range of 513 nm.



Figure 7. Absorption spectrum of **3** (10^{-2} M) in benzene in the absence of anthracene (left) and presence of anthracene (10^{-2} M) (right) upon irradiation at 425 nm.

In the presence of anthracene (triplet quencher) (Figure 7), there was simultaneous increase in intensity in the peak at 513 nm and a decrease of the 453 nm peak upon irradiation, suggesting photochemical formation of the rearranged dione from 3^{22} . The isobestic point in the absorption spectra and gradual increase in the 513 nm peak suggest formation of the allylic rearrangement

product through a singlet excited state. However, the photodecarbonylation product was formed via the triplet manifold. Hence, anthracene quenched bisdecarbonylation, which proceeds from a quenchable triplet state, but not rearrangement, which is an excited singlet state reaction.²²



Figure 8. Fluorescence emission of **3** (10^{-2} M) in toluene before irradiation (left) and after irradiation (right).

Fluorescence spectrum of compound **3** in toluene (Figure 8) exhibited the emission at 500 nm before irradiation. However, after irradiation of 1 hour there was complete quenching of the fluorescence at 500 nm. The lifetime of fluorescence ($\tau_{f (500 \text{ nm})}$) at 500 nm was 4.2 ns (singlet manifold) and the quantum yield of fluorescence (ϕ_f) was 0.21. The large difference between the absorption maxima and fluorescence, and a high fluorescence intensity for the α -diketone **3** were unexpected. The nature of the emission properties of the α -diketone compared with that of other diketones (Figure 9) is shown in Table 1. However, the appearance of the 400 nm peak in the emission spectrum was not interpreted. There was no phosphorescence observed for the α -diketone at 77k.⁴³



Compound	Solvent	UV abs	λ_{fluo}	T fluo	Φ_{fluo}	λ_{phos}	Tphos	$\Phi_{ m phos}$
		(nm)	(nm)	(ns)		(nm)		
1-Phenyl-1,2- propanedione ⁴⁴	Acetonitrile	391	482	2.6	0.0013	530	4900 ns	Not reported
Benzil ⁴⁵	Acetonitrile	378	502	2.2	0.0025	560	450 ns	Not reported
Camphorquinone ^{46,4}	Methyl Cyclohexane	483	497, 518	17.4	0.0032	561, 591, 620	190 µs	0.00265
Pivalil ^{47,48}	Not reported	370	485, 515	Not reported	Not reported	550	Not reported	Not reported
Biacteyl ^{47,49,50}	Cyclohexane (for emission)	422	460	21	0.0025	510	1800 s	0.82

Table 1. Emission properties of several α -diketones

2.4 NMR and GC-MS experiment for the characterization of the allylic rearranged product

The allylic product formed upon rearrangement of **3** was highly unstable. The ¹H NMR spectra (Figure 10) upon irradiating the diketone in benzene- d_6 in the NMR tube at 425 nm for 100 minutes are shown below.



Figure 10. Irradiation of the α -diketone 3 at 425 nm in the presence of anthracene for 100 minutes.

The ¹H NMR spectra did not correspond to the allylic rearranged product. No evidence in the ¹H NMR was seen for the diketone without anthracene upon irradiation. The ¹H NMR spectra for the control experiments may be viewed in the appendix. The GC-MS spectra for **3** upon irradiation at 425 nm also did not give any evidence of the rearranged product (spectra is given in the appendix).

This shows that the alleged allylic rearranged product was highly unstable to light and air, and was not stable enough to characterize through ¹H NMR and GC-MS spectroscopy. We next attempted to trap the proposed biradical during the photodecarbonylation process (Strating-Zwanenburg reaction) to detect the presence of biradicals, discussed below.

2.5 Trapping experiment with 3

The trapping of the proposed biradical (Scheme 11) from **3** was attempted using several acrylate monomers (1:200 ratio of the α -diketone to the monomers, see experimental section) upon irradiation at 395 nm light using Scheme 11. Several acrylates (Figure 11), namely methyl acrylate, hexyl acrylate, lauryl acrylate, and 2-phenoxy ethyl acrylate, were used.²⁷







Figure 11. Acrylates/monomers used for the trapping experiment.

Characterization was attempted using ¹H NMR spectroscopy and MALDI-TOF of the irradiated sample at different time intervals (see attached spectra's in the appendix) to detect any presence of the biradical-monomer adduct. Table 2 shows the results upon irradiating the sample with the acrylates at 395 nm.

Compound	Monomer	Irradiation wavelength	Result
α-Diketone	Methyl acrylate (MA)	395 nm	No polymerization or formation of any adduct with the diketone
α-Diketone	Hexyl acrylate (HA)	395 nm	The solution became viscous but no adduct was observed in the mass spectra and NMR spectra
α-Diketone	Lauryl acrylate (LA)	395 nm	No evidence of any adduct in the mass and NMR spectra
α-Diketone	2-phenoxy ethyl acrylate (PEA)	395 nm	Rapid polymerization into solid elastic polymer but no such evidence of any adduct in the mass and NMR spectra

Table 2. Trapping experiment of the diketone 3 with acrylates upon irradiation at 395 nm

Upon irradiating the sample, there was rapid polymerization observed for PEA and hexyl acrylate (Scheme 12), however neither gave information about the trapped biradical in the mass spectra or by ¹H NMR spectroscopy. Control experiments were carried out with the acrylates, but no polymerization was observed. This led to the conclusion that the biradical is highly unstable and has an extremely short lifetime making it difficult to be detected by acrylate

traaping experiments. However, the α -diketone **3** was observed to be an initiator for radical polymerization of the several acrylates without the addition of coinitiator.



Scheme 12. Polymerization mechanism with PEA involving biradicals from 3.

2.6 Trapping experiments with 4, 13, 14



Scheme 13. α -Diketones used for the trapping experiment.^{19,27}

α-Diketones 9,10-Dihydro-9,10-ethanoanthracene-11,12-dione (**4**), 2,3,9,10-Tetra(2methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**13**), and 2,3,9,10-Tetrabromo6,13-dihydro-6,13-ethanopentacene-15,16-dione (**14**) were subjected to the trapping experiment with acrylates (Scheme13). The above diketones, upon irradiation at 395 nm, should form different adducts with different acrylates (Scheme14), which on analysis should correspond to the formation of corresponding biradicals.²⁷



Scheme 14. Expected 1:1 adduct of the α -diketones (4, 13, 14) with different acrylates.

Upon irradiation at 395 nm, 4 in the presence of acrylate monomer, showed no change other than formation of anthracene. 4 did not initiate photopolymerization. However, in presence of the coinitiator 2,6-diidopropyl-N,N,dimethylaniline (Norrish type II initiator),^{51, 52} polymerization was observed.27



However, **13** and **14** under similar conditions showed formation of something other than the formation of the corresponding polyacene (pentacene derivative). **14** with a PEA monomer system gave a blue polymer upon irradiation for 20 minutes.²⁷

Careful analysis of the MALDI-TOF of the mixture and a control experiment with the dione revealed the blue color was because of the pentacene derivative, and the polymerization resulted from formation of 2,3,9-tribromopentacene radical⁵² from the photochemistry of **14** (Scheme 15).³⁰ The molecular mass observed of 1028 (Figure 12) in MALDI-TOF suggests the formation of the dimer of the bromopentacene derivative, formed from tribromopentacene radical.



Figure 12. MALDI-TOF of 14 with PEA monomer system after 20 minutes of irradiation at 395 nm.³⁰

The most interesting observation was with dione **13**, when it was irradiated with ethyl acrylate in benzene at 395 nm light for about 20 minutes. The MALDI-TOF spectra (Figure 13) revealed formation of 1:1 and 1:2 adducts of the dione and acrylate.²⁷ The spectra also showed peaks for **13**, the decarbonylated pentacene adduct (Scheme 16). This was the first experimental evidence of formation of biradical during photodecarbonylation reaction.²⁷



Figure 13. Formation of 1:1 and 1:2 adduct of α -dione 13 and monomer after irradiation.²⁷

The biradical lived long enough to be detected by instrumental technique (MALDI-TOF). There exists a competition between the intramolecular photobisdecarbonylation reaction of the α -diketone to give the polyacene and the intermolecular reaction between the diketone and reaction



Scheme 16. Biradical adduct photoformation of 13 with ethyl acrylate.²³

with the monomer. As diffusion–controlled rate constants in benzene are moderate $(10^{10} \text{ L mol-} 1 \text{ s-}1)^{53}$, the biradical with the longer lifetime will react with the monomer rather than undergoing decarbonylation. The longer lifetime of the biradical from **13** was attributed to the better delocalization of the biradical. Additionally, biradicals with shorter lifetimes will undergo photodecarbonylation faster than they will react with acrylates. This was observed in the other α -diketones **3** and **4**.

3. Conclusion

Compound **3**, when irradiated, showed an absorption maxima at 453nm because of (n, π^*) transition. Formation of the alleged allylic rearranged product has been observed in the absorption spectra. However, it was not characterized because of its instability. Irradiation of **13** with ethyl acrylate has shown evidence of the formation of biradical adduct in MALDI-TOF. This was the first experimental proof for the formation of the proposed biradical formation during Strating-Zwanenburg reaction. However, it was not characterized using ¹H NMR. No such adducts were observed with other α -diketones, indicating a very short biradical lifetime.

4. Future Research

Diketone **13**, has shown evidence in the MALDI-TOF spectrum for the formation of the biradical-acrylate adduct (Figure 14).²⁷



Figure 14. Trapped biradical adduct with ethyl acrylate/monomer.

Additional research is going on for further characterization of the biradical adduct. More of **13** is being synthesized, and further trapping experiments are to be done for additional characterization.

5. Experimental Section

5.1 General Remarks

Solvents, standard grade silica gel, and chemicals were used as received. Anhydrous solvents were obtained from Manual Solvent Purification System, and other organic solvents were spectroscopic grade. Air-sensitive reactions were carried out in Ar-atmosphere.

All melting points were obtained using a Mel-Temp apparatus and were recorded in degrees Celsius. Mass spectra were obtained using GC-MS-QP5050A, equipped with a DIP (direct ionization probe, 70 ev) and MALDI-TOF mass spectra were measured by Bruker Daltronics Omniflex Spectrometer with N₂ laser. ¹H NMR spectra were recorded on Bruker 300 NMR and 500 NMR instruments working at frequencies of 300 MHz and 500 MHz respectively with TMS as a standard. FT-IR data were obtained from an ATR (Attenuated Total Reflectance) spectrometer. The irradiation experiments were carried out using a 395 nm (±25 nm) UV-LED lamp. UV- VIS absorption data were obtained from Shimadzu UV-2401. Absorption spectrophotometer and fluorescence emission and lifetime data were obtained using Spex Fluorolog-3 Spectrometer. Fluorescence quantum yields (Φ_{fluo}) were measured in toluene with DPA in toluene with a quantum yield of 1 as the reference.⁵⁴ All measurements were executed with a degassed sample at room temperature (22 ± 3^{0} C) unless otherwise specified.

5.2 Irradiation Experiment

Two different sets of solutions of the compound **3** (10^{-2} M) were made in toluene and benzene and put in sealed tubes, degassed with Argon gas, and protected from light. Pure anthacene (10^{-2} M) was added to one tube. An additional solution of **3** was prepared in an NMR tube (benzened₆) for NMR measurements and simultaneous irridiation. All three solutions were irradiated with light from a xenon lamp using 425 nm cut off filter. During frequent time intervals the absorbance was measured using a Shimadzu Absorption spectrophotometer. A control experiment was carried out with just anthracene to compare with the results.

5.3 Biradical Trapping Experiments

 α -Diketone (1mg) and 200 equiv. monomer (ethyl, hexyl, lauryl or 2-phenoxy ethyl acrylate) were added into a UV-cuvette containing 3 mL of benzene. The cuvette was sealed and degassed with argon. Then irradiation was carried out using 395 nm LED and the UV-VIS spectrum was monitored. Finally, the MALDI-TOF spectrum was taken to look for products. An NMR tube with **13** and ethyl acrylate in benzene-d₆ was also irradiated to track the NMR spectra of the biradical- monomer adduct.

5.4 Synthetic Procedures

cis-2,3-Bicyclo[2.2.2]octyl carbonate (1). A mixture of vinylene carbonate (3 g, 37.5 mmol) and 1,3-dicyclohexadiene (3 g, 35 mmol) in 20 ml of benzene was sealed in an autoclave and heated for 12 hrs at 180°C. The autoclave was cooled and opened. Evaporation of the solvent using a rotary evaporator gave 5 g of a paste-like residue. Recrystallization from benzene gave 2.2 g (44%) of white crystals of **1**. Mp 142-143 °C (Ref. Mp 143- 144 °C);^{32 1}H NMR, 300 MHz (CDCl₃): δ 1.5 (m, 4H), 3.02 (broad s, 2H), 4.7 (s, 2H,), 6.32 (t, 2H); Mass spectrum (GC-MS) *m/z* M⁺ 166 (100).

cis-endo-2,3-Bicyclo[2.2.2]oct-5-enediol (2). A solution of **1** (2 g, 12.04 mmol) and 4 M NaOH (50 mL) in 1,4-dioxane was refluxed for 1 hour. The reaction flask was cooled to room temperature, and the resulting solution extracted with CHCl₃. The combined organic layers were washed thoroughly with water and then Na₂SO₄. The solvent upon evaporation using rotary

evaporation gave 1.2 g (60%) of light yellow crystals of **2**. Mp: 204-205 °C (Ref. Mp 205- 206 °C);³³ ¹H NMR 300 MHz, (CDCl₃): δ 1.25 (m, 2H,), 1.45 (m, 2H), 2.35 (broad, 2H), 2.85 (broad, 2H), 3.95 (s, 2H), 6.35 (m, 2H).

Bicyclo[2.2.2]oct-5-ene-2,3-dione (3). Trifluoroacetic anhydride (5.4 g, 25.71 mmol) was added to a stirred solution of DMSO (2.3 g, 30 mmol) and dichloromethane (40 mL), very slowly at -78°C. The mixture was stirred for about 10 minutes after which a solution (10 mL of dichloromethane) of 2 (1.2 g, 8.57 mmol) was added slowly at the reduced temperature. The resulting solution was stirred for 2 hrs under argon atomsphere after which triethylamine (5.2 g, 51.42 mmol) was added slowly, and stirred for 2 more hours. The solution was warmed to room temperature, and extracted with dichloromethane, followed by washing the organic phase several times with water, dried with Na₂SO₄, and filtered. The solvent upon evaporation using rotary evaporator gave deep yellow color liquid. The crude product was purified using column choromatography (silica gel, ethyl acetate) to obtain 350 mg (30%) of bright yellow **3**. Further recrystallization from hexane gave 200 mg of pure **3** was: Mp 75-77 °C (Ref. Mp 81 °C);^{35 1}H NMR (300 MHz, CDCl₃): δ 1.87 (dm, 2H), 2.06 (dm, 2H), 3.50 (m, 2H), 6.5 (dd, 2 H); Mass spectrum (GC-MS) *m/z* M+ 136 (25), 80 (93) [M⁺-2CO], 79 (100) [C₆H₇], 51 (28) [C₄H₃].

Bicyclo[2.2.2]oct-2-ene-5,6,7,8-tetracarboxylic acid, tetrabutyl ester (5). p-Toluenesulfonic acid (0.25 g, 1.45 mmol) was added to a stirred solution of Bicyclo[2.2.2]oct-7-ene-2,3,5,6-tetracarboxylic-2,3,5,6-dianhydride (25 g, 0.1mol) and n-butanol (50mL) (0.68 moles) in toluene (150 mL). The reaction mixture was heated under reflux for 22 hours with azeotropic removal of water in a dean-stark apparatus. After cooling to room temperature, a solution (5 mL of butanol) sodium hydride (0.4 g, 0.01 mol) was added and heated at 125-130°C for 6 hours. After cooling, additional sodium hydride (0.1 g, 4.1 mmol) was added followed by heating for 2 more hours.

The mixture was cooled to room temperature and the solvent upon evaporation with rotary evaporator gave 50 g (98%) liquid residue of **5** which was used as such for the next step. ¹H NMR (300 MHz, CDCl₃): δ 0.8-1.7 (m, 28H), 3.0 (s, 4H), 3.35 (bs, 2H), 4.0 (m, 8H), 6.4 (bs, 2H). The ¹H NMR was in agreement with the literature values.^{36,37}

5,6,7,8-Tetra(hydroxymethyl)-bicyclo[2.2.2]oct-2-ene (6). To a stirring solution of LiAlH₄ (15 g, 0.4 mol) in THF (400 mL), **5** (50 g, 0.1 moles) was added slowly over a period of 5 hours under argon atmosphere. After forming a thick suspension towards the end, the reaction was stirred for 30 minutes, and cooled to room temperature. Then the solution was quenched very slowly with a solution (30 mL water). The suspension was filtered and the solids were washed with THF, treated with methanol (200 mL) and boiled, followed by hot-filtration. The filtrate was neutralized with hydrochloric acid followed by filtration to get rid of the inorganic salt. On further rotary evaporation and filtration gave 18.5 g (83 %) of tetrol (6). Mp 154-155 °C. (Ref. Mp 155-156 °C); ³⁶ ¹H NMR (300 MHz, CDCl₃): δ 2.08 (m, 4H), 2.67 (bs, 2H), 3.35 (m, 4H), 3.5 (m, 4H), 6.2 (bs, 2H).

5,6,7,8-Tetra(**tosylmethyl**)-**bicyclo**[**2.2.2**]**oct-2-ene** (**7**). A solution of **6** (5.3 g, 0.023 moles) and tosyl chloride (22.1 g, 0.11 moles) in anhydrous pyridine (170 mL) was stirred for 5 hours at 0° C under argon atmosphere. After warming to room temperature, the mixture was extracted with (2 x 60 mL) dichloromethane. The organic layer was washed repeatedly with water, dried with Na₂SO₄ and filtered. The solvent, upon evaporation, gave 9 g of a solidifying oil of crude tosylate (**7**). The crude tosylate was used for the next step.

5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene (8). To a stirred solution of **7** (9 g, 10.7 mmoles) in DMSO (40 mL), potassium tertiary butoxide (4.8 g, 43 mmoles) at 0°C was added. It was

warmed to room temperature and stirred for 2 hours. The reaction mixture was quenched with crushed ice and extracted with hexane (2x 50mL). The organic layer was washed repeatedly with water, dried with magnesium sulfate, and filtered. Rotary evaporation and further recrystallization from pentane gave 320 mg (20 %) of white crystals of Pentaene, **8**. Mp 97-98 ^oC; ¹H NMR (300 MHz, CDCl₃): δ 3.85 (dd, 2H), 4.95 (s, 4H), 5.15 (s, 4H), 6.4 (dd, 2H). The ¹H NMR was in agreement with the literature values.³⁷

2,3,9,10-Tetrabromo-5,6,7,12,13,14-hexahydro-6,13-ethenopentacene (**9**). n-BuLi (1.6M in Hexane) (1.8 mL, 2.88 mmol) was added dropwise in an argon atmosphere to a stirred solution of **8** (0.150 g, 1 mmol) and tetrabromobenzene (0.980 g, 2.48 mmol) in dry toluene (60 mL) at -50 to -60°C. The reaction mixture was stirred for 6 hours and slowly warmed to room temperature by stirring for another hour. Methanol (5 mol) was added to quench the excess BuLi, the solvent was evaporated, and the crude solid was purified using silica gel column chromaography. Elution starting with hexane and ending with 20% DCM in hexane gave 180 mg (34 %) of white **9**. Mp 294-296 °C (Ref. Mp 295-296 °C);^{29 1}H NMR (300 MHz, CDCl₃): δ 3.5 (s, 8H), 4.3 (m, 2H), 6.8 (m, 2H), 7.4 (s, 4H); Mass spectrum (DIP-MS) *m/z*M+ 624 (40), 544 (10), 384 (8), 151 (100).

2,3,9,10-Tetrabromo-6,13-dihydro-6,13-ethenopentacene (10). A mixture of **9** (0.180 mg, 0.30 mmoles) and chloranil (0.15 mg, 0.6 mmoles) in dry toluene (30 mL) was refluxed under argon atmosphere for 2 hours. It was cooled to room temperature and the solvent was evaporated. The solid mixture was dissolved in DCM (50 mL) and extracted with (2x 10 mL) of 2N NaOH followed by 10 ml of brine. The organic layer was dried with MgSO₄, filtered, and the solvent was evaporated using rotary evaporator to yield 140 mg (74 %) of **10**.²⁹ The crude product obtained was used directly for the next step.

2,3,9,10-Tetra(**2-methylphenyl**)-**6,13-dihydro-6,13-ethenopentacene** (**11**). Pd(PPh₃)₄ (0.20 g, 0.017 mmol) was introduced to a stirred solution of **10** (0.320 g, 0.5 mmol), o-tolylboronic acid (0.408 g, 3 mmol) and Cs₂CO₃ (1.30 g, 4 mmol) in the degassed mixture of toluene (40 mL) and water (20 mL). After 48 hours of reflux under argon atmosphere, the reaction mixture was cooled to room temperature. The solvent was evaporated and the mixture was applied to silica gel column chromatography. The column was eluted starting with hexane and ending with 20 % DCM in hexane. Evaporation of the solvent gave 166 mg (50 %) of **11**. (Ref.Mp 214-216 °C);²⁹ ¹H NMR (300 MHz, CDCl₃): δ 2.889 and 2.969 (s, 12H), 5.387 (m, 2H), 6.978 and 7.069 (18H), 7.653 (s, 3H), 7.774 (s, 3H), 8.036 (s, 2H); Mass spectrum (DIP-MS) *m/z*M+ 664 (100), 574 (40), 332 (40).

2,3,9,10-Tetra(2-methylphenyl)-6,13-dihydro-6,13-ethanopentacene-15,16-diol (12).

Osmium tetroxide [1 mL solution of 2.5 % (w)] in tert-butyl alcohol was added to 100 mL of a mixed solution of acetone and water (1:5 in volume) containing 4- methylmorpholine N-oxide (0.250 g, 2.14 mmol). After 10 minutes of stirring, an acetone solution containing **11** (0.5 mmol) was added and a suitable amount of acetone added to make the solution transparent. The reaction mixture was then stirred at room temperature for 48 hours. Sodium dithionite (0.400 g) was added to this reaction mixture, and it was stirred for another 20 minutes to yield a heterogenous solution. The suspension in the mixture was removed by filtering it through a pad of cerite and washing the pad with acetone. The solvent was evaporated, and the residue was applied to silica gel column choromatography. Elution of the column was started with heaxane and ended with 35 % of ethyl acetate in hexane. Removal of solvent gave 82% of pure **12** as a pale vellow white solid. (Ref Mp 235-237 °C);²⁹ ¹H NMR (300 MHz, CDCl₃): δ 1.997-2.264

(m, 14H), 4.270 (b, 2H), 4.704 (s, 2H), 6.987-7.283 (m, 16H), 7.728 -7.886 (m, 8H); Mass spectrum (DIP-MS) *m/z* (M+ -C2H4O2) 638 (100), 548 (75); MALDI-TOF 721 (M+ + Na).

2,3,9,10-Tetra(**2-methylphenyl**)-**6,13-dihydro-6,13-ethanopentacene-15,16-dione** (**13**). Under argon atmosphere, trifluoroacetic acid anhydride (4.5 g, 21.42 mmol) was added dropwise to a stirred solution of dimethyl sulfoxide (1.32 g, 16.9 mmol) in DCM (30 mL) at -50 to -60°C. After 15 minutes, a solution (1.2 mL of dry DMSO in 15 mL of DCM) of **12** (0.150 g, 0.29 mmol) was added very slowly. The resulting mixture was stirred for 2 hours after which 2 mL of diisopropylethylamine was introduced dropwise, and this reaction mixture was stirred for another 2 hours. The mixture was maintained at reduced temperaturs under argon after which the solution was warmed to room temperature and extracted with DCM followed by washing the organic layer with water thoroughly. Evaporation of the solvent provided crude dione. Purification with silica gel column choromatography gave 54 % of yellow **13**.²⁹ ¹H NMR (300 MHz, CDCl₃): δ 1.982 (m, 12H), 5.313 (s, 2H), 6.949 and 7.022 (16H), 7.738 (s, 4H), 7.942 (s, 4H); Mass spectrum (DIP-MS) *m/z* (M+ -C₂O₂) 639 (25), 548 (20).

6. References

- 1. Schon, J. H.; Kloc, C.; Batlogg, B. Nature 2000, 406, 702.
- 2. Dimitrakopoulos, C. D.; Malenfant, P. R. L. Adv. Mater. 2002, 14, 99.
- (a) Clar, E. Polycyclic Hydrocarbons; Academic Press: London and New York, 1964;
 Vols. 1 and 2. (b) Harvey, R. G. Polycyclic Aromatic Hydrocarbons; Wiley-VCH: New York, 1997.
- 4. Wolak, M. A.; Jang, B. B.; Palilis, L. C.; Kafafi, Z. H. J. Phys. Chem. B 2004, 108, 5492.
- 5. Chung, D. D. L. J. Mater. Sci. 2002, 37, 1475.
- 6. Iijima, S.; Ichihashi, T. Nature 1993, 363, 603.
- 7. Anthony, J. E. Angew. Chem., Int. Ed. 2008, 47, 452.
- 8. Allen, C. F. H.; Bell, A. J. Am. Chem. Soc. 1942, 64, 1253.
- 9. Yasuda, T.; Goto, T.; Fujita, K.; Tsutsui, T. Appl. Phys. Lett. 2004, 85, 2098.
- 10. Clar, E. Ber. Dtsch. Chem. Ges. 1942, 75B, 1330.
- 11. Boggiano, B.; Clar, E. J. Chem. Soc. 1957, 2681.
- 12. Marschalk, C. Bull. Soc. Chim. 1943, 10, 511.
- 13. Bailey, W. J.; Liao, C. W. J. Am. Chem. Soc. 1955, 77, 992.
- 14. Mondal, R.; Shah B. K.; Neckers D. C. J. Am. Chem. Soc. 2006, 128, 9612.
- 15. Strating, J.; Zwanenburg, B.; Wagenaar, A.; Udding, A. C. *Tetrahedron Lett.* **1969**, *3*, 125.
- Yamada, H.; Yamashita, Y.; Kikuchi, M.; Watanabe, H.; Okujima, T.; Uno, H.; Ogawa, T.; Ohara, K.; Ono, N. *Chem. Eur. J.* **2005**, *11*, 6212.
- 17. Satchell, M. P.; Stacey, B.E. J. Chem. Soc. C 1971, 3, 468.
- 18. Meinwald, J.; Klingele, H. O. J. Am. Chem. Soc. 1966, 88, 2071.

- Mondal, R.; Okhrimenko, A. N.; Shah, B. K.; Neckers, D. C. J. Phys. Chem. B 2008, 112, 11.
- Mondal, R.; Tonshoff, C.; Khon, D.; Neckers, D. C.; Bettinger, H. F. J. Am .Chem. Soc.
 2009, 131, 14281.
- Schroder, D.; Heinemann, C.; Schwarz, H.; Harvey, J. N.; Dua, S.; Blanksby, S. J.;
 Bowie, J. H. *Chem. Eur. J.* **1998**, *4*, 2550.
- 22. Rubin, M. B.; Kapon, M. J. Photochem. Photobiol., A 1999, 124, 41.
- 23. (a) Rubin, M. B.; Patyk, A.; Sander, W. *Tetrahedron Lett.* 1988, 29, 6641. (b) Rubin, M. B. *Top. Curr. Chem.* 1985, *129*, 1.
- 24. Hasson, S.; Rubin, M. B.; Speiser, S. J. Photochem. 1984, 26, 295.
- 25. Wintgins, V.; Johnston, L. J.; Scaiano, J. C. J. Am. Chem. Soc. 1988, 110, 511.
- 26. (a) Ermoshkin, A. A.; Neckers, D. C.; Federov, A. V. *Macromolecules* 2006, *39*, 5669.
 (b) Polykarpov, A. Y.; Hasson, S.; Neckers. D. C. *Macromolecules* 1996, *29*, 8274.
- 27. Zhao, Y.; Neckers, D. C. unpublished data.
- 28. Meek, J. S.; Stacy, R. D. J. Org. Chem. 1961, 26, 300.
- 29. Zhao, Y.; Mondal, R.; Neckers, D. C. J. Org. Chem. 2008, 73, 5506.
- Zhao, Y.; Cai, X.; Danilov, E.; Li, G.; Neckers, D. C. Photochem. Photobiol. Sci. 2009, 8, 34.
- 31. Xiao, P.; Dai, M.; Nie, J. J. Appl. Polym. Sci. 2008, 108, 665.
- 32. Lambert, J. B.; Holcomb, A. G. J. Am. Chem. Soc. 1971, 93, 3952.
- Yamada, H.; Kawamura, E.; Sakamoto, S.; Yamashita, Y.; Okujima, T.; Uno, H.; Ono, N. *Tetrahedron Lett.* 2006, 47, 7501.
- 34. Omura, K; Swern, D. Tetrahedron 1978, 34, 1651.

- 35. Kobayashi, T.; Kobayashi, S. Eur. J. Org. Chem. 2002, 13, 2066.
- 36. Rigaudy, J.; Scribe, P.; Breliere, C. Tetrahedron 1981, 37, 2585.
- 37. Ten Hoeve, W.; Huisman, B H. PCT Int. Appl. 2004, 21.
- 38. Chollet, M.; Wismer, A.; Vogel, P. Tetrahedron Lett. 1976, 47, 4271.
- 39. Herwig, P. T.; Mullen, K. Advanced Materials 1999, 116, 480.
- Kobayashi, K.; Shimaoka, R.; Kawahata, M.; Yamanaka, M.; Yamaguchi, K. Organic Letters 2006, 811, 2385.
- 41. Miyaura, N.; Suzuki, A. Chem. Commun. 1979, 866.
- 42. Miyaura, N.; Suzuki, A. Chem. Rev. 1995, 95, 2457.
- 43. Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. Pure Appl. Chem. 1989, 61, 198.
- 44. Malvel, J. P.; Allonas, X. J. Photochem. Photobiol., A. 2007, 192, 66.
- 45. Flamigni, L.; Barigelletti, F.; Dellonte, S; Orlandi, G. J. Photochem. 1983, 21, 237.
- 46. Romani, A.; Favaro, G. J. Lumin. 1995, 63, 183.
- 47. Evans, T.; Leermakers, A. J. Am. Chem. Soc. 1967, 89, 4380.
- 48. Oliff, S.; Agosta, W. M. Can. J. Chem. 1984, 62, 2429 .
- Pina, F.; Parola, A. J.; Ferreira, E.; Maestri, M.; Armaroli, N.; Ballardini, R.; Balzani, V.
 J. Phys. Chem. 1995, 99, 12701.
- 50. Parmenter, C. S.; Poland, H. M. J. Chem. Phys. 1969, 51, 1551.
- 51. (a) Raumer, M. V.; Suppan, P.; Haselbach, E.; Chem. Phys. Lett. 1996, 252, 263. (b)
 Aydin, M.; Arsu, N.; Yagci, Y.; Jockush, S.; Turro, N. J. Macromolecules 1994, 27, 7794.

- Haszeldine, R. N.; Osborne, J. E. J. Chem. Soc. 1956, 61. (b) Scherzer, T.; Knolle, W.;
 Naumov, S.; Elsner, C.; Buchmeiser, M. R. J. Polym. Sci., Part A: Polym. Chem. 2008, 46, 4905.
- 53. Murov, S. L.; Carmichael, I.; Hug, G. L. In Handbook of Photochemistry, 2nd ed., rev. and expanded, Marcel Dekker, Inc., 1993; Section 7, 207.
- 54. Du, H.; Fuh, R. H.; Li, J.; Corkan, A.; Lindsey, J. S. Photochem. Photobiol. Sci. 1998, 68, 141.

7. Appendix

Appendix 1. GC-MS spectra of *cis* 2,3-Bicyclo[2.2.2]octyl carbonate (1).



Appendix 2. ¹H NMR spectra of *cis* 2,3-Bicyclo[2.2.2]octyl carbonate (1) in CDCl_{3.}







Appendix 4. GC-MS spectra of Bicyclo[2.2.2]oct-5-ene-2,3-dione (3).







Appendix 6. ¹H NMR Spectra of Anthracene in Benzene-D₆ before irradiation.



Appendix 7. ¹H NMR Spectra of Anthracene with Bicyclo[2.2.2]oct-5-ene-2,3-dione (**3**) in Benzene-D₆ before irradiation.



Appendix 8. ¹H NMR Spectra of Anthracene in after irradiation for 100 minutes in Benzene-d₆.



Appendix 9. ¹H NMR Spectra of 1,3-Cyclohexadiene in Benzene-d₆.



Appendix 10. GC-MS spectra of Anthracene with Bicyclo[2.2.2]oct-5-ene-2,3-dione (3) after

irradiation for 100 minutes.

Appendix 11. GC-MS spectra of Bicyclo[2.2.2]oct-5-ene-2,3-dione (**3**) with ethyl acrylate upon irradiation.



Appendix 12. GC-MS spectra of Bicyclo[2.2.2]oct-5-ene-2,3-dione (**3**) with hexyl acrylate upon





Appendix 13. MALDI-TOF spectra of Bicyclo[2.2.2]oct-5-ene-2,3-dione (**3**) with Lauryl acrylate upon irradiation.



Appendix 14. GC-MS spectra of Bicyclo[2.2.2]oct-5-ene-2,3-dione (**3**) with 2-phenoxy ethyl acrylate upon irradiation.



Appendix 15. ¹H NMR Spectra of 2,3,9,10-tetrabromo-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**14**) in CDCl_{3.}



Appendix 16. ¹H NMR Spectra of Bicyclo[2.2.2]oct-2-ene-5,6,7,8-tetracarboxylic acid, tetrabutyl ester (**5**) in CDCl₃.





Appendix 17. ¹H NMR Spectra of 5,6,7,8-Tetra(hydroxymethyl)-bicyclo[2.2.2]oct-2-ene (6) in

Appendix 18. ¹H NMR Spectra of 5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene (8) in CDCl₃.



Appendix 19. DIP-MS spectra of 2,3,9,10-Tetrabromo-5,6,7,12,13,14-hexahydro-6,13-



ethenopentacene (9).

Appendix 20. ¹H NMR Spectra of 2,3,9,10-Tetrabromo-5,6,7,12,13,14-hexahydro-6,13ethenopentacene (**9**) in CDCl₃.



Appendix 21. DIP-MS spectra of 2,3,9,10-Tetrabromo-6,13-dihydro-6,13-ethenopentacene (10).



Appendix 22. MALDI-TOF spectra of 2,3,9,10-tetrabromo-6,13-dihydro-6,13-ethanopentacene-15,16-dione (**14**) with ethyl acrylate upon irradiation.

