SELECTIVE SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRENE CORED NEW CLASS OF POLYCYCLIC AROMATIC HYDROCARBONS

September 2010

Division of Energy and Material Science
Graduate School of Science and Engineering
Saga University

Arjun Paudel

SELECTIVE SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRENE CORED NEW CLASS OF POLYCYCLIC AROMATIC HYDROCARBONS

A Thesis Presented

By

Arjun Paudel

Submitted to the Graduate School of
Science and Engineering Saga University in partial fulfillment of the requirements
for the degree of

DOCTOR OF PHILOSOPHY

Organic Chemistry
September 2010

DEDICATION

For my Parents, Keshav Paudel & Bhim kumari Paudel.

For my wife, Anjana.

&

Daughter, Araya.

ACKNOWLEDGEMENTS

I would like to thank my advisor ***Prof*. Takehiko Yamato (TY),** for his guidance, insight, and for sharing his encyclopedic knowledge of chemistry.

I would like to thank **Ministry of Education, Culture, Sports, Science and Technology** for providing me scholarship and platform for research through Monbushu scholarship and always proud to be a recipients of most prestigious Japanese Government Monbusho Scholarship for my doctoral study. I would also like to thanks **Cannon Company** for additional financial support for this research.

I wish to convey my sincere thanks to ***Prof*. Masanao Era,** and ***Prof*. Mishinori Takeshita** for the determination of the fluorescence-emission spectra and quantum yields of my synthesized compounds and valuable suggestions during this work. I also wish to convey my special thanks to ***Dr*. Mark R. J. Elsegood** (Loughborogh University, UK) and ***Prof*. Junnji Tanaka** (Institute for Material Chemistry and Engineering, Kyushu University,) for single-crystal X-ray analysis in my research works. To ***Prof*. Tsugio Kitamura, and *Prof*. Takeshi Hanamoto,** thank you for always being a source of inspiration. I would like to thank the rest of my thesis committee for their kind cooperation and suggestions.

I would also like to express my sincere gratitude to my MS supervisor ***Prof*. M.D. Manandhar**, ***Prof*. M.B. Gewali** and all my teachers of CDC Tribhuvan University, Nepal for their constant suggestions and inspiration. I owe my deepest gratitude to ***Prof*. Kedar Ghimire** for his kind suggestions and support during this study and ***Dr*. Arjun K. Thapa** for his kind support and co-operation during my stay in Japan.

I thank the entire TY group for their friendship and support especially for ***Dr*. Sulfur Rahman, Katsuhiro Hida, Yamashita Kosuke, Iizuka Fuminori, Yoshizawa Akina, Tomiyasu Hirotsugu, Uchikawa Yuki, Xin-long Ni,** and **Bigyan Sharma,** who made my research so intellectually stimulating and enjoyable. I would also like to thank many people who contributed their time, helping me with literatures and advices to this project; especially ***Dr***. **Hari. D. Bhattarai**, **Bishnu Guragain**, **Sudhina Guragain** and all of my colleagues from Nepal.

I would like to thank all my friends and family that have supported me over my many years as a student. To my parents, **Keshav Paudel** and **Bhim K. Paudel**, thank you for always being there to support me financially, emotionally, and spiritually. To my sister **Arati Thapa**, brother-in-law **Shree Ram Thapa**, brothers **Krishana Paudel** and **Luxman Paudel**, thanks for your constant encouragement and support. I would also like to thank my father- and mother-in-law, **Hit B. Thapa** and **Bindu Thapa** for their constant support and inspiration. I am grateful to sister **Rekha Karki**, brother ***Er*. Suraj Thapa**, sister ***Dr*. Radha KC** and **Sabina Thapa** and all of my family members for their kind support and encouragement during my study.

Last, but not the least, I want to thank my wife **Anjana** and daughter **Araya**, for supporting me in every way possible and I would like to dedicate this thesis to my beloved **parents**, caring wife **Anjana Thapa** and loving daughter **Araya Paudel**. Thank you.

ABSTRACT

SELECTIVE SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRENE CORED NEW CLASS OF POLYCYCLIC AROMATIC HYDROCARBONS

September 2010

Arjun Paudel, Saga University, Japan
Directed by: *Prof.* Takehiko Yamato

Combining tools of traditional organic synthesis with those of the emerging field of helicene chemistry, we have designed novel concept to obtain the helicene compounds. With the background of limited use of polycyclic aromatic hydrocarbons as the core material for the synthesis of helicene compounds, herein we report the use of pyrene as core material for the synthesis of [*4*] and [5] mono and bis-helicenes for the first time. We have developed and established technique of extending the helicene framework to the higher members. We have also demonstrated that synthesis of helicene motifs around the pyrene core molecules is the novel procedure and techniques to get desired helicene compounds having unique molecular architecture, consequently a novel class of polycyclic aromatic hydrocarbons. The synthesis strategies included the regioselective formylation of pyrene moiety at novel positions and consecutive conversion of formylated pyrene to the corresponding arylethenyl pyrenes using Wittig reaction and followed by photo induced cyclization. The compound's structure were established by using most modern techniques like ^{1}HNMR, ^{13}C NMR, GC, Mass, Single-crystal X-ray crystallography etc and finally characterized by their optoelectronic properties.

SELECTIVE SYNTHESIS AND PHOTOPHYSICAL PROPERTIES OF PYRENE CORED NEW CLASS OF POLYCYCLIC AROMATIC HYDROCARBONS

By

Arjun Paudel

A thesis submitted in partial fulfillment of the requirements for the degree of

DOCTOR OF PHILOSOPHY
(Organic Chemistry)
Graduate School of Science and Engineering
Saga University
September 2010

Approved by_____

Prof. Takehiko Yamato

Supervisor /chair

_____

Prof. Tsugio Kitamura

_____

Prof. Takeshi Hanamoto

_____

Prof. Mishinori Takeshita

Program authorized to offer degree: **Doctor of Philosophy**
Date: 2010-09-24

TABLE OF CONTENTS

Chapter 1

General Introduction
Pyrene, Pyrene Cored Polycondensed Aromatic Hydrocarbons As Advanced Materials.

In this chapter general introduction of pyrene and pyrene cored material with respect to their applications are presented, and a brief introductory outline of present thesis are also discussed.

1.2 General Introduction

1. 1.a Pyrene and Pyrene cored compounds as advance materials

Pyrene is an alternant polycyclic aromatic hydrocarbon (PAH) and consists of four fused benzene rings, resulting in a large, flat aromatic system, which chemical structure as shown in Figure: 1. Pyrene is a colorless or pale yellow solid. Pyrene forms during incomplete combustion of organic material and therefore can be isolated from coal tar together with a broad range of related compounds. In last four decades, a number of works have been carried out and published which included both the theoretical and experimental investigation of pyrene concerning on its electronic structure, UV-Vis absorption and fluorescence emission spectrum.[1,2] Recently pyrene has proved as potential component for advanced material. Their different structural derivatives were reported as useful materials in field effect transistors, photovoltaic cell, light emitting diodes etc. Due to optoelectronic properties, pyrene is not only limited to the these applications but also used in the field of ionic.[3,4,5] and molecular recognition.[6]

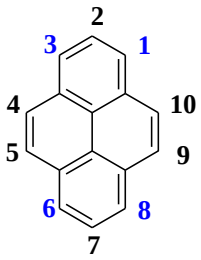


Fig. 1 Pyrene ($C_{16}H_{10}$)

Since the first great discoveries of multilayer thin film structures in organic light emitting diodes (OLEDs) was reported by Tang and co-workers.[7] Organic materials such as naphthalene, anthracene, fluorenes, pyrenes etc are supposed to be suitable for the application as light emitters in OLEDs. Pyrene; although contains extensive π-conjugated system, high thermal stability and good performance in solution, previously it was not considered as good OLED material because of its nature to form π-aggregates leading to long wave excimer emission. But upon modification in the structure, pyrene derivatives were reported as useful blue emitting material.[8,9] Recently pyrene derivatives like fluorene substituted[8] and carbazol-substituted[9] were found to be exhibited as very good blue fluorescence material with quantum yield up to 100%. In 1997, Yamana *et al.* proposed the synthesis of fluorescence-labeled oligonucleotides, which exhibit enhanced emission on

hybridization to complementary nucleic acid for DNA sequences.[10] Pyrene has strong π-electron delocalization energy and efficient fluorescence property due to its large planar conjugated aromatic characteristic. Thus, its derivatives widely used as probes in recognized DNA labels.[10]

At present, there are a number of stable blue emitting materials concerning on pyrene that have been disclosed in the literature, which can be roughly categorized into three types of materials: firstly, Function-substituted pyrene derivatives.[11,-14] were used as a conjugation center due to its extensive π-electron delocalization and electron accepting nature. These compounds were synthesized by the introduction of various kinds of chromophores into pyrene molecules by using several powerful cross coupling reactions. Secondly, pyrene-substituted PAHs derivatives[15,16] that make it an attractive chromophore include its well-characterized long-lived excited state, the sensitivity of its fluorescence to quenching, the sensitivity of its excitation spectra to microenvironment changes, and its properties for forming excimers. These compounds can be developed by the introduction of pyrene into various kinds of PAHs molecules to afford pyrene derivatives. Finally pyrene-bridged polymers unit as the π-conjugated system[13,17] that have been using always be used as hole-transporting materials in PLEDs.

Pyrene with its unique character to form excimer leading to the excimer emission has been using by many researchers as fluorogenic unit in fluorescent chemosensor in recent years. Pyrene with different type of recognition units (Ionophore) were found to be excellent chemosensor for the detection of biologically, chemically and environmentally important metals cations like Hg^{2+}, Cu^{2+}, Pb^{2+},Ag^{+}, K^{+} etc.

In last few years many fluorescence chemosensor based on pyrene moiety were synthesized and characterized with different metal ions and neutral molecules having excellent selective and sensitive nature. e.g. Photo induced charge transfer (PCT) based 1,3-alternetcalix[4]crown was reported,[5] which is able to recognize metal cations like Hg^{2+}, Cu^{2+}, Pb^{2+}, K^{+} etc. in excellent manner. Cyclams bearing diametrically disubstitued pyrenes exhibiting significant selectivity towards Hg^{2+} and Cu^{2+} ions with detecting limits 1.45×10^{-6} and 1.30×10^{-6} M respectively had reported by Suk-Kyu Chang et al.[4] Highly selective ratiometric fluorescence determination of Ag^{+} based on molecular motif with one pyrene and two adenine moieties[6] has recently reported and found to be the best method instead of most expansive and time consuming methods like potentiometric methods for Ag^{+} assay

based on ion-selective electrodes, atomic absorption spectroscopy and inductively coupled plasma-mass spectroscopy etc.

Not only in the field of ionic recognition but also in the field of molecular recognition based on PAHs, have many works been reported. Recently Danaboyina Ramaiah et al.[7] reported the selective recognition of tryptophan through inhibition of intramolecular charge transfer interaction in an aqueous medium based on novel donor-acceptor conjugate 1-[(pyren-1-yl)methyl]-1'-butyl-4,4'-bipyridinium dibromide. This compound was reported as having unusual high selectivity for tryptophan among all the other amino acids.

On the other hand, the material properties for the application of any compound in the area of field effect transistor and photovoltaic cell, basically measure as cyclic aromatic hydrocarbons like Hexabenzocorones (HBC) and its derivatives were found to be exhibited good charge carrier mobility ranging from 0.02 to 1.1 $cm^2\ V^{-1}s^{-1}$.[18,19] Recently discotic materials based on pyrene were reported by P. Kaszynski et al.[20] as ambipolar compound having charge carrier mobility (μ) $10^{-3}\ cm^2\ V^{-1}s^{-1}$.

Therefore the synthesis of pyrene cored material leads to the synthesis of potentially useful materials that could be used in different practical aspects of chemistry. Accordingly, inspired by intriguing applications in the broad area of applied chemistry, the aim of this thesis is to design, synthesis and investigation of variety of pyrene cored PAHs, with unique structural architectures namely helicenes. The second motivation of this thesis is to investigate and discuss complete structural properties using most modern techniques like ^1H NMR, ^{13}C NMR, IR, UV-Vis and single X-ray crystal analysis. The application approach was studied through the fluorescence spectroscopy and calculation of absolute quantum yields. The reminder of thesis is organized as follows. Chapter **2**; provides a brief description of the existing literature concerning PAHs, pyrene cored helicened polycyclic aromatic hydrocarbons. This chapter also provides a brief description of the existing literature concerning helicenes and their synthetic approaches via non photochemical as well as photochemical methods, including the present propose of study.

Because of unique regioselective reactions around pyrene molecules, the inactive positions namely 2, 4, 5, 7, 9 and 10 can only participate in the electrophilic substitution reactions by indirect methods. Moreover the regioselectively towards 4, 5, 9 and 10 positions of pyrene moiety can only achieved by the introduction of alkyl substitution at 2 and 7 positions. In **Chapter 3**, the more efficient synthesis routes to substituted and unsubstituted

pyrene based [4]helicene compounds with their optoelectronic properties are presented. A Complete description of Wittig reaction of 2,7-di-*tert*-butylpyrene-4-carboaldehyde with benzyltriphenylphosphonium salt in the presence of *n*-BuLi to afford 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrenes, from which naphthalene condensed aromatic compounds, 2,7-di-*tert*-butyl-dibenzo[*ij,no*]tetraphenes derivatives were obtained by photo-induced cyclization in presence of iodine and propylene oxide alone with the photophysical properties of compounds were presented. The structures of these new classes of pyrene based polycyclic aromatic hydrocarbons were fully determined on the basis of their ^{1}H NMR, ^{13}C NMR, mass spectroscopy as well as elemental analysis. Because of introduction of *tert*-butyl group at 2 and 7 positions of pyrene, synthesized compounds were found to be highly soluble in common organic solvents such as dichloromethane, chloroform and hexane.

Chapter 4 describes a complete synthetic strategies of first member of new class of double [4]helicene polycyclic aromatic hydrocarbons namely, tetrabenzo[*a,fg,j,op*]tetracene, and tetrabenzo[*a,de,h,mn*]tetracene derivatives from the respective 2,7-di-*tert*-butyl-4,9-diformylpyene and 2,7-di-*tert*-butyl-4,10-diformylpyene derivatives respectively. These compounds features bearing of naphthalene condensed pyrene molecule having unique double helicene structure. The structures of compounds were fully characterized by ^{1}H / ^{13}C NMR, Mass spectroscopy, elemental analysis. Similarly a complete analysis of single crystal X-ray analysis was presented. The applicability of the synthesized compounds were fully characterized by theirs photophysical properties using UV-Vis and fluorescence spectroscopy alone with the quantum yield determination.

Introducing alkyl groups of pyrene at 1, 3 and 7 positions interestingly show regioselectively towards electrophilic substitution at 5 and 9 positions. Considering this particular nature of pyrene, the more efficient synthesis routes to substituted and unsubstituted 7-*tert*-butyl-1,3-dimethylpyrene pyrene based [4] helicene compounds with their optoelectronic properties are presented in **Chapter 5**. A complete scenarios of Wittig reaction of 7-*tert*-butyl-1,3-dimethyl-5-formylpyrene with benzyltriphenylphosphonium salt in the presence of *n*-BuLi to afford 7-*tert*-butyl-1,3-dimethyl-5-(phenylethenyl)pyrenes, to obtain naphthalene condensed aromatic compounds, 7-*tert*-butyl-1,3-dimethyl-13-methoxydibenzo[*ij,no*]tetraphene, and 7-*tert*-butyl-1,3-dimethyl-12,14-dimethyldibenzo[*ij,no*]tetraphe by photo-induced cyclization in the presence of iodine and propylene oxide were also discussed. Along with X-ray crystal structure, optoelectronic

properties, and the effects of introduced of methyl groups in the fjord region i.e the methyl groups induced helicity in the synthesis of [4]helicene compounds were also discussed.

In **Chapter 6**, Synthesis and properties of new class of polycyclic aromatic hydrocarbons derivatives containing double [5]helicene motifs are presented. These compounds features bearing of phenanthrene condensed pyrene cored Polycyclic aromatic hydrocarbons having bis [5]helicene structural patterns . The structures of compounds were fully characterized by $^{1}H/\ ^{13}C$ NMR, Mass spectroscopy, elemental analysis. The method proceeds with the Wittig reaction of 2,7-di-*tert*-butyl-4,9-diformylpyene with (2,7-di-*tert*-butyl-pyrene-4-yl)triphenylphosphonium chloride in the presence of n-BuLi and followed by intramolecular photo-induced cyclization in the presence of iodine and propylene oxide to afford a the novel expanded π-conjugated systems, 2,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg,op*]dipyreno[*a,j*]tetracene. Similarly photophysical properties of compounds were carefully examined also presented in this chapter.

1.1 b References

[1] T. Azumi, S. P. McGlynm, *J. Chem. Phys*. **1964**, 41, 3131-3138.

[2] E. Clar, W. Schmidt, *Tetrahedron.* **1976**, 32, 2563-2566.

[3] S. M. Park, M.H. Kim, J-I. Choe, K. Tai, S-K. Chang, *J .Org. Chem*. **2007**, 72, 3550-3553.

[4] J. Xiang, D. Zhu, *Org. Lett*. **2008,** 10(11), 2271-2274.

[5] J. K. Choi, S. H. Kim, J. Yoon, K-H. Lee, R. A. Bartsch, J. S. Kim, *J.Org.Chem*. **2006**, 71, 8011-8015.

[6] M. Hariharan, S. C. Karunakaran, D. Ramaiah, *Org. Lett.* **2007**, 9(3), 417-420.

[7] C.W. Tang, S. A. Vanslke, *Appl.phys. letter*. **1987**, 51, 913-915.

[8] Y. Xing, X. Xu, P. Zhang, W. Tian, G. Yu, P. Lu, Y. Liu, D. Zhu, *Chem. Phys. Letter*. **2005**, 408, 169-173.

[9] C. Tang, F. Liu, Y-J. Xia, J. Lin, L-H. Xie, G-Y. Zhong, Q-Li. Fan, W. Huang, ***Organic** Electronics* **2005**, 7, 155-162.

[10] K. Yamana, M. Takei, H. Nakano, *Tetrahedron Lett.* **1997**, 38, 6051.

[11] Z. H. Li, and M. S. Wong., *Org. Lett.* **2006**, 8, (7), 1499-1502.

[12] S. Tang, M. Liu, C. Gu, Y. Zhao, P. Lu, D. Lu, L. Liu, F. Shen, B. Yang, and Y. Ma,. *J. Org. Chem.* **2008**, 73, 4212-4218.

[13] R. M. Adhikari, R. M., B. K. Shah, and D. C. Neckers., *J. Org. Chem*. **2007**, 72, 4727-4732.

[14] Y. Xing, P. Lu, Y. Liu, and D. Zhu. *Chemical Physics Letters,* **2005,** 408, 1169-173.

[15] A. Saitoh, N. Yamada, M. Yashima, K. Okinaka, A. Senoo, K. ueno, D. Tanaka, and R. Yashiro, " Novel fluorine-based blue emitters for high performance OLEDs," in Proc. Soc. Information Display, Seattle, WA, **2004**, 150-153.

[16] C. Yang, T. Guo, and I. Sun. *Journal of Luminescence,* **2007**, 124, 93-98.

[17] Joji Ohshita, Kazuhiro Yoshimoto, and Kazuo Yamashita, *Journal of Organometallic Chemistry,* **2003**, 678, 33-38.

[18] J. Wu, W. Pisula, K. Müllen, *Chem., Rev.,* **2007**, 107, 718- 747.

[19] L. Schmidt-Mende, A. Fechtenkötter, K. Müllen, E. Moons, R. H. Friend, J. D. MacKenzie *Science*, **2001**, 293 1119-1122.

[20] M. J. Sienkowska, H. Monobe, P. Kaszynski, Y. Shimizu, *J .Mater. Chem.,* **2007**, 17, 1392-1398.

Chapter 2

Polycyclic Aromatic Hydrocarbons, Helicenes and Present Propose of Study.

In this chapter recent literature concerning synthesis and development of polycyclic aromatic hydrocarbons, helicenes and present proposed of study are presented. From the earliest development to the present achievements towards the field of PAHs, Helicenes and photochemical and non photochemical methods for the synthesis of [n]helicenes are discussed. Based on this literature reviews, the present propose of study are also discussed.

2.1 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons (PAHs) are polycondensed aromatic hydrocarbons which are formed during pyrolysis or incomplete combustion of various kind of organic materials.[1] PAHs have been designated as human carcinogens by WHO and are reported as neurological, reproductive, development effecting and genotoxic substances in human and animals. These are most potent class of carcinogens commonly present in urban environment.[2,3] However polycyclic aromatic hydrocarbons have proven their potential active components as advance materials in present time like in field effect transistors, photovoltaic cell, light emitting diode, photochromism etc, due to their optoelectronic properties.[4] PAHs are now extensively used in different area of chemistry like ionic [4,5,8] and molecular recognition[6] too. Because of this unique optoelectronic properties and many other applications as advanced material; many effort have been devoted in the synthesis and characterization of PAHs.

The research on polycyclic aromatic hydrocarbons simply carbon-rich compounds began with the isolation of polycycles from coal-tar and other petroleum products in the mid of 19th century. The late 19th century initiated the first synthetic efforts on two, three, and four linearly-annelated polycyclic systems, most of which had been previously isolated from fossil fuels, as well as pericondensed benzenoid systems such as terphenyl and tetraphenyl. The most of the common techniques applied at that time were pyrolysis or pyro-condensation and consisted of passing precursor molecules through red-hot tubes or distillation over broken glass at red heat.[9a] Example include Graebe's formation of fluorine from diphenylmethane in 1874 and Radziszewski's production of naphthalene from (α,β-dibromobutyl)benzene in 1876.[9b] The most important early cyclization technique were

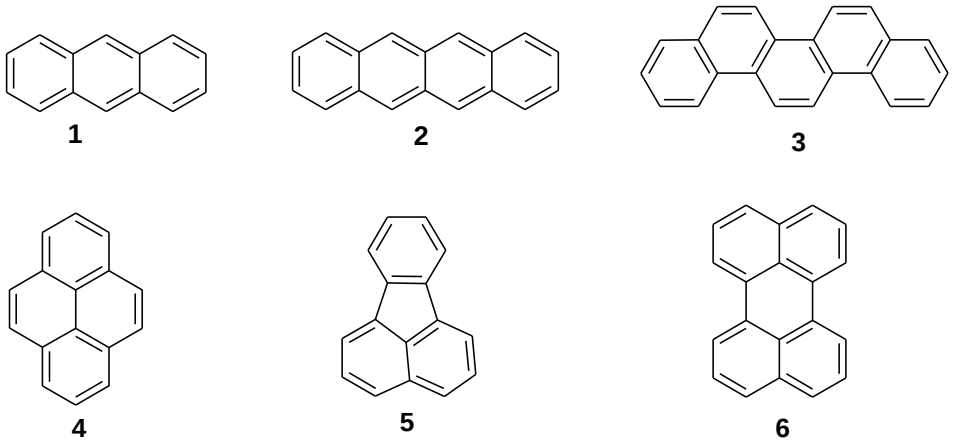
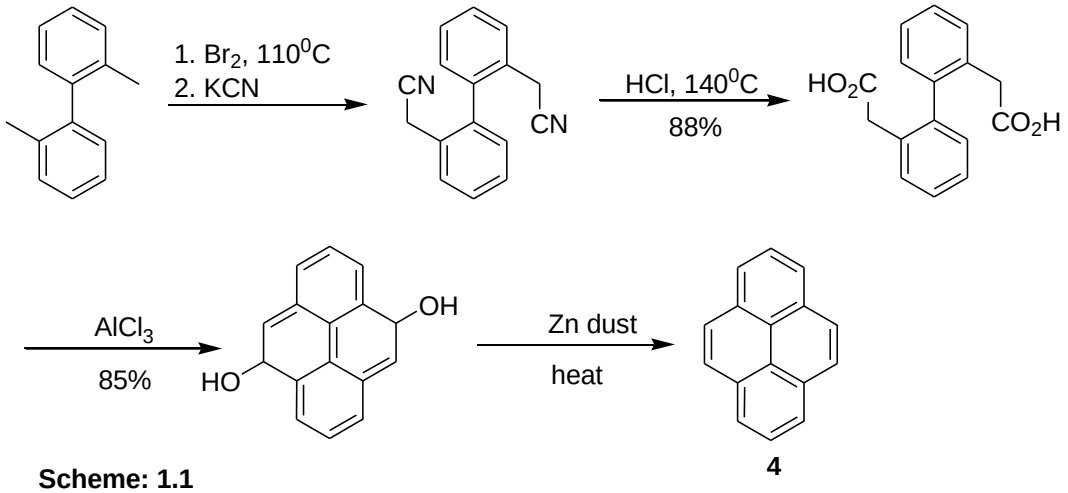


Fig: 1.1. Structures **1-6**

developed was von Baeyer's Zn-dust distillation[9c] and multistep production of phenanthrene by Pschorr.[9d]

The production of tetracene prior to the turn of the 19th century marked the largest linearly-annelated polycyclic hydrocarbon at that time.[10a] However the most important polycycles produced prior to 1920 were perylene **6** and pyrene **4**, both of notes as parent structures for numerous fused benzenoid analogs produced in the following decades. In 1913, Weitzen-bock first produced pyrene from o,o'-ditolyl.[10b] The five step synthesis began with bromination of o,o'-ditolyl followed by conversion into dicarboxylic acid via a dinitrile intermediate(Scheme 1.1). Cyclization and Zn-dust distillation afforded the tetra fused structure in a well-designed synthesis, confirming the structure through intermediate analysis.



Scheme: 1.1

In contrast to the numerous Zn-distillation cyclization, Cook et. al. in 1930s utilized an atypical selenium dehydrogenation of a partially saturated keto-derivative to afford pyrene.[10c] Cook and coworkers also successfully synthesized and correctly elucidated the structure of several new polycycles and numerous derivatives like new isomers of benzopyrene, anthraceneotetraphene **7**, benzopentaphene **8**, dibenzanthracene **9**,[9d] as well as several condensed fluorine structure such as **10**, **11** and **12**. (Figure: 1.2).[10d] His work on perylene and the first helicenes is of note. The confirmed isolation of first two helicene, tetra-**13** and pentahelicene **14**, did not occur until the early 1930s when Cook et al. reinvestigated the work[10e] and modified the techniques.

A number of linear annelated benzenoid derivatives of the high reactive hexa- and heptacene as well as the first octacene derivative with pyrene as one of the notable structural

motif present, which likely added stability over purely linear structures were also reported by scientists in different time intervals. In 1963, dibenzoctacene **18** (Figure: 1.2c) was produced and reported by Clar et al.via two fold condensation of derivatized naphthalene compounds to a central substituted pyrene, di and tetrabenzoheptacene, **16**, **17** representing two heptacene derivatives were also been reported in 1960s. Clar et al. in 1956 also produced tetrabenzopentacene **15** in a similar fashion to his other pentacene derivatives and reported.[9a] Similarly, Halleux et.al in 1958 synthesized and reported the hexabenzocoronene (HBC) **19** from NaCl-$ZnCl_2$ melt of hexaphenylbenzene.[11] In the modern contest HBC materials are very interested due to their physical properties,[12a,b] and have been extensively exploited in organic electronic devices, such as field-effective transistors, injection layers, and solar cells.[12c,d]

Increased surface area of aromatic core leads to a more pronounced π-stacking propensity, but it also reduces solubility and thus complicates purification, characterization, and processing.[12e,f] Most recently Mullen et al. reported the electron deficient N-heteroaromatic linkers **20** for the elaboration of large, soluble polycyclic aromatic hydrocarbon having unique molecular architecture. The improved solubility of heteroatom-containing PAHs have been synthesized by introducing of *tert*-butyl groups in the corona of aromatic system and reported.[13]

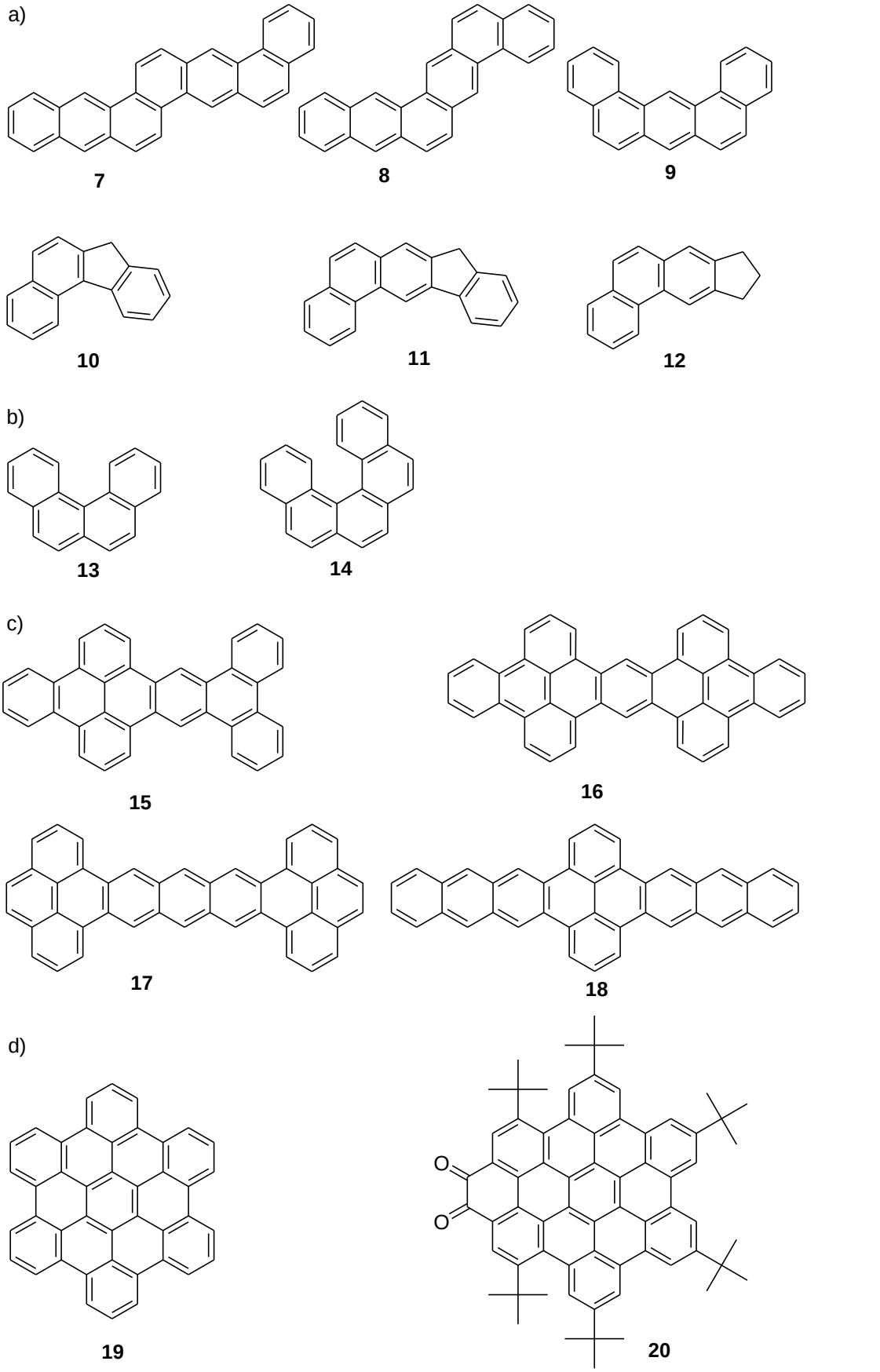


Fig: 1.2. (a) Structures **7-12,** (b) structure **13** and **14**, (c) structure **15-16**, (d) structure **19** and **20**.

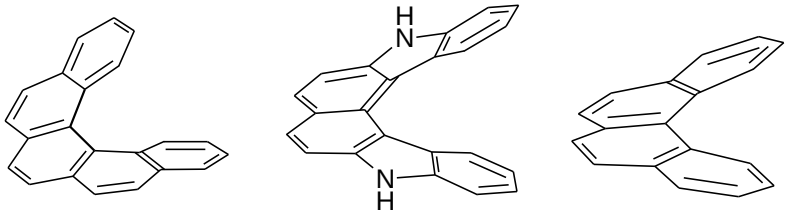
2.2 The Helicenes

"*Helicene is the name introduced by Newman in 1955, to describe the benzologues of phenanthrene in which the extra ortho-condensed rings give rise to a (regular) cylindrical helix."*

The helicenes are characterized by a helical structure made up of *ortho*-condensed aromatic rings, by the presence of a powerful inherently chiral chromophore and by the possibility of interaction between overlapping aromatic rings. The scientific interest raised by these compounds is due to the unique combination of these three properties in a single molecule.[14] [*n*]Helicenes possess *n* angularly annelated aromatic rings, forming a helically shaped π-conjugated system. For [*n*]helicenes with $n \geq 4$, the distortion from planarity due to steric repulsion of terminal rings is sufficient to allow for resolution of enantiomers. Because both high degree of annelation and significant strain have to be introduced in such systems, efficient syntheses of [*n*]helicenes are challenging.

2.2.a Non photochemical Syntheses

The First [*n*]helicenes, [*6*]pyrrolohelicene **22** by Fuchs et al. in 1927, [4]helicene **13**, and [5]helicene **23** by Cook et al. in 1933 were reported respectively[15a,b,10d] The first enantiomerically pure helicene namely phenanthro[3,4-c]phenanthrene or hexahelicene was synthesized in 1956 by Newman and Lednicer in 12 steps involving the resolution of a charge-transfer complex.[16]

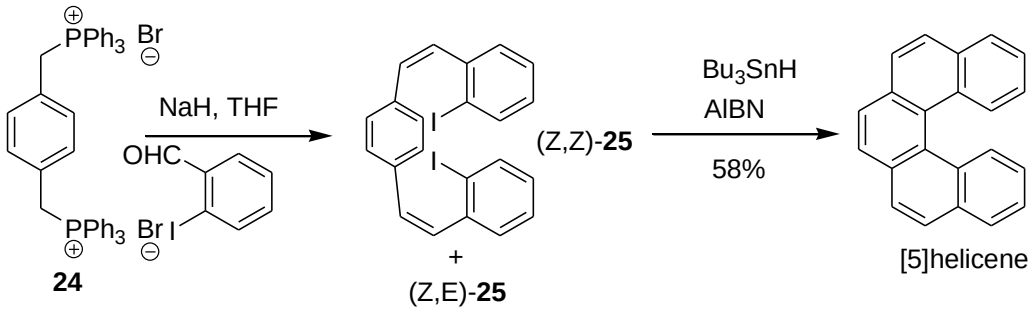


21 **22** **23**

Fig:1.2. Structure 21-23:[n]helicenes

In the recent work by Katz et al. led to the production of racemic helicene bis quionones through a Diels-Alder approach[17a,b,c] supplemented by an efficient procedure for effecting the required resolutions. Despite remarkable progress in helicene chemistry, the

task of developing new, short and efficient strategies to racemic and enantiopure helicene which fulfill criteria of atom economy remains a challenge. The first non photochemical preparation of [7]helicene, which was the first carbohelicene to be synthesized by dehydrophotocyclization,[18] was not described until 1999 when Gingras and Dubois[19] reported a five step approach using a carbenoid coupling strategy. A related strategy was presented by Rajca and co-worker in 2002 for the synthesis of a novel oligothiophene in which the thiophene rings are cross-conjugated and annelated into a helix.[20] A new route to [5]helicenes, based on a tin mediated, non reducing tandem radical cyclization of (Z,Z)-1,4-bis(2-iodostyryl)benzene derivatives **25** starting from ylide **24** was recently described by Horrowven et al. (Scheme: 1.2).[21a,b]



Scheme: 1. 2. [5]helicene by tandem radical cyclization,(Z,Z)-1,4-bis(2-iodostyryl)benzene **25.** AIBN = azobisisobutylronitrile.

An innovative approach to helicene **26** that exploited atom-economic isomerization of aromatic *cis, cis* dienetryines under transition-metal catalysis have recently been reported by Stara, Stary and co-workers,[22a] The scope of this efficient procedure was clearly demonstrated with the synthesis of different substituted [5], [6], and [7]helicene with yields ranging from 60-83%. Similarly Carreno et al. in 2001 described the first enantioselective synthesis of 7,8-dihydro[5]helicene quinines and bisquiones **27** based on the three-step one pot domino process.[22b] In another asymmetric approach to helical conjugated molecules, Karikomi et al. in developed a practical method for the synthesis of chiral [5]helicene **28** using and aromatic oxy-cope rearrangement strategy.[22c] In an independent study, Jan Storch et al. in 2009 reported the new approach of nonphotochemical synthesis of hexahelicene **29** e.g. 1-methoxyhexahelicene via cycloisomerization of biphenyl-naphthalene derivatives.[23]

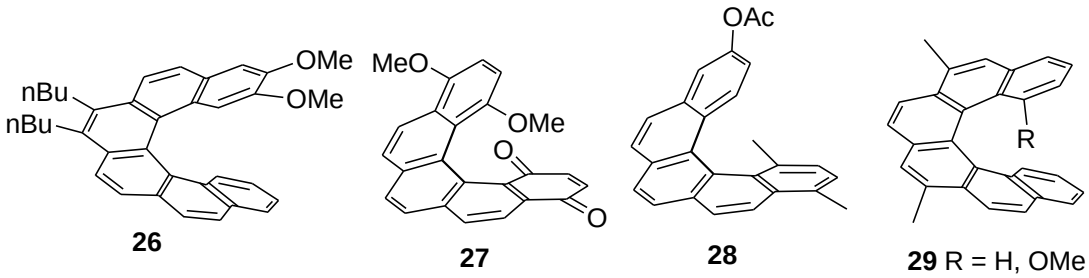


Fig:1.3. Structure 26-29:[n]helicenes

Recently, a new palladium catalyzed cyclotrimerization of arenas, developed by Guitian and co-workers was very recently applied to the synthesis of **30** in 26% yield, the first double helicene formed by a pentahelicene and a heptahelicene with two rings in common.[24] The ^{1}HNMR spectrum for racemic **30** showed better agreement with the calculated spectrum for the diastereomer with homochiral versus heterochiral helicene. A conjugated double helicene, in which two hydrazine-based [5]helicene **31** that are highly annelated in the mid section was also reported by non photochemical methods.[25a] The structure of compound was established by X-ray crystallography. The extended C_3-symmetry PAHs, which may be viewed as graphite disks with [*n*]helicene like unit have been prepared via efficient oxidative cyclodehydrogenation by Mullen and co-workers.[25b] The hexabenzotriphenylene **32** was reported as the best studied example of chiral, overcrowded PAHs with significant steric congestion of the bay hydrogens.

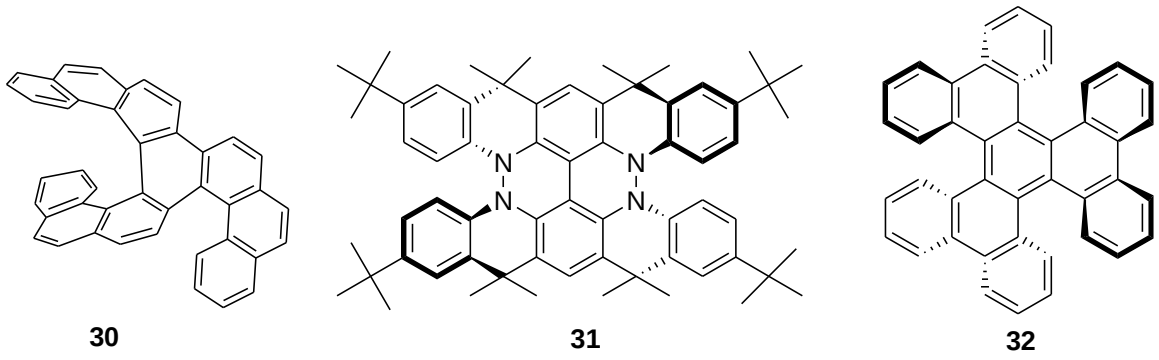


Fig:1.4. Structure 30-32: double and triple[n]helicenes

2.2b Photochemical Syntheses

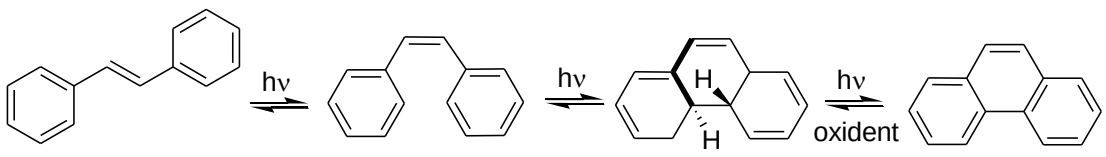
The photocyclodehydrogenation in solution of *cis*-stilbenes and its analogues have been extensively studied since long. An Intensive research into this field has been carried out by Fischer, Muszkat, Bromberg et al. and other laboratories [14] since very beginning.

Irradiation with ultraviolet light of solutions containing stilbenes in the presence of suitable oxidant such as dissolved oxygen has been found to lead the formation of phenanthrene in good yield.[26] This photoreaction of stilbenes or substituted stilbenes has been discovered and developed independently by several workers. [27, 15]

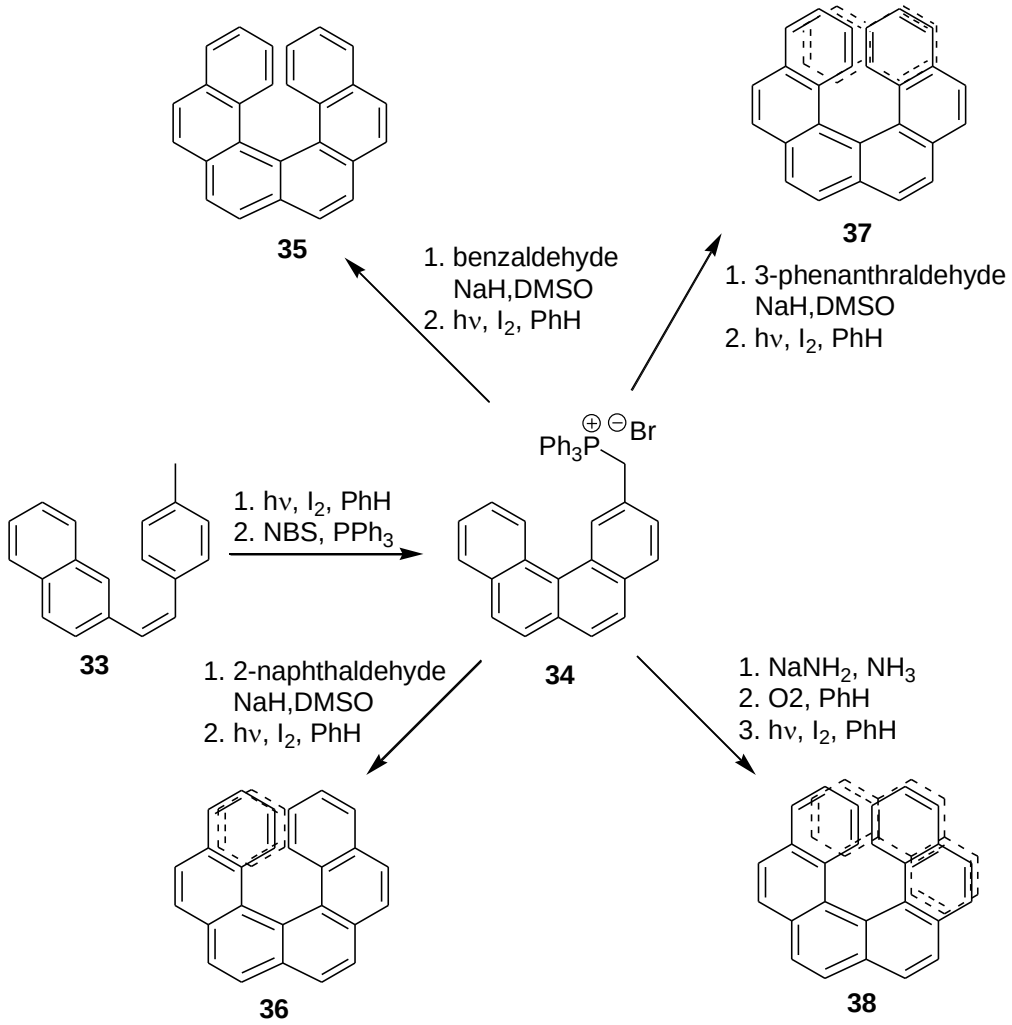
In 1964, Wood and Mallory prepared phenanthrene via enhanced methods i.e. iodine catalyzed photochemical induced cyclization of stilbenes and opened the basis for modern helicene cyclization chemistry.[28] The new method effectively provided efficient pathways to substituted phenanthrene derivatives, easier access to existing and new helicene structure, as well as sufficient quantities for proper studies. In the 1967, Martin and coworkers successfully applied the method to the synthesis of previously prepared hexahelicene **35**, as well as hepta- **36**, octa- **37**, and nonahelicene **39**.[14,26,18] These preparations culminated in photo-induced cyclization of bisarylethylenes with I_2 oxidation and Hg-lamp radiation source. The key improvement over previous efforts included production of phenanthrene derivatives via photo-induced cyclization of intermediate **33** and subsequent conversion to Wittig ylide **34**, a common intermediate to the four helicenes (Scheme: 1.3).

This approach was further extended to the synthesis of long [*n*]helicenes (n ≤14) and [*n*]thiahelicene ($n \leq 15$), using both mono and diannelations. Numerous [*n*]helicenes ($n \leq 13$) and [*n*]thiahelicene ($n \leq 13$) were also reported in non-racemic form via different methods like seeded crystallization,[29,30] chromatography[31] and photocyclization from a resolved precursor.[32]

Introduction of improved methodology for photocyclization reaction by Katz et al. in 1991, using stoichiometric amount of iodine plus propylene oxide in the absence of air as superior to the catalytic amount of iodine in air has became the important landmark in the field of photochemical reaction in modern contest.[35] The method improved the yield and purities in photocyclization of stilbenes, exemplified by Scheme: 1.4, transformations widely used to prepare complex ring systems.



Scheme: 1. 4. Mechanism of photocyclization



Scheme: 1. 3. Photochemical route to [n]helicenes by Martin et al.

The first double helicene, consisting of head-to-tail annelated [6]helicene, were prepared by oxidative photocyclization of stilbenes to helicenes.[33a] The double photocyclization have proved very useful in many cases, as illustrated by the two step synthesis of [6]helicene,[33b] the preparation of [13],[33c] [11]-,[12]-, and [14]-helicene and by the synthesis of double helicenes and heterohelicenes.[33d] An impressive demonstration of the ability of transition metal catalysis to build up helicene framework is the recently described total synthesis of angular [*n*]phenylenes, comprised of *n* alternating benzene units fused with n-1 cyclobutadiene rings the first helical phenylenes, called heliphenes by the author Vollhardt et al.[34] The group adopted the cobalt-catalyzed photochemical cyclotrimerization of alkynes for the rapid conversion to a novel class of helicenes.

Helicene Synthesis via photodehydrocyclization of stilbenes derivatives is known to have a somewhat restricted application as the scale up is hampered at the photocyclization

step, which must be performed in dilute hydrocarbon solutions.[35] Nevertheless; it is still the method of choice for the preparation of selected [*n*]helicenes and their heteroatom analogs.[27,36]

2.3. Pyrene cored photochemical syntheses and present proposed of study

Pyrenes and its derivatives, which belong to the class of polycyclic aromatic hydrocarbons consists of four benzene rings, resulting in a large, flat aromatic system. Pyrene is a colorless or pale yellow solid. Pyrene forms during incomplete combustion of organic material and therefore can be isolated from coal tar together with a broad range of related compounds. Pyrene derivatives have been developed as a basic synthetic unit in the synthesis of wide range of applicable organic materials. In the last four decades, a number of works have been carried out and published which included both theoretical and experimental investigation of pyrene concerning on its electronic structure, UV-vis absorption and fluorescence emission spectra.[37] At present, naphthalene, anthracene, perylene, fluorene and their derivatives have been widely developed as emitting materials in OLED but the use of pyrene molecules is limited, because of its unique character of forming π-aggregates/excimers and π-aggregates/excimers leading an additional emission band in long wavelength, decreasing electroluminescence nature of it. However the introduction of long or branched side chains or expansions of π-conjugation system in pyrene have been widely used to overcome such problems. Most recently pyrene derivatives have been used in blue fluorescent light emitting materials for organic light-emitting device due to its excellent properties like extensive π-conjugated system, excellent electron acceptor nature, excellent thermal stability, good performance in solution etc.[38]

On the other hand, helical compounds currently provide an active field of research in supramolecurlar chemistry, related to their self assembly and physicochemical properties.[39] Also their unique chiral array can provide functionalized helicenes, e.g. alcohols,[40] nitriles,[41], amines, and phosphanes,[42] for use as ligands and auxiliaries in asymmetric syntheses. Most recently the helically shaped molecules have found applications as potentially useful components in chiral discotic liquid crystalline materials building blocks for helical conjugated polymers, sensors, dyes, molecular recognition and more fascinatingly as catalysts and ligand in asymmetric synthesis because of their rigid structure and high optical stability. However the development of helicene chemistry was long hampered by the lack of convenient synthetic methods and despite much recent progress, the preparation of helicenes still requires improvements. During the last decade, huge efforts have been made to search

for new synthetic process. The most classical helicene synthesis, Martin's photochemically mediated cyclization of stilbenes derivatives, has been optimized and widely applied.[43] In modern contest, the key improvement over previous efforts includes production of helicenes compounds via photochemical process in presence of iodine oxidant and propylene oxide with Hg-lamp radiation source having Wittig ylide, a common intermediate to the helicenes.

Although pyrene and its derivatives have extensively been used in the synthesis of various organic advanced materials and applied in huge practical areas, syntheses of helicene compounds based on pyrene core have not yet reported. Recently synthesis of benzohexathia[7]helicenes, a naphthalene core double helicene with its synthetic route and crystal properties have reported by H. Wang et. al.[44] Therefore using PAHs as basic core for the synthesis of helicene compounds would open the new assess for the synthetic route to helicene compounds. Based on this assumptions, present research purpose is focused on the synthesis and characterization of pyrene cored single and double [4] and [5] helicene compounds using improved photochemical methods.[35] All these developed materials are expected as novel helicene compounds and thus new class of polycyclic aromatic hydrocarbons.

The structural properties of prepared compounds will be determined by ^{1}H NMR, ^{13}C NMR, mass spectroscopy, elemental analysis, IR etc. meanwhile, the UV-vis absorption and fluorescent emission spectrum for each compound will also be studied and established.

2. 4. References

[1] A. K. H. Kabzinski, J. Cyran, R. Juszczak. *Polish Journal of Environmental Studies*, **2002**, 11, 695-706.

[2] D. Xu, Y. Duan, I. A. Blair, T. M. Penning, R. G. Harvey, *Org. Lett.* **2008**, 10 (6) 1059-1062.

[3] Toxicologial profile for PAHs, US department of health and health services, August 1995.

[4] S. M. Park, M. H. Kim, J. Choe, K. T. No, S.Chang, *J. Org. Chem*. **2007**, 72(9), 3550-3553.

[5] L. Liu, D. Zhang, G. Zhang, U. Xiang, Z. Daoben, *Org. Lett*. **2008,** 10(11), 2271-2274.

[6] M. Hariharan, S. C. Karunakaran, D. Ramaih, *Org. Lett.* **2007,** 9(3), 417-420.

[7] C.W. Tang, S. A. Vanslke, *Appl.phys. letter*, **1987**, 51, 913-915.

[8] J. K. Choi, S. H. Kim, J. Y. Yoon, K-H, Lee, R. A Bartsch, J. S. Kim, *J. Org. Chem*. **2006**, 71(21), 8011-8015.

[9] a) E. Clar, *Polycyclic Hydrocarbonons*, Vol. I-II, Academic Press London, **1964.** b) B.Radiszewski, *Ber. Dtsch. Chem. Ges*. **1876**, 9, 260-262. c) A. V. *Baeyer, Ann. Chem. Pharm.*, **1866**, 140, 295-313. d) R. Pschorr, *Ber. Dtsch. Chem*. Ges. **1896,** 29, 496-501.

[10] a) S.Gabriel, A. Michael, *Ber. Dtsch. Chem. Ges.* **1877**, 10, 2199-2210. b) K. Diziewonski, S. Suknarowski, *Ber. Dtsch. Chem. Ges.* **1918**, 51, 457-465. c) V. Bruckner, A. Karczag, K. Kormendy, M. Meszag, J. Tomasz, *Tetrahedron Lett*. **1960**, 5-6. d) J. W. Cook, C. L. Hewett, *J. Chem. Soc,* **1933**, 1098-1111. e) J. W. Cook, *J. Chem. Soc*. **1931**, 2524-2528, 2529-25-32. 1**933**, 1592-1597.

[11] A. Halleux, R. H. Martin, G. S. D. *King, Helv. Chim. Acta*. **1958**, 41, 1177-1183.

[12] a) A. M. Van de Craats, M. J. Warman, A. Fechtenkotter, D. J. Brand, M.A. Harbison, K. Mullen, *Adv. Mater.* **1999**, 11, 1469-1472. b) E.W. Meijer, A.P. H. J. Schenning, *Nature*, **2002**, 419, 353-354. c) M. Kastler, W. Pisula, D. Wasserfallen, T. Pakula, K. Mullen, *J. Am. Chem. Soc*. **2005**, 127, 4286-4296. d) L. Schmidt-Mende, A. Fechtenkotter, K. Mullen, E. Moons, R. H. Friend, J.D. MacKenzie, *Science*, **2001**, 293, 1119-1122. e) Z. Tomovic, M.D. Watson, k. Mullen, *Angew. Chem. Int. Ed*. **2004**, 43, 755-758. f) D. Wasserfallen, M. Kastler, W. Pisula, W.A. Hofer, Y. Fogel, Z. H. Wang, K. Mullen, *Chem. Mater*., **2006**, 18, 3634-3640.

[13] F. Yulia, K. Marcel, Z. Wang, D. Andrienko, G. J. bodwell, K. Mullen, *J. Am. Soc.* **2007**, 129, 11743-11749.

[14] R. H. Martin, *Angew, Chem. Internat. Ed*. **1974**, 13, 649-660, and references therein.

[15] a) W. Fuches, F. Niszel, *Ber. Dtsch. Chem. Ges.* **1727**, 60, 209-112. b) I. Pischel, S. Grimme, S. Kotila, M. Nieger, F. Vogtle, *Tetrahedron:Asymmetry* **1996**, 7, 109-116.

[16] a) T. J. Katz, *Angew. Chem.* **2000**, 112, 1997-1999; *Anglew. Chem. Int. Ed.* **2000**, 39, 1921-1923. b) S. Grimme, J. Harren, A. Sobanski, F. Vogtle, *Eur. J. Org. Chem*. **1998**, 1491-1509.

[17] a) L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem*. **1991**, 56, 3769-3775. b) K. E. S. Philips, T. J. Katz, S. Jockusch, A. J. Lovinger, N. J. Turro, *J. Am. Chem. Soc*. **2001**, 123, 11899-11907. c) T. Thongpanchang, K. Paruch, T. J. Katz, A. L. Rheingold, K. Lam, L. Liablesands, *J. Org. Chem*. **2000**, 65, 1850-1856.

[18] M. Flammange-Barbieux, J. Nasielski, R. H. *Martin, Tetrahedron Lett*. ***1967***, 743-744.

[19] M. Gingras, F. Dubois, *Tetrahedron Lett*. **1999**, 40, 1309-1312.

[20] A. Rajca, H. Wang, M. Pink, S. Rajca, *Angew. Chem*. **2000**, 112, 4655-4657; *Angew. Chem. Int. Ed.* **2000**, 39, 4481-4483.

[21] a) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Letter* **2002**, 43, 7345-7347. b) D. C. Harrowven, I. L. Guy, L. Nanson, *Angew. Chem. Int. Ed*. **2006**, 45, 2242- 2245.

[22] a) F. Teply, I. G. Stara, I. Stary, a. Kollarovic, D. Saman, L. Rulisek, P. Fiedler, *J. Am. Chem. Soc*. **2002**, 124, 9175-9180; *Collect. Czech, Chem. Commun*. **2003**, 68, 917-930. b) M. C. Carreno, S. Garcia-Cerrada, A. Urbano, *J. Am. Chem. Soc*. **2001**, 123, 7929-7930. c) Y. Owagwa, M. Toyama, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahedron Lett*. **2003**, 44, 2167-2170.

[23] J. Storch, J. Sykora, J. Cermak, J. Karban, I. Cisarova, A. Ruzicka, *J. Org. Chem*. **2009**, 74, 3090-3093.

[24] a) D. Pena, A. Cobas, D. Perz, E. Guitian, L. Castedo, *Org. Lett*. **2003**, 5, 1863-1866. b) D. Pena, D. Perez, E. Guitian, L. Castedo, *Org. Lett*. **1999**, 1, 1555-1557.

[25] a) K. Shiraishi, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**, 127, 9312-9313. b) J. Wu, Z. Tomovic, V. Enkelmann, K. Mullen, *J. Org. Chem.* **2004**, 69, 5179-5186.

[26] F. J. Mallory, J. T. Gordon, C.S. Wood, *J. Am. Chem. Soc*. **1963**, 35, 828; **1964**, 86, 3094-3102.

[27] a) A. Satrijo, T. M. Swager, *Macromolecules,* **2005**, 38, 4054-4057. b) W. N. Herman, *J. Opt. Soc. Am. A.* **2001**, 18, 2806-2818. c) N. Wilson, W. Steffen, T. G. McKenzie, G. Lieser, M. Oda, D. Neher, U. H. Bunz, *J. Am. Chem. Soc*. **2002**, 124, 6830-6831. d) G. L. J. A. Rikken, J. Foiling, P. Wyder, *Phys. Rev. Lett.* **1996**, 76, 2121-2124. e) Y. Dai, T. J. Katz, *J. Org. Chem.* 1997, 62, 1274-1285.

[28] C. S. Wood, F.B. Mallory, *J. Org. Chem*. **1964**, 29, 3373-3377.

[29] R. H. Martin, M, -J. Marchant, *Tetrahedron* **1974**, 30, 343-345.

[30] B. S. Green, M. Knossow, *Science* **1981**, 214, 795-797.

[31] H. Nakagawa, S. Ogashiwa, H. Tanaka, K. Yamada, h. Kawazura, *Bull. Chem. Jpn*. **1981**, 1903-1904.

[32] R. H. Martin, V. Libert, *J. Chem. Res (s),* **1980**, 130-131.

[33] a) P. P. Meurer, F. Voltle, *Top. Curr. Chem*. **1985**, 127, 1-76. b) L. Brunsveld, B. J. B. Folmer, E. W. Meijer, R. P. Sijbesma, *Chem. Rev*. **2001**, 101, 4071-4098. c) E. Yashima, K. Maeda, T. Nishimura, *Chem. Eur. J*. **2004**, 10, 42-51. d) H. Goto, K. Akagi, *Angew. Chem. Int. Ed.* **2005**, 44, 4322-4328.

[34] S. Han, A.D. Bond, R. L. Disch, D. Holmes, J. M. Schulman, S. J. Teat, K. P. C. Vollhardt, G. D. Whitener, *Angew. Chem. Int. Ed.* **2002**, 114, 3357-3361; *Angew. Chem. Int. Ed.* **2002**, 41, 3223-3227.

[35] L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem*. **1991**, 56, 3769-3775.

[36] a) C. Wachmann, E. Weber, M, Czugler, W. Seichter, Eur, *J. Org. Chem*. **2003**, 2863-2876. b) J. Lasen, K. Bechgaard, *Acta. Chem. Scand*. **1996**, 50, 71.76. c) E. Murguly, T. R. McDonald, N. R. Banda, *Org. Lett.* **2000**, 2, 3169-3172. d) T. Caronna,, R. Sinisa, M. Catellani, S. Luzzati, L.Malpezzia, S. V. Meillea, A. Melea, C. Richer, R. Sinisi, *Chem. Mater.* **2001**, 13, 3906-3914. e) K. Sato, S. Okazaki, T. Yamaguchi, S. Aral, *J. Heterocyl. Chem.* **2004**, 41, 433-447. f) C. Bazzinni,, S. Brovelli, T. Caronna, C. Gambarotti, M. Giannone, P. Macchi, F. Meinardi, A. Male, W. Panzeri, F. Rocupero, A. Sironi, R. Tubino, *Eur. J. Org. Chem.* ***2005***, 1247-1257. g) R. E. Abed, B. B.Hassine, J. -P. Genet, m. Gorsane, A. Marinetti, *Eur. J. Org. Chem*. **2004**, 1517-1522. h) K. -H. Ernst, M. Neuber, M. Grunze, U.Ellerbeck, *J. Am. Chem. Soc*. **2001**, 123, 493-495.

[37] a) T. Azumi, S.P. McGlynm, *J. Chem. Phys*. **1964**, 41, 3131. b) E. Clar, W. Schmidt, *Tetrahedron Lett.* **1976**, 32, 2563.

[38] a) A. Saitoh, N. Yamada, M. Yashima, K. Okinaka, A. Senoo, K. Ueno, D. Tanaka, R. Yashiro, Proc. Soc. Information Display, *Seattle*, WA, **2004**, 150-153. b) L. H. Zhong, W. S. Wong, *Org. Lett.* **2006**, 8, 1499-1502. c) J. Ohshita, K. Yoshimoto, K. Yamashita, *J. Organomet. Chem*. **2003**, 678, 33-38.

[39] a) C. Nukolls, T. J. Katz, T. Verbiest, S. Vand Elschoct, H-G. Kuball, S. Kiesewalter, A. J. Lovinger, A. Persoons, *J. Am. Chem. Soc.* **1998**, 120, 8656-8660. b) C. Nukolls, T. J. Katz, *J. Am. Chem. Soc.* **1998**, 120, 9541-9544. c) T. Verbiest, S. Sioncke, A. Persoons, l. Vyklicky, T. J. Katz, *Angew. Chem. Int. Ed.* **2002**, 41, 3882-3884.

[40] a) K. Yamamoto, T. Ikeda, T. Kitsuki, Y. Okamoto, H. Chikamastu, M. Nakazaki, *J . Chem. Soc. Perkin Trans. 1* **1990**, 271-276. b) K. Tanaka, H. Osuga, Y. Shogase, H. Suzuki, *Tetrahedron Lett.* **1995**, 36, 915-918. c) Y. Ogawa, M. Toyama, M. Karikomi, K. Seki, K. Haga, T. Uyehera, *Tetrahedron Lett.* **2003**, 44, 2167-2170.

[41] B. B. Hassine, M.Gorsane, J. Pecher, R. H. Martin, *Bull. Soc. Chem. Belg*. **1986**, 95, 547-556.

[42] a) P. M. Op den Brouw, W. H. Laarhoven, *Recl. Trav. Chim. Pays-Bas*, **1978**, 97, 265, 5925-5928. b) K. Tanaka, H. Suzuki, H. Osuga, Y. Kawai, Tetrahedron *Lett*. **1996**, 37, 5925-5928. c) T. Terfort, H. Gorls, H. Brunner, *Synthesis*, **1997**, 79-86. d) M. T. Reetz, S. Sastmann, *J. Organomet. Chem*. **2000**, 603, 105-109.

[43] a) M. Flammang-Barbieux, j. Nasielski, R. H. Martin, *Tetrahedron Lett*. **1967**, 743-744. b) L. Liu, B. Yang, T.J. Katz, M.K Poindexter, *J. Org. Chem*. **1991**, 56, 3775.

[44] a) Z. Wang, J. Shi, Jiange Wang, C. Li, X. Tian, Y. Cheng, H. Wang, *Org. Lett*. **2009**, 12 (3), 456-459.

Chapter 3

Synthesis, Structural and Photo Physical Properties of Pyrene Cored First Member of New Single Helicened Polycyclic Aromatic Hydrocarbons Derived From 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrenes.

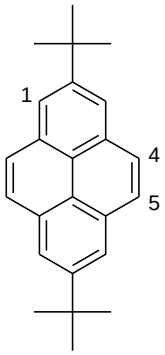
In this chapter the more efficient synthesis routes to substituted and unsubstituted pyrene based [4] helicene compounds with their optoelectronic properties are presented. Wittig reaction of 2,7-di-tert-butypyrene-4-carboaldehyde with benzyltriphenylphosphonium salt in the presence of n-BuLi to afford 2,7-di-tert-butyl-4-(phenylethenyl)pyrenes, from which naphthalene condensed aromatic compounds, 2,7-di-tert-butyl-dibenzo[ij,no]tetraphenes derivatives were obtained by photo-induced cyclization in the presence of iodine and propylene oxide. The photophysical properties were carefully examined

Parts of this work have been published: (a) Arjun Paudel, Jian-yong Hu, and Takehiko Yamato*, *J. Chem. Res.*, **2008**, 457-460. (b) Jian-yong Hu, Arjun Paudel, and Takehoko Yamato*, *J. Chem. Res.*, **2009**, 109-113.

3.1 Introduction

Helical compounds currently provided an active field of research in supramolecurlar chemistry, related to their self assembly and physicochemical properties.[1] The phenanthrene nucleus is present in a great number of natural substances, some of them having valuable chemotherapeutic properties, which has resulted in considerable efforts being made to synthesize them.[2-5] Recently methyl group induced helicity in 1,4-dimethylbenzo[c]phenanthrene have been reported by M.K. Lakshman et al.[6], where one of its two methyl groups resides in the highly congested fjord- regions. Such compounds have been widely studies in chiral recognition in the charge transfer complexation[7], asymmetric reduction[8], and in the synthesis of oligomers.[9] The Chemical structures of several parents benzo[c]phenanthrene based [4]helicene compounds that have been published in recent literatures are summarized in Figure: 3.2[7-11] Despite the various approaches now available, there exist no efficient method for the preparation of a phenanthrene annulated pyrenes at positions 4 and 5 as in Figure:3.1 .

On the other hands, since electrophilic substitution of pyrene occurred at 1, 3, 6, and 8 positions, but not at the other positions (2, 4, 5, 7, 9, and 10).[12-19] Therefore, pyrenes substituted at the latter positions must be prepared in ways other than by direct electrophilic substitution of pyrene itself.[20] For example, Moyle et al.[17] prepared 4,9-diethylpyrene in a low total yield from ethylbenzene in 14 steps using Friedel-Crafts in tramolecular acylation to construct a pyrene ring. Thus there is substantial interest in investigating the selective introduction of substituents at positions 4, 5, 9 and 10 in ways other than by direct electrophilic substitution of pyrene itself.



1

Fig:3. 1 2,7-di-*tert*-butylpyrene

It has been previously reported the $TiCl_4$-catalyzed formylation of 2,7-di-*tert*-butylpyrene with dichloromethyl methyl ether using the *tert*-butyl group as a positional protective group to afford only 4-monoformylated product, 2,7-di-*tert*-butypyrene-4-carboaldehyde in excellent yield.[20-21] This compound afforded a convenient starting material for the preparation of various 4,5-naphthalene annulated pyrenes derivatives by using photo-induced cyclization of 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrenes based derivatives.

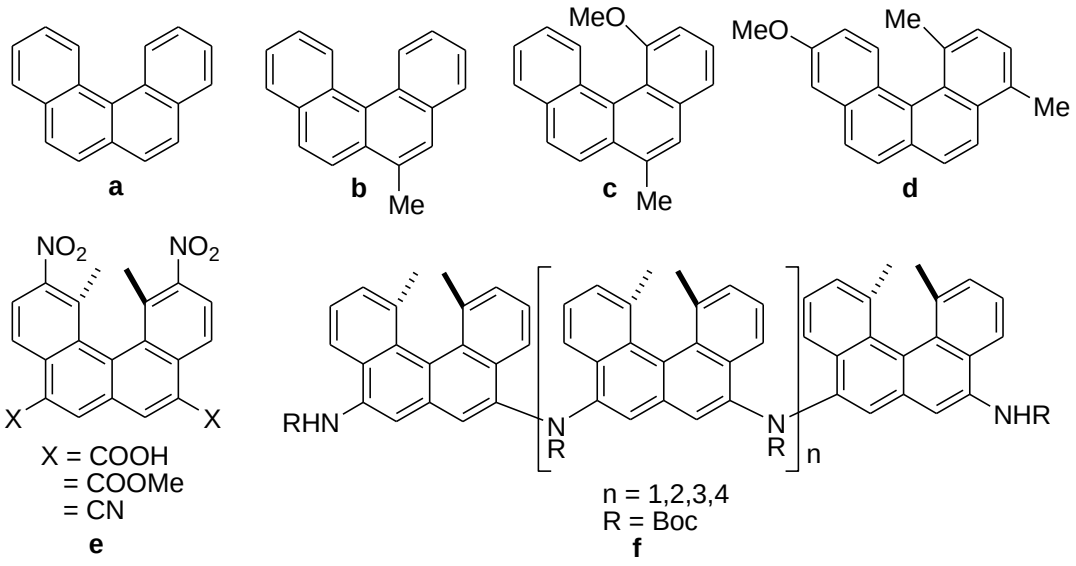


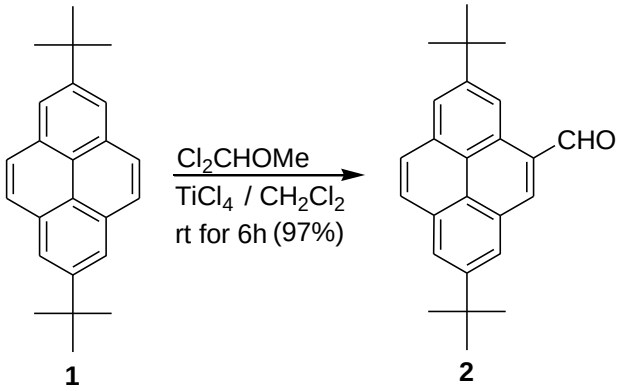
Fig: 3. 2 Chemical structure of [4]helicene derivatives, structure (**a-d**),[23] structure **e,**[7]structure **f**[11]

In this chapter, the synthesis and structural properties, along with the photo physical properties of novel 4,5-naphthalene condensed pyrenes, in which the [4]helicene[22,23,24] structures are contained, will be fully presented.

3.2 Results and Discussion

3.2.a Synthesis and Spectral Properties

The preparation of 2,7-di-*tert*-butypyrene-4-carboaldehyde **2** was carried under various conditions. Thus, formylation of **1** with dichloromethyl methyl ether at room temperature for 3 h in the presence of titanium tetrachloride occurred selectively only at 4-position to afford the corresponding 4-*mono*-formyl derivative **2** in 93 % yield. Prolong the reaction time to 6 h to 12 h, reaction lead to the increase of yield of **2** to 97%. (Scheme: 3.1 and Table 3.1) The compound was purified by washing through column chromatography using mixture of hexane: chloroform (3:1) as eluent and recrystallized from hexane to afford yellow crystalline solid.



Scheme: 3.1 Synthetic routes to 2,7-di-*tert*-butylpyrene-4-carbaldehyde

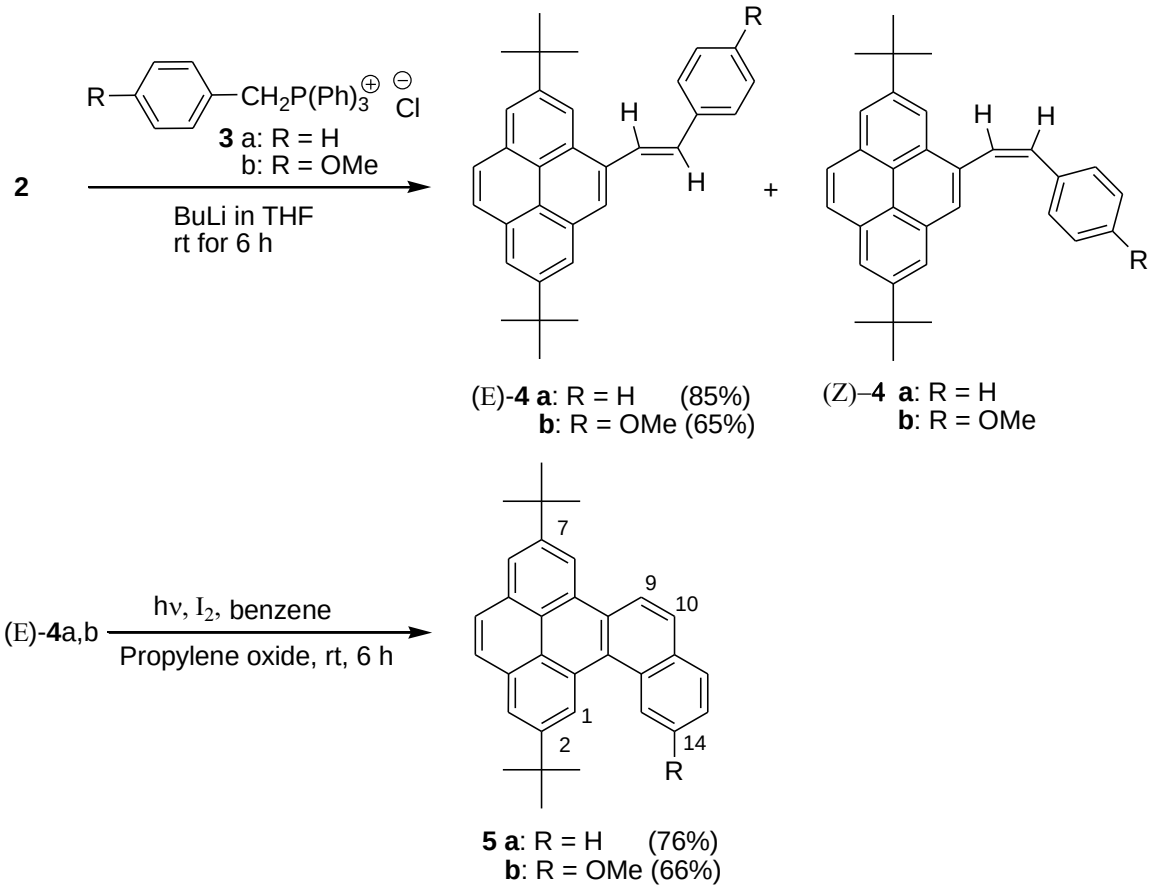
Table 3.1 Formylation of 2,7-di-*tert*-butylpyrene with Cl_2CHOMe.

Run	Lewis acid	Reaction time (h)	Product Yields **2** (%)[b]
1	$TiCl_4$	3	93 [84][c]
2	$TiCl_4$	6	97 [87][c]
3	$TiCl_4$	12	97 [87][c]

[a] Yields are determined by G. L. C. analyses. [b] Isolated yields are shown in square parentheses. [c] The starting compound 1 was recovered in 7 and 3% yields, respectively.

The structure of compound **2** was assigned by spectra data and elemental analysis. The ^1H NMR spectral data (300 MHz, $CDCl_3$) shows a pairs of doublet with meta coupling (J = 1.8 Hz) at δ 8.34, 8.36 ppm for aromatic protons H_1 and H_8, pairs of doublet with meta

coupling (J = 1.5 Hz) at δ 8.71, 9,73 ppm for aromatic protons H_3 and H_6, and a singlet at δ 8.57 ppm for aromatic H_5 protons respectively. Similarly ^{1}H NMR spectra shows a pairs of doublet with ortho coupling (J = 9.0 Hz) at δ 8.01, 8.07 ppm for H_9 and H_{10}, Proton of aldehyde group was found to be resonanced at lower field in δ 10.54 ppm. Also the *t*-butyl protons were observed δ 1.69, 1.59 ppm. The structure of the compound was further established on the basis of the base peak molecular ion at m/z 341. 20 in mass spectrum.



Scheme: 3.2 Synthetic routes to 2,7-di-*tert*-butyldibenzo[*ij,no*]tetraphene **5a** and 2,7-di-*tert*-butyl-13-methoxydibenzo[*ij,no*]tetraphene **5b**

Thus The reaction of **2** and the (4-methoxybenzyl)-triphenylphosphonium chloride **3b** with *n*-butyllithium in THF gave the desired 2,7-di-*tert*-butyl-4-(4-methoxyphenylethenyl)pyrene **4b** in 65% yield, whose *E*/*Z* ratio was 80:20. The *E*/*Z* ratio of the product was determined by its ^{1}H NMR spectrum. The *E* isomer was isolated pure by silica gel column chromatography and recrystallisation from hexane. However, attempted to

isolate *Z*-isomer in pure form failed. Similarly, (*E*)-2,7-di-*tert*-butyl-4-(phenylethenyl)pyrene **4a** was prepared in 85 % yield.

The structures of products *(E)*-**4b** and *(Z)*-**4b** were determined on the basis of their elemental analyses and spectral data. ^{1}H NMR signals of the olefinic protons for *E*-olefins should be observed at lower magnetic field (δ > 7.4 ppm) than that of *Z*-olefins (δ< 6.9 ppm).[25] ^{1}H NMR spectrum of *(E)*-**4b** in $CDCl_3$ shows a singlet at δ 3.88 for methoxy protons, a pair of doublets (*J* = 15.9 Hz) at δ 7.35, 7.91 ppm for olefinic protons, and a pair of doublets (*J* = 8.4 Hz) at δ 6.99, 7.63 ppm for aromatic protons. The structure of the *(Z)*-isomer, *(Z)*-**4b** is also readily assigned from the smaller coupling constant (*J* = 8.8 Hz) than that of (*E*)-**4b** (*J* = 15.9 Hz) at δ 7.14, 7.43 ppm for olefinic protons. Furthermore, the methoxy protons and the aromatic protons are observed much higher field (δ 3.62 ppm and δ 6.52, 6.85) than those of (*E*)-**4b** (δ 3.88 ppm and δ 7.35, 7.91 ppm) due to the ring current of the pyrene ring. Also one of the *tert*-butyl protons of (*Z*)-**4b** was observed at higher field, δ 1.46 ppm due to the shielding effect of the aromatic ring. These data strongly support that the structure of (*E*)-**4b** is the *(E)*-configuration, and the structure of *(Z)*-**4b** is the *(Z)*-configuration.

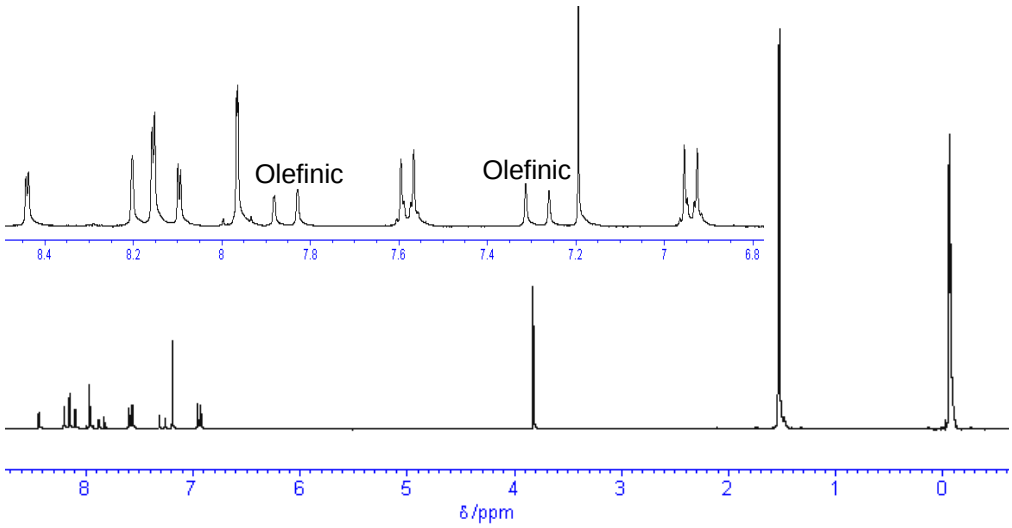


Fig: 3. 3. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of (*E*)-**4b**

When a solution of (*E*)-**4a** and a stoichiometric amount of iodine in benzene was irradiated with a high pressure murcury lamp (400W) at room temperature for 6 h, the photocyclization product, 2,7-di-*tert*-butyl-dibenzo[*ij*,*no*]tetraphene **5a** was obtained only 20

% along with the recovery of the starting compounds. Prolonging the reaction time to 24 h reaction led to the increase of the yield to 30 %. Interestingly, when the irradiation was carried out at room temperature for 6 h with a stoichiometric amount of iodine plus a large amount of propylene oxide[26,27,] in the absence of air led to increase the yield of the desired cyclization product **5a** to 76 %. (Table 3.2) The propylene oxide prevents HI from photoreducing double bond. Also absence of air prevents photooxidative side reactions, such as causing by a photogenerated oxidant, possibly hydrogen peroxide. Similar result was obtained in the case of (*E*)-**4b** and 2,7-di-*tert*-butyl-13-methoxydibenzo[*ij,no*]tetraphene **5b** was obtained in 66% (Table 3.2) yield as light-yellow prisms.

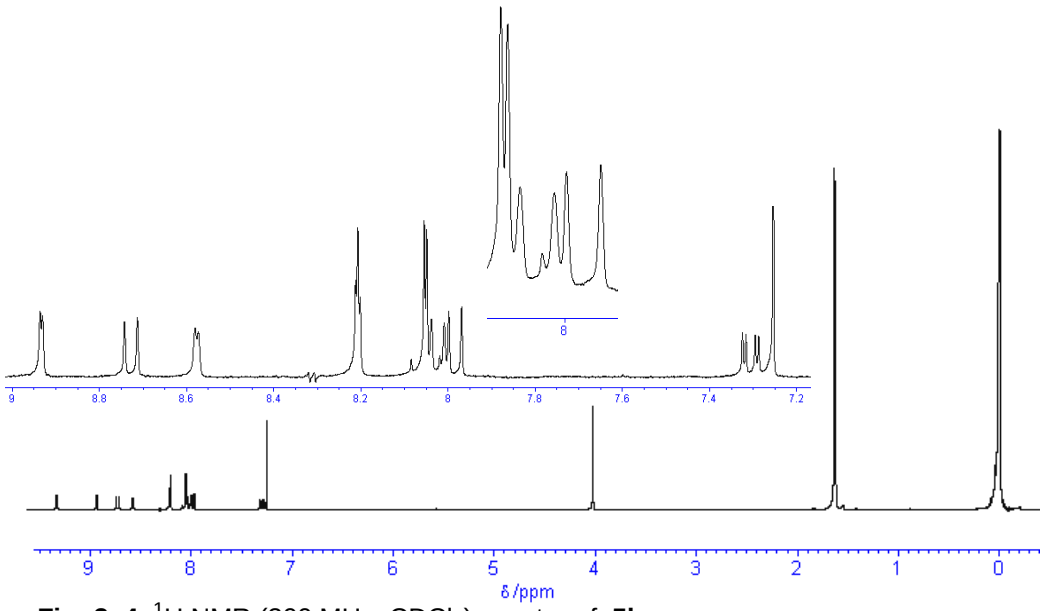
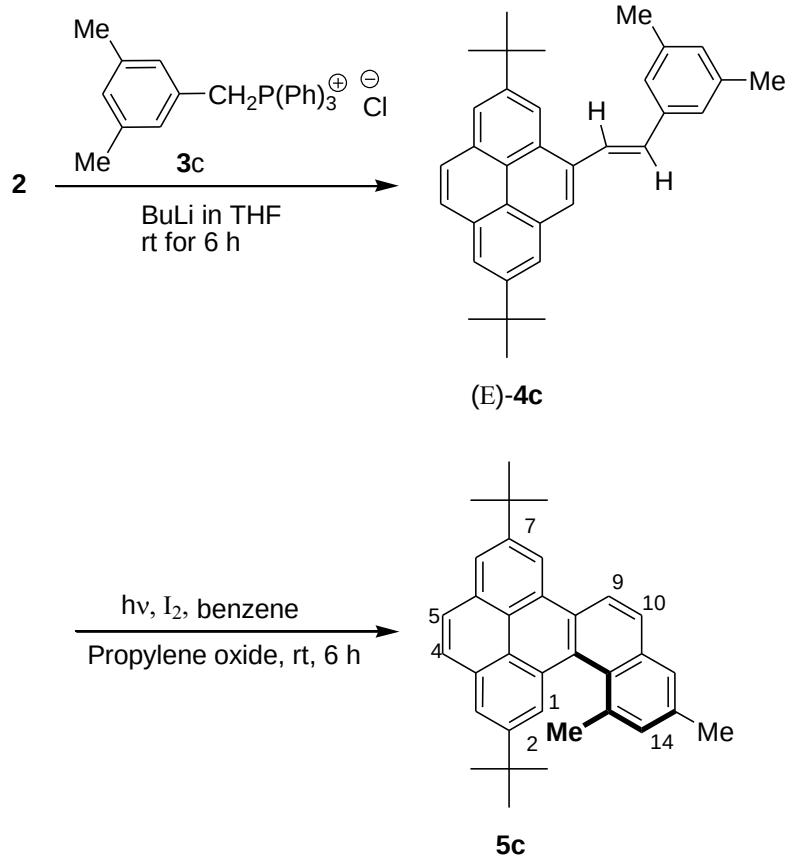


Fig: 3. 4. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **5b**

The structures of products **5a** and **5b** were determined on the basis of their elemental analyses and spectral data. Thus, the structures of **5a** and **5b** were established on the basis of the base peak molecular ion at *m*/*z* 414 and 444 in their mass spectrum, respectively. ^{1}H NMR spectrum of **5b** in $CDCl_3$ shows a singlet at δ 4.02 ppm for methoxy proton, a pair of doublets (J = 9.0 Hz) at δ 8.72, 7.98 ppm for H_9, H_{10} protons, and a pair of doublets (J = 8.3 Hz) at δ 8.03, 8.06 ppm for H_4, H_5 protons. Further the 1- and 14-aryl hydrogens can clearly be seen as deshielded at δ 9.33 ppm (J = 1.5 Hz) and 8.57 ppm (J = 2.4 Hz), respectively by the adjacent ring, a common consequence of the expanded benzene ring.[23]



Scheme: 3.3 Synthetic routes to 2,7-di-*tert*-butyl-12,14-dimethyldibenzo[*ij,no*]tetraphene **5c**

To investigate this finding in more detail, we have introduced methyl group at C_{14} position for dibenzo[*ij*,*no*]tetraphenes which could lead the increased skeletal distortion like benzo[c]phenanthrenes.[23] Thus, the reaction of **2** and the (3,5-dimethylbenzyl)triphenylphosphonium bromide **3c** with *n*-butyllithium in THF gave the desired (*E*)-2,7-di-*tert*-butyl-4-(3,5-dimethylphenylethynyl)pyrene (*E*)-**4c** in 35 % yield. The structure of product (*E*)-**4c** was determined on the basis of elemental analyses and spectral data. Thus the structure of **4c** was established on the basis of base peak molecular ion at m/z 446.67 in mass spectrum. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) shows a pairs singlets for *tert*-butyl groups at δ 1.58, 1.59 ppm, a singlet for methyl protons at δ 2.42 ppm, a pairs of doublets (J = 15.9 Hz) at δ 7.32, 8.00 ppm for olefinic protons, a pairs of doublets (J = 1.8 Hz) at δ 8.21 ppm for aromatic protons. These data strongly supports the structure of **4c** is of (*E*)-configuration.

When a solution of (*E*)-**4c** and a stoichiometric amount of iodine in the presence of propylene oxide in benzene was irradiated with a high pressure mercury lamp (400W) under

the same conditions as in (*E*)-**4a**, the photocyclization product, 2,7-di-*tert*-butyl-12,14-dimethyl- dibenzo[*ij*,*no*]tetraphene **5c** was obtained in 24 % yield (table 3.2) as light yellow prisms. Low yield of the compound may be because of steric congestion of methyl protons in the fjord regions. ^{1}H NMR spectrum of **5c** in $CDCl_3$ shows singlets at δ 2.30, 2.63 ppm for methyl protons, a pair of doublets (J = 8.7Hz) at δ 8.67, 7.96 ppm for H_9, H_{10} protons, and a pair of doublets (J = 8.3 Hz) at δ 8.03 ppm for H_4, H_5 protons. Further, as expected, the 1-hydrogen H_1 and one of the methyl groups at the 14-position can clearly be seen to be deshielded at δ 8.88 ppm (J = 1.5 Hz) and δ 2.63 ppm, respectively by the adjacent ring, a common consequence of the expanded benzene ring.[23] Consequently, we have succeeded to prepare a series of substituted (phenylethenyl)pyrene derivatives **4** and dibenzo[*ij*,*no*]tetraphene derivatives **5**.

Table 3.2 Effect of catalyst in photo induced cyclization reactions

Run	Catlyst	Reaction time (h)	Product Yields (%)		
			5a	**5b**	**5c**
1	I_2	6	20	20	10
2	I_2	12	30	30	15
3	I_2 /PO*	6	76	66	24

* PO = Propylene oxide

3.2.b Photo Physical Properties

The UV-Vis absorption and fluorescence spectroscopic data of novel polycondensed aromatic compounds with [4]helicene structure derived from 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrenes in dilute dichloromethane solution at room temperature were measured and presented in Table 3.5, together with 2, 7-di-*tert*-butyl-pyrene (**1**). The comparative UV-Vis absorption spectra of **4** (before cyclization) and **5** (after cyclization) are shown in Figure: 3.5 and 3.6 respectively. For 2, 7-di-*tert*-butylpyrene (**1**), the absorption spectra are almost identical compared with that of the parent pyrene with three well-resolved, sharp absorption bands observed in the region 300-350 nm. The slight bathochromic shift is

ascribed to the increased electron density to the pyrene ring, arising from the electron-donating nature of *tert*-butyl groups at the 2 and 7 positions.

The UV-Vis absorption spectra of compounds **4** (before cyclization) with **1**, all spectra are broad, less well resolved and the longest wave length hyperchromic absorption maximum of **4a**, **4b** and **4c** occurs at 351, 356, and 354 nm respectively (Table: 3.6), which are bathochromically red-shifted by 12-17 nm arising from the introduced phenylethenyl units at 4 positions. In addition, among these compounds **4**, the methoxy substituted phenylethenylpyrene **4b** display the largest bathochromic shift of the absorption bands, which could be attributed by the strongest electron donating nature of methoxy group compared to -H or -alkyl substituent. This result also shows a slight substitution effects in UV-vis spectra of **4**. With the increase of electron donating nature of the substituent, the UV-vis spectra were found to be more bathochromically red shifted i.e. **4a** < **4c** < **4b**.

The UV spectra of dibenzo[*ij*,*no*]tetraphene derivatives **5** are almost identical and absorption bands were observed in the range of 300-380 nm. The quite different shapes in the UV spectrum of **5** in comparison with those of **4** are ascribed to the expanded conjugation of π-electron system by the cyclization reaction. The pronounced decrease (hypochromic absorption) of absorption bands at 370-380 nm after cyclization was ascribed as because of absence of phenylethenyl units, decrease of aromaticity and increase of distortions from the plane. The UV-spectra of **5** in CH_2Cl_2, showed a large number of transition bands (Figure 3.5), typical for PAHs[28]. Similarly the departures from co-planarity with the aromatic rings are also pronounced with substituent methoxy group, which is ascribed by the absorption bands at 401 for **5b**. Interestingly, the slight different shape in the UV-Vis spectrum of **5c** confirms the increased non planarity of the aromatic ring to avoid the sterically crowding by the overlapping at the C_1 protons and the methyl groups at C_{14} leading to the increased of strain in the system.[23,24]

Upon excitation, a dilute solution (~10^{-7} M) of compound **4** and **5** along with **1** in dichloromethane at room temperature shows broad band blue emission, (Figure 3.6). Compared with the lower energy emission band of 2, 7-di-*tert*-buylpyrene **1**, the lower emission band of 4**a**, **4b** and **4c** were found to be bathochromically red shifted at 476, 434 and 446 nm respectively. All the fluorescence emission bands are broad but almost identical. The emission band was observed in the visible pure-blue region with a small shoulder at longer wave length. However the fluorescence stokes shift increases in the order of **4c** > **4a** > **4b**. On the other hand, compared with the lower emission band of **1**, the lower energy

emission band of **4a** was found to be bathochromically red shifted at 476 nm where as the lower emission band of **4b** and **4c** were found at 434 and 446 respectively.

Table 3.3 Optical absorption and emission spectroscopic data for4**6a-c**, **5a-c**, in CH_2Cl_2 (~ 10^{-6}-10^{-7}M) at room temperature, compared with that of 1 [a]

Compd	Absorption [b] λ_{abs} [nm]	Fluorescence[c] λ_{max}[nm] (λ_{ex})[d]	Stokes-shifts [nm]	F.Q.Y Φ_f[e]
1	339	460 (240)	121	0.10
4a	351	476 (308)	125	0.94
4b	356	434, 454 (321)	78	0.71
4c	354	446 (314)	92	0.84
5a	363	437 (311)	74	0.086
5b	362	426 (321)	64	0.16
5c	374	440 (316)	66	0.13

[a] all measurements were perfomed under degassed conditions. [b] ~10^{-6} M in CH_2Cl_2, λ_{abs} is absorption band appearing at the longest wavelength. [c] ~ 10^{-6} M in CH_2Cl_2, λ_{ex} fluorescence band appearing at the shorest wavelength. [d] wavelength of excitation.[e]absolute quantum yields (± 0.01- 0.03) in dichloromethane.

Similarly the maximum emission spectra of compound **5** (after cyclization) in CH_2Cl_2 are shown in Figure 3.6 and Table 3.3. Compared with the lower energy band of **1**, the lower energy band of **5a**, **5b**, **5c** were found to be hypsochromically blue shifted at 437, 426, 440 nm respectively. All of the fluorescence emission bands are sharper than the corresponding starting compound **4** with small shoulder at longer wavelength and were observed in the visible pure-indigo regions (420-440 nm). The fluorescence stokes shift increases in the order of **7a** > **7c** > **7b**. Compared the quantum yield of compounds, all the 4-ethenyl derivatives showed considerable extent of higher quantum yield yields than all the cyclized compounds **5**. These higher quantum yields of compounds were ascribed to be because of extended π-conjugation of electrons. Despite the electron pushing methoxy group and methyl substitutions, **4b** and **4c** exhibited low quantum yields than **4a**, which were assumed to be because of lost of co-planarity of molecules.

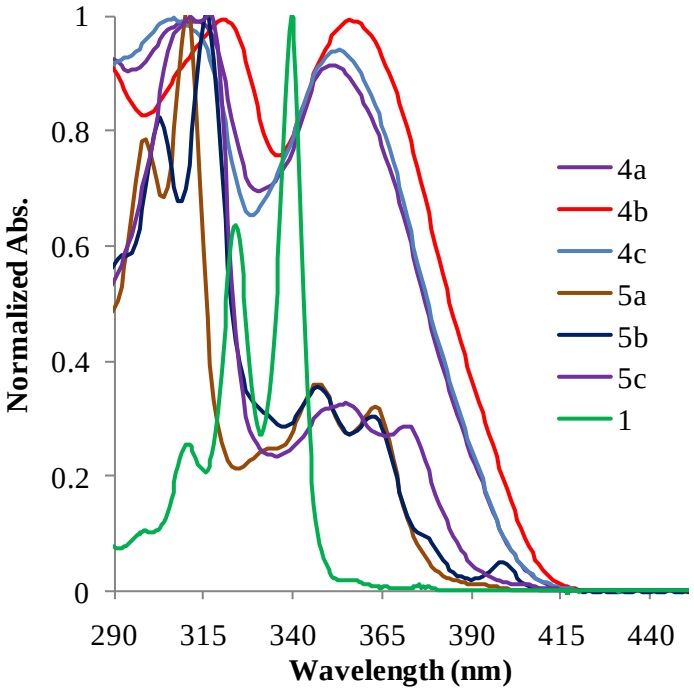


Fig 3.5 Normalized UV-vis absorption spectra of **4** (before cyclization) and **5** (after cyclization) recorded at ~10^{-5} M concentration at 25℃, compared with that of **1**

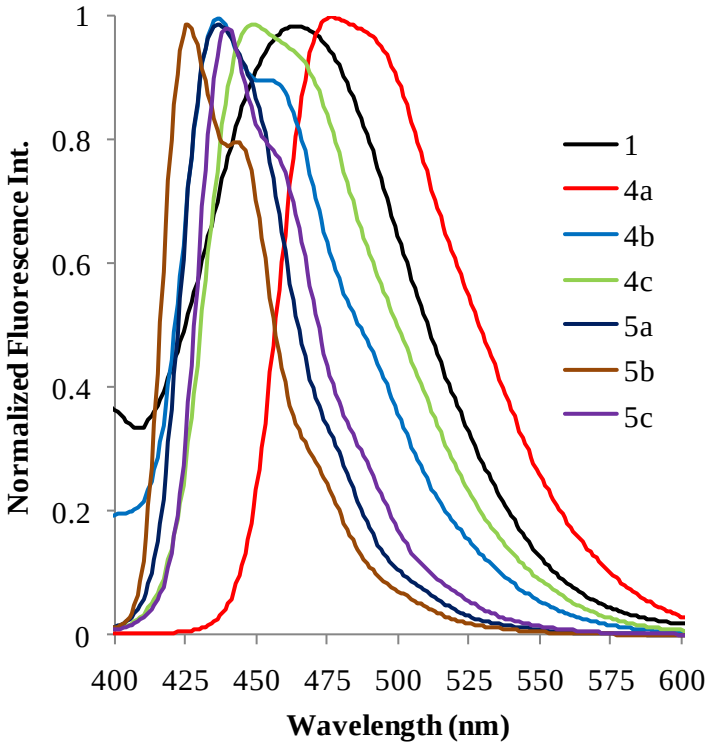


Fig 3.6 Normalized fluorescence spectra of **4** (before cyclization) and **5** (after cyclization) recorded at ~10^{-7} M concentration at 25°C,

After cyclization, because of extended aromatic rings, helicene nature of compounds there is considerable extent of decrease of aromaticity and consequently lesser extent of π-electron delocalization leading hypochromical shift of emission band and low quantum yields. However lesser substitution effect was also observed in the quantum yields of compounds after cyclization, However the quantum yields of the compounds were observed as similar with the 2,7-di-*tert*-butylpyrene **1**.

3.3. Conclusions

We conclude that the Wittig reaction of 2,7-di-*tert*-butylpyrene-4-carboaldehyde with benzyltriphenylphosphonium salt in the presence of *n*-BuLi should be useful for the preparation of 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrenes **4**. Photo-induced cyclization in the presence of iodine and propylene oxide led to the novel expanded π-conjugated systems, dibenzo[*ij,no]*tetraphene derivatives **5**, in which the first number of the [*n*]helicene structures are contained. Introduction of methyl group in the fjord region of [4] helicene compounds were found to be more distorted from the plane. The result obtained through inspecting the absorption and emission spectra of these compounds serves to shift the wavelength to pure blue regions. The result also shows a slight substitution effects in UV-Vis spectra of compound 4 (before cyclization). With the increased of electron donating nature of the substitution, the UV-vis spectra were found to be more bathochromically red shifted. However after cyclization, the wavelengths of emission spectra of compounds were observed to be shifted to the pure indigo regions. All the synthesized 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrene and its derivatives showed considerable extent of higher quantum yields because of extended π-conjugation in the molecules. The higher quantum yields were also enhanced by the central electron accepting pyrene core structural architecture. On the other hand because of increased distortion in the structures of compounds leading to the decrease of π-conjugation, all to the cyclized compounds showed lower quantum yields as expected.

3.4. Experimental

All melting points are uncorrected. The ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with TMS as an internal reference. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. UV/Vis spectra were obtained with a Perkin Elmer Lambda 19

UV/VIS/NIR spectrometer in various organic solvents. Fluorescence spectroscopic studies were performed in various organic solvents in a semimicro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were measured using absolute methods. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyser.

Materials

Preparation of 2,7-di-*tert*-butylpyrene **1** was previously described.[21, 22]

2,7-di-*tert*-butylpyrene-4-carbaldehyde 2: To a stirred solution of 2,7-di-*tert*-butyl-pyrene (5.72g, 20.0mmol) and dichloromethyl methyl ether (3.94g, 34.4mmol) in CH_2Cl_2 (200 mL) was added a solution of titanium tetrachloride (5.0mL, 20.0mmol) in CH_2Cl_2 (100 mL) at 0° C. This mixture was stirred for 3 hrs at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 x 250 mL). The organic layer was washed with water (2 x 300 mL), dried over $MgSO_4$, and evaporated. The residue was chromatographed over silica gel (Wako, C-300; 200g) with hexane as eluent to give a yellow solid, which was recrystallized from hexane: chloroform (1 : 1) to afford the title compound **2** (5.24g, 84%) as yellow prisms. m.p. 268-269 ^{0}C; ^{1}H-NMR (300 MHz, $CDCl_3$): δ (ppm): 1.59 (9H, s, *t*-Bu), 1.61 (9H, s, *t*Bu), 8.01 (1H, d, *J* = 9.0 Hz, Ar-H), 8.07 (1H, d, *J* = 9.0Hz, Ar-H), 8.27 (1H, d, *J* = 1.5 Hz, Ar-H), 8.34 (1H, d, *J* = 1.8 Hz, Ar-H), 8.36 (1H, d, *J* = 1.8 Hz, Ar-H), 8.58 (1H, s, Ar-H), 9.73 (1H, d, *J* = 1.8 Hz, Ar-H), 10.54 (1H, s, CHO). MS (EI): m/z: 342 (M^+). Elemental Analysis for $C_{25}H_{26}O$ (342.20): C; 87.68, H; 7.65, O; 4.67. Found: C; 87. 56, H; 7.75, O; 4.55.

(*E*)-2,7-di-*tert*-butyl-4-(phenylethenyl)pyrene 4a: Wittig reagent was prepared from triphenylphosphine and benzyl chloride in dry benzene. To a solution of Wittig reagent (benzyltriphenylphophonium chloride) **3a** (1.15 g, 3.0mmol) in THF (15mL) was added *n*-BuLi (3.5 mL, 3.0 mmol) at room temperature. After the solution was stirred for 10 min, the solution of 2,7-di-*tert*-butyl-pyrene-4-carbaldehyde **2** (342 mg, 1.0 mmol) in THF (15 mL) was added. The reaction mixture was stirred at room temperature for 6 h under argon, and then it was poured into a large amount of ice-water and extracted with ethyl acetate (2 x 100 mL). The extract was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane: ethyl acetate (5:1) as eluent to give (*E*)-**4a** as light-yellow

solids. Recrystallization from hexane afforded (*E*)-2,7-di-*tert*-butyl-4-(phenylethenyl)pyrene (*E*)-**4a** (437 mg, 85%) as light-yellow prisms. m.p. 188-190°C (dec.); ^{1}HNMR (300 MHz, $CDCl_3$): δ(ppm): 1.59 (9H, s, *t*Bu), 1.60 (9H, s, *t*Bu), 7.34 (1H, t, *J*= 7.5 Hz, Ar-H), 7.40 (1H, d, *J* = 15.9 Hz, Pyrene-CH_b=CH_a-Ar), 7.46 (2H, t, *J* = 7.5 Hz, Ar-H), 7.70 (2H, d, *J* = 7.5 Hz, Ar-H), 8.03 (2H, s, Ar-H), 8.06 (1H, d, *J* = 15.9 Hz, Pyrene-CH_b=CH_a-Ar), 8.16 (1H, d, *J* = 1.8 Hz, Pyrene-H), 8.22, 8.25 (2H, each d, *J* = 1.8 Hz, Ar-H), 8.29 (1H, s, Ar-H), 8.49 (1H, d, *J* = 1.8 Hz, Ar-H). MS (EI): *m*/*z*: 416 (M^+). Elemental Analysis for $C_{32}H_{32}$ (416.60): C; 92.26, H; 7.74. Found: C; 91.78, H; 7.94.

Similarly, (*E*)-**4b** and (*E*)-**4c** were obtained in 65% and 35% yields, respectively. In the case of **4b**, a mixture of (*E*)-**4b** and (*Z*)-**4b** was obtained in the ratio of 80:20 (determined by ^{1}H NMR spectrum) in 85% yield. (*E*)-**4b** isomer was obtained pure by recrystallisation from hexane in 65% yield as light-yellow prisms, but several attempts to obtain (*Z*)-isomer in pure failed.

(*E*)-2,7-di-*tert*-butyl-4-(4-methoxyphenylethenyl)pyrene(*E*)-4b: Wittig reagent was prepared from triphenylphosphine in dry benzene. To a solution of Wittig reagent (benzyltriphenylphophonium chloride) **3b** (838 mg, 2 mmol) in THF (15mL) was added *n*-BuLi (1.7 mL, 2 mmol) at room temperature. After the solution was stirred for 10 min, the solution of 2,7-di-*tert*-butyl-pyrene-4-carbaldehyde **2** (342.4 mg, 1 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature for 6 h under argon, and then it was poured into a large amount of ice-water and extracted with dichloromethane (2 x 100 mL). The extract was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane: dichloromethane (5:1) as eluent to give light-yellow solids. Recrystallization from hexane afforded (*E*)-**4b** (250 mg, 65%) as light-yellow prisms; m.p. 224-226 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.59 (18H, s, *t*Bu), 3.88 (3H, s, O*Me*), 6.99 (2H, d, *J* = 8.4 Hz, Ar-*H*), 7.35 (1H, d, *J* = 15.9 Hz, Pyrene-CH_b=CH_a-Ar), 7.63 (2H, d, *J*= 8.4 Hz, Ar-*H*), 7.91 (1H, d *J* = 15.9 Hz, Pyrene-CH_b=CH_a-Ar), 8.02 (2H, s, Pyrene-$H_{9,10}$), 8.15 (1H, d, *J* = 1.8 Hz, Pyrene-H_1), 8.21 (2H, d, *J* = 1.8 Hz, Pyrene-$H_{6,8}$), 8.26 (1H, s, Pyrene-H_5), 8.49 (1H, d, *J* = 1.5 Hz, Pyrene-H_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ(ppm): 31.94 (Me), 32.04 (Me), 35.19 (C), 35.42 (C), 55.38 (OMe), Pyre-C = 114.112, 114.27, 118.50, 121.88, 122.29, 122.49, 123.06, 124.44, 124.57, 127.27, 127.39, 127.66, 128.03, 129.75, 130.70, 130.72, 131.38, 134.87(C), 148.34(C), 148.76(C); MS (EI): *m*/*z*:

446 (M^+). Elemental Analysis for $C_{33}H_{34}O$ (446.26): C, 88.74; H, 7.67. Found: C, 88.36; H, 7.61.

(*Z*)-2,7-di-*tert*-butyl-4-(4-methoxyphenylethenyl)pyrene(*Z*)-4b: ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.46 (9H, s, *t*Bu), 1.55 (9H, s, *t*Bu), 3.62 (3H, s, O*Me*), 6.52 (2H, d, *J* = 7.5 Hz, Ar-*H*), 6.85 (2H, d, *J* = 7.5 Hz, Ar-*H*), 7.14 (1H, d, *J* = 8.8 Hz, Pyrene-CH_b=C*H*$_a$-Ar), 7.43 (1H, d *J* = 8.8 Hz, Pyrene-*CH*$_b$=CH_a-Ar), 7.71 (2H, s, Pyrene-H_5), 7.82 (1H, d, *J* = 1.5 Hz, Pyrene-H_6), 7.98, 8.12 (1H, each d, *J* = 1.5 Hz, Pyrene-$H_{9,10}$), 8.15 (1H, d, *J* = 1.5 Hz, Pyrene-H_1), 8.23 (1H, d, *J* = 1.5 Hz, Pyrene-H_8), 8.36 (1H, d, *J* = 1.5 Hz, Pyrene-H_3),

(*E*)-2,7-di-*tert*-butyl-4-(3,5-dimethylphenylethenyl)pyrene(*E*)-4c: Wittig reagent was prepared from triphenylphosphine and 1-(bromomethyl)-3,5-dimethylbenzene in dry benzene. To a solution of Wittig reagent **3c** (403.6 mg, 0.87mmol) in THF (10mL) was added *n*-BuLi (0.74 mL, 0.87 mmol) at room temperature. After the solution was stirred for 10 min, the solution of 2,7-di-*tert*-butyl-pyrene-4-carbaldehyde **2** (300 mg, 0.87 mmol) in THF (10 mL) was added. The reaction mixture was stirred at room temperature for 6 h under argon, and then it was poured into a large amount of ice-water and extracted with dichloromethane (3 x 50 mL). The extract was washed with water and brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane: dichloromethane (9:1) as eluent to give pale-yellow solids. Recrystallization from hexane and dichloromethane afforded (*E*)-**4c** (128 mg, 35 %) was obtained as light-yellow prisms; m.p. 141-142 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.58 (9H, s, *t*Bu), 1.59 (9H, s, *t*Bu), 2.41 (6H, s, *Me*), 7.00 (1H, s, Ar-*H*), 7.31 (2H, s, Ar-*H*), 7.32 (1H, d, *J* = 15.9 Hz, Pyrene-CH_b=C*H*$_a$-Ar), 8.00 (1H, d *J* = 15.9 Hz, Pyrene-C*H*$_b$=CH_a-Ar), 8.028, 8.031 (2H, each s, , Pyrene-$H_{9,10}$), 8.16 (1H, d, *J* = 1.8 Hz, Pyrene-H_1), 8.21 (2H, d, *J* = 1.8 Hz, Pyrene-$H_{6,8}$), 8.25 (1H, s, Pyrene-H_5), 8.48 (1H, d, *J* = 1.5 Hz, Pyrene-H_3); ^{13}C NMR (300 MHz, $CDCl_3$): δ(ppm): 21.39 (Me), 31.55 (Me), 31.95 (Me), 35.20 (C), 35.43 (C), Pyre-C = 118.61, 121.99, 122.23, 122.56, 124.75, 124.98, 126.35, 127.28, 127.67, 129.60, 129.75, 130.66, 131.13, 132.24, 134.92, 137.80, 138.29, 148.38(C), 148.79(C); 165.54(C) MS (EI): *m*/*z*: 444 (M^+). Elemental Analysis for $C_{34}H_{36}$ (444.66): C, 91.84; H, 8.16. Found: C, 91.63; H, 8.25.

General procedure for photocyclization:

Photo reactor was a cylindrical glass vessel with an immersion well and two tapered joints, one vertical attached with condenser to which argon source was fitted. Another angled for

withdrawal and addition of samples. The vessel was flat bottom to allow a magnetic stirring bar to rotate. The immersion well was a double walled pyrex tube cooled by water and containing high pressure quartz Hg-vapour lamp. Argon gas was bubbled through benzene for 20-30 min and used to dissolved sample and iodine. To the dissolved solution of sample, iodine and propylene oxide were added to the reaction vessel through angled joint and the lamp was turned on. The reaction was carried out under argon atmosphere. Photo reactions were monitored by ^{1}H NMR and iodine color change. After complete irradiation, work up included washing with 15% $Na_2S_2O_3$. H_2O and saturated brime, drying with anhydrous $MgSO_4$, filtering and concentrated to dryness on a rotary evaporator. The residue obtained was washed either through a short column of silica gel or different solvent systems were used to obtain the pure compounds.

2,7-di-*tert*-butyl-dibenzo[*ij,no*]tetraphene 5a: 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrene **4a** (50 mg, 0.119 mmol), I_2 (28.27 mg, 0.12 mmol) and propylene oxide (1.53 mL, 21.1 mmol) was dissolved in benzene (260 mL), and the solution was irradiated with a high pressure Hg lamp (400 W) for 6 h. The reaction mixture was poured into ice-water (300 mL) and extracted with ethyl acetate (3 × 50 mL). After the ethyl acetate solution had been washed successively with 15% sodium thiosulfate, water and brine the extract was dried over anhydrous sodium sulfate and concentrated. The residue was washed with methanol (10 mL) to afford 2,7-di-*tert*-butyl-dibenzo[*ij,no*]tetraphene **5a** (37.6 mg, 76%) as light-yellow prisms; mp 163-165 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.62 (9H, s, *t*Bu), 1.64 (9H, s, *t*Bu), 7.65-7.68 (2H, m, $H_{12,13}$), 8.05, 8.06 (2H, each d, J = 8.3 Hz, $H_{4,5}$), 8.08 (1H, d, J = 5.7 Hz, H_{11}), 8.09 (1H, d, J = 9.0 Hz, H_{10}), 8.21, 8.23 (2H, each d, J = 1.5 Hz, $H_{3,6}$), 8.86 (1H, d, J = 9.0 Hz, H_9), 8.95 (1H, d, J = 1.5 Hz, H_8), 9.16 (1H, dd, J = 1.2, 7.8 Hz, H_{14}), 9.27 (1H, d, J = 1.2 Hz, H_1); ^{13}C NMR (300 MHz, $CDCl_3$): δ(ppm): 31.85 (CH_3), 32.00 (CH_3), 35.413 (C), 35.479(C), Pyre-C = 118.14, 121.33, 122.30,122.39, 122.74, 123.34, 124.48, 125.84, 127.20, 127.61, 128.15, 128.33, 128.80, 129.16, 130.92, 130.92, 131.03, 131.148, 133. 78, 147.81 (C), 148.70 (C), MS (EI): *m*/*z*: 414 (M^+). Elemental Analysis for $C_{32}H_{30}$ (414.58): C, 92.71; H, 7.29. Found: C, 91.78; H, 7.94.

2,7-Di-*tert*-butyl-13-methoxydibenzo[*ij,no*]tetraphene 5b: (*E*)-2,7-di-*tert*-butyl-4-(4-methoxyphenylethenyl)pyrene **4b** (50 mg, 0.111 mmol), I_2 (28.27 mg, 0.12 mmol) and propylene oxide (1.53 mL, 21.1 mmol) was dissolved in benzene (260 mL), and the solution was irradiated with a high pressure Hg lamp (400 W) for 6 h. The reaction mixture was

poured into ice-water (300 mL) and extracted with ethyl acetate (2 ×50 mL). After the ethyl acetate solution had been washed successively with 15% sodium thiosulfate, water and brine the extract was dried over anhydrous sodium sulfate and concentrated. Washed with 20% hexane/dichloromethane in column chromatogram to afford 2,7-di-*tert*-butyl-dibenzo[*ij,no*]tetraphene **5b** (34 mg, 66%) light-yellow prisms; m.p. 173-174 °C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.63 (9H, s, *t*Bu), 1.62 (9H, s, *t*-Bu), 4.02 (3H, s, O*Me*), 7.30 (1H, dd, *J* = 2.4, 9.0 Hz, H_{12}), 7.98 (1H, d, *J* = 9.0 Hz, H_{10}), 8.02 (1H, d, *J* = 9.0 Hz, H_{11}), 8.03, 8.06 (2H, each d, *J* = 8.3 Hz, $H_{4,5}$), 8.18, 8,20 (2H, each d, *J* = 1.5 Hz, $H_{3,6}$), 8.57(1H, d, *J* = 2.4 Hz, H_{14}), 8.72 (1H, d, *J* = 9.0 Hz, H_9), 8.93 (1H, d, *J* = 1.5 Hz, H_8), 9.33 (1H, d, *J* = 1.5 Hz, H_1); ^{13}C NMR (300 MHz, $CDCl_3$): δ(ppm): 31.99 (Me), 32.03 (Me), 35.47 (C), 55.50 (OMe), Pyre-C = 108.24, 117.66, 118.32, 119.14, 122.20, 122.75, 123.27, 123.42, 127.23, 127.43, 127.59, 128.55, 128.94, 128.81, 131.03, 131.10, 147.71 (C), 148.69 (C), 158.26(C); MS (EI): *m*/*z*: 444 (M^+). Elemental Analysis for $C_{33}H_{32}O$ (444.61): C, 89.15; H, 7.25. Found: C, 89.09; H, 7.26.

2,7-di-*tert*-butyl-12,14-dimethyldibenzo[*ij,no*]tetraphene 5c: (*E*)-2,7-di-*tert*-butyl-4-(3,5-dimethylphenylethenyl)pyrene(*E*)-4c (50 mg, 0.111 mmol), I_2 (28.27 mg, 0.12 mmol) and propylene oxide (1.53 mL, 21.1 mmol) was dissolved in benzene (250 mL), and the solution was irradiated with a high pressure Hg lamp (400 W) for 6 h. The reaction mixture was poured into ice-water (200 mL) and extracted with ethyl acetate (3 ×50 mL). After the ethyl acetate solution had been washed successively with 15% sodium thiosulfate, water and brine the extract was dried over anhydrous sodium sulfate and concentrated. Washed with hexane in column chromatogram to afford 2,7-di-*tert*-butyl-dibenzo[*ij,no*]tetraphene **5c** (15.3 mg, 24%) as white prisms; m.p. 110-111°C; ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.54 (9H, s, *t*Bu), 1.63 (9H, s, *t*Bu), 2.30 (3H, s, Me_{12}), 2.63 (3H, s, Me_{14}), 7.35 (1H, s, H_{13}), 7.69 (1H, s, H_{11}), 7.96 (1H, d, *J* = 8.7 Hz, H_{10}), 8.03 (2H, each d, *J* = 8.3 Hz, $H_{4,5}$), 8.15, 8.21 (2H, each d, *J* = 1.5 Hz, $H_{3,6}$), 8.26 (1H, each d, *J* = 1.5 Hz, H_8), 8.67 (1H, d, *J* = 8.7 Hz, H_9), 8.88 (1H, d, *J* = 1.5 Hz, H_1); ^{13}C NMR (300 MHz, $CDCl_3$): δ(ppm): 21.31 (Me), 24.71 (Me), 31.82 (Me), 32.02 (Me), 35. 34 (C), 35.48(C), Pyre-C = 118.01, 120.94, 122.03, 122.14, 122.24, 124.85, 125.51, 127.03, 127.55, 127.61, 127.94, 128.62, 128.82, 129.87, 131.03, 131.62, 134.50(C), 135.49(C), 135.71(C), 148.70(C); MS (EI): *m*/*z*: 442 (M^+). Elemental Analysis for $C_{34}H_{34}$ (442.65): C, 92.26; H, 7.77. Found: C, 92.87; H, 7.49.

3.5. References

[1] (a) M.S. Newmann, D. Lednicer, *J.Am.Chem. Soc*. **1956**, 78, pp.4765-4774. (b) A. Rajca, M. Miyasaka, *Synthesis and charaterization of Novel chiral conjugated materials*. *Functional Organic Material.* (c) A. Urbano, *Angew. Chem*. **2003**, 115, 4116-4119C. S. Wood, F. B. Mallory, *J. Org. Chem.* **1964**, 29, 3373-3377.

[2] F. B. Mallory, C. S. Wood and J. T. Goedon, *J. Am. Chem. Soc.* **1964**, 86, 3094-3102.

[3] L. Castedo, J. M. Saá, R. Suau and G. Tojo, *Tetrahedron Lett.* **1983**, 24, 5419-5421.

[4] A. J. Floyd, S. F. Dyke and S. E. Ward, *Chem. Rev.* **1976**, 76, 509-562.

[5] D. Pena, A. Cobas, D. Perz, E. Guitian, L. Castedo, *Org. Lett.* **2003**, 5 (11), 1863-1866.

[6] H. Okubo, D. Nakano, S. Anzai, M. Yamaguchi, *J. Org. Chem*. **2001**, 66(2), 557-563.

[7] H. sugiura, k. Teranishi, R. Amermiya, M. Yamaguchi, *Chem. Lett.* **2008**, 37(2), 158-159.

[8] J. Mizukami, H. Sugiura, M. Yamaguchi, K. Mushiake, *Bull. Chem. Soc. Jpn.* **2006**, 79(2), 317-332.

[9] M. K. Lakshman, P.L. Kole, S. Chaturvedi, J. H. Saugier, H. J. C. Yeh, j. P. Glusker, H. L. Carrell, A. K. Katz, C. E. Afshar, W-M. Dashwood, G. Kenniston, W. M. Baird, *J. Am.Chem. Soc.* **2002**, 122, 12629-12636.

[10] H. Sugiura, k. Teranishi, R. Amermiya, M. Yamaguchi, *J.Org. Chem.* **2005**, 70, 5698-5708.

[11] A. Bjørseth and T. Ramdahl, *Handbook of Polycyclic Aromatic Hydrocarbons*, eds. A. Bjørseth and T. Ramdahl, Marcel Dekker, New York, **1985**.

[12] E. Cavalieri and E. Rogan, *Environ. Health Perspect.* **1985**, 64, 69-84.

[13] E. Clar, *Polycyclic Hydrocarbons*, Academic Press, New York, **1964**, Vol. II.

[14] H. Vollmann, H. Becker, M. Correl and H. Streeck, *Justus Liebigs Ann. Chem.* **1937**, 531, 1-159.

[15] A. Streitwieser, R. G. Lawler and D. Schwaab, *J. Org. Chem*. **1965**, 30, 1470-1473.

[16] M. Moyle, E. Ritchie, *Aust. J. Chem.* **1958**, 11, 211-224.

[17] R. G. Harvey, J. Pataki and H. Lee, *Org. Prep. Proced. Int.* **1984**, 16, 144-148.

[18] M. Minabe, S. Takeshige, Y. Soeda, T. Kimura and M. Tsubota, *Bull. Chem. Soc. Jpn.* **1994**, 67, 172-179.

[19] A. M. Braken-van Leersum, J. Cornelisse and J. Lugtenburg, *J. Chem. Soc., Chem. Commun.* **1987**, 1156-1157.

[20] T. Yamato, A. Miyazawa and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 3127-3137.

[21] T. Yamato and J. Hu, *J. Chem. Research*, **2006**, 12, 762-765.

[22] C. Brulé, K. K. Laali, T. Okazaki and M. K. Lakshman, *J. Org. Chem.* **2007**, 72, 3232-3241.

[23] G. Portella, J. Poater, J. M. Bofill, P. Alemany and M. Solá, *J. Org. Chem.* **2005**, 70, 2509-2521.

[24] A. Merz, A. Karl, T. Futterer, N. Stacherdinger, O. Schneider, J. Lex, E. Lubochand J. F. Biernat, *Liebigs Ann. Chem.***1994**, 12, 1199-1209.

[25] L. Liu, B. Yang, T. J. Katz and M. K. Poindexter, *J. Org. Chem.* **1991**, 56, 3769-3775.

[26] I. Ben, L. Castedo, J. M. Saá, J. A. Seijas, R. Suau and G. Tojo, *J. Org. Chem.* **1985**, 50, 2236-2240.

[27] D. Wasserfallen, M. Kastler, W. Pisula, W.A. Hofer, Y. fogel, Z. Wang, and K. Mullen, *J. Am. Chem. Soc.* **2006**, 128, 1334-1339.

Chapter 4

Synthesis, Spectral and Photo Physical Properties of Pyrene Cored First Member of New Double Helicened Polycyclic Aromatic Hydrocarbons Derived From 4,9-bis(arylethenyl)pyrenes and 4,10-bis(arylethenyl)pyrene.

Synthesis and spectral properties of first member of new class of double [4]helicened polycyclic aromatic hydrocarbons derivatives are presented. These compounds features bearing of naphthalene condensed pyrene molecule having double helicene structure. The structures of compounds were fully characterized by ^{1}H / ^{13}C NMR, Mass spectroscopy, elemental analysis. The method proceeds with the Wittig reaction of 2,7-di-tert-butyl-4,9-diformylpyene and 2,7-di-tert-butyl-4,10-diformylpyene with benzyl triphenylphosphonium salt in the presence of n-BuLi and followed by intramolecular photo-induced cyclization in the presence of iodine and propylene oxide leading to the novel expanded π-conjugated systems, tetrabenzo[a,fg,j,op]tetracene, and tetrabenzo[a,de,h,mn]tetracene derivatives. Similarly suitable crystal analysis of the compound indicates the presence of first member of laterally condensed bis [4]helicenes structures. There photophysical properties were carefully examined and these data are in support of helicene structural architecture in the synthesized compounds.

Parts of this work have been submitted to *Eur. J. Org. Chem*. **Arjun Paudel**, Mark R. J. Elsegood, Junnji Tanaka, Takehiko Yamato* 2010.

4. 1 Introduction

As described in previous chapters, for many years, helicenes were considered academic curiosity because of their twisted shape as a result of repulsive steric overlap of the terminal aromatic nuclei.[1] The scientific interest revised due to the unique properties of helicene like *ortho*-condensed aromatic rings a powerful inherently chiral chromophore and by the possibility of electronic interaction.[2] Most recently the helically shaped molecules have found applications as potentially useful components in chiral discotic liquid crystalline materials[3] building blocks for helical conjugated polymers,[4] sensors,[5] dyes,[5] molecular recognition and more fascinatingly as catalysts and ligand in asymmetric synthesis because of their rigid structure and high optical stability.[6] Consequently, there is a sudden surge of interest in helicene with unique properties and in the development of novel synthetic protocols to access them and therefore various methods have been developed and reported for the synthesis of these class of compounds.[1,7]

Although huge efforts have devoted for the new synthetic procedures and been continuously improving. The Friedel-Crafts approach to fused rings was the first example known by Newman[1a] and the photochemically mediated cyclization of stilbenes derivatives developed by Martins have been optimized and widely applied[7b,8] On the other hand, double helicene consists of two annelated helical like subunits with extended π-conjugated system. The first double helicene consisting of head to tail annelated [6]helicene were reported by oxidative photocyclization of stilbene to helicene.[9] Similarly, a conjugated double helicene[10] compound in which two benzene rings are shared by [5]- and [7]helicene was prepared by non photochemical Pd-catalyzed cyclo-trimerization of 3,4-didehydrophenanthrene and also reported. More recently, a conjugated double helicene with two hydrazine-based [5]helicenes, highly annelated in their mid sections were also reported.[11]

However applying polycyclic aromatic hydrocarbons as the core material for the synthesis of helicene compounds have not been reported to that extent. For this propose; particularly we have selected pyrene as core material for the synthesis of mono[14] and bis-helicenes with lots of possibility of extending the helicene framework to the higher members. Synthesis of helicene motifs around the pyrene core molecules is the novel procedure and techniques to get desired helicene compounds having unique molecular architecture consequently novel class of polycyclic aromatic hydrocarbons. On the other hand, we have selected pyrene as core material because of its unique fluorescence properties that have been using as fluorescence probe or fluorescence sensor since long.

Despite the various approaches now available, there exists no efficient method for the synthesis of phenanthrene annulated pyrene at position 4, 5 and 9, 10 as in **1.** On the other hand, the electrophilic substitutions of pyrene occur at 1, 3, 6, and 8 positions but not the other positions (2, 4,5,7,9 and 10). Therefore pyrene substituted at the later positions must be prepared in ways others than by direct electrophilic substitution of pyrene itself.[12] For example Moyle et.al.[13] prepared 4,9-diethylpyrene in a low total yield from ethyl benzene in 14 steps using Friedel-Crafts intramolecular acylation to construct a pyrene ring. Therefore there is substantial interest to investigate the selective introduction of substituent at 4, 5, 9 and 10 positions. Based on these knowledge and reports we synthesized and studied a series of novel polycyclic aromatic hydrocarbons containing bis[*4*]helicene using a simple and most common method i.e. photo induced intramolecular cyclization of series of novel 2,7-di-*tert*-butyl-4,9-bis(phenylethenyl)pyrene and 2,7-di-*tert*-butyl-4,10-bis(phenylethenyl)pyrene.

4.2 Results and Discussion

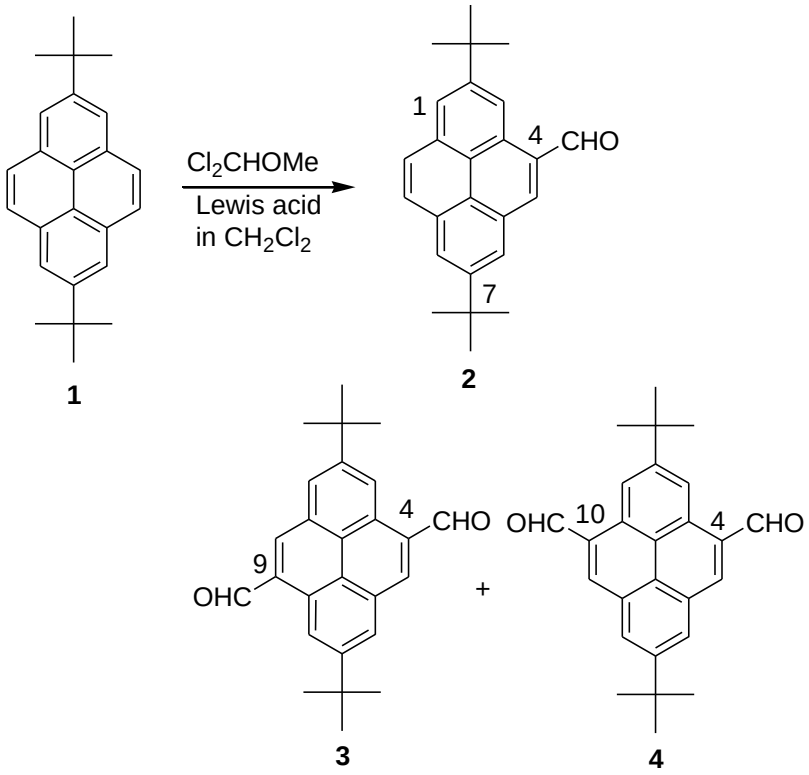
4.2.a Synthesis and Spectral Properties

We have previously reported the $TiCl_4$-catalysed formylation of 2,7-di-*tert*-butylpyrene (**1**) with dichloromethyl methyl ether using *tert*-butyl group as a positional protective group to afford only 4-mono-formylted product (Chapter 3), 2,7-di-*tert*-butylpyrene-4-carbaldehyde **2** in excellent yield.[14] However different regioselectively was observed in the formylation of **1** with dichloromethyl methyl ether (4.0 equiv) in the presence of $AlCl_3$ for 3 h selectively at 4 and 9-position to afford a mixture of the corresponding difomylated product **3** and **4** in which ratio is determined as 74:26 by ^{1}H NMR spectrum, along with 4-formylated derivative **2** in 65% yield (Scheme: 4.1). Interestingly the formylation of **1** with large excess (8.0 equiv) of dichloromethyl methyl ether in methylene dichloride solution in presence of $AlCl_3$ for 12 h increased the yields of the diformylated derivatives **3** and **4** in 65% yield (Table: 4. 1). However several attempts to isolate **4** in pure failed. The ^{1}H NMR data of **3** shows a sets of doublets with the meta-coupling constant (J= 1.8 Hz) at δ 8.44 ($H_{1,6}$) and 9.93 ($H_{3,8}$) ppm as well as a singlet at δ 8.61 ppm, which is assigned to the protons of positions 5, 10 on pyrene ring respectively. On the other hand, ^{1}H NMR spectral data of **4** shows three singlets (relative intensity 1:1:1) at δ 8.51 ($H_{6,8}$), 8.57 ($H_{1,3}$) and 9.82 ($H_{5,9}$) ppm and two singlets (relative intensity 1:1) at δ 1.62 and 1.64 for *tert*-butyl protons. Therefore these data are strong supports for the structure of 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **3** and 2,7-di-*tert*-butylpyrene-4,10-biscarbaldehyde **4**. These results also strongly suggest the *tert*-butyl group on the pyrene ring protects the electrophilic attack at the 1, 3, 6, 8-positions permitting the electrophilic attack at 4,9 and 4,10-positions.[12] These compounds afforded a convenient starting material for the preparation of corresponding bis(arylethenyl)pyrenes by Wittig reaction with arylmethylphosphonium ylide which is followed by photo-induced cyclization reaction.

The reaction of compound **3** and benzyltriphenyl phosphonium chloride **5a** with *n*-butyllithium in THF gave the desired 2,7-di-*tert*-butyl-4,9-bis(phenylethenyl)pyrene (*E*,*E*)-**6a** in 78% yield as major product, while other isomer were not observed (Scheme: 2). The (*E*,*E*)-**6a** was isolated pure by silica gel column chromatography and recrystallisation from hexane. Similarly the series of (*E*,*E*)-**6b** and (*E*,*E*)-**6c** were also prepared in 82 and 75% yields, respectively.

The structures of product (*E*,*E*)-**6a**, (*E*,*E*)-**6b** and (*E*,*E*)-**6c** were determined on the basis of their elemental analyses and spectral data. ^{1}H NMR signals of the olefinic protons

for *E*-olefins should be observed at the lower magnetic field (δ > 7.4 ppm) than that of Z-olefins (δ < 6.9 ppm).[14b] ^{1}H NMR spectrum of (*E,E*)-**6b** in $CDCl_3$ shows a singlet at δ 3.89 ppm for methoxy protons,



Scheme 4.1 Formylation of 2, 7-di-*tert*-butylpyrene

Table 4.1 Formylation of 2,7-di-*tert*-butylpyrene (1) with Cl_2CHOMe[a]

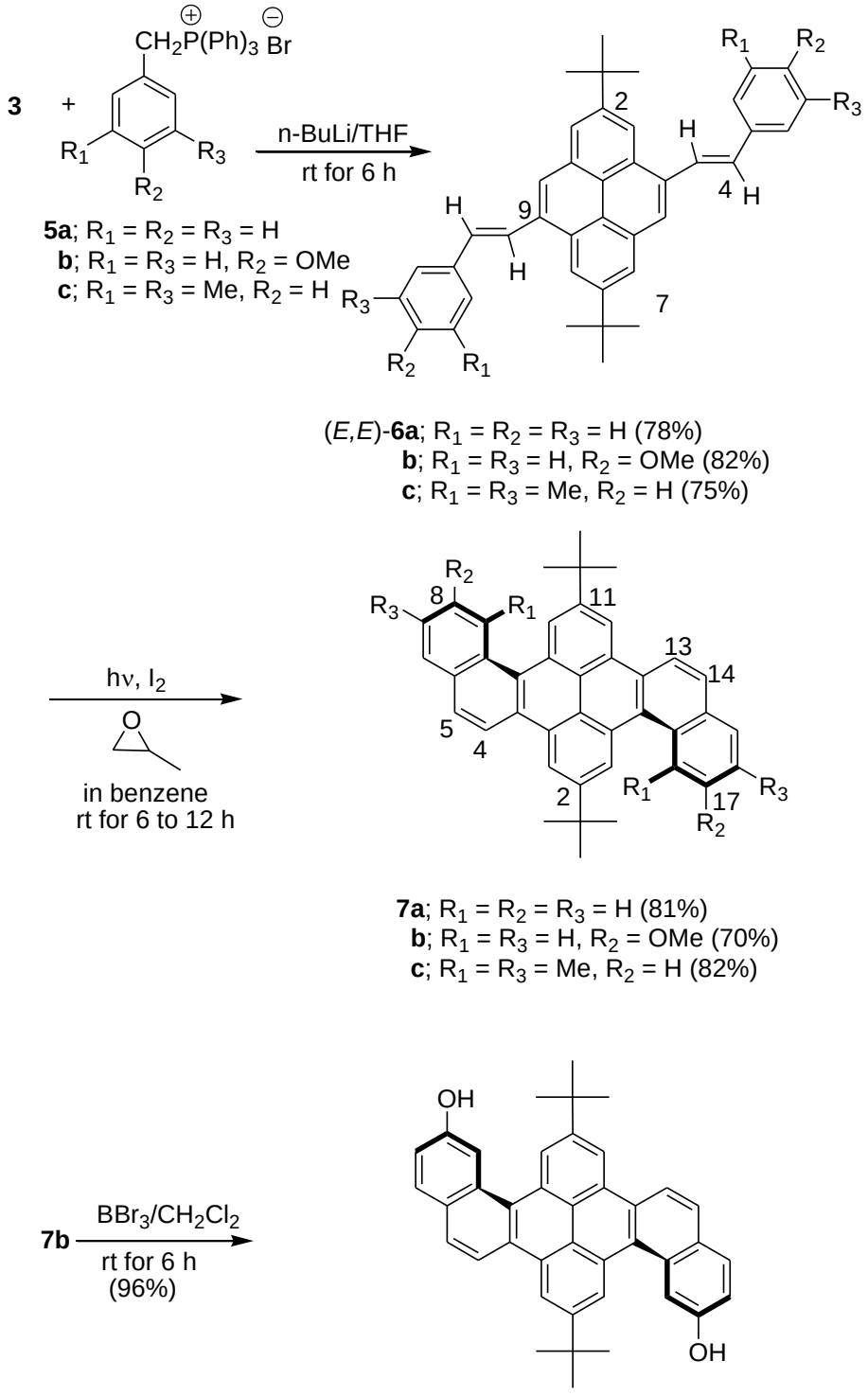
Run	Lewis acids	Reaction time (h)	Product Yields(%)[b]		
			2	**3**	**4**
1	$TiCl_4$	3	93 [84][c]	0	0
2	$TiCl_4$	12	97 [87][c]	0	0
3	$AlCl_3$	3	65	26	9
4	$AlCl_3$	12	3	73 [65]	24

[a]Yields are determined by GLC analysis. [b]Isolated yields are shown in square parentheses. [c]The starting compound 1 was recovered in 7 and 3% yields respectively.

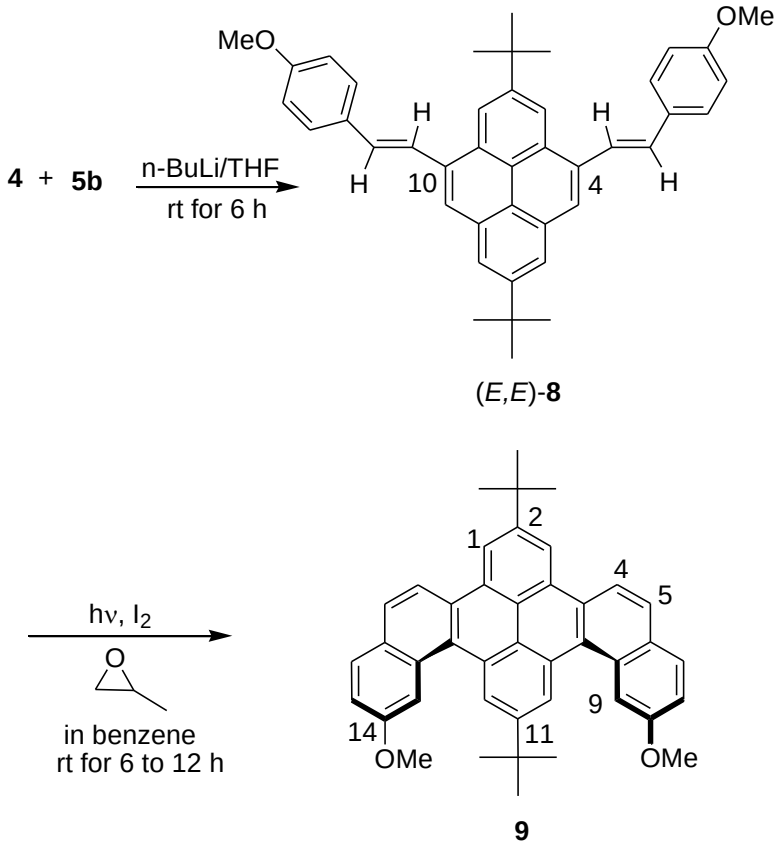
a pair of doublets (J = 15.6 Hz) at δ 7.34, 7.92 ppm for olefinic protons, and a pair of doublets (J = 8.7 Hz) at δ 7.01, 7.65 ppm for aromatic protons. These data strongly supports that the structure of (*E,E*)-**6b** is (*E,E*)-configuration. When a solution of (*E.E*)-**6a** and stoichiometric amount of iodine in benzene was irradiated under pressure mercury lamp (400

W) at room temperature for 6h, the photocyclization product 2,11-di-*tert*-butyltetrabenzo[*a,fa,i,op*]*tert*racene **7a** was obtained in 52% along with the recovery of the starting compound. Prolonging the reaction time to 24h led to an increase of yield to 60%. Interestingly, when the irradiation was carried out at room temperature for 6h with stoichiometric amount of iodine plus an excess amount of pyropylene oxide[8,15] in the absence of air led to increase the yield of desired cyclized product to 81%. The propylene oxide prevents HI from photo-reducing double bond and also reactions, such as causing by photo generated oxidant, possibly hydrogen peroxide. A similar result was obtained in the case of (*E,E*)-**6b** and 2,11-di-*tert*-butyl-8,17-dimethoxytetrabenzo- [*a,fg,j,op*]tetracene **7b** was also obtained in 70% yield as light yellow prisms. The structures of products **7a** and **7b** were determined on the basis of their elemental analyses and spectral data. Thus the structures of **7a** and **7b** were established on the basis of the base peak molecular ion at m/z 514.28 and 574.28 in their mass spectrum respectively. ^{1}H NMR spectrum of **7b** in $CDCl_3$ shows a singlet at δ 4.02 ppm for methoxy proton, a pair of doublets (J = 8.7 Hz) at δ 7.99, 8.07 ppm for $H_{6,15}$ and $H_{5,14}$ protons. Further the protons $H_{1,10}$ and $H_{9,18}$ were found to be deshielded at δ 8.97 ppm (J = 1.5 Hz) and δ 8.52 ppm (J = 2.4 Hz) respectively by the adjacent ring, a common consequence of the expanded benzene ring.[16]

The motto of synthesis of compound **6c** was to introduce methyl groups in 7, 9, 16 and 18 positions in compound **7c** leading to the increased skeletal distortion like benzo[c]phenanthrene.[16] The compound **7c** (82%) was prepared as white solid by using similar method describe above and the structure was determined by elemental analyses and the spectral data. ^{1}H NMR spectra of compound **7c** in $CDCl_3$ shows two singlets at δ 2.36 and 2.65 for methyl protons, two sets of singlets at δ 7.37, 7.72 for $H_{8,17}$ and $H_{6,15}$ respectively. Similarly a pair of doublets (J = 8.7 Hz) at δ 8.02, 8.75 ppm for $H_{5,14}$ and $H_{4,13}$ protons and a pair of doublets (J = 1.65 Hz) at δ 8.18, 8.89 ppm for $H_{1,10}$ and $H_{3,12}$ were observed in ^{1}H NMR spectra. Further as expected the protons $H_{1,10}$ and one of the methyl groups at the 9,18-position can clearly be seen to be deshielded at δ 8.18 ppm (J = 1.8 Hz) and δ 2.63 ppm respectively by the adjacent ring, a common consequence of expanded benzene ring.[16] Interestingly, compared with the ^{1}H NMR values of compounds **7a** and **7b**, the protons $H_{1,10}$ of compound **7c** were observed to be more shielded by 0.80 ppm indicating more twisted structure of **7c** by virtue of Van der Waals steric effect. Consequently, we have demethyled[5b] compound **7b** using boron tribromide led to 2,11-di-*tert*-butyl-8,17-dihydroxytetrabenzo[*a,fg,j,op*]tetracence **7d** in 96% yield (Scheme: 4. 2).



Scheme 4.2 Synthetic routes to bis-[4]helicenes



Scheme 4. 3 Synthetic routes to bis-[4]helicenes

Although several attempted isolation of 4,10-diformyl compound **4** in pure form failed, we have carried out the Wittig reaction of a mixture of **3** and **4** (1:1) with (4-methoxybenzyl)-triphenylphosphonium chloride **5b** in presence of *n*-butyllithium in THF to afford a mixture of desired (*E,E*)-2,7-di-*tert*-butyl-4,10-bis(4-methoxyphenylethenyl)pyrene **8** and 4,9-isomer (*E,E*)-**6b** in 85% yield. Fortunately, we have isolated (*E,E*)-**8** in a pure form by careful column chromatography with ethyl acetate as an eluent. The ^{1}H NMR of the compound **8** shows three singlets relative intensity (1:1:1) at δ 8.19, 8.26 and 8.54 ppm for $H_{1,3}$, $H_{6,8}$ and $H_{5,9}$ respectively for characteristics peaks of 4,10 isomer, a singlet at δ 3.89 for methoxy, a pairs of doublets (J = 15.9 Hz) at δ 7.34, 7.92 ppm for the trans olefinic protons. Similarly we have succeeded to convert (*E,E*)-**8** to 2,11-di-*tert*-butyl-8,14-dimethoxytetrabenzo- [*a,de,h,mn*]tetracene **9** (Scheme: 4. 3). The structure of compound **9** was further confirmed by ^{1}H NMR, elemental analysis and mass spectra. ^{1}H NMR of the compound 9 shows characteristic two sets of singles at δ 9.02, 9.22 for $H_{1.3}$, $H_{10,12}$, respectively. The fjord region protons H_{10} and H_{12} of **9** were found as singlet and observed

more deshielded as compared to that of **7b**, a common consequences for the different orientation of helicene motifs other than the **7b**.

4.2.b X-ray crystal analysis

In order to investigate the helical nature of molecule in detail, suitable crystals of compound **7b** was obtained as pale yellow prisms by using binary solvent systems of methylenechloride (in) and hexane (out). The crystallographic data for this compound are presented in table 4.2. The X-ray analysis of compounds **7b** was carried out on a single crystal obtained[18] as shown in Figure: 4. 1. As shown in figure: 4. 1, compound **7b** lies in two fold axis. Of course, for this crystal where slight structural disorder was observed, the accuracy of the molecular geometry is lower, though in general sufficient to draw some conclusion.

The molecular geometry of helicene skeleton contains short and long C-C bonds. The longer bonds are those mostly affected by the intramolecular torsion (namely C11-C12, C12-C13, C13-C14, C14-C15), average of 1.43 Å. It is noteworthy to mention that in the peripheral rings, the C20-C21 bond length [1.353 (Å)] is significantly shorter than counterpart C13-C14 [1.466 (Å)], showing more twisted structure of peripheral rings because of rigid pyrene core. Similarly the torsonal angles along the inner helical rim of upper limbs C11-C12-C13-C14 and C12-C13-C14-C15 are measured as 18.54° and 19.84° respectively and the torsonal angles along the inner helical rim of lower limbs C26-C27-C28-C29, and C27-C2-C29-C30 are measured as -18.43° and -21.54° respectively. On the other hand nonbonding distances (Å) were calculated as; C37-O; 5.951 Å; C25-C1; 5.397 Å; and C26-C3, 2.991 Å. These values are also a convenient measure of the helicity.[17]

The crystal packing of pyrene molecules has been studied previously. A card-packed structure was observed and the molecules exhibits inter planar separation of ca. 3.5 Å with strong π-π stacking by the involvements of 14 carbons in π-π interactions in pyrene molecules.[18] As shown in figure 4.2 (i) and 3, the present molecule **7b** are packed in herringbone pattern of arrangement in a single dimension. However the overall arrangement of the molecules in a crystal lattice shows pattern of the ladder-like arrays [Figure: 4.2 (ii)]. Interesting, the intermolecular distance ca. 6.214 Å between the pyrenyl planes of two adjacent **7b** molecules is not especially short at ca. 3.50-3.70 Å in the crystal lattice. These results strongly indicated that the two bulky *tert*-butyl groups attached in the pyrene rings at

2 and 11 positions play an important role for suppressing the fact to face π-π stacking in the solid state.

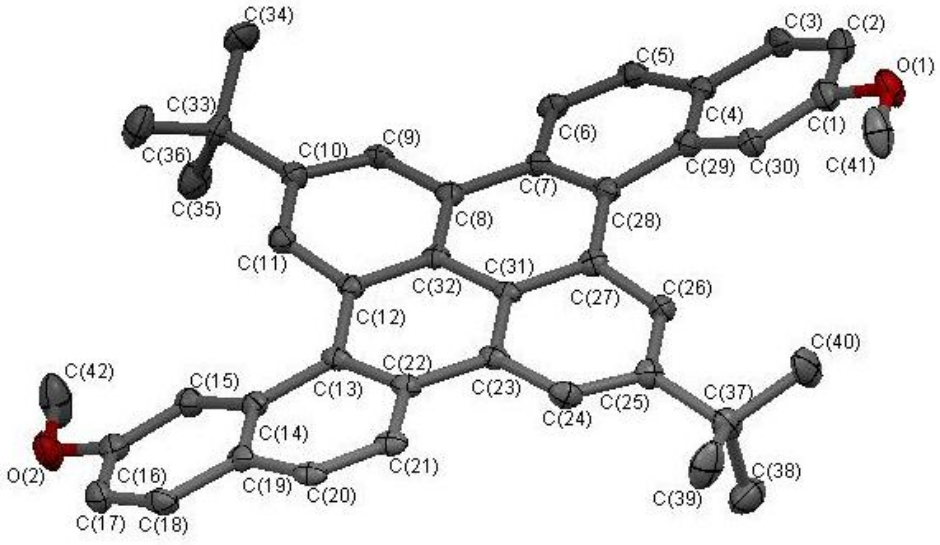


Figure 4.1 X-ray structure diagram of compound **7b** (top view)

These longer inter planar distance, which is due to the presence of the bulky *tert*-butyl group, could justify the greater solubility of synthesized compounds. On the other hand crystal structure suggested that **7b** was synthesized in the conformation in which both helicene rotate in opposite sense (Figure 4. 1)

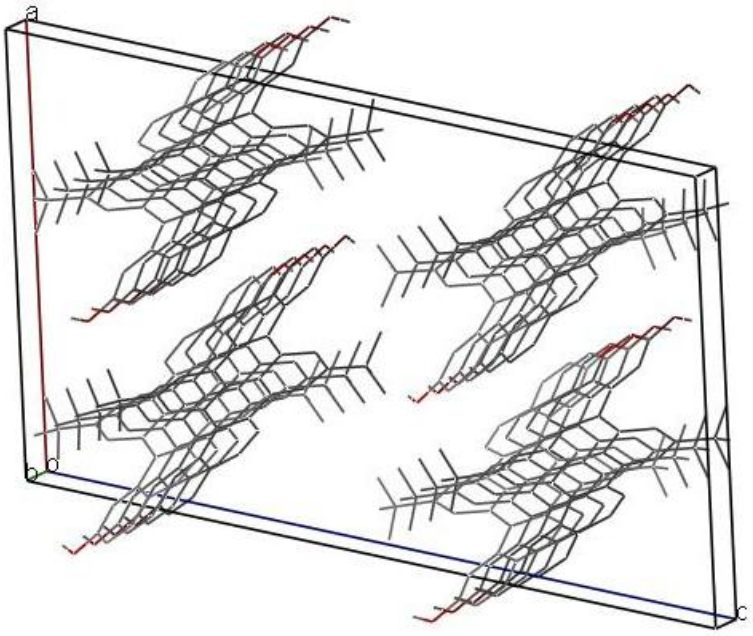
However, the parallel pseudo-stacking between pyrenyl and sideways aromatic rings were observed in the crystal packing of **7b** [Figure: 4.3 (ii)]. In crystal packing, the pyrenyl and lateral rings of adjacent molecules lies on planes at the average distance of short contact ca. 3.262 Å (Table: 4.3) which is suggestive of partial but remarkable intermolecular interaction leading to the strong herring- bone array of molecules [Figure: 4. 3 (i)] in crystal lattice.

Table: 4. 2 Summary of crystallographic data of **7b**

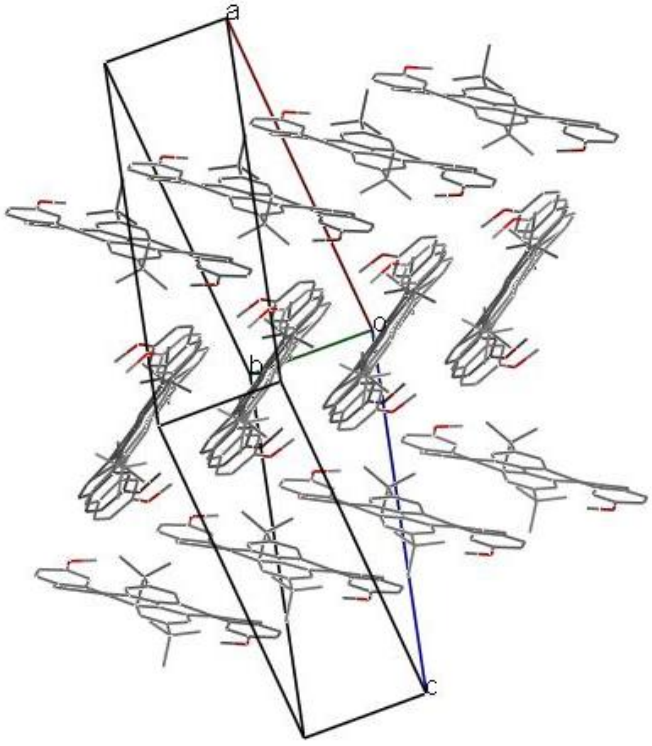
Parameters	**7b**
Empirical Formula	$C_{42}H_{40}O_2$
Formula Weight	576.78
Crystal Color, Habit	colorless, prism
Crystal Dimensions	0.30 X 0.15 X 0.15 mm
Crystal System	monoclinic
Lattice Type	Primitive
Detector Position	55.00 mm
Pixel Size	0.137 mm
Lattice Parameters	a = 17.855(2) Å b = 6.2136(7) Å c = 27.618(3) Å b = 104.3513(17) ^{o} V = 2968.5(6) Å^3
Space Group	$P2_1/c$
Z value	4
D_{calc}	1.290 g/cm^3
F_{000}	1232.00
m(MoKa)	0.771 cm^{-1}
Data Images	1080 exposures
Structure Solution	Direct Methods
No. Observations (All reflections)	6774
No. Variables	398
Reflection/Parameter Ratio	17.02
Residuals: R1 (I>2.00s(I))	0.1180
Residuals: R (All reflections)	0.1356
Residuals: wR2 (All reflections)	0.2846
Goodness of Fit Indicator	1.231
Max Shift/Error in Final Cycle	0.000
Maximum peak in Final Diff. Map	0.52 e$^-$/Å^3
Minimum peak in Final Diff. Map	-0.55 e$^-$/Å^3

Table: 4. 3 Showing the intermolecular distance of short contact < [sum of vdw radii]

Number	Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length(Å)	Length-VdW
1	C(5)	C(31)	x,y,z	x,-1+y,z	3.234	-0.166
2	C(7)	C(22)	x,y,z	x,-1+y,z	3.328	-0.072
3	C(32)	C(20)	x,y,z	x,-1+y,z	3.226	-0.174
4	H(1)	H(33)	x,y,z	x,-1+y,z	2.288	-0.112



(i)

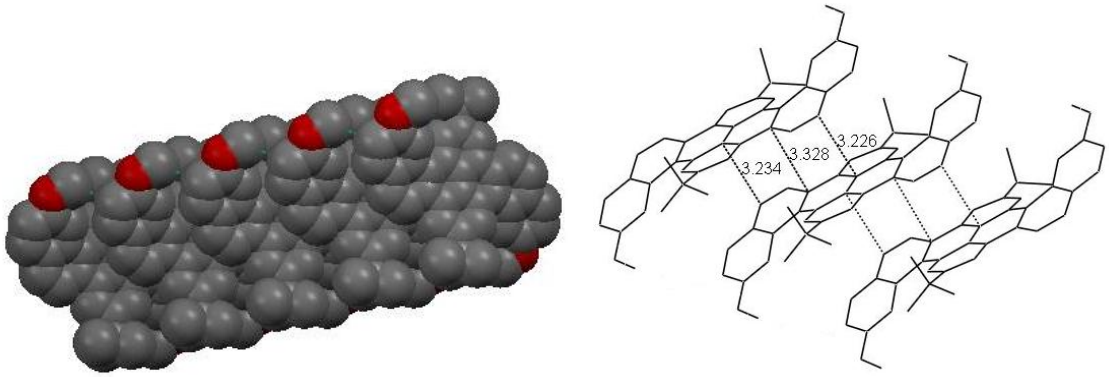


(ii)

Figure 4.2 Packing diagram of compound **7b** (i) highlighting π-π stacking; (ii) showing the packing pattern of the ladder-like arrays.

Similarly the sterically congested non planar polycyclic arene **7c** also contains a double tetrahelicene with none of the ring in common. On the other hand non planar

polycyclic arene **9** also contains a double tetrahelicene but with one of the rings in common [figure: 4.4]. The study of possible Van der Waals interaction and patterns of crystal packing of compound **7d** with x-ray crystallography analysis is under study in our laboratory



(i) **(ii)**

Figure 4.3 (i) Space filled diagram of **7b** showing the π-π -stacking and herringbone pattern of arrangement (ii) . showing intermolecular distance for pseudo-stacking pattern by pyrenyl and lateral rings of **7b**.

.

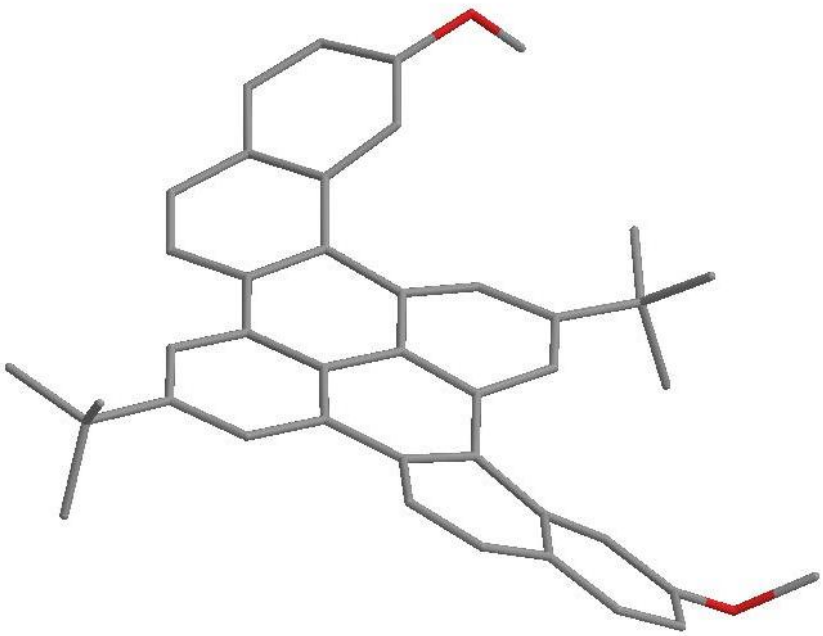


Figure 4. 4 Optimized geometry (MM2) for the proposed conformation of double helicene **9.**

Table: 4. 4 Crystal data and structure refinement for **7c**

Parameters	**7c**	
Chemical formula	$C_{44}H_{42}$	
Formula weight	570.78	
Temperature	150(2) K	
Radiation, wavelength	synchrotron, 0.7749 Å	
Crystal system, space group	triclinic, P $\bar{1}$	
Unit cell parameters	a = 11.3212(6) Å	α = 96.268(4)°
	b = 11.3699(6) Å	β = 96.618(4)°
	c = 25.0897(14) Å	γ = 90.287(4)°
Cell volume	3188.4(3) $Å^3$	
Z	4	
Calculated density	1.189 g/cm^3	
Absorption coefficient μ	0.067 mm^{-1}	
F(000)	1224	
Crystal colour and size	colourless, 0.09 × 0.09 × 0.02 mm^3	
Reflections for cell refinement	8583 (θ range 2.69 to 33.68°)	
Data collection method	Bruker APEX 2 CCD diffractometer	
	ω rotation with narrow frames	
θ range for data collection	2.25 to 30.00°	
Index ranges	h −14 to 14, k −14 to 14, l −32 to 32	
Completeness to θ = 30.00°	99.6 %	
Intensity decay	0%	
Reflections collected	38306	
Independent reflections	14294 (R_{int} = 0.0405)	
Reflections with $F^2>2\sigma$	10105	
Absorption correction	semi-empirical from equivalents	
Min. and max. transmission	0.994 and 0.999	
Structure solution	direct methods	
Refinement method	Full-matrix least-squares on F^2	
Weighting parameters a, b	0.0869, 1.4160	
Data / restraints / parameters	14294 / 0 / 814	
Final R indices [$F^2>2\sigma$]	R1 = 0.0609, wR2 = 0.1558	
R indices (all data)	R1 = 0.0890, wR2 = 0.1721	
Goodness-of-fit on F^2	1.030	
Extinction coefficient	0.0058(9)	
Largest and mean shift/su	0.000 and 0.000	
Largest diff. peak and hole	0.383 and −0.227 e $Å^{-3}$	

As expected, upon the introduction of methyl groups in fjord region of helicene, there is considerable extent of increased distortion in helicene structure. For this, suitable crystals of compound **7c** was obtained as colorless prisms by using binary solvent systems of methylenechloride (in) and hexane(out). The crystallographic data for this compound are presented in Table 4.4.The X-ray analysis of compound **7c** was carried out on a single crystal obtained 18 as shown in figure: 4.5 and 4.6. The X-ray crystal analysis of compound **7c** showed that two molecules in the asymmetric units with centrosymmetric space group. The Compound lies in two fold axis having both of the methyl groups on the same side of pyrene core leading to the surprisingly cured pyrene core. These properties of compounds were quite different than that of compound **7c**, in which the methyl groups were observed to be on opposite direction of the pyrene core.

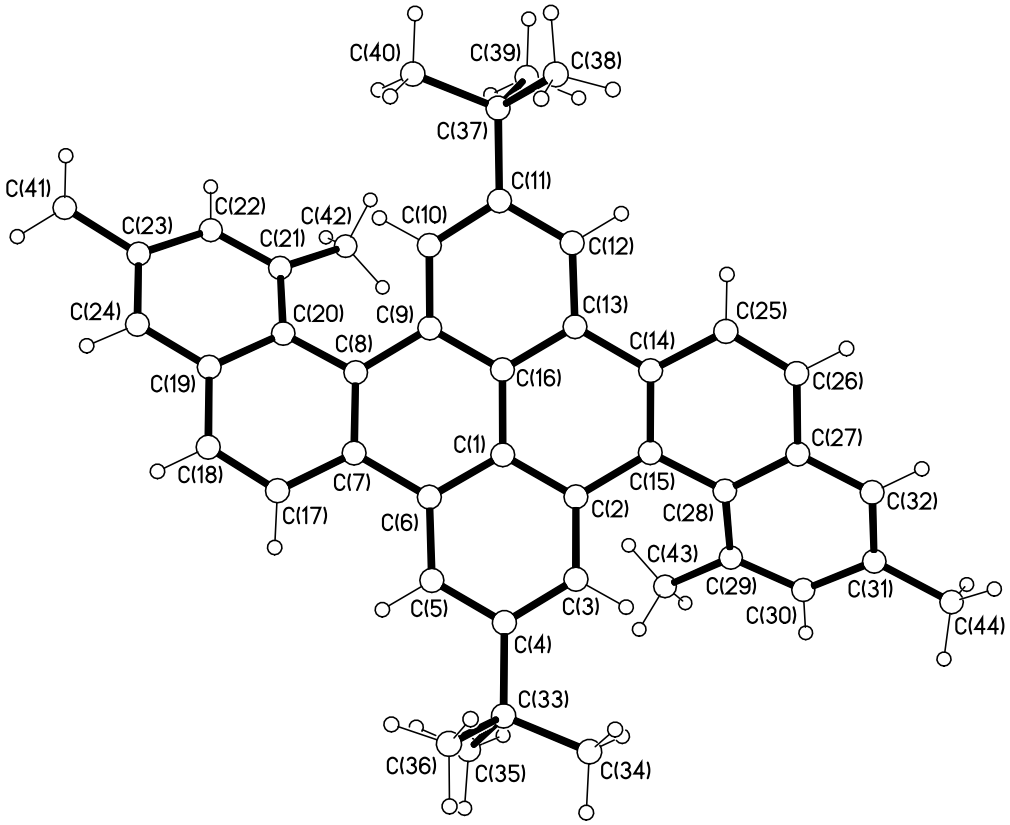


Figure 4. 5 X-ray structure diagram of compound **7c (top view)**

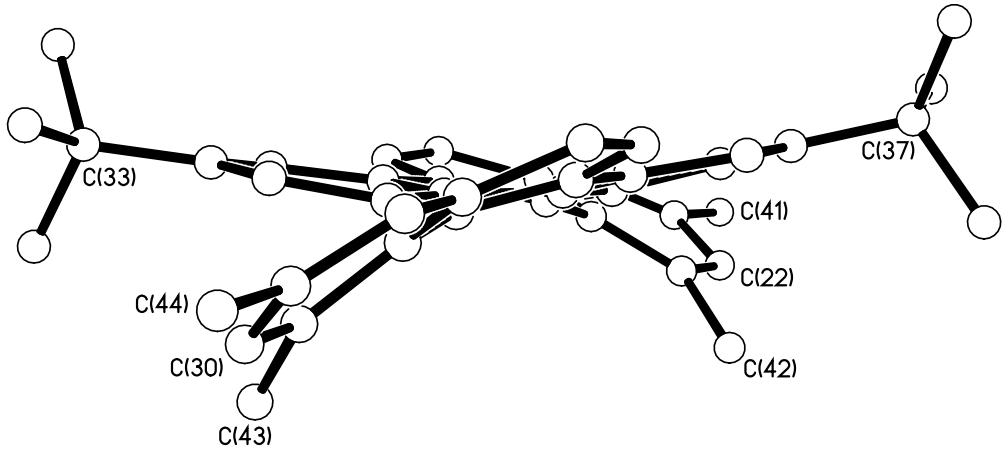


Figure 4.6 X-ray structure diagram of compound **7c (lateral view)**

The molecular geometry of the helicene skeleton contains short and long C-C bonds similar with compound **7c**. The longer bonds are those mostly affected by the intramolecular torsion. The torsonal angles along the inner helical rim of one limb C10-C9-C8-C20 and C9-C8-C20-C21 are measured as 19.32° and 33.34° respectively and the torsonal angles along the inner helical rim of other limb C28-C15-C2-C3 and C29-C28-C15-C2 were measured as 21.79° and 34.55° respectively.

Compared with the torsonal angles of compound **7b**, the helicene motifs of compound **7c** were found to be exhibiting highly distorted structure, a clear indication of effect of introduced methyl groups at fjord regions. In order to study the distortion of the molecules, after the introduction of methyl groups at fjord region, the various planes with in the molecules of **7b** and **7c** were considered and studied as shown in figure 4.7. The figure clearly shows that, twisting of naphthalene motifs from the existing pyrene core of **7b** is 23.04°, whereas same for **7c** is 45.05°. This value is almost double then that of compound **7b**. On the other hand the comparison of twisting of pyrene core for compound **7b** was observed to be 1.15°, where as for **7c**, it is 15.70°. From these data it was concluded that the introduction of methyl group at fjord region is highly responsible for distorted structure of compound **7c**.

The crystal packing of the compound **7c** shows a slanted layers packing parallel to the a, but do not π-π stack because of introduced bulky *tert*-butyl groups on pyrene core and

distorted structure of compound with the introduction of methyl groups at fjord regions. Figure: 4.8.

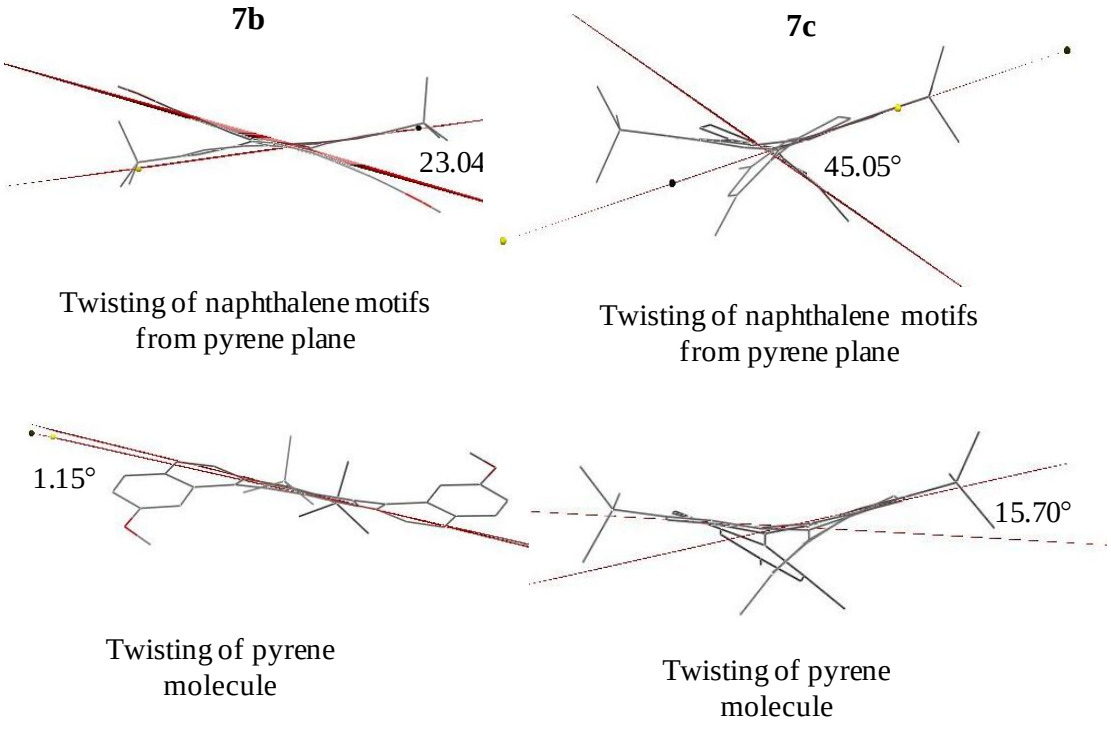


Figure: 4.7 Effect of substitutions in the twisting of molecule from the plane

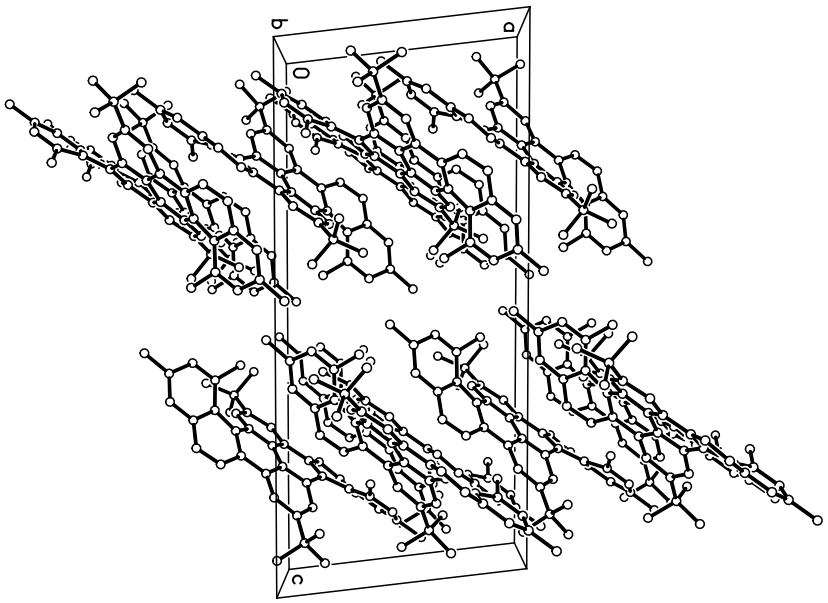


Figure 4.8 Packing diagram of **7c** showing a slanted layeres packing Parallel to a .

4.2.c Photo Physical Properties

The UV-Vis absorption and fluorescence spectroscopic data of novel polycondensed aromatic compounds with 4- *double*-helicene structure derived from 4,9-bis(arylethenyl)pyrenes in dilute dichloromethane solution at room temperature were measured and presented in Table: 4.5, together with 2,7-di-*tert*-butyl-pyrene (**1**) and **9**. The comparative UV-Vis absorption spectra of **6**, **8** (before cyclization) and **7**, **9** (after cyclization) are shown in Figure: 6 and 7 respectively. For 2,7-di-*tert*-butylpyrene (**1**), the absorption spectra are almost identical compared with that of the parent pyrene with three well-resolved, sharp absorption bands observed in the region 300-350 nm. The slight bathochromic shift is ascribed to the increased electron density to the pyrene ring, arising from the electron-donating nature of *tert*-butyl groups at the 2 and 7 positions. The UV-Vis absorption spectra of compounds **6** (before cyclization) with **1**, all spectra are broad, less well resolved and the longest wave length hyperchromic absorption maximum of **6a**, **6b** and **6c** occurs at 370, 376, and 373 nm respectively, which are bathochromically red-shifted by 32-34 nm arising from the introduced phenylethenyl units at 4 and 9 positions. Although the same vibronic feature for 4,10-isomer **8** was observed, the UV-spectra shows less bathochromically red shifted (10 nm) compared with that of **l** and 4,9-derivatives **7** (Figure: 4.6).

A reasonable explanation for these different shifts between 4,9- and 4,10-isomers is that there are quite different conjugation pathways within these molecules. In addition, among these compounds **6**, the methoxy substituted phenylethenyl pyrene **6b** display the largest bathochromic shift of the absorption bands, which could be attributed by the strongest electron donating nature of methoxy group compared to -H or -alkyl substituent. This result also shows a slight substitution effects in UV-Vis spectra of **6**. With the increase of electron donating nature of the substituent, the UV-Vis spectra were found to be more bathochromically red shifted i.e. **6a** < **6c** < **6b**.

The UV spectra of tetrabenzo[*a,fg,j,op*]tetracene derivatives **7** and **9** are almost identical and absorption bands were observed in the range of 300-380 nm. The UV-spectra of **7** and **9** in CH_2Cl_2, showed a large number of transition bands (Figure: 4.5 and 4.6), typical for PAHs[20]. The quite different shapes in the UV spectrum of **7** in comparison with those of **6** are ascribed because of expanded ring system by the cyclization reaction. The pronounced decrease (hypochromic absorption) of absorption bands at 370-380 nm after cyclization was ascribed as because of absence of phenylethenyl unit, decrease of aromaticity and increase of

distortions from the plane and consequently decrease of π-conjugation. Similarly the departures from co-planarity with the aromatic rings are also pronounced with substituent methoxy group, which is ascribed by the absorption bands at 405 and 408 nm for **7b** and **9** respectively. Interestingly, the slight different shape in the UV spectrum of **7c** confirms the increased non planarity of the aromatic ring to avoid the sterically crowding by the overlapping at the $C_{1,10}$ protons and the methyl groups at $C_{9,18}$ leading to the increased of strain in the system.

Table 4.5 Optical absorption and emission spectroscopic data for **6a-c**, **7a-c**, **8** and **9** in CH_2Cl_2 (~ 10^{-6}-10^{-7}M) at room temperature, compared with that of 1 [a]

Compd	Absorption [b] λ_{abs} [nm]	Fluorescence[c] λ_{max}[nm] (λ_{ex})[d]	Stokes-shifts [nm]	F.Q.Y Φ_f[e]
1	339	460 (240)	121	0.10
6a	370	484 (304)	114	0.77
6b	376	481 (308)	105	0.84
6c	373	480 (308)	107	0.85
7a	370	434 (313)	64	0.13
7b	368	430 (319)	62	0.22
7c	381	433 (321)	52	0.15
8	349	433 (345)	94	0.60
9	342	409 (270)	67	0.23

[a] all measurements were performed under degassed conditions. [b] ~10^{-6} M in CH_2Cl_2, λ_{abs} is absorption band appearing at the longest wavelength. [c] ~ 10^{-6} M in CH_2Cl_2, λ_{ex} fluorescence band appearing at the shorest wavelength. [d] wavelength of excitation.[e]absolute quantum yields (± 0.01- 0.03) in dichloromethane.

Upon excitation, a dilute solution (~10^{-7} M) of compound **6** and **8** along with **1** in dichloromethane at room temperature shows broad band blue emission, (Figure: 4.7 and 4.8). Compared with the lower energy emission band of 2,7-di-*tert*-buylpyrene **1**, the lower emission band of **6a**, **6b** and **6c** were found to be bathochromically red shifted at 484, 481 and 480 nm respectively. All the fluorescence emission bands are broad but almost identical.

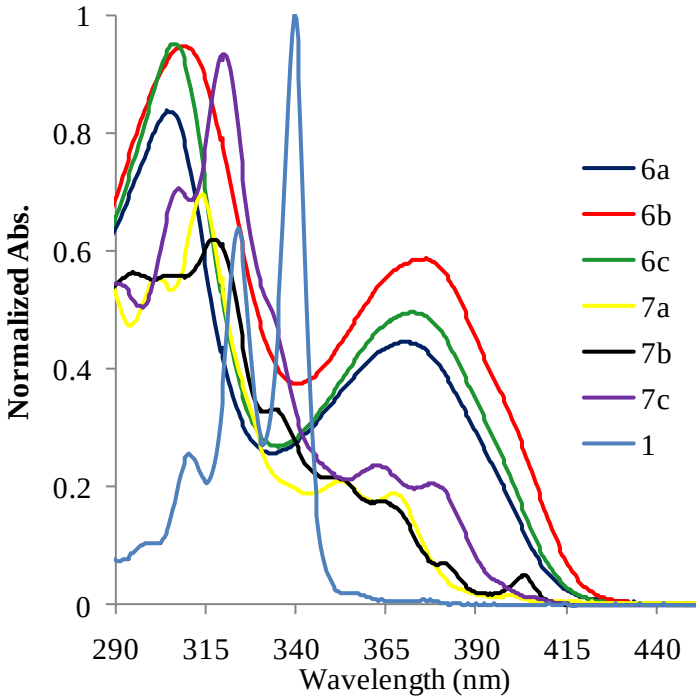


Fig 4.9 Normalized UV-vis absorption spectra of **6** (before cyclization) and **7** (after cyclization) recorded at ~10^{-5} M concentration at 25℃, compared with that of **1**

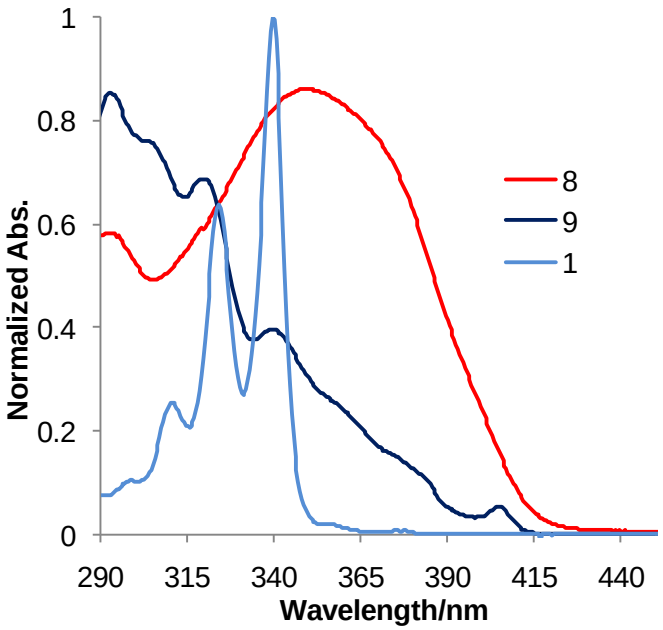


Fig 5.0 Normalized UV-vis absorption spectra of **8** (before cyclization) and **9** (after cyclization) recorded at ~10^{-5} M concentration at 25℃, compared with that of **1** in dichloromethane.

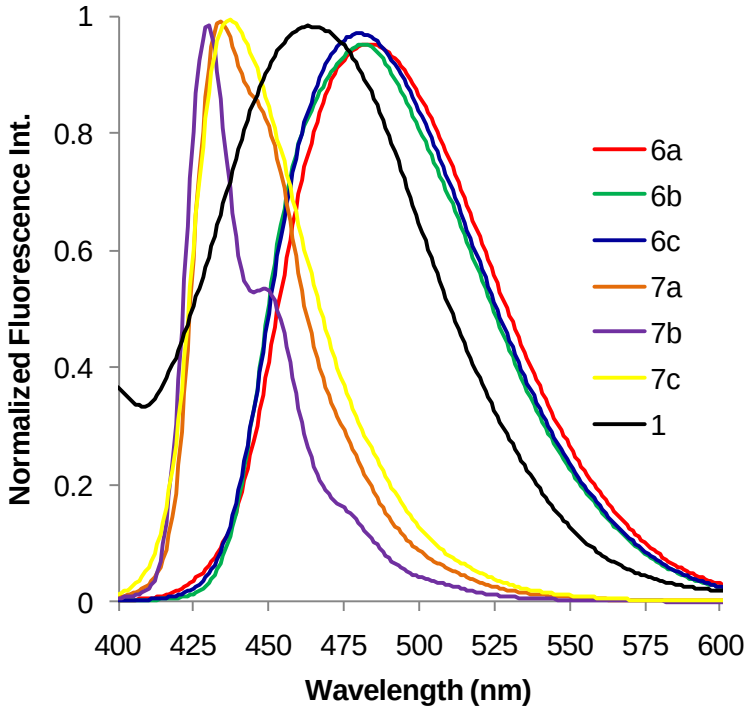


Fig 5.a Normalized fluorescence spectra of **6** (before cyclization) and **7** (after cyclization) recorded at ~10^{-7} M concentration at 25°C, compared with that of **1**

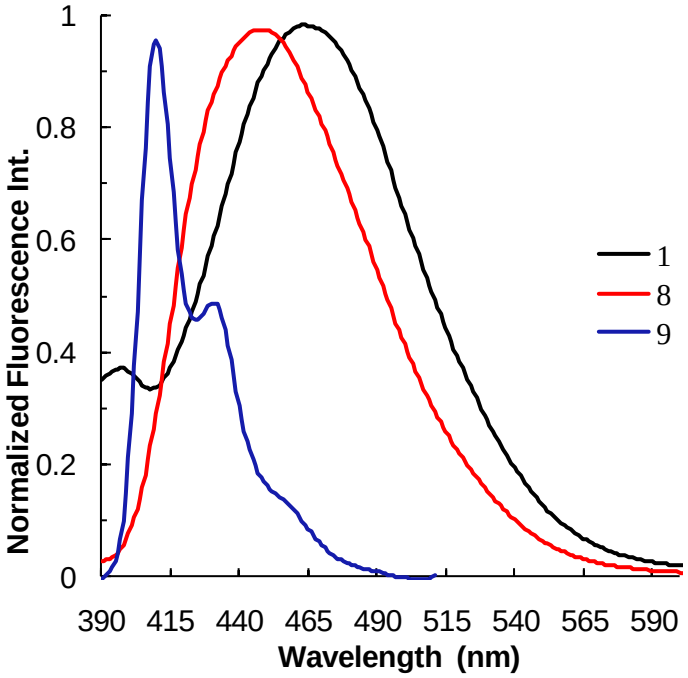


Fig 5.b Normalized fluorescence spectra of **8** (before cyclization) and **9** (after cyclization) recorded at ~10^{-7} M concentration at 25°C, compared with that of **1**

Only one emission band was observed in the visible pure-blue region, a strong indication of emission from the lowest excited state with the largest oscillator strength. However the fluorescence stokes shift increases in the order of **6a** > **6c** > **6b**. On the other hand, compared with the lower emission band of **1**, the lower emission band of **8** was found to be hypochromically shifted at 443 nm.

Similarly the maximum emission spectra of compound **7** and **9** (after cyclization) in CH_2Cl_2 are shown in Figure: 4.7 and 4.8 and Table: 4. 4. Compared with the lower energy band of **1**, The bands of **7a**, **7b**, **7c** were found to be hypsochromically shifted at 434, 430, 433 nm with a small shoulder in each respectively. All of the fluorescence emission bands are sharper than the corresponding starting compounds **6** and were observed in the visible pure-indigo regions (420-440 nm).

The fluorescence stokes shift increases in the order of **7a** > **7c** > **7b**. Interestingly, compared with the starting compound **1**, the emission band of **9** strongly hypsochromically shifted at 409 nm, a visible pure-violet-region (400-420 nm). The fluorescence absolute quantum yields of 1, 6a-c, 8 and, 9 recorded in dilute CH_2Cl_2 solution at room temperature are also listed in Table: 4.4. We found the Φ_f values before cyclization were quite high ranging from 0.77 to 0.85 while as after cyclization was ranging from 0.13 to 0. 23.

4. 3 Conclusions

We conclude that Wittig reaction of 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde (**3**) and 2,7-di-*tert*-butylpyrene-4,10-biscarb- aldehyde (**4**) with benzyl triphenylphosphonium salt in the present of *n*-BuLi should be useful for the preparation of 2,7-di-*tert*-butyl-4,9-bis(phenylethenyl)pyrenes (**6**) and 2,7-di-*tert*-butyl-4,10-bis(phenyl-ethenyl)pyrene (**8**) and their derivatives **6** and **8** respectively. Photo induced cyclization of **6** and **8** in the presence of iodine and propylene oxide led to the novel expanded π-conjugated systems derivatives **7** and **9**, in which the first member of new class of [*n*]helicene structure are contained. The result obtained through inspecting the absorption and emission spectra of these compounds serves to shift the wavelength to pure blue regions. However after cyclization, the wavelengths of emission spectra of compounds were observed to be shifted to the pure indigo and violet regions. The fluorescence spectra of two isomers **7b** and **9** were found to be exhibited quite different fluorescence properties. The single X-ray crystal study revealed that the two *tert*-butyl group on the pyrene moiety play very important role for inhibiting the close face to face π-π stacking interactions between neighboring pyrene units. These longer inter planar

distance, which is due to the presence of the bulky *tert*-butyl group, could justify the greater solubility of synthesized compounds. The parallel pseudo-stacking between pyrenyl and sideways aromatic rings were also observed in the crystal packing of **7b**. In crystal packing, the pyrenyl and lateral rings of adjacent molecules lies on planes at the average distance of short contact ca. 3.262 Å, which is suggestive of partial but remarkable intermolecular interaction leading to the strong herringbone array of molecules in crystal lattice.

4.4 Experimental

All melting points are uncorrected. The ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with TMS as an internal reference. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. UV/Vis spectra were obtained with a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer in various organic solvents. Fluorescence spectroscopic studies were performed in various organic solvents in a semimicro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were measured using absolute methods. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyser.

Materials:

Preparation of 2,7-di-*tert*-butylpyrene (**1**) was previously described.[12]

Formylation of 2,7-di-*tert*-butylpyrene (1) with Cl_2CHOMe in the presence of $TiCl_4$: To a stirred solution of **1** (5.72 g, 20.0 mmol) and dichloromethyl methyl ether (3.1 mL, 34.4 mmol) in CH_2Cl_2 (200 mL) was added a solution of titanium tetrachloride (5.0 mL, 45.5 mmol) in CH_2Cl_2 (100 mL) at 0°C. This mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 × 500 mL). The organic layer was washed with water (2 × 300 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was chromatographed over silica gel (Wako, C-300; 200 g) with a toluene as eluent to give a yellow solid, which was recrystallized from hexane-$CHCl_3$ (1:1) to afford 2,7-di-*tert*-butylpyrene-4-carbaldehyde **2** (5.95 g, 87%) as yellow prisms, m.p 175-177°C (lit.[12a] mp 175-177°C).

Formylation of 2,7-di-*tert*-butylpyrene (1) with Cl_2CHOMe in the presence of $AlCl_3$: To a stirred solution of **1** (5 g, 16.0 mmol) and dichloromethyl methyl ether (20 mL, 224 mmol) in CH_2Cl_2 (150 mL) was gradually added a powdered aluminum chloride (13.3 g, 100 mmol) at 0°C. This mixture was stirred for 12 h at room temperature. The reaction mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 × 300 mL). The organic layer was washed with water (2 × 100 mL), dried over $MgSO_4$, and evaporated in vacuo. The residue was washed with a hot mixture of hexane-ethyl acetate (5:1) (2 × 300 mL) and filtered. The filtrate was concentrated and washed with a hot mixture of hexane-methanol (10:1) (100 mL) to afford the pure 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **3** (3.8 g, 65%) as a yellow solid. Recrystallization from hexane afforded 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **3** (3.26 g, 55%) as pale yellow prisms. m.p. 246-248°C. IR (KBr) ν: 1680 (C=O) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm):1.63 (s, 18H, *t*B u), 8.44 (d, 2H, *J* = 1.8 Hz, Ar-$H_{1,6}$), 8.60 (s, 1H, Ar-$H_{5,10}$), 9.92 (d, 2H, *J* = 1.8 Hz, Ar-$H_{3,8}$), 10.52 (s, 2H, C*H*O). MS (EI) m/z: 370 [M^+]. Elemental Analysis: $C_{26}H_{26}O_2$ (370.5): cacld. C. 84.29, H. 7.07; found C. 84.37, H. 6.99.

On the other hand, the filtrate was evaporated to leave the residue which was chromatographed over silica gel (Wako, C-300; 200 g) with a toluene as eluent afforded a mixture of 4,9-di-formyl- (**3**) and 4,10-diformylpyrene (**4**) in which ratio is determined as 50:50 by ^1H NMR spectrum. Although several attempted isolations of 2,7-di-*tert*-butylpyrene-4,10-biscarbaldehyde **4** in pure failed, However the compound **4** was confirmed by ^1H NMR spectra and GC analysis in a mixture and used crude for next Wittig reaction. ^1H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.62 (s, 9H, *t*Bu), 1.64 (s, 9H, *t*Bu), 8.51 (s, 2H, Ar-$H_{6,8}$), 8.57 (s, 2H, Ar-$H_{1,3}$), 9.82 s, (2H, Ar-$H_{5,9}$), 10.56 (s, 2H, C*H*O).

Synthesis of (*E,E)*-2,7-di-*tert*-butyl-4,9-bis(phenylethenyl)pyrene (*E,E)*- (6a): The Wittig reagent was prepared from triphenylphosphane and benzyl chloride in dry benzene. To a solution of this Wittig reagent (2.33g, 6.0 mmol) in dry THF (15 mL) was slowly added *n*-butyllithium in hexane (3.5 mL, 3.0 mmol) at 0°C under argon. The mixture was stirring for 10 minutes and a solution of 2,7-di-*tert*-butyl-4-formylpyrene (372 mg, 1.0 mmol) in dry THF (15 mL) was injected into this mixture under same conditions.The mixture was heated to room temperature stirring for 6h under argon. The mixture was quenched by large amount of water, extracted with ethyl acetate (2 × 100 mL). The combined extracts were washed with brine and water, dried with $MgSO_4$ and concentrated. The residue was chromatographed over

silica gel (Wako C-300, 200 g) with hexane-ethyl acetate (5 : 1) as eluent to give light-yellow solids. Recrystallization from hexane only afforded **(***E,E)*-2,7-di-*tert*-butyl-4,9-bis(phenylethenyl)pyrene **(***E,E)*-**6a** (404 mg. 78%) as light-yellow solids. m.p. 302-304°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.61 (s, 18H, *t*Bu), 7.33(t, 2H, Ar-*H*), 7.40 (d, 2H, *J*= 15.9 Hz, -CH=C*H*$_a$-), 7.46 (t, 4H, Ar-*H*), 7.70 (t, 4H, Ar-*H*), 8.05 (d, 2H, *J*= 15.9 Hz, -C*H*$_b$=CH-), 8.27 (d, 2H, *J*= 2.7 Hz, Py-*H*$_{3,8}$), 8.30 (s, 2H, Py-*H*$_{5,10}$), 8.49 (d, 2H, *J*= 15 Hz, Py-H$_{1,6}$). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 32.02 (Me), 35.45 (C), 118.55 (C), 122.68 (CH), 125.24 (CH), 126.50 (CH), 126.84, 126.84 (CH), 127.83 (CH), 128.85 (CH), 129.60 (C), 130.98 (CH), 132.00 (CH), 134.49 (C), 137.85 (C), 148.67 (C). MS (EI) m/z: 518 [M^+]. Elemental Analysis: $C_{40}H_{38}$ (518.73): cacld. C. 92.62, H. 7.38; found C. 92.12, H. 7.43.

Synthesis of (*E,E)*-2,7-di-*tert*-butyl-4,9-bis(4-methoxyphenylethenyl)- pyrene (*E,E)*-(6b): The Wittig reagent was prepared from triphenyl- phosphane and 4-methoxy- benzyl chloride in dry benzene. To a solution of this Wittig reagent (2.53 g, 6.0 mmol) in dry THF (15 mL) was slowly added *n*-butyllithium in hexane (3.5 mL, 6.0 mmol) at 0°C under argon. The mixture was stirred for 10 minutes and a solution of 2,7-di-*tert*-butyl-4,9-diformylpyrene (371 mg, 1.0 mmol) in dry THF (15 mL) was injected into this mixture under same conditions. The mixture was heated to room temperature stirring for 6h under argon. The mixture was quenched by large amount of water, extracted with dichloromethane (2 × 100 mL), the combined extracts were washed with brine and water, dried with $MgSO_4$ and concentrated. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane as eluent to give light-yellow solids. Recrystallization from hexane afforded **(***E,E)*-2,7-di-*tert*-butyl-4,9-bis(4-methoxyphenyl- ethenyl)pyrene **(***E,E)*-(**6b**) **(**475 mg, 82%) as light-yellow prisms. m.p. 229-230°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.61 (s, 18H, *t*Bu), 3.89 (s, 6H, OMe), 7.01 (d, 4H, *J*= 8.7 Hz, Ar-*H*), 7.34 (d, 2H, *J*= 15.6 Hz, -CH=C*H*$_a$-), 7.65 (d, 4H, *J*= 8.7 Hz, Ar-*H*), 7.92 (d, 2H, *J* = 15.6 Hz, -C*H*$_b$=CH-), 8.25 (d, 2H, *J*= 1.5 Hz, Ar-*H*), 8.28 (s, 2H, Ar-*H*), 8.47 (d, 2H, *J*= 1.5 Hz, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 32.02 (Me), 35.42 (C), 55.40 (OMe), 114.30 (CH), 118.36 (C), 122.48 (CH), 122.71 (CH), 124.34 (CH), 124.81 (C), 128.04 (CH), 128.04 (CH), 130.74 (CH), 131.05 (C), 131.45 (CH), 134.70 (C), 148.54 (C), 158.51 (C). MS (EI) m/z: 578.3 [M^+]. Elemental Analysis: $C_{42}H_{42}O_2$ (578.78): cacld. C. 87.16, H. 7.31; found C. 86.32, H. 7.28.

Synthesis of (*E,E)*-2,7-di-*tert*-butyl-4,9-bis(3,5-dimethylphenylethynyl)- pyrene (*E,E)*-(6c): The Wittig reagent was prepared from triphenylphosphane and 3,5-dimethylbenzyl bromide in dry benzene. To a solution of this Wittig reagent (1.384 g, 3.0 mmol) in dry THF

(15 mL) was slowly added *n*-butyllithium (in hexane) (1.87 mL, 3.0 mmol) at 0°C under argon. The mixture was stirring for 10 minutes and a solution of 2,7-di-*tert*-butyl-4,9-diformylpyrene (372 mg, 1.0 mmol) in dry THF (15 mL) was injected into this mixture under same conditions. After this addition, the mixture was heated to room temperature stirring for 6 h under argon. The mixture was quenched by large amount of water and extracted with dichloromethane (2 × 100mL). The combined extracts were washed with brine and water, dried with $MgSO_4$ and concentrated. The residue was chromatographed over silica gel (Wako C-300, 200 g) with hexane as eluent to give desired compounds (NMR analysis) as yellow solids. Recrystallization from toluene and hexane afforded **(***E,E)*-2,7-di-*tert*-butyl-4,9-bis(3,5-dimethylphenylethynyl)pyrene **(***E,E)*-**6c** (432 mg, 75.0%) as yellow solid. m.p. 205-207°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.60 (s, 18H, *t*Bu),2.42 (s, 12H, Me), 7.00 (s, 2H, Ar-*H*), 7.33 (d, 2H, *J*= 15.9Hz, -CH=C*H*$_b$-), 7.31 (s, 4H, Ar-H), 7.99 (d, 2H, *J* = 15.9 Hz, -C*H*$_a$=CH-), 8.25 (2H, d, *J* = 1.8 Hz, Py-*H*), 8.26 (2H, s, Py-*H*), 8.47 (d, 2H, *J*= 1.5 Hz, Py-*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 21.40 (py-Me), 32.03 (Me), 35.42 (C), 118.57 (C), 122.56 (CH), 122.74 (CH), 124.75 (CH), 124.75 (CH), 125.21 (CH), 126.21 (C), 130.98 (C), 132.28 (C), 134.74 (CH), 137.78 (C), 138.28 (C), 148.58 (C). MS (EI) m/z: 574.39 [M^+]. Elemental Analysis: $C_{44}H_{46}$ (574.84): cacld. C. 91.93, H. 8.07; found C. 91.99, H. 7.99.

Synthesis of (*E,E)*-2,7-di-*tert*-butyl-4,10-bis(4-methoxyphenylethenyl)- pyrene (*E,E)*-(8): Separation of compound pure 2,7-di-*tert*-butyl-4,10-di-formylpyrene by direct method failed by chromatography as well as solvent treatment methods. For this, the mixture (400 mg) of isomers (2,7-di-*tert*-butyl-4,9 and 4,10-di-formylpyrene 1:1) was treated with 4-methoxybenzyl triphenyl- phosphonium chloride in the presence of *n*-butyllithum in THF (Wittig reaction) was performed to afford a mixture of the 2,7-di-*tert*-butyl-4,9-bis(4-methoxyphenylethenyl)pyrene **6b** and 2,7-di-*tert*-butyl-4,10-bis(4-methoxy-phenylethenyl)pyrene **8**. The careful chromatography with ethyl acetate as eluent afforded the desired compound (*E,E)*-(**8**) (260 mg, 45%) as light-yellow prisms.

m.p. 218-220°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.60 (9H, s, *t*Bu), 1.61 (9H, s, *t*Bu), 3.89 (6H, s, *OMe*), 6.97 (4H, d, *J*= 8.7 Hz, Ar-*H*), 7.34 (2H, d, *J*= 15.9 Hz, Py-CH$_b$=*CH*$_a$-Ar), 7.64 (4H, d, *J*= 8.7 Hz, Ar-*H*), 7.92 (2H, d, *J*= 15.9 Hz, Py-*CH*$_b$=CH$_a$-Ar), 8.19 (2H, s, Py-$H_{1,3}$) 8.26 (2H, s, Py-$H_{6,8}$) and 8.54 (2H, s, Pyrene-$H_{5,9}$). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 31.13 (Me), 35.67 (C), 55.41 (OMe), 114.29 (CH), 118.74 (C), 122.10 (CH), 123.25 (CH), 124.62 (C), 128.05 (C), 130.10 (C), 130.53 (CH), 130.74 (C), 131.47 (C), 135.05

(CH), 148.96 (C), 159.50 (C) ppm. MS (EI) m/z: 578.3 [M^+]. MS (EI): *m*/*z*: 578.3 (M^+). Elemental Analysis: $C_{42}H_{42}O_2$ (578.78): cacld. C. 87.16, H. 7.31; found C.87.16, H.7.31.

General procedure for photocyclization: Photo reactor was a cylindrical glass vessel with an immersion well and two tapered joints, one vertical attached with condenser to which argon source was fitted. Another angled for withdrawal and addition of samples. The vessel was flat bottom to allow a magnetic stirring bar to rotate. The immersion well was a double walled pyrex tube cooled by water and containing high pressure quartz Hg-vapour lamp. Argon gas was bubbled through benzene for 20-30 min and used to dissolved sample and iodine. The dissolved solutions of sample, iodine and propylene oxide were added to the reaction vessel through angled joint and the lamp was turned on. The reaction was carried out under argon atmosphere. Photo reactions were monitored by ^{1}H NMR and iodine color change. After complete irradiation, work included washing with 15% $Na_2S_2O_3{\cdot}H_2O$ and saturated brime, drying with anhydrous $MgSO_4$, filtering and concentrated to dryness on a rotary evaporator. The residue obtained was washed either through a short column of silica gel or different solvent systems were used to obtain the pure compounds.

Synthesis of 2,11-di-*tert*-butyl-tetrabenzo[*a,fg,j,op*]tetracene (7a): (*E,E*)-2,7-Di-*tert*-butyl-4,9-bis(phenylethenyl)pyrene (*E,E*)-**6a** (50.0 mg, 0.0960 mmol) in 230 mL of benzene was irradiated in presence of I_2 (48.73 mg, 0.19 mmol) and propylene oxide (1.64 mL, 18.83 mmol) for 8h. Work up and washed with hexane: EtOAc (1:1) and followed by excess methanol. Recystallisation from dichloromethane and hexane affored 2,11-di-*tert*-butyltetrabenzo[*a,fg,j,op*]tetracene **7a** (40 mg, 81%) as colorless prisms. m.p. 243-245°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.66 (s, 18H, *t*Bu), 7.62-7.72 (m, 4H, Ar-*H*), 8.08 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 8.14 (d, 2H, *J*= 9.0 Hz, Ar-*H*), 8.09 (d, 2H, *J*= 9.0 Hz, Ar-*H*), 8.99 (d, 2H, *J*= 1.5 Hz, Ar-*H*), 9.11 (d, 2H, *J*= 7.5Hz, Ar-*H*), 9.18(d, 2H, *J*= 1.5Hz, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 31.87 (Me), 35.67 (C), 117.84 (C), 121.11 (CH), 123.24 (C), 125.25 (CH), 125.91 (CH), 126.04 (C), 127.89 (CH), 127.99 (C), 128.08 (CH), 128.24 (CH), 128.45 (CH), 128.45 (CH), 128.73 (C), 130.81 (C), 133.75 (C), 148.02 (C) ppm. MS (EI) m/z: 514.28 [M^+]. Elemental Analysis: $C_{40}H_{34}$ (514.27): cacld. C. 93.34, H. 6.66; found C. 93.12, H. 6.55.

Synthesis of 2,11-di-*tert*-butyl-8,17-dimethoxy-tetrabenzo[*a,fg,j,op*] tetracene (7b): (*E,E*)-2,7-Di-*tert*-butyl-4,9-bis(4-methoxyphenylethenyl)- pyrene (50.0 mg, 0.086 mmol) in 200 mL of benzene was irradiated in presence of I_2 (43.6 mg, 0.172 mmol) and propylene oxide (1.54 mL, 22.02 mmol) for 6 h. Work up and chromatography (30% CH_2Cl_2 in hexane)

gave pale yellow solid. Recystallisation from dichloromethane and hexane afforded 2,11-di-*tert*-butyl-8,17-dimethoxytetrabenzo[*a,fg,j,op*]- tetracene **7b (**34.4 mg, 70.0%) as colorless prisms. m.p. 248-249°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm):1.65 (s, 18H, *t*Bu), 4.02 (s, 6H, OMe),7.31 (dd, 2H, *J*= 2.4, 2.4 Hz, Ar-*H*), 7.99 (d, 2H, *J*= 8.7 Hz, Ar-H), 8.07 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 8.52 (d, 2H, *J*= 2.4 Hz, Ar-*H*), 8.76 (d, 2H, *J* = 9.0 Hz, Ar-*H*), 8.97(d, 2H, *J*= 1.5 Hz, Ar-*H*), 9.22 (d, 2H, *J* = 1.8 Hz, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 32.01 (Me), 35.72 (C), 55.43 (OMe), 107.78 (CH), 117.86 (CH), 117.92 (C), 118.88 (CH), 123.25 (C), 124.25 (CH), 127.20 (C), 127.70 (CH), 128.35 (CH), 128.50 (CH), 128.96 (C), 129.34 (CH), 129.92 (C), 132.02 (C). MS (EI) m/z: 574.28 [M^+]. Elemental Analysis: $C_{42}H_{38}O_2$ (574.75): cacld. C. 87.77, H. 6.66; found C. 87.38, H. 6.55.

Synthesis of 2,11-di-*tert*-butyl-7,9,16,18-tetramethyltetrabenzo[*a,fg,j,op*]- tetracene (7c): (*E,E*)-2,7-Di-*tert*-butyl-4,9-bis(3,5-dimethylphenylethynyl)- pyrene (50.0 mg, 0.0867 mmol) in 200 mL of benzene was irradiated in presence of I_2 (43.9 mg, 0.173 mmol) and propylene oxide (1.54 mL, 22.016 mmol) for 12 h. After work up and chromatography (30% CH_2Cl_2 in hexane), The compound thus obtained was further washed with hexane and recrystallized from dichloromethane and hexane to give 2,11-di-*tert*-butyl-7,9,16,18-tetramethyl-tetrabenzo[*a,fg,j,op*]tetracene **7c** (40.3 mg, 82%) as white solid. m.p. 260-261°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.54 (9H,s, *t*Bu), 1.58 (s, 9H, *t*Bu), 2.36 (s, 6H, Me), 2.63 (s, 6H, Me), 7.37 (s, 2H, Ar-*H*), 7.72 (s, 2H, Ar-*H*), 8.02 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 8.184 (d, 2H, *J*= 1.8 Hz, Ar-*H*), 8.752 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 8.89 (d, 2H, *J*= 1.5 Hz, Ar-*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 21.33 (py-Me), 24.90 (Me), 31.87 (Me), 35.63 (C), 117.15 (C), 120.31 (CH), 121.62 (C), 125.10 (CH), 125.84 (C), 127.67 (CH), 127.89 (CH), 128.09 (C), 128.93 (CH), 129.12 (CH), 129.54 (C), 131.81 (C), 134.57 (C), 135.49 (C), 135.75 (CH), 147.38 (C). MS (EI) m/z: 570 [M^+]. Elemental Analysis: $C_{44}H_{42}$ (570.8): cacld. C. 92.58, H. 7.42; found C. 91.49, H. 7.34.

Synthesis of 2,11-di-*tert*-butyl-8,17-dihydroxy-tetrabezo[*a,fg,j,op*]- tetracene (7d): A Schlenk flask was charged with methyl ether **7b** (110.1 mg, 0.191 mmol) and flushed with argon. The material was dissolved in dichloromethane (10 mL) and BBr_3 in 5 mL dichloromethane, (0.85 mL, 0.85 mmol, 4.5 equiv.) was added drop wise. The mixture was stirred at r,t. for 6 h. the mixture was diluted with water (10 mL), extracted with dichloromethane (3 × 20 mL). The organic portion was washed with brine and water and finally dried over anhydrous $MgSO_4$ and solvent was evaporated in vacco. The residue was washed with hexane and recrystallized in chloroform and hexane to afford 2,11-di-*tert*-butyl-

8,17-dihydroxytetrabezo[*a,fg,j,op*]tetracene **7d** (100 mg 96%) as white solid. m.p. 253-254°C. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.66 (s, 18H, *t*Bu), 5.174 (s, 2H, -*OH*),7.22 (dd, 2H, *J*= 2.7, 2.7 Hz, Ar-*H*), 7.99 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 8.515 (d, 2H, *J*= 2.1 Hz, Ar-*H*), 8.73(d, 2H, *J*= 9.3 Hz, Ar-*H*), 8.946 (d, 2H, *J*= 1.5 Hz, Ar-*H*), 9.180 (d, 2H, *J*= 1.5 Hz, Ar-*H*). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 32.01 (Me), 35.62 (C), 111.46 (CH), 116.86 (CH), 117.86 (C), 118.97 (CH), 123.18 (C), 124.56 (CH), 126.83 (C), 128.15 (CH), 128.96 (C), 129.38 (C), 130.30 (CH), 132.93 (C), 147.93 (C), 154.17 (C). MS (EI) m/z: 546.7 [M^+]. Elemental Analysis: $C_{40}H_{34}O_2$ (546.7): cacld. C. 87.88, H. 6.27; found C. 86.58, H. 6.49.

Synthesis of 2,11-di-*tert*-butyl-8,14-dimethoxy-*tert*abenzo[*a,de,h,mn*]- *tert*acene (9): (*E,E*)-2,7-di-*tert*-butyl-4,10-bis(4-methoxyphenylethenyl)- pyrene (50.0 mg, 0.086 mmol) in 100 mL of benzene was irradiated in presence of I_2 (43.6 mg, 0.172 mmol) and propylene oxide (1.54 mL, 22.016 mmol) for 6 h. Work up and chromatography (30% CH_2Cl_2/ Hexane) gave pale yellow solid. of as white crystalline solid. Recystallisation from chloroform and hexane afforded 2,11-di-*tert*-butyl-8,14-dimethoxy-*tert*abenzo[*a,de,h,mn*]-*tert*acene **9** (34.4 mg, 70%) as colorless prisms. m.p. 255-257°C (decomposed). ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.58 (s, 9H, *t*-Bu), 1.70 (s, 9H, *t*-Bu), 4.08 (s, 6H, OMe), 7.32 (dd, 2H, *J*= 2.1, 2.1 Hz, Ar-*H*), 8.00 (d, 2H, *J*= 8.7Hz, Ar-*H*), 8.06 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 8.64 (d, 2H, *J*= 1.8 Hz, Ar-*H*), 8.75 (d, 2H, *J*= 8.7 Hz, Ar-*H*), 9.02 (s, 2H, Ar-*H*), 9.22 (s, 2H, Ar-*H*) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 32.01 (Me), 35.47 (C), 55.48 (0Me), 107.88 (CH), 177.97 (CH), 119.00 (CH), 199.04 (CH), 122.45 (C), 123.69 (CH), 124,65 (C), 127.27 (C), 127.58 (C), 128.04 (CH), 128.86 (CH), 129.09 (CH), 129.96 (CH), 132.06 (C), 146.48 (C), 158.32 (C). MS (EI) m/z: 574.25 [M^+]. Elemental Analysis: $C_{42}H_{38}O_2$ (574.75): cacld. C. 87.77, H. 6.66; found C. 87.77, H. 6.50.

Crystal data and refinement details for 7b and 7c: Diffraction data were collected using a Bruker SMART APEX II CCD diffractometer using narrow frames to θ_{max}= 26.46°.[26] Data were corrected for absorption on the basis of symmetry equivalent and repeated data (min. and max. transmission factors: 0.861, 0.999) and Lp effects. The structure was solved by direct methods and refined on F^2 using all data.[27] H atoms were constrained in a riding model. Further details can be found in Table **4.2** and Table **4.4**.

4. 5 References

1. (a) M.S. Newmann, D. Lednicer, *J.Am.Chem. Soc*. **1956**, 78, 4765-4774. (b) A. Rajca, M. Miyasaka, *Synthesis and charaterization of Novel chiral conjugated materials*. *Functional Organic Material.* (c) A. Urbano, *Angew. Chem*. **2003**, 115, 4116-4119.
2. (a) R, H. Martin, *Angew. Chem.* **1974,** 13, 649-660. (b) D.Z. Wang, T. J. Katz, *Org.Chem.* **2005**, 70, 8497-8502.
3. (a) T. Verbist, S. Sioncke, A. Persoons, L. Vyklicky, T. J. Katz, *Angew. Chem. Int. Ed*. **2002**, 41, 3882-3884. (b) C. Nuckolls, R. Shao, W. G. Jang, N. A. Clark, D. M. Walba, T. J. Katz, *Chem. Mater*. **2002,** 14,773-776 .
4. (a) Y. Dai, T.J. Katz, *Org.Chem*. **1997,** 62, 1274-1285. (b) J. M. Fox, D. Lin, *J. Org.Chem*. **1998**, 63, 2031-2038.
5. (a) B. Laleu, P. Mobian, C. Herse, B. W. Lauresen, G. Hopfgartner, G. Berandinelli, Lacour, *Angew.Chem.* **2005,** 44, 1879-1883. (b) M. T. Reetz, S. Sostmann, *Tetrahedron* **2001**, 57, 2515-2520.
6. (a) Y. Xu, X. Y. Zhang, H. Sugiyama, T. Umano, H. Osuga, K. Tanaka, *J. Am. Chem*. **2004**, 126, 6566-6567. (b) I. Sato, K. Yamashima, K. Kadowaki, J. Yamamoto, T. Shibata, K. Soal, *Angew. Chem. Int. Ed.* **2001,** 40, 1096-1098. (c) S. D. Dreher, T. J. Katz, K. -C. Lam, A. L. Rheingold, *J. Org. Chem.* **2000,** 65, 815-822. (d) H. Sugiura, Y. Takahira, M. Yamaguchi, *J. Org. Chem*. **2005**, 70, 5698-5708. (e) E. Murguly, R. McDonald, N. R. Brandra, *Org. Lett.* **2000**, 2, 3169-3172.
7. (a) H. A. Staab, M. Diehm, C. Kriger, *Tetrahedron Lett*. **1994**, 35,8357-8360. (b) M. Flammang-Barbieux, J. Nasielski, R. H. Martin, *Tetrahedron Lett*. **1967,** 8, 743-744. (c) R. H. Martin, M. Flammang-Barbieux, J. P. Cosyn, M. Gelbcke, *Tetrahedron Lett*. **1968,** 31, 3507-3510. (d) D. C. Harrowven, M.I.T Nunn, D. R. Fenwick, *Tetrahedron Lett.* **2002,** 43, 3189-3191. (e) Y. Ogawa, T. Ueno, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahderon Lett.* **2002**, 43, 7827-7829. (f) J. N. Moorthy, P. Venkatakrishnan, S. Sengupta, M. Baidya, *Org. Lett.* **2006**, 8, 4891-4894. (g) R. E Abed, B. Hassine, J-P. Genet, M. Gorsane, A. Marinetti, *Eur, J. Org. Chem.* **2004**, 1517-1522. (h) D. C. Harrowven, I. L. Guy, L. Nanson, *Angew,Chem. Int.Ed*. **2006**, 45, 2242-2245. (i) F. Aloui, C. B. Hassine, *Tetrahderon Lett*. **2009**, 50, 4321-4323.
8. L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, 56, 3769-3775.
9. P. P. Meurer, F. Vogtle, *Top. Curr. Chem*. **1985**, 127, 1-76.
10. D. Pena, A. Cobas, D. Perez, E. Guitian, L. Castedo, *Org. Lett.* **2003**, 5, 1863-1866.

11.K. Shiraishi, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**, 127, 9312-9313.

12.(a) T. Yamato, A. Miyazawa, M. Tashiro, *J. Chem. Soc. Perkin Trans. 1*, 24, **1993**, 3127-3137. (b) M. Tashiro, T. Yamato, *J. Am. Chem. Soc.* **1982**, 104, 3707-3710 (c) T. Yamato, J. Hu, *J. Chem. Res***. 2006**, 762-765.

13.M. Moyle, E. Ritchie, *Aust. J. Chem*. **1958,** 11, 211224.

14.J. Hu, A. Paudel, T, Yamato, *J. Chem. Res*. **2009**, 109-113. (b) A. Paudel, J. Hu, T. Yamato, *J. Chem. Res*. **2008**, 457-460.

15.(a) I. Ben, L. Castedo, J. M. Saa, J. A. Seijas, R, Suau, G. Tojo, *J. Org. Chem*. **1985**, 50, 2236-2240. (b) Y. Kitahara, K. Tanaka, *Chem. Commun.**2002***, 932-933.

16.C. Brule, K. K. Laali, T. Okazaki, M. K. Lakshman, *J. Org. Chem.* **2007**, 72, 3232-3241.

17.M. K. Lakshman, L. P. Kola, S. Caturvedi, H. Saugier, H. J. C. Yeh, P. J. Glusker, H. L. Carrell, K. A. Katz, C, E. Afshar, W-M. Dashwood, G. Kenniston, W.M. Baird, *J. Am.Chem.Soc*. **2000,** 122, 12629-12636.

[18] M.Pope, C. E. Swenberg, *Electronic Processes in Organic Crystals and Polymers*, 2nd edition, Oxford University Press, Oxford 1999, 48-53.

Chapter 5

Synthesis, Structural and Photo Physical Properties of Pyrene Cored First Member of New Single Helicened Polycyclic Aromatic Hydrocarbons Derived from 7-*tert*-butyl-1,3-dimethyl-5-(phenylethenyl)pyrenes.

In this chapter, more efficient routes to substituted and unsubstituted 7-tert-butyl-1,3-dimethylpyrene based [4] helicene compounds with their optoelectronic properties are presented. Wittig reaction of 7-tert-butyl-1,3-dimethyl-5-formylpyrene with benzyltriphenylphosphonium salt in the presence of n-BuLi to afford 7-tert-butyl-1,3-dimethyl-5-(phenylethenyl)pyrenes, from which naphthalene condensed aromatic compounds, 7-tert-butyl-1,3-dimethyl-13-methoxydibenzo[ij,no]tetraphene, and 7-tert-butyl-1,3-dimethyl-12,14-dimethyldibenzo[ij,no]tetraphe were obtained by photo-induced cyclization in the presence of iodine and propylene oxide. The methyl group induced helicity in the synthesized [4] helicene compounds were also discussed. The structure of these new compounds were determined on the basis of their elemental analyses and spectral data, On the other hand, studies on the electronic UV-Vis absorption and fluorescence emission properties for these novel pyrene derivatives are fully presented by using UV-vis absorption and photoluminescence spectroscopy analysis.

Part of this work have been published: Jian-young Hu, **Arjun Paudel** and Takehiko Yamato, *J. Chem. Res*, **2008**, 6, 308-311.

5. 1 Introduction

Although described in earlier 20th century literature by Weitzenbock and co-worker, as well as Mayer and Oppenheimer,[1] confirmed isolation of the first tetra helicene **1**, did not occur until the early 1930s when Cook et al. reinvestigated the work.[2,3] Parent benzo[c]phenanthrene (B[C]Ph) **1** is the smallest polycyclic aromatic hydrocarbon (PAH) with a fjord region. As the first member of the [n]helicene family.[4] it has a twisted framework with an angle of 27° between the A and D rings from the x-ray structure.[5] Focusing on structure /activity relationships, the 3-, 4-, 5-, and 6 methylated derivatives of such compounds were found to be tumorigenic in mouse skin, but the 1-Me and 2-Me derivatives were reported as less active than the parent (B[C]Ph).[6] Fluorine substitution on the benzo ring found to be exhibit enhanced tumorigenicity relative to parent **1**, except for the 2-fluoro derivative which was less active.[7] Nitration, acetylation, and bromination of parent **1** were studied by Newman and Koask in 1940s, showing preferential substitution at C-5.[8]

The influence of planarity on the metabolic activation and DNA binding properties of PAHs have been studied M.K. Lakshman et al. in 2000[9] and reported the increased nonplanarity in this type of PAH lowered its ability to be metabolically activated to form DNA-damaging adducts. Interestingly the report also described the convenient synthetic route to 1,4-DMBcPh, its (±)-trans 9,10-dihyrodiol as well as the (±)-9 β,10α,1α-epoxide and comparative metabolic activation and DNA binding of BcPh, 1,4-DMBcPh and their dihydrodiols has been investigated using mammary carcinoma MCF-7 cells. The study also showed that a fjord region methyl can induced helicity in this small hydrocarbons which then results in the hydrocarbon demonstrating atropisomerism (P and M helicity).Methyl substitution into the highly congested fjord region increased skeletal distortion from 27° for A/D ring angle in B[C]Ph to 30° for that in 1, 4-dimethyl-B[C]Ph **2.** [10]

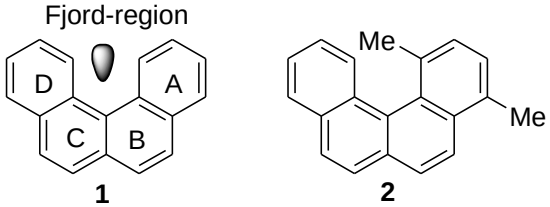


Fig: 5.1. Structures **1 and 2**

Photochemical ring closure of appropriate stilbenes to phenanthrenes has proven to be a good method for the synthesis of several angular fused PAHs,[11] and as extensions of this method the synthesis of fjord-region dihydrodiols have been documented.[12] However, for the present study, the suitability of this method was not known since the introduction of a fjord-region by at least one methyl group on the course of the pyrene based photocyclization had not been documented.

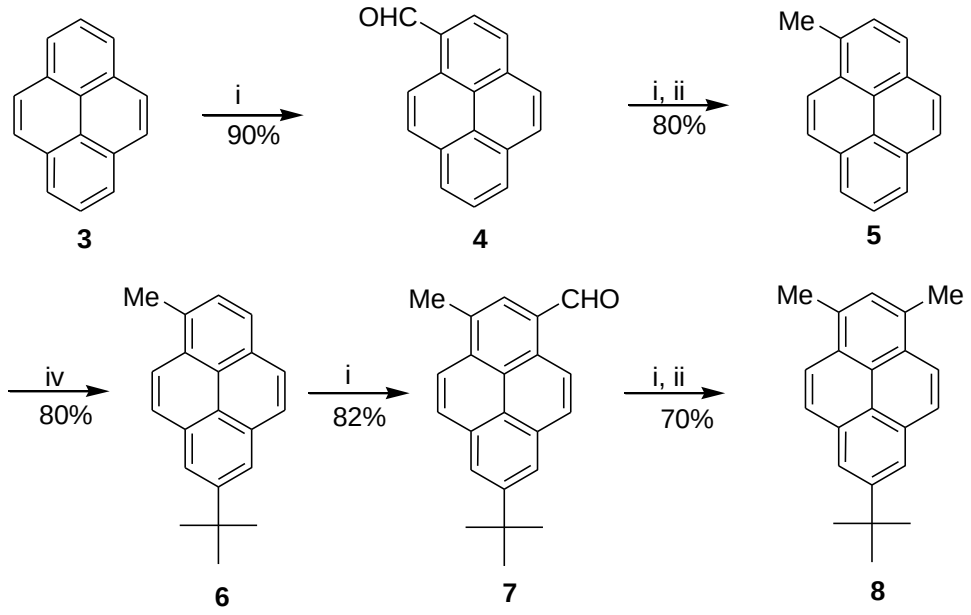
As described in previous chapters, electrophilic substitution of pyrene occurs at 1. 3. 6. And 8 positions, but not the other positions(2,4,5,7,9 and 10).[13,14] The substitutions at the later positions must be prepared in ways other than by direct electrophilic substitutions of pyrene itself. Regioselective electrophilic substitution at the positions 5 and 9 is still challenging. We have previously reported the convenient preparative route for 7-*tert*-butyl-1.3-dimethyl pyrene form pyrene in 5 steps, which involves formylation of 7-*tert*-butyl-1.3-dimethyl pyrene and Wolff-Kishner reduction.[15,16] The compound is a convenient starting material for the preparing a series of 5 mono- and 5,9-disubstituted 1,3-dimethylpyrene by electrophilic substitution because one of the active positions of pyrene at 6 and 8 position is protected by the *tert*-butyl group.

Therefore In this chapter, the electrophilic aromatic substitution of 7-*tert*-butyl-1.3-dimethyl pyrene which selectively afforded 5-mono and 5,9-diformyl substitution products depending on the Lewis acid catalyst that were used for the synthesis of first member of new class of pyrene based [4]helicenes polycyclic aromatic hydrocarbons containing at least one methyl group at fjord regions along with their photo physical properties will be fully presented.

5. 2 Result and Discussion

5. 2. a Synthesis and Spectral Properties

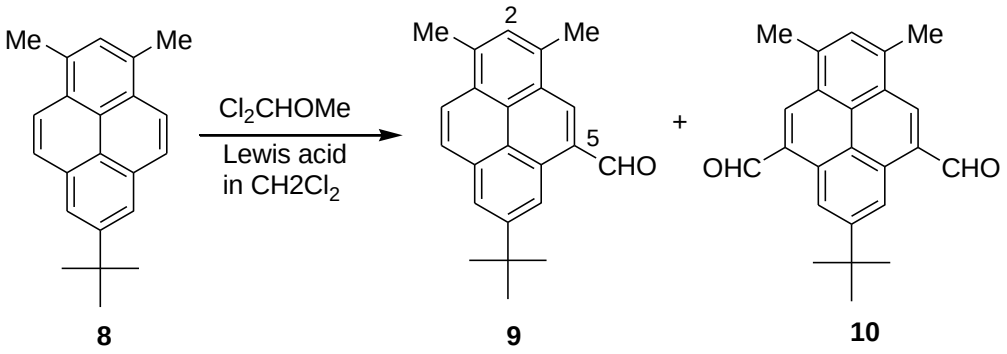
The preparation of 7-*tert*-butyl-1,3-dimethylpyrene **8** was carried out according to the reported procedure.[15,16] The formylation of pyrene with dichloromethyl methyl ether was carried out in the presence of $TiCl_4$ to afford 1-formylpyrene **4** at 90% yield, upon which Wolff-Kishner reduction was carried out to give 1-methylpyrene **5** in 80% yield. The $AlCl_3$-catalysed *tert*-butylation of compound **5** with *tert*-butyl-chloride afforded 7-*tert*-butyl-1-methylpyrene **6** in 80% yields. 7-*tert*-butyl-1,3-dimethylpyrene **8** was obtained by the successive formylation of 7-*tert*-butyl-1-methylpyrene **6** with dichloromethyl methyl ether followed by the reduction of the obtained 7-*tert*-butyl-1-formyl-3-methylpyrene **8**.



Scheme 5. 1. Reagent and conditions:[15,16] i, Cl_2CHOMe, $TiCl_4$, CH_2Cl_2; ii, NH_2NH_2, toluene-diethylene glycol, reflux, 1h; iii, KOH, 180^oC, 3h; iv, Bu^tCl, $AlCl_3$, room temperature, 1h

The formylation of 7-*tert*-butyl-1,3-dimethylpyrene **8** with dichloromethyl methyl ether was carried out under the various conditions. Thus formylation of **8** with dichloromethyl methyl ether at room temperature for 3h in presence of titanium chloride occurred only selectively at 5-position to afford the corresponding 5-*mono*-formyl derivative **9** in 69% yield. The formylation of **8** with large excess (4.0 equiv.) of dichloromethyl methyl

ether in methylene dichloride solution in presence of $AlCl_3$ afforded regioselectively the diformylated product **10** in 85% yield arising from the two fold formylation at 5,9- positions.



8 **9** **10**

Scheme 5. 2. Formylation of 7-*t*-butyl-1, 3-dimethylpyrene

Table 5.1 Formylation of 7-*t*-butyl-1,3-dimethylpyrene (**8**)[a]

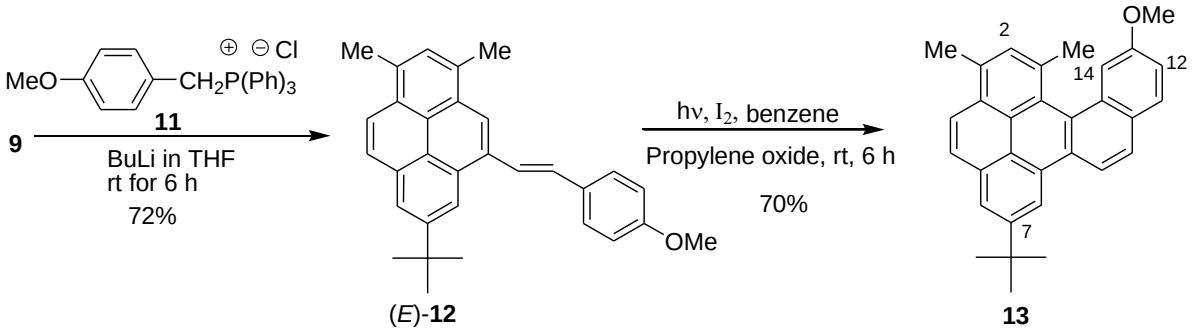
Run	Reagent	Lewis acid	Reaction time/h	Product yields/%[b]	
				9	**10**
1	Cl_2CHOMe	$TiCl_4$	3	93[69][c]	0
2	Cl_2CHOMe	$AlCl_3$	6	0	89[85]

[a]Yields are determined by GLC analysis. [b]Isolated yields are shown in square parenthesies. [c]The starting compound 8 was recovered in 7% yields.

The structure of **9** and **10** were assigned by spectral data and elemental analysis. Thus ^{1}H NMR spectra data (300MHz, $CDCl_3$) of **9** shows a set of doublets with *meta*-coupling constant (J = 1.8Hz) at δ 8.26 (H_8) and 9.75 (H_6) ppm as well as two singlets at δ 7.75 (H_2) and 8.69 (H_4) ppm. Similarly a set of doublets with *ortho*-coupling constant (J = 9.3 Hz) at δ 8.05 and 8.15 ppm were assigned for the protons of position 9, 10-on pyrene ring respectively. On the other hand, ^{1}H NMR spectral data (300MHz, $CDCl_3$) of **10** shows characteristics four singlets at lower field. The picks at δ 7.82, 8.68 and 9.89 were assigned for H_2, $H_{4,10}$ and $H_{6,8}$ respectively and similarly the singlet pick at δ 10.56 was assigned for two protons of aldehyde groups. These data strongly supports the assignment of 7-*tert*-butyl-5-formyl-1,3-dimethylpyrene **9** and 7-*tert*-butly-5,9-diformylpyrene **10**.Therefore this result also strongly suggest that the *tert*-butly group on the pyrene ring protects the electrophilic

attack at the 6,8- position as well as the methyl groups at the 1,3- position, inhibiting the electrophilic attack at 4,10 position.

The reaction of **9** and the (4-methoxybenzyl)triphenylphosphonium chloride **11** with n-butyllithium in THF gave the desired 7-*tert*-butyl-1,3-dimethyl-5-(4-methoxyphenylethenyl)pyrene (*E*)-**12**. Only (*E*)-isomer was isolated in 72% yield by silica gel column chromatography and recrystallisation from hexane and dichloromethane. Similarly (*E*)- 7-*tert*-butyl-1,3-dimethyl-5-(3,5-dimethylphenyethenyl)pyrene **15** was prepared in 75% yield (Scheme: 5.3). The structure of product (*E*)-**12** was determined on the basis of its elemental analyses and spectral data. ^{1}H NMR single of olefinic protons for *E*-isomer should be observed at lower field ($\delta > 7.4$ ppm) than that of *Z*-olefinic ($\delta < 6.9$ppm) proton.[17] As expected ^{1}H NMR (300 MHz, $CDCl_3$) shows a pair of doublets (J = 15.9 Hz) at δ 7.32, 7.92 ppm for *E*-olefinic protons and a singlet at δ 3.88 for methoxy protons. Similarly two methyl protons of pyrene ring were observed as singlets at δ 2.94, 2.98. These data also strongly support that the compound (*E*)-**12** is of *E*-configuration. The structure of compound was further established on the basis of base peak molecular ion at m/z 418 in mass spectra.

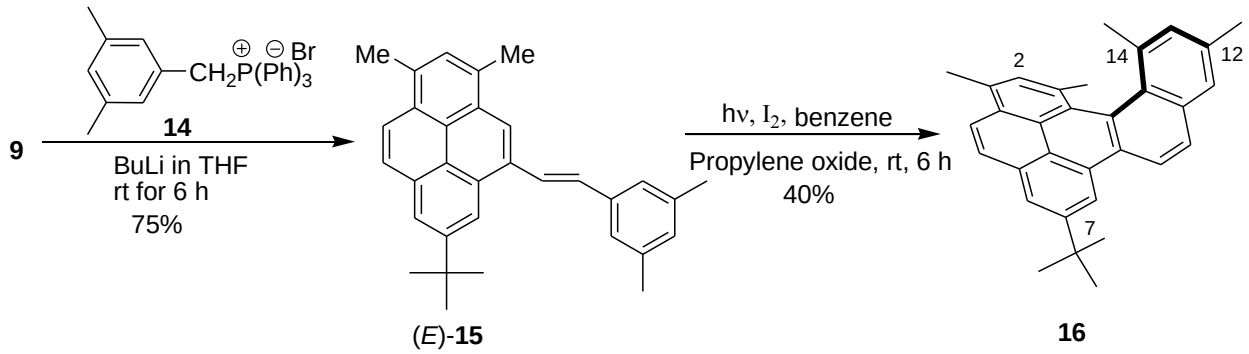


Scheme 5. 3 Sythetic route to 7-*tert*-butly-1,3-dimethyl-13-methoxydibenzo[*ij,no*]tetraphene

When a solution of (*E*)-**12** and a stoichiometric amount of iodine in benzene was irradiated with high-pressure mercury lamp(400W) at room temperature for 6 h, the photocyclized product, 7-*tert*-butyl-1,3-dimethyl-13methoxydibenzo[*ij,no*]tetraphene **13** was obtained only 10% along with the recovery of the starting compound. Prolonging reaction time to 12h led to an increase the yield to 25%. When the irradiation with stoichiometric

amount of iodine plus a large amount of propylene oxide[18,19] in the absence of air led to an increase of the yield to 70% (Scheme: 5.3 and Table: 5.2).

The structure of product **13** was determined on the basis of their elemental analyses and spectral data. The structure of **13** was established on the basis of the base peak molecular ion at m/z 416 in mass spectrum. ^{1}H NMR spectrum of **13** (300 MHz in $CDCl_3$) shows singlet at δ 1.61 for *t*-butyl group, two singlets at δ 2.50 and 2.96 for two methyl peaks and a singlet at δ 3.90 for methoxy peak. Compared with the methyl peaks of (*E*)-**12**, methyl peak at δ 2.50 that of **13** was found to be more shielded by 0.41 ppm. Similarly ^{1}NMR of compound shows a pair of doublets (J = 9.3 Hz) at δ 8.71 and 7.69 ppm for H_9, H_{10} protons, a pair of doublets (J = 9.0 Hz) at δ 8.01, 8.70 ppm for H_4, H_5 protons. A set of characteristic double doublet (dd, J = 2.4, 2.4 Hz) for H_{12} was assigned at δ 7.22 ppm. Similarly 14-arylhydrogen can clearly be seen to be deshielded at δ 9.0 ppm by the adjacent rings, a common consequence of the expanded benzene rings. Further the helical structure of compound **13** was confirmed by single crystal x-ray analysis (Fig: 5, 7).



Scheme: 5. 4 Sythetic route to 7-*tert*-butly-1,3,12,14-tetramethydibenzo[*ij,no*]tetraphene

In order to investigate this finding in more detail, two methyl groups were introduced at fjord regions of the synthesized [4]helicene compounds. Additional methyl groups at C_{14} position could lead the increased skeletal distortion even more than reported in benzo[c]phenanthrene.[20] Thus the reaction of **9** and (3,5-dimethylbenzyl)triphenylphosphonium bromide **14** in n-butyllithium in THF gave the desired 7-*tert*-butyl-1,3-dimethyl-5-(3,5-dimethylphenylethynyl)pyrene (*E*)-**15** in 75% yield. (Scheme: 5.4) The structure of compound (*E*)-**15** was established on the basis of elemental analyses and spectral data. Thus the structure of (E)-**15** was determined on the basis of base

peak molecular ion at m/z 416 in its mass spectra. ^{1}H NMR spectrum (300 MHz, $CDCl_3$) of (*E*)-**15** shows singlet at δ 2.40 for six protons of methyl groups while as two set of singlet at δ 2.96 and 2.97 for two pyrene methyl groups. ^{1}H NMR spectra of compound also shows, a pair of doublets (J = 15.3 Hz) at δ 7.08, 8.01 ppm for (*E*)-olefinic protons. This spectral analyses strongly supports that the structure (*E*)-**15** has (*E*)-configuration.

Table 4.2 Effect of catalyst in photo induced cyclization reactions

Run	Catlyst	Reaction time (h)	Product Yields (%)	
			13	**16**
1	I_2	6	10	5
2	I_2	12	25	15
3	I_2 /PO*	6	70	40

* PO = Propylene oxide

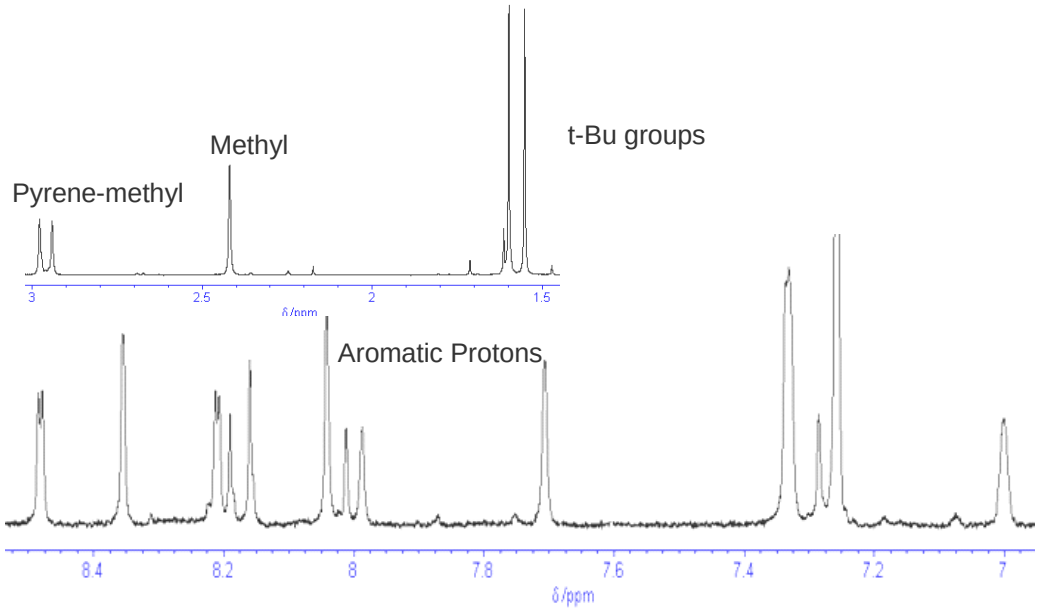


Fig: 5. 2. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of (E)-**12**

When a solution of (*E*)-**15** and a stoichiometric amount of iodine in presence of propylene oxide in benzene was irradiated with high pressure mercury lamp (400 W) as same condition described above, the photocyclization product, 7-*tert*-butyl-1,3,12,14-tetramethyldibenzo[*ij*,*no*]tetraphene **16** was obtained at 40% yield as white crystalline solid.

(Scheme: 5.4 and Table: 5.2.). The low yield of the compound is because of substituted two methyl groups in the fjord regions which contribute pronounced steric hindrances during cyclization.

The structure of compound **16** was determined on the basis of its elemental analyses and spectral data. Thus the structure of compound was established on the basis of the base peak molecular ion m/z 414 in mass spectra. ^{1}H NMR (300 MHz, $CDCl_3$) shows four distinct singlets at δ 2.06, 2.29, 2.59. 2.96 ppm for four methyl protons, two set of doublets (J = 8.7 Hz) at δ 7.89, 8.74 ppm for H_{10} and H_9 protons, and two sets of doublets (J = 9.1 Hz) at δ 7.98, 8.21 ppm for H_5 and H_4 protons respectively. Interestingly, further as expected, two methyl protons at fjord regions of [4]helicene structure were found to be pronounced shielded at 1.82, 2.59 ppm by adjacent rings, and absence of meta coupling in any of the aromatic protons, a common consequences of the distorted structure of the expanded rings.[20]

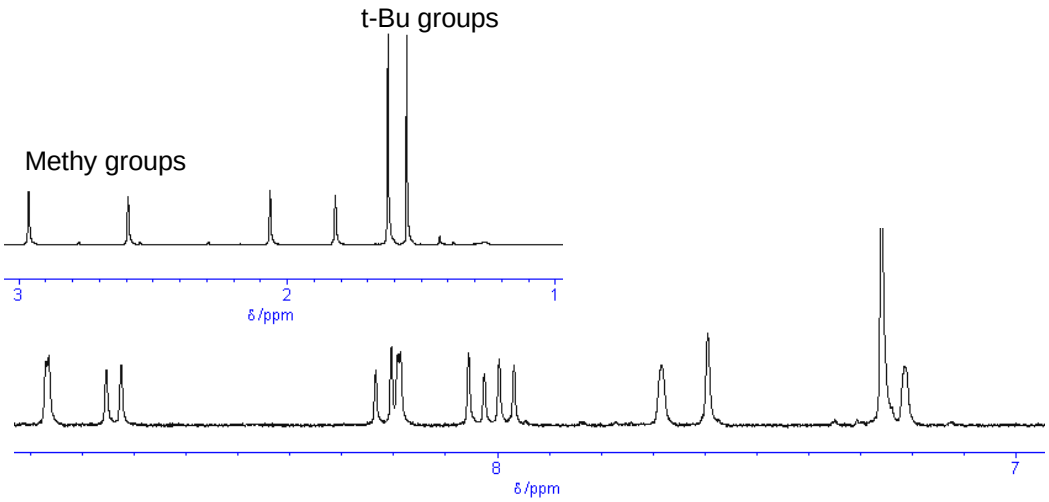


Fig: 5. 3. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of (E)-**16**

5. 2. b Photo Physical Properties

The UV-Vis absorption and fluorescence spectroscopic data of novel polycondensed aromatic compounds with [4]helicene structure derived from 7-*tert*-butyl-1,3-dimethyl-5-(phenylethenyl)pyrene in dilute dichloromethane solution at room temperature were measured and presented in Table 5.3, together with 7-*tert*-butyl-1,3-dimethylpyrene (**8**). The comparative UV-Vis absorption spectra of **12** and **15** (before cyclization) and **13** and **16** (after cyclization) are shown in Figure: 5.4, 5.5 and 5.6 respectively. For 7-*tert*-butyl-1,3-

dimethylpyrene (**8**), the absorption spectra are almost identical compared with that of the parent pyrene with three well-resolved, sharp absorption bands observed in the region 300-350 nm. The slight bathochromic shift is ascribed to the increased electron density to the pyrene ring, arising from the electron-donating nature of *tert*-butyl groups and methyl groups at the 7 and 1, 3 positions respectively.

The UV-Vis absorption spectra of compounds **12** and **15** (before cyclization) with **8** , all spectra are broad, less well resolved and the longest wave length hyperchromic absorption maximum of **12**, and **15** occurs at 386 and , 372 nm respectively (Table: 5.3), which are bathochromically red-shifted by 17-19 nm arising from the introduced phenylethenyl units at 5 positions. The newly substituted pyrene **8** was found to be exhibited more bathochromically red shifted, compared with the 2,7-di-*tert*-butyl pyrene (compound **1**, chapter 3).

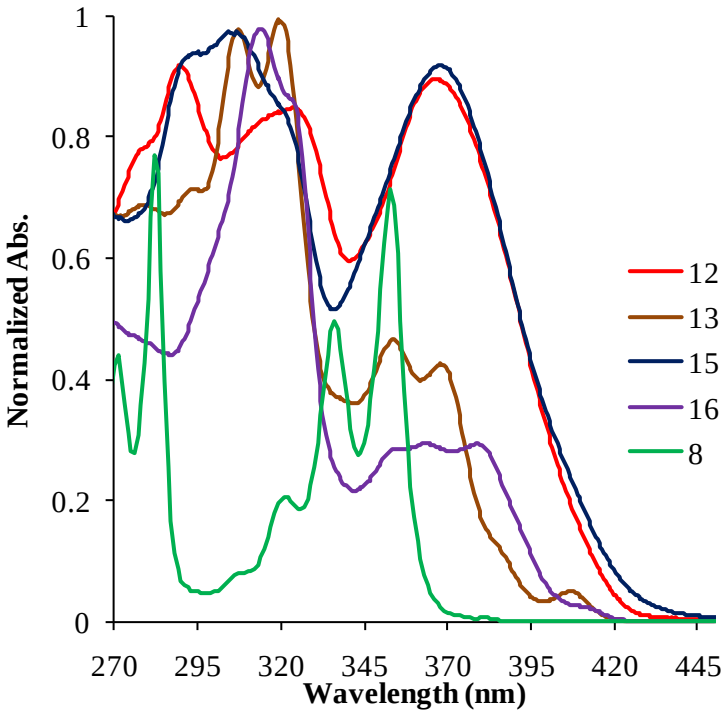


Fig 5.4 Normalized UV-vis absorption spectra of **12, 15** (before cyclization) and **13,16** (after cyclization) recorded at ~10^{-5} M concentration at 25°C, compared with that of **8**

Table:5. 3 Optical absorption and emission spectroscopic data for **12**, **13**, **15** and **16**, in CH_2Cl_2 (~10^{-6}-10^{-7}M) at room temperature, compared with that of **8** [a]

Compd	Absorption [b] λ_{abs} [nm]	Fluorescence[c] λ_{max}[nm] (λ_{ex})[d]	Stokes-shifts [nm]	F.Q.Y Φ_f[e]
8	353	403 (222)	50	0.091
12	368	433[452] (222)	65	0.77
15	372	455 (221)	83	0.88
13	371	419[449] (220)	49	0.11
16	382	422[442] (219)	40	0.13

[a] all measurements were performed under degassed conditions. [b] ~10^{-6} M in CH_2Cl_2, λ_{abs} is absorption band appearing at the longest wavelength. [c] ~ 10^{-6} M in CH_2Cl_2, λ_{ex} fluorescence band appearing at the shorest wavelength(major). [d] wavelength of excitation. [e]absolute quantum yields (± 0.01- 0.03) in dichloromethane.

In addition, among these compounds, the 3, 5 alkyl substituted phenylethenyl pyrene **15** display slightly more bathochromic shift (4 nm) in the absorption bands, which could be attributed by the strongest electron donating nature of large number of alkyl groups in the molecules. However the shifting is not so pronounced as compared with the **12,** containing methoxy group.The UV spectra of dibenzo[*ij,no*]tetraphene derivatives **13** and **16** are almost identical and absorption bands were observed in the range of 440- 490 nm. However the quite different shapes in the UV spectrum of **12,** and **15** in comparison with those of **13** and **16** are ascribed to be because of the expanded conjugation of π-electron system by the cyclization reaction. The pronounced decrease (hypochromic absorption) of absorption bands at 370-382 nm after cyclization was ascribed as because of absence of phenylethenyl units after cyclization, decrease of aromaticity, increase of distortions from the plane and consequently decrease of π-conjugation. The UV-spectra of **13** and **16** in CH_2Cl_2, showed a large number of transition bands (Figure 5.1), typical for PAHs.[21] Similarly the departures from co-planarity with the aromatic rings are also pronounced with substituted methoxy group, which is ascribed by the absorption bands at 404 nm for **13**. On the other hand different shape in the UV spectrum of **16** confirms the increased non planarity of the aromatic ring to avoid the sterically crowding by the overlapping at the C_1 methyl groups and the methyl groups at C_{14} leading to the increased of strain in the system.

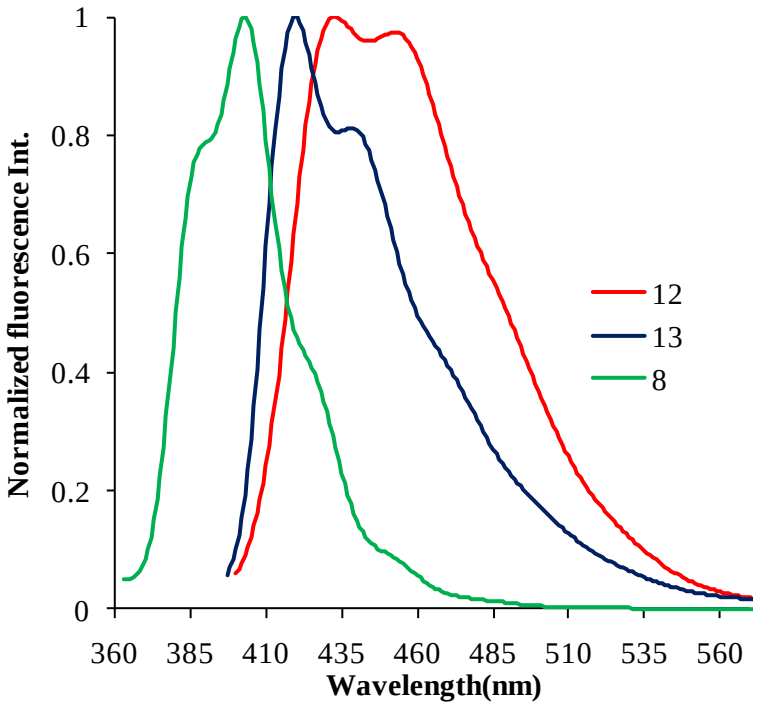


Fig 5.5 Normalized fluorescence spectra of **12** (before cyclization) and **13** (after cyclization) recorded at ~10^{-7} M concentration at 25°C, compared with that of **8**

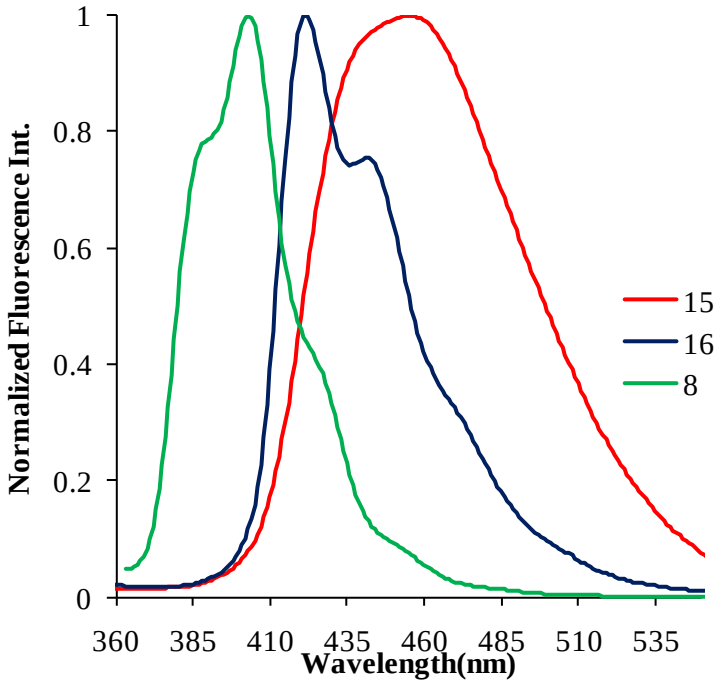


Fig 5.6 Normalized fluorescence spectra of **15**(before cyclization) and **16** (after cyclization) recorded at ~10^{-7} M concentration at 25°C, compared with that of **8**

Upon excitation, a dilute solution (~10^{-7} M) of compound **12** and **15** along with **8** in dichloromethane at room temperature shows broad band blue emission, (Figure: 5.5 and 5.6). Compared with the lower energy emission band of 7-*tert*-butyl-1,3-dimethylpyrene (**8**), the lower emission band of **12** and **15** were found to be bathochromically red shifted at 433 and, 455 respectively. All the fluorescence emission bands are broad but not identical to each other. Emission band of **12** shows small shoulder at 452 nm. Both compounds were observed in the visible pure-blue region. The emission bands of compound **15** was found to be broad but slight bathochromically red shifted (11 nm) compared with **12** which is ascribed to be because of highly alkyl substituted compound. Therefore the fluorescence stokes shift increases in the order of 15 > 12. Similarly the maximum emission spectra of compound **13** and **16** (after cyclization) in CH_2Cl_2 are shown in Figure: 5.5, 5.6 and Table: 5.3. Compared with the lower energy bands of **8**, the lower energy bands (major) of **13** and **16** were found to be bathochromically red shifted at 419 and 422 nm respectively. All of the fluorescence emission bands are sharper than the corresponding starting compound **12** and **15** with small shoulder at longer wavelength.

Because of higher extent to π-conjugation along the phenylethenyl units at 5 position of pyrene core, remarkably high quantum yields of compounds **12** and **15** were observed. The higher values of quantum yields were contributed by the electron donating groups attached with the phenylethenyl units. However the quantum yields of **13** and **16** were low compared with **12** and **15** that are ascribed to be because of low aromaticity after cyclization and consequently lesser extent to of electron delocalization around the aromatic core.

Compared with the maximum absorption bands of 2,7-di-*tert*-butylpyrene and the maximum absorption bands of 7-*tert*-butyl-1,3-dimethylpyrene was observed as slight bathochromically red shifted (14 nm) which is because of newly substituted alkyl groups in different positions of pyrene core. Even though small bathochromical red shift in the later compounds, the alkyl groups in the later compounds clearly shows different mode of contribution then that of 2,7-di-*tert*-butylpyrene and this effect of different mode of contributions of alky substitution at 1 and 3 positions was clearly observed in longest wave length absorption bands of compounds **12** and **15** (before cyclization) which were characteristically bathochromically red shifted than that of series of **4** (chapter 3). Although the shifting is not pronounced, the maximum emission bands of **12** and **15** were observed less bathochromically red shifted, compared with that of series of **4** (chapter 3). This lesser

bathochromically red shifted values of **12** and **15** were also because of substituted methyl groups leading to the loss of co-planarity. On the other hand, the different structural characteristics of compounds after cyclization were clearly being observed in emission spectra. Upon excitation, the lower energy bands of all the series of compounds **5** (chapter 3) were observed bathochromically red shifted as compared with cyclized **13** and **16**. Therefore the considerable extent of hypsochromically blue shifting of **13** and **16** were ascribed to be because of more twisted structural architecture.

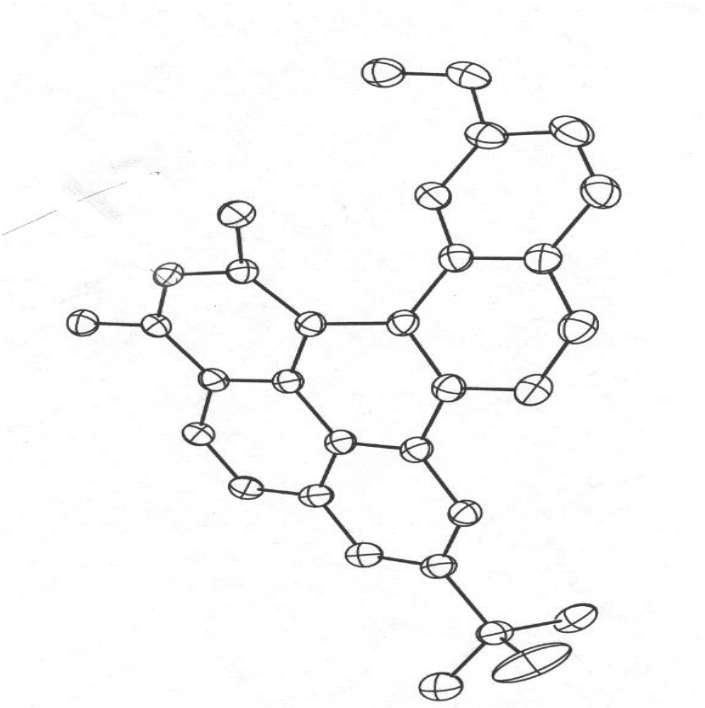


Fig: 5.7 X-ray structure diagram of compound 13(top view)

5. 3 Conclusion

In summary the formylation of 7-*tert*-butyl-1,3-dimethylpyrene with dichloromethyl methyl ether in the presence of $TiCl_4$ or $AlCl_4$ successfully offered 5-mono-formylated and 5,9-difromylated pyrene respectively. The Wittig reaction of 7-*tert*-butyl-1,3-dimethylpyrene-5-carbaldehyde with (4-methoxybenzyl)triphenylphosphonium chloride and (3,5-dimethylbenzyl)triphenylphosphonium bromide gives corresponding arylethenyl pyrene. Photo induced cyclization in presence of iodine and propylene oxide led to the corresponding novel expanded π-conjugated dibenzo[*ij*,*no*]*tert*aphene derivatives containing methyl group at fjord region. As expected the introduction of two methyl groups at fjord

region of [4]helicene was found to be more distorted in structure. Studies on electronic absorption and fluorescence emission properties of these compounds were fully examined in dilute solution. Introduction of methyl groups in 1and 3 positions of pyrene core was observed as contributing remarkably in the red shifting the absorption band though out the series. However the same substitution and similar substitutions in phenylethenyl units were observed as contributing remarkable blue shifting in emission spectra leading to the more distorted structural architecture.

5. 4 Experimental

All melting points are uncorrected. The ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with TMS as an internal reference. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. UV/Vis spectra were obtained with a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer in various organic solvents. Fluorescence spectroscopic studies were performed in various organic solvents in a semimicro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were measured using absolute methods. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyser.

Materials

Preparation of 7-*tert*-butyl-1,3-dimethylpyrene 8 was previously described.[15,16]

7-*tert*-butyl-5-formyl-1,3-dimethylpyrene 9: To a stirred solution of **8** (106mg, 0.37 mmol) and dichloromethyl methyl ether (74 mg, 0.64 mmol) in CH_2Cl_2 (5mL) was added at 0°C a solution of titanium tetrachloride (0.1 mL, 0.91 mmol) in CH_2Cl_2 (1 mL). This mixture was stirred for 2 h at room temperature. The mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 x 25mL). The organic layer was washed with water (2 x 25 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was recrystallized from hexane to afford **9** (80mg, 69%) as pale yellow prisms; m.p.268-269°C; ^{1}H NMR (300 MHz, CDCl3): δ (ppm): 1.62 (9H, s,*t*Bt), 2.93 (3H, s, Me), 2.95 (3H, s, Me), 7.69(1H, s, Ar-H), 8.02 (1H, d, *J* = 9.2 Hz, Ar-H), 8.12 (1H, d, *J* = 9.2 Hz, Ar-H), 8.25 (1H, d, *J* = 2.0 Hz, Ar-H), 8.61 (1H, S, Ar-H), 9.73 (1H, d, *J* = 2.0 Hz, Ar-H), 10.49 (1H, s.

CHO). MS (EI): m/z 314 (M^+). Elemental Analysis For $C_{23}H_{22}O$ (314.4): C 87.9; H, 7.1. Found: C, 88.1; H, 7.1.

7-*tert*-butyl-5,9-diformyl-1,3-dimethylpyrene 10: To a stirred solution of **8** (268 mg, 1 mmol) and dichloromethyl methyl ether (463 mg, 4 mmol) in CH_2Cl_2 (10mL),was added aluminum chloride (534 mg, 4 mmol) at 0°C. After this addition this mixture was stirred for 6 h at room temperature. The mixture was poured into a large amount of ice-water and extracted with CH_2Cl_2 (2 x 100mL). The organic layer was washed with water (2 x 50 mL), dried over Mg_2SO_4, and concentrated under reduced pressure. The residue was column chromatographed with hexane: Chloroform (1: 3) as eluent to give orange solid. The compound was recrystallized from hexane to afford **10** (273mg, 85%) as pale yellow prisms; m.p.256-258°C; ^{1}H NMR (300 MHz, CDCl3): δ (ppm): 1.64 (9H, s,*t*Bt), 3.05 (6H, s, Me), 7.82(1H, s, Ar-H), 8.68 (2H, s, Ar-H), 9.84 (1H, s, Ar-H), 10.56 (2H, s. CHO). MS (EI): m/z 342 (M^+). Elemental Analysis for $C_{24}H_{22}O_2$ (342.44): C 84.2; H, 6.5. Found: C, 84.2; H, 6.4..

7-*tert*-butyl-1,3-dimethyl-5-(4-methoxyphenylethenyl)pyrene (*E*)-12: The Wittig reagent was prepared from triphenylphosphane and 4-methoxybenzyl chloride in dry benzene. To a solution of this Wittig reagent (794 mg, 1.89 mmol) in dry THF (15mL) was slowly added *n*-butyllithium in hexane (1.17mL, 1.89 mmol) at 0^{o}C under argon. The mixture was stirring for 10 minutes and the solution of 7-*tert*-butyl-5-formyl-1,3-dimethylpyrene **9** (200 mg, 0.632 mmol) in dry THF (15mL) was injected under same conditions. After this addition, the mixture was warmed to room temperature, stirring for 6 h under argon. The mixture was quenched by large amount of ice-water and extracted with ethyl acetate (2 x 100mL). The combined extracts were washed with water followed by drying with brine and $MgSO_4$ and concentrated. The residue was adsorbed in silica gel and column chromatographed over silica gel (Wako C-300, 200 g) with hexane: dichloromethane (5:1) as eluent to give (*E*)-**12** (NMR analysis) as light-yellow solids. Recrystallization from hexane and dichloromethane afforded the *anti*-compound (190.2 mg, 72% yield) : m.p. 150-152 ^{0}C; ^{1}H NMR ($CDCl_3$): (*E*)-**12**: δ (ppm): 1.59 (9H, s *t*Bu), 2.94 (3H, s, -Me), 2.98 (3H, s, -Me), 7.00 (2H, d, *J* = 8.7Hz, Ar-H), 7.33 (1H, d, *J* = 15.9Hz -CH=CH_b-), 7.65 (2H, d *J* = 8.7Hz, Ar-H), 7.70(1H, s, Ar-H), 7.92 (1H, d *J* = 16.2 Hz, -CH=CH_a-), 8.02 (1H, d, *J* = 9.0 Hz, Ar-H), 8.18 (1H, d, *J* = 1.8Hz, Ar-H), 8.36 (1H, s, Ar-H), 8.48 (1H, d ,*J* = 1.8Hz, Ar-H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 19.73 (2Me), 31.98 (3Me), 35.34 (C), 55.38 (OMe), 114.22 (CH), 118.36 (CH), 121.08 (C), 122.18 (C), 123.48 (C), 125.05 (C), 126.53 (C), 127.41 (C), 127.48 (CH), 128.01

(C), 129.97 (CH), 130.71 (CH), 131.15 (CH), 131.51 (CH), 131.79 (CH), 133.60 (C), 148.45 (C), 159.39 (C). MS (EI): m/z: 418 (M^+). Elemental Analysis for $C_{31}H_{32}O$ (418): C, 88.95; H, 7.22; O, 3.80. Found: C, 88.54; H, 7.22.

7-*tert*-butyl-1,3-dimethyl-5-(3,5-dimethylphenylethynyl)pyrene (*E*)-15: The Wittig reagent was prepared from triphenylphosphane and 3,5-dimethylbenzyl bromide in dry benzene. To a solution of this Wittig reagent (692 mg, 1.50mmol) in dry THF (15mL) was slowly added n-butyl lithium in hexane (0.933mL, 1.50 mmol) at 0^oC under argon. The mixture was stirring for 10 minutes and the solution of 7-*tert*-butyl-5-formyl-1,3-dimethylpyrene **9** (316.44 mg, 1 mmol) in dry THF (20mL) was injected under same conditions. After this addition, the mixture was warmed to room temperature stirring for 6 h under argon. The mixture was quenched by large amount of ice-water, extracted with ethyl acetate (2 x 100mL), the combined extracts were washed with water followed by drying with brine and $MgSO_4$ and concentrated. The residue was adsorbed in silica gel and column chromatographed over silica gel (Wako C-300, 200 g) with hexane-ethyl acetate (5: 1) as eluent to give (***E***)-**15** (^{1}H NMR analysis) as light-yellow solids. Recrystallization from hexane: toluene (2:1) and finally washed with hexane afforded the *anti*-compound (215 mg, 75% yield). m.p = 106°C; ^{1}H NMR (300Hz, $CDCl_3$): (*E*)-**15**: δ (ppm): 1.59 (9H, s *t*Bu), 2.41 (3H, s, Ar-Me), 2.94 (3H, s, Ar -Me), 2.98 (3H, s, -Me), 7.00 (2H, s, Ar-H), 7.30 (1H, d, *J* = 15.3Hz -CHa=CH-), 7.33 (2H, s, Ar-H), 7.70 (1H,s, Ar-H), 8.01 (1H, d *J* = 15.3Hz, -CHb=CH-), 8.05 (1H, d, *J* = 9.9Hz, Ar-H), 8.18 (1H, d, *J* = 9.0Hz, Ar-H), 8.21 (1H, d, *J* = 1.8Hz Ar-H), 8.36 (1H, s, Ar-H), 8.482 (1H,d, *J* = 1.8Hz, Ar-H). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 21.40 (2Me), 30.94 (2Me), 32.00 (3Me), 35.35 (C), 118.48 (C), 121.49 (CH), 122.20 (CH), 123.48 (CH), 124.72 (C), 126.55 (CH), 126.94 (CH), 127.38 (C), 129.55 (C), 129.95 (C), 129.98 (CH), 131.41 (C), 131.61 (C), 131.86 (C), 132.03 (C), 133.66 (C), 137.79 (C), 138.28 (C), 148.51(C) MS (EI): m/z: 416 (M^+). Elemental Analysis for $C_{32}H_{32}$ (416.6): C, 92.26; H, 7.74; Found: C, 91.52 ; H, 7.71

General procedure for photocyclization

Photo reactor was a cylindrical glass vessel with an immersion well and two tapered joints, one vertical attached with condenser to which argon source was fitted. Another angled for withdrawal and addition of samples. The vessel was flat bottom to allow a magnetic stirring bar to rotate. The immersion well was a double walled pyrex tube cooled by water and containing high pressure quartz Hg-vapour lamp. Argon gas was bubbled through benzene

for 20-30 min and used to dissolved sample and iodine. The dissolved solutions of sample, iodine and propylene oxide were added to the reaction vessel through angled joint and the lamp was turned on. The reaction was carried out under argon atmosphere. Photo reactions were monitored by ^{1}H NMR and iodine color change. After complete irradiation, work included washing with 15% $Na_2S_2O_3 \cdot H_2O$ and saturated brime, drying with anhydrous $MgSO_4$, filtering and concentrated to dryness on a rotary evaporator. The residue obtained was washed either through a short column of silica gel or different solvent systems were used to obtain the pure compounds.

7-*tert*-butyl-1,3-dimethyl-13-methoxydibenzo[*ij,no*]tetraphene 13: 7-*tert*-butyl-1,3-dimethyl-5-(4-methoxyphenylethenyl)pyrene (*E*)-**12** (50.0 mg, 0.118 mmol) in 260 mL of benzene was irradiated in presence of I_2 (28.27 mg, 0.12 mmol) and propylene oxide (1.53 mL, 21.1 mmol) for 6 h. Worked up and adsorbed over silica gel using dichloromethane and proceed for column chromatography using hexane only. The viscous material obtained from column was dissolved in ether and left for overnight to obtain the white solid. The compound was further recrystallized in ether and washed with hot hexane to afford **13** (34 mg, 70%) as white compound. m.p. = 140-141°C; ^{1}H NMR (300, $CDCl_3$): 1.62 (9H, s, t-Bu), 2.50 (3H, s, -Me), 2.97 (3H, s, Me), 3.90 (3H, s, OMe), 7.02, 7.24 (1H, dd, J = 2.4,2.7 Hz, Ar-H_{12}), 7.50 (1H, s, Ar-H_2), 7.688 (1H, d, J = 1.2, Ar-H_{10}), 7.90 (1H, d, J = 9.0Hz, Ar-H_{11}), 8.03 (1H, s, Ar-H_{14}),8.018 (1H, d, J = 9.0Hz, Ar-H_5) 8.17(1H, d, J = 1.8Hz, Ar-H_6), 8.20 (1H, d, J = 9.3Hz, Ar-H_4), 8.70 (1H, d, J = 9.3Hz, Ar-H_9), 8.89 (1H, d, J = 1.8Hz, Ar-H_8). ^{13}C NMR (300 MHz, $CDCl_3$): δ (ppm): 19.42 (Me), 25.11 (Me), 31.89 (3Me), 35.35 (C), 55.24 (OMe), 107.84 (CH), 109.20 (CH), 113.67 (C), 115.44 (C), 117.08 (C), 117.86 (C), 118.47 (C), 122.79 (CH), 123.02 (CH), 126.09 (CH), 126.79 (CH), 127.05 (CH), 127.62 (CH), 128.93 (CH), 130.30 (CH), 130.88 (C), 131.91 (C), 132.32 (C), 133.29 (C), 148.68 (C), 157.55 (C). MS (EI): m/z: 416 (M^+). Elemental Analysis for $C_{31}H_{30}O$ (416.55): C, 88.38; H,6.78 ; O, 3.82. Found: C: 86.48, H: 6.28.

7-*tert*-butyl-1,3,12,14-tetramethyldibenzo[*ij,no*]tetraphene 16: 7-*tert*-butyl-1,3-dimethyl-5-(3,5-dimethylphenylethynyl)pyrene (*E*)-**15** (50.0 mg, 0.12 mmol) in 250 mL of benzene was irradiated in presence of I_2 (31.4 mg, 0.12 mmol) and propylene oxide (1.45 mL, 21.0 mmol) for 10h. Worked up and adsorbed over silica gel using dichloromethane and proceed for column chromatography using hexane as eluent to obtain pure **16** (20.0 mg, 40.%) as white crystalline compound. m.p = 165-166 °C; ^{1}H-NMR (300MHz, $CDCl_3$): δ(ppm): 1.62 (9H, s, tBu), 1.82 (3H ,s, -Me), 2.06 (3H, s, -Me), 2.59 (3H, s,-Me), 2.96 (3H, s, -Me),

7.21(1H, s, Ar-H), 7.59 (1H,s, Ar-H) 7.68(1H, s, Ar-H), 7.98(1H, d, *J* = 8.7Hz, Ar-H), 8.04 (1H, d, *J* = 9.0Hz, Ar-H), 8.19 (1H, d, *J* = 1.5Hz, Ar-H), 8.21 (1H, d, *J* = 9.3Hz, Ar-H), 8.74 (1H, d, *J* = 8.4Hz, Ar-H), 8.86 (1H, d, *J* = 1.5Hz, Ar-H_8). ^{13}C NMR (300 MHz, CDCl3): δ (ppm): 19.48 (Me), 21.39 (Me), 23.29, 23.32 (Fjord 2Me), 31.94 (3Me), 35.39 (C), 117.61, (CH), 119.68 (CH), 122.28 (CH), 123.23 (CH), 124.68 (CH), 125.99 (CH), 126.66 (CH), 127.15 (CH), 127.29 (CH), 128.94 (CH),130.33 (C), 130.58 (C), 130.67 (C), 130.83 (C), 131.08 (C), 131.89 (C), 133.02 (C), 134.42 (C), 135.18 (C), 136.44 (C), 146.85 (C), 148.65 (C). MS (EI): m/z: 414 (M^+). Elemental Analysis for $C_{32}H_{30}$ (414.23): C, 92.71; H, 7.29. Found: C, 86.14, H, 7.10

5.5 References

[1] a) R. Weitzenbock, H. Lieb, *Manatsh. Chem*. **1912**, 33, 549-565. b) R. Weitzenbock, A. Klinger, *Manatsh, Chem*. **1918**, 39, 315-324.

[2] J. W. Cook, *J. Chem. Soc.* **1931**, 2524-2528.

[3] J. W. Cook, C.L. Heweit, *J. Chem. Soc*. **1933**, 549-565.

[4] a) G. Portella, J. Poater, J. M. Bofill, P. Alemany, M. Sola, *J. Org. Chem*. **2005**, 70, 2509-2521. b) H. Hopf, *Classical Hydrocarbon Chemistry*, Wiley-VCH, Weinheim, **2000**, Chapter 12

[5] F. L. Hirshfeld, S. Sandler, G. M. J. Schmidt, *J. Am. Chem. Soc*. **1963**, 2108-2125.

[6] S. S. Hecht, A. A. Melikian, S. Amin, in *Polycyclic aromatic hydrocarbon carcinogenesis: Structrue- Activity Relationships*, CRC Press, Boca Raton, FL, **1988**, 1, Chapter 4.

[7] D. M. Jerina, J. M. Sayer, H. Yagi, M. Croisy-Delcey, Y. Ittah, D. R. Thakker, A. W. Wood, R. L Chang, W. Levin, In *Biological Reactive Intermediate II* Part A, Plenum Press, New York, **1982**, 501-523.

[8] S. Mirsadeghi, G. K. B. Prasad, N. Whittaker, D. R. J. Thakker, *J. Org. Chem*. **1989**, 54. 3091-3096.

[9] M. K. lakshman, P. L. Kole, S. Chaturvedi, J. H. Saugier, H. J. C. Yeh, J. P. Glusker, H. K. Carrell, A. K. Katz, C. E. Afshar, W-M. Dashwood, G. Kenniston, W. M. Baird, *J. Am. Chem. Soc.* **2000**, 122, 12629-12636.

[10] H. Goto, K. Akagi, Angew. *Chem. Int. Ed*. **2005**, 44, 4322-4328.

[11] J. Szeliga, A. Dipple, Chem. Res. Toxicol, 1998, 11, 1-11.

[12] a) S. Amin, J. Camanzo, K. Huie, S. S. Hecht, *J. Org. Chem.* **1984**, 49, 381-384. b) C. M. Utermoehlen, M. Singh, R. E. J. Lehr, *J. Org. Chem*. **1987**, 52, 5574-5582. c) S. Amin, G. Balanikas, K. Huie, S. S. Hecht, *Chem. Res. Toxicol.* **1988**, 1, 349-355. d) B. Mishra, S. Amin, *J. Org. Chem*. **1990**, 55, 4478-4480.

[13] E. Clar, *Polycyclic hydrocarbons*, Academic Press, New York, **1964**, Vol II.

[14] M. Minabe, S. Takeshige, Y. Soeda, T, Kimura, M. Tsubata, *Bull. Chem. Soc. Jpn*. **1994**, 67, 172-179.

[15] T. Yamato, A. Miyazawa, M. Tashiro, *J. Chem. Soc. Perkin Trans*. 1, **1993**, 3127-3137.

[16] T. Yamato, J. Hu, *J. Chem. Res.* **2006**, 762-765.

[17] A. Merz, A. Karl, T. Futterer, N. Stacherdinger, O. Schneider, J. Lex, E. Lubochand, J. F. Biernt, *Liebigs Ann. Chem*. **1994**, 1199-1209.

[18] L. Liu, B. Yang, T. J. Katz, M. K. Piondexter, *J. Org. Chem.* **1991**, 56, 3769-3775.

[19] I. Ben, L. Castedo, J. M. Saa, J. A. Seijas, R. Suau, G. Tojo, *J. Org. Chem.* **1985**, 50, 2236-2240.

[20] C. Brule, K. K. Laali, T. Okazaki, M. K. Lakshman, *J. Org. Chem*. **2007**, 72, 3232-3241.

[21] D. Wasserfallen, M. Kastler, W. Pisula, W. A. Hofer, Y. Borgel, Z. Wang, K. Mullen, *J. Am. Chem. Soc.* **2006**, 128, 1334-1339.

Chapter 6

Synthesis, Structural and Photo Physical Properties of Pyrene Cored New Class of Polycyclic Aromatic Hydrocarbons With Bis [5] Helicene Motifs, Derived From 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene

.

Synthesis, spectral and photo physical properties of pyrene cored new class of polycyclic aromatic hydrocarbons derivatives containing double [5] helicene motifs are reported in this chapter. These compounds features bearing of phenanthrene condensed pyrene cored Polycyclic aromatic hydrocarbons having bis [5]helicene structural patterns . The structures of compounds were fully characterized by $^{1}H/^{13}C$ NMR, Mass spectroscopy, elemental analysis. The method proceeds with the Wittig reaction of 2,7-di-tert-butyl-4,9-diformylpyene with (2,7-di-tert-butyl-pyrene-4-yl)triphenylphosphonium chloride in the presence of n-BuLi and followed by intramolecular photo-induced cyclization in the presence of iodine and propylene oxide to afford a the novel expanded π-conjugated systems, 2,7,12,15,20,25-hexa-tert-butyl-dibenzo[fg,op]dipyreno[a,j]tetracene. Similarly photophysical properties of compounds were carefully examined and are also presented.

6.1 Introduction

In the previous chapters, the synthesis of pyrene cored PAHs with helicene structural motifs in which a pyrene molecules have been used as a core molecules contributing at least two aromatic rings of it in the helicene architecture to obtained mono and bis [*4*]helicenes were introduced. There has been a growing interest in large polycyclic aromatic hydrocarbons LPAHs as environmental contaminants which were assumed to be sparingly soluble and therefore not environmentally relevant, has been questions[1] It has been recently shown that the majority of PAHs must adopt nonplanar conformation as global minima.[2]The nonplanarity motif is especially frequent in LPAHs.[2] However the synthesis and characterization of PAHs cored fused π-conjugated molecules are of current interest to their potential applications in organic optoelectronic materials and devices.[3,4] The chemistry of overcrowding polycyclic aromatic hydrocarbons on the other hand became a field of interest during the past decade. The synthesis of PAHs cored compounds with huge structural diversity is particularly appealing but also important efforts have been directed to the construction of highly symmetric PAHs with different shapes, such as saddles or twists,[5,6] and to the synthesis of other structures that exhibits distortion from the planarity, such as helicenes.[7] In general, the syntheses of these kinds of compounds have in common the lack of general applicability, use of harsh reaction conditions and low yields.

Most recently it was reported that the aromatic hydrocarbon pyrene is an important and thoroughly investigated organic chromophore. Substitution in the pyrene ring at the most active centers (1, 3, 6, and 8 positions) exclusively by pyrene units leads to the interesting potential useful compounds.[1] Similarly at these positions, lot of works, 1'1'-bipyrenyl,[8] linear 1,6-disubstitued oligopyrenes,[9] and polypyrene dendrimers have been reported.[10] (Fig: 6.1. 1) Similarly most recently, Yamato et al.[11] (2010) also reported the introduction of *p*-functionalized phenylacetyleninc groups in the selected reactive positions of pyrene molecules. (Figure: 6.1. 2). The regiosective introductions of substitutions around the other centers (4, 5, 9, and 10 positions) were extensively carried out in our laboratory. Most recently Yamato et al.[11] (2010) reported the regioselective introduction of *p*-functionalized phenylacetyleninc groups in these positions too, and demonstrated by the introduction of *tert*-butyl groups in 2 and 7 positions of pyrene molecules **(Figure: 6.1. 3)** Therefore, introduction of helicene motifs around the later positions of pyrene molecules proceeding by adopting the regioselective introduction of formyl groups in 4, and 9 positions has not been studied yet. Interestingly, increasing the surface area of aromatic core leads to a more

pronounced π-stacking propensity, but it also reduces solubility and thus complicated purification, characterization, and processing.[12,13] Improved solubility is thus can simply achieve by the introduction of long alky chains in the corona of the aromatic system.[14]

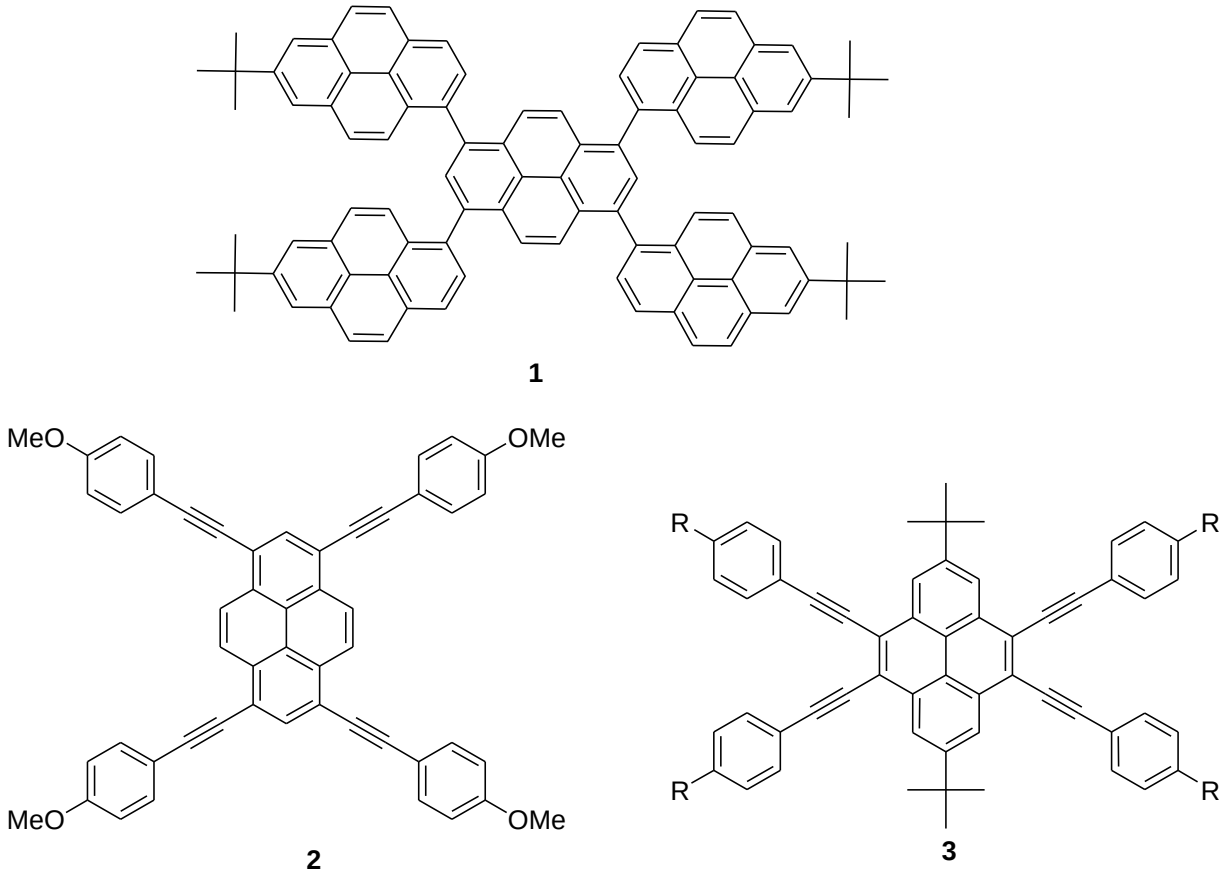


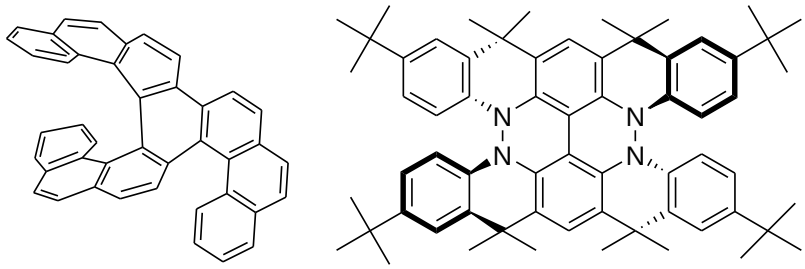
Fig: 6.1. Structures **1- 3**, showing different orientation around pyrene molecule

As a classical methods helicenes have been prepared by the oxidative photocyclization of bis(stilbene)s.[15,16] though useful, complex product mixtures often arise as a result of poor regiocontrol in the photocyclization step or competitive side reaction, such as photo induced dimerization formation.[16] The challenges of developing efficient strategies based on Diels-Alder cycloadditions,[17,18] carbenoid insertions,[19] radical cyclization, and metal-mediated cycloisomerization.[20.21] However the major drawback of photocyclization reaction obtaining complex mixture arises from photo induced cyclization can be overcome by using basic PAHs core for the synthesis. Herein we have demonstrated that the use of pyrene as a core material always leads pure and desired product rather than obtaining complex mixture.

The first helicene, consisting of head to tail annelated [6] helicenes, were first prepared by photo induced cyclization of stilbenes to helicenes.[22] Recently, a conjugated double helicene, in which two hydrazine-based [5]helicene are highly annelated in their mid-sections[23](Figure: 6.2. 5) and double helicenes (Figure: 6.2. 4) in which two benzene rings are shared by [5]- and [7]helicene prepared via non photochemical Pd-catalyzed reaction were reported. However the pyrene annelated pyrene cored double helicene were not reported yet.

We have previously demonstrated that applying polycyclic aromatic hydrocarbons as the core materials for the synthesis of helicenes compounds have not been reported to that extent. On the other hand uses of phenylethenyl based stilbenes have only been remained the practiced methods for the synthesis of helicenes. However use of pyrenylethenyl based stilbenes for the synthesis of helicenes via photo induced cyclization reaction has not been reported so far. Therefore, herein we intended to introduce the pyrene cored helicenes containing pyrene motifs in helicened architectures.

The synthesis strategies included the regioselective formylation of pyrene moiety at novel positions and consecutive conversion of formylated pyrenes to the corresponding pyrenylethenyl pyrenes using Wittig reaction and followed by photo induced cyclization. Herein we describe the efficient synthesis and photophysical properties of novel pyrene cored pyrene annelated pentahelicene: 2,7,12,15,20,15-hexa-*tert*-butyl-dibenzo[*fg,op*]dipyreno[*a,j*]tetracene, a bis pentahelicene. In order to improve the selectivity and solubility of the large pyrene based helicene, we even used *tert*-butyl group at the 2 and 7 positions of each pyrene motifs.



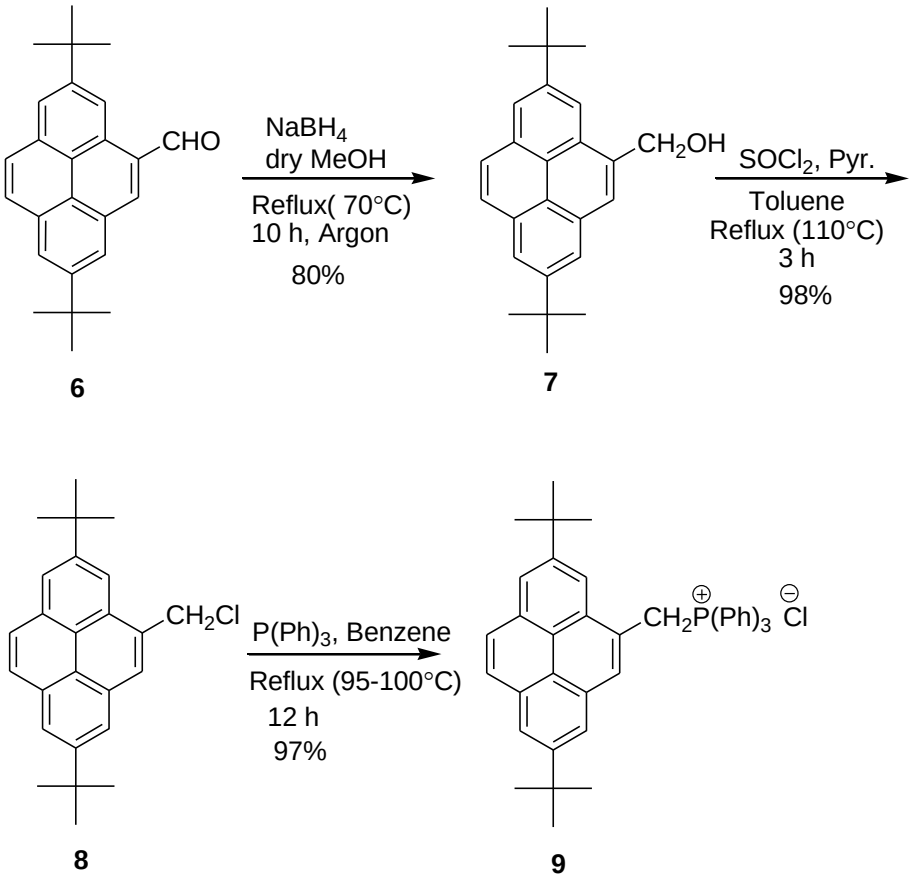
4 **5**

Fig: 6.2. Structures **4 - 5**, double helicenes

6.2 Result and Discussion

6.2.a Synthesis and Spectral Properties

Phosphorous ylide was prepared according to the Scheme: 6.1. Preparation method for 2,7-di-*tert*-butylpyrene-4-carboaldehyde **6** was carried out according to our previous procedure starting from pyrene (chapter 3). Thus the reduction of **6** with $NaBH_4$ in dry ether by refluxing the mixture at 70°C for 10h afforded alcohol **7** at 80% yield. The compound was purified by washing through column chromatography using hexane as eluent and recrystallized with a mixture of chloroform and hexane to afford white crystalline solid. The structure of compound **7** was assigned by spectral data, G.C and elemental analysis. The ^1H NMR data (300 MHz, $CDCl_3$), shows a pairs of doublet with meta coupling (J = 1.8 Hz) at δ 8.77, 8.19 ppm for aromatic protons H_1 and H_8, pairs of meta coupling (J = 1.6Hz) at δ 8.20, 8.41 ppm for aromatic protons H_3 and H_6, and singlet at δ 8.08 ppm for aromatic H_5 protons respectively. Similarly the ^1H NMR spectra shows a singlet at δ 8.01 ppm for H_9 and H_{10} protons. Protons for a methylene



Scheme: 6. 1 Sythetic route to phosphorous ylide

group was found to be resonanced a lower field in δ 5.36 ppm and a protons of hydroxyl group was found at δ 1.70 ppm. Also the *tert*-butyl protons were observed at δ1.59, 1.57 ppm. The reaction of **7** with $SOCl_2$ in toluene in presence of pyridine gave a chlorinated compound **8** in 97%. The structure was conformed directly by 1H NMR spectra, GC analysis. ^{1}H NMR spectra of compound **8** shows almost similar patterns of resonance at aromatic regions. The methylene protons were observed as singlet at δ5.28 ppm, a slight higher field that that of methylene protons in compound **8**. Similarly the disappearance of hydroxyl proton at δ 1.70 was strong support of compound **8**.

The Wittig reagent was prepared by adopting similar methods described in previous chapters. The Wittig reagent (2,7-di-*tert*-butyl-pyrene-4-yl)triphenylphosphonium chloride **9** was prepared in 97% yield by refluxing a mixture of **8** and triphenylphosphine in benzene for 12h. The compound was purified by washing with hexane and followed by benzene. The structure of compound was confirmed by ^{1}H NMR spectra and directly used for the Wittig reaction.

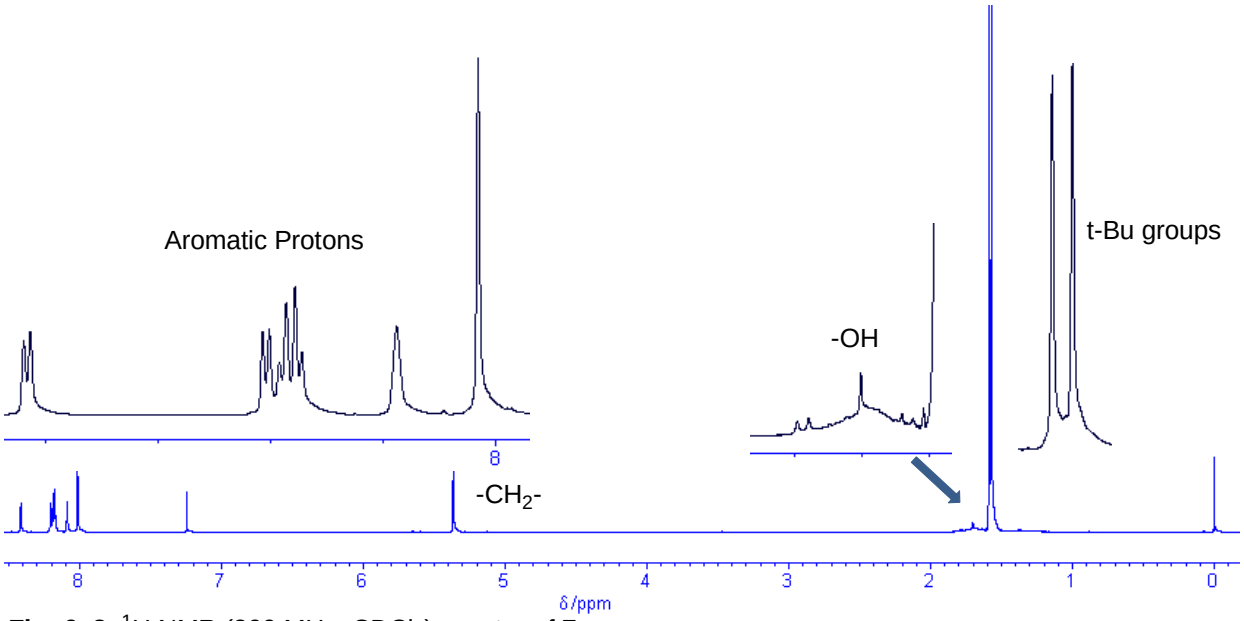


Fig: 6. 3. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **7**

On the other hand the regioselective preparation of 2,7-di-*tert*-butyl-4,9-di-formylpyrene **10** was carried out according to the method described in Chapter 5. Thus the reaction of **10** and (2,7-di-*tert*-butylpyrene-4-yl)triphenylphosphonium chloride **9** with n-butyllithium in THF gave the desired 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene **11** in 51% yield. The ^{1}H NMR spectra of compound shows most

complicated splitting patters because of the mixture of (*E, E*), (*E. Z*) and (*Z, Z*)-isomers. However the *tert*-butyl groups were found to be resonanced as three singlets at δ 1.16 ppm for peripheral pyrene and at δ 1.62 and 1.63 ppm for the central pyrene motif. The structures of compound as a mixture of different isomers were identified with the ^{1}H NMR spectra. The structure of Z- isomers is readily assigned from smaller coupling constant (J = 7.2 Hz) than that of (E)-isomer (J = 16.5 Hz). Being the complicated ^{1}H NMR spectral nature of the compound the structure of the compounds was further conformed by elemental and mass analysis. Therefore the compound was confirmed by the molecular ion at m/z 990.7 [M^{+}].

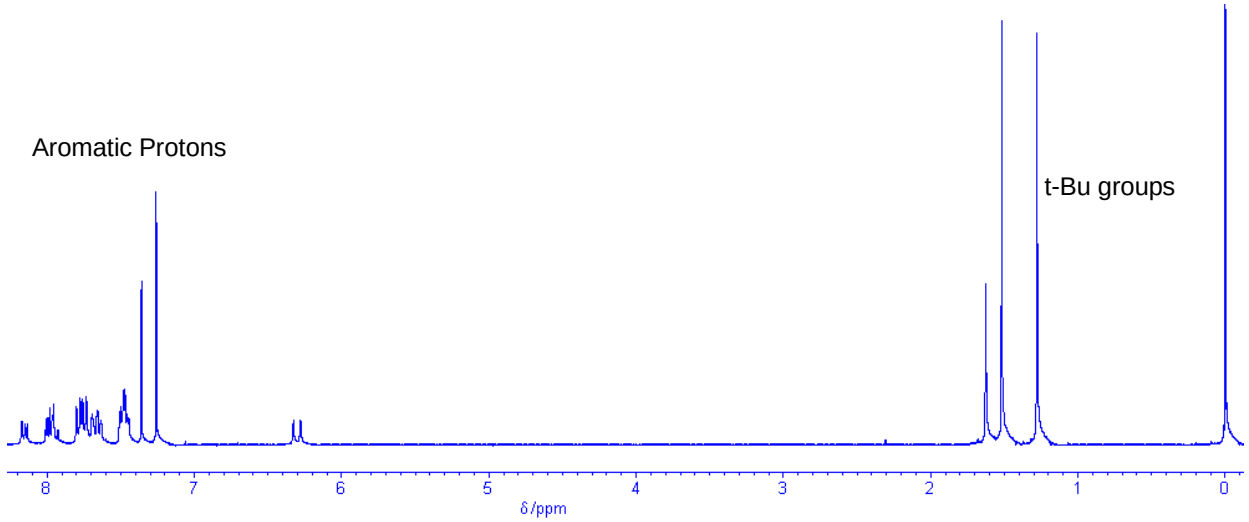
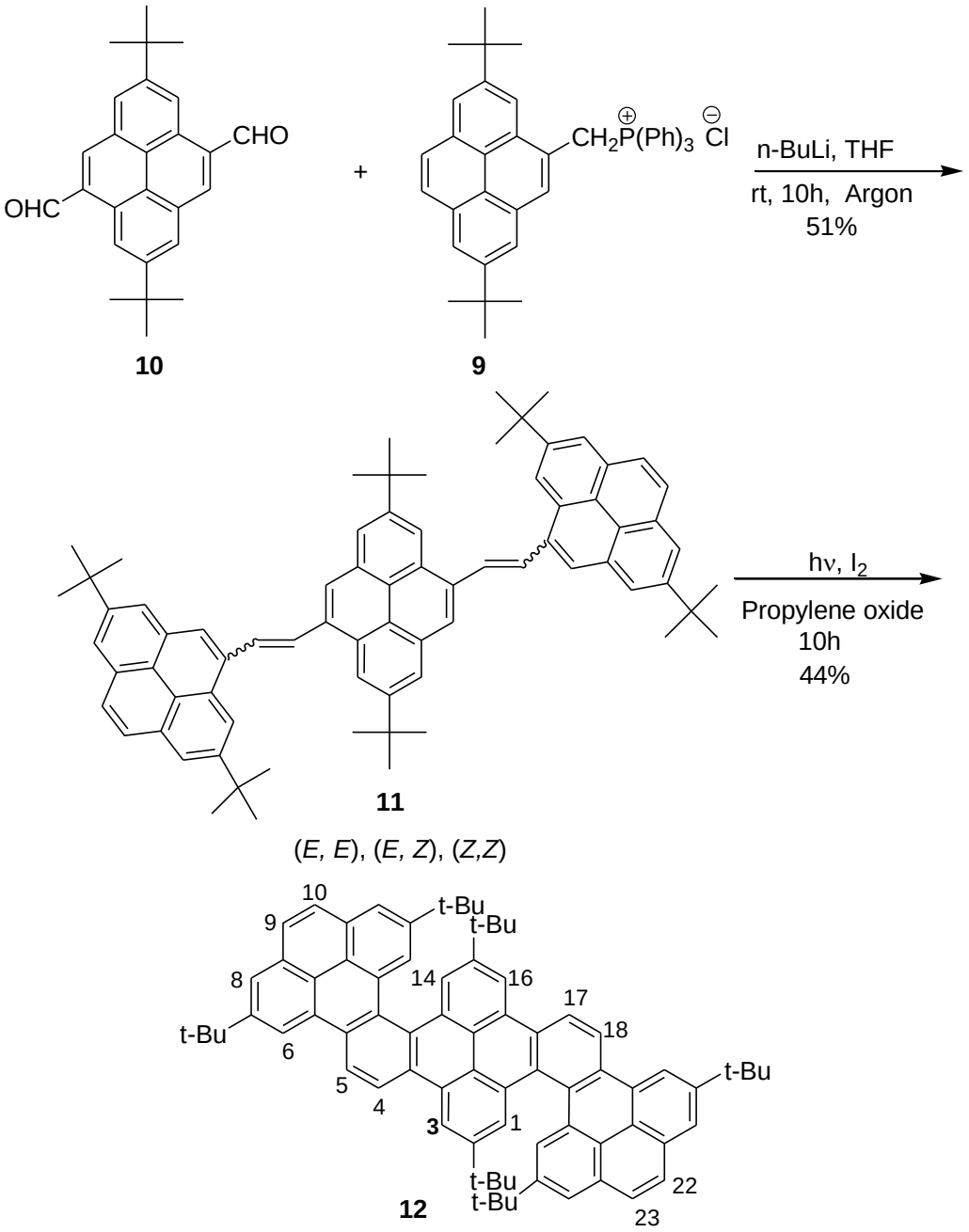


Fig: 6. 4. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of **9**

When a solution of (*E, E*), (*E. Z*) and (*Z, Z*)-**11** and a stoichiometric amount of iodine and excess amount of propylene oxide in benzene was irradiated under mercury lamp (400 W) at room temperature for 10h, photo cyclized product 2,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg,op*]dipyreno[*a,j*]tetracene **12** was obtained in 44%. Despite of being six *tert*-butyl groups in the compound, the compound bears low solubility and because of this the compound was purified by washing with different solvents and the column chromatography and recrystallized by slow evaporation of dilute solution. The structure of the compound was further determined by ^{1}H NMR spectra and mass analysis. The ^{1}H NMR spectra in $CDCl_3$ of compound, shows very simple patterns of splitting. As expected, the ^{1}H NMR (300 MHz, $CDCl_3$) shows two sets of singlets for outer *tert*-butyl groups that were found to be resonanced at δ 1.19, 1.22 ppm that were at the shielded region than that of inner *tert*-butyl groups that were found to deshielded at of δ 1.70 ppm. One of the *tert*-butyl groups of

peripheral pyrene motifs were observed at slight higher field than that of the other *tert*-butyl groups of peripheral pyrene motif, a common consequence of



Scheme: 6. 2 Synthetic route to 2,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg,op*]-dipyreno*[a,j]*tetracene

pronounced interaction with nearby aromatic rings. Similarly the ^{1}H NMR spectra of at aromatic regions shows a singlet at δ 8.07 ppm, six sets of meta coupling aromatic protons at δ 8.07, 8.26, 8.56,8.70, 8.79, 8.90 for $H_{9,10,22,23,}$ $H_{11,24,}$ $H_{13,26}$, $H_{8,21}$, $H_{1,14}$, H6,19, $H_{3,16}$ respectively. Furthermore the 1, 14 and 13, 26-arylhydrogens at fjord regions were found to

be deshielded at δ 8.70 and 8.26ppm, a common consequence of expanded aromatic rings. Similarly a doublet (J = 6.9 Hz) at δ 8.90 was observed as ortho coupled protons for H $_{4,5}$ and H $_{17,18}$.

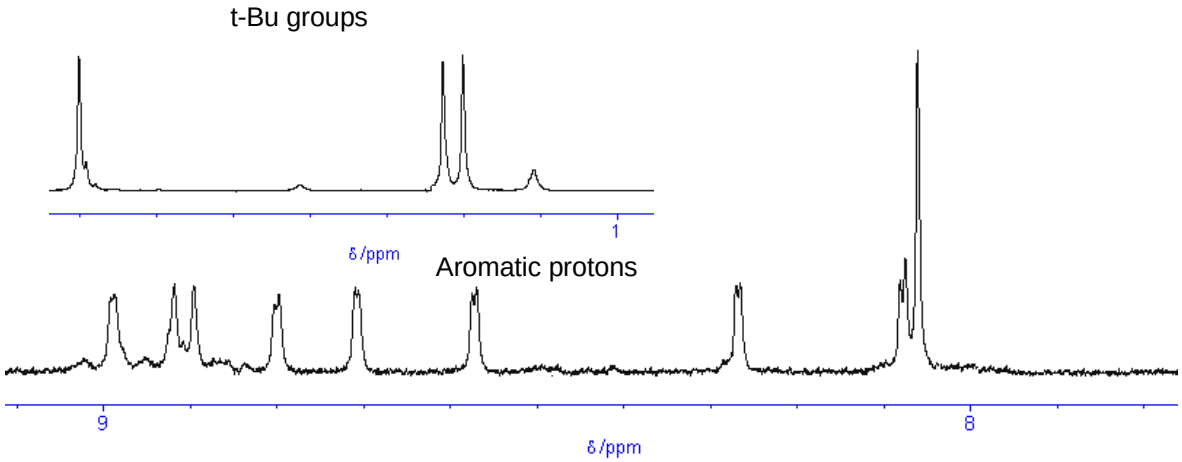


Fig: 6. 5. ^{1}H NMR (300 MHz, $CDCl_3$) spectra of compound **12**

Therefore well resolved ^{1}H NMR spectra recorded for the compound **12**. The sharp resonance in the aromatic region implied low self-association propensities in solution. The low self association propensities in the solution were because of bulky *tert*-butyl groups at the terminal regions of each pyrene molecules and helicene structural pattern associated with them. Study of characteristic splitting of ^{1}H NMR picks and the study of energy minimized, optimized geometry (MM2) of the compound **12**, suggested that compound **12** was also synthesized in the conformation in which both helicenes rotate in opposite sense (Figure: 6. 6). However the primary observation in energy minimized structure shows both of the double cyclization have occurred in a same direction with respect to the central pyrene core resulting in the formation of left handed (M) helicene in both of the sides, quite different mode of cyclization as compared to that of 2,11-di-*tert*-butyl-tetrabenzo[*a,fg,j,op*]tetracene and its derivatives (Chapter: 4). This different mode of cyclization was because of the bulky *tert*-butyl groups presence in the all of the pyrene motifs. Because of non concerted photo induced cyclization reactions, after the cyclization occurred in one side, the counter terminal of pyrene core with *tert*-butyl group would have been bent in opposite direction and resulting the most favorable left handed (M) mode of cyclization for next cyclization reaction. However the single X-ray crystal analysis and introduction of different substitutions in the

fjord regions of helicene in order to investigate the mode of cyclization and study of other parameters are under study in our laboratory. However, the structure also shows that both of the helicene motifs are attached laterally without sharing any common benzene rings, similar with that of previously described compounds (Chapter: 4)

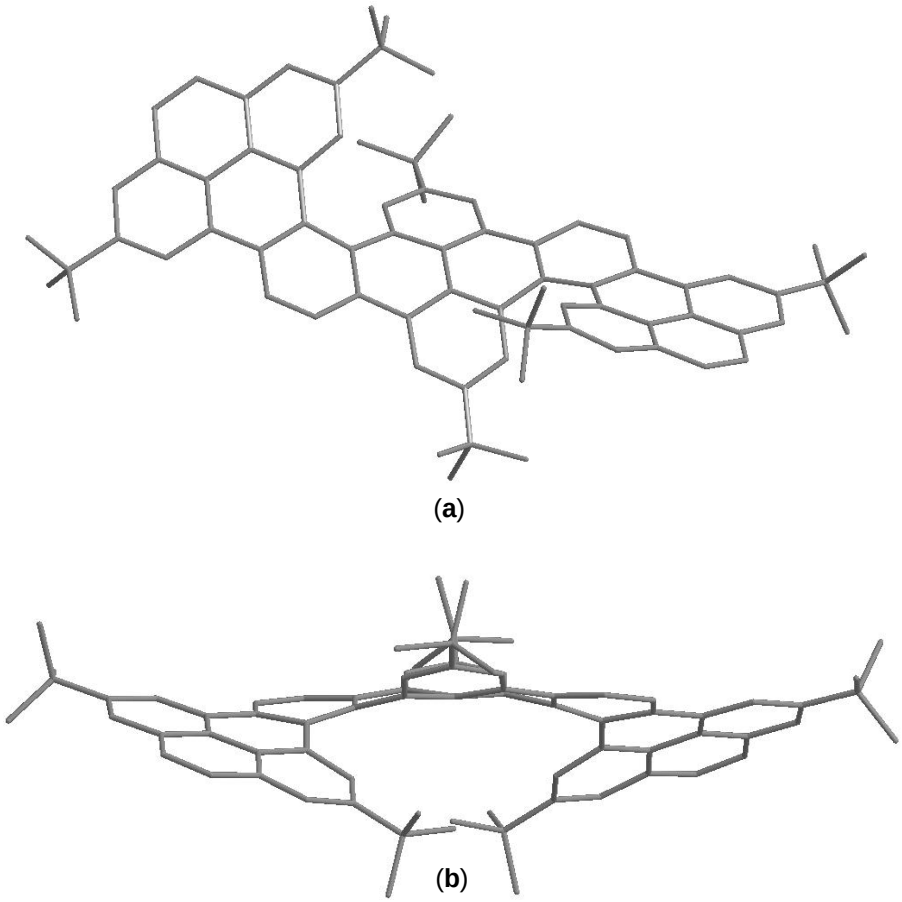


Fig: 6. 6. Energy minimized, optimized (MM2) for the proposed conformation of double helicenes (**a**) vertical view (**b**) lateral view

6.2.b Photo Physical Properties

The UV-Vis absorption and fluorescence spectroscopic data of novel polycyclic aromatic compounds with bis[5]helicenes structure **12**, derived from 2,7-di-*tert*-butyl-4,9-bis-(2'-7'-di-*tert*-butylpyrenylethenyl)pyrene **11** in dilute dichloromethane solution at room temperature, were measured and tabulated in Table.6.1, together with 2,7-di-*tert*-butyl pyrene. The comparative UV-Vis absorption spectra of **11**(before cyclization) are shown in Figure: 6.7. For 2,7-di-*tert*-butyl pyrene the absorption bands are almost identical with the

pyrene itself as described in previous chapters. As usual, slight bathochromic shifts is ascribed to the increased electron density to the pyrene rings, arising from the electron donating nature of *tert*-butyl groups at 2 and 7 positions. From Figure: 6.7, the UV-Vis absorption shows even broader, less well resolved bands than that of all the compounds described in previous chapters. The longest wave length with hyperchromic absorption maximum of **11** at 387 nm was observed as extreme broad absorption band. The absorption band was found to be bathochromically red-shifted by 48 nm arising from the introduced 2', 7'-di-*tert*-butyl-pyrenylethenyl units at 4 and 9 positions of central pyrene core as compared with 2,7-di-*tert*-butylpyrene. Compared with series of compounds 6 (Chapter 4), the compounds **11** displays the longest bathochromic shift of the absorption band, which could be attributed by the electron donating *tert*-butyl groups and pyrene incorporated to the both ends in the molecules. Longer conjugation will lead to the longer absorption wavelength. However the absorption maxima of the compound **11** is found slight lesser as expected because of being two electron accepting pyrene incorporated to the both ends with the electron accepting pyrene core.[11]

The UV-Vis spectra of 2,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg, op*]dipyreno[*a,j*]tetracene **12** the absorption bands were observed in the range of 317-362 nm. The quite different shape in Uv-Vis spectra of **12** in comparison with those of **11** is ascribed to be because of the expanded ring system by cyclization reaction. The sharp hypochromic absorption bands at 317-362 nm, after cyclization was ascribed as because of absence of 2', 7'-di-*tert*-butyl-pyrenylethenyl units leading to the decrease of aromaticity, increased distortions from the plane and decrease of π-conjugation in ring.

Compared with the absorption bands (300-376nm) series of compounds **6** (Chapter 4), the absorption bands of compound **11** was observed in as more bathochromically red shifted (311- 387 nm), a common consequences of extended π-conjugation in the later compounds. Similarly compared with the absorption bands (300-380 nm) of series of compounds **7** (chapter 4), the absorption band of compound **12** was observed as hypsochromically blue sifted in the range of 317-362 nm, a strong support of sudden decrease of π-conjugation, which is because of even more expanded bis [5]helicened aromatic rings leading to the distorted structural architecture. Upon excitation, a dilute solution of (~10^{-7}M) of compound **11** along with 2,7-di-*tert*-butyl pyrene in dichloromethane

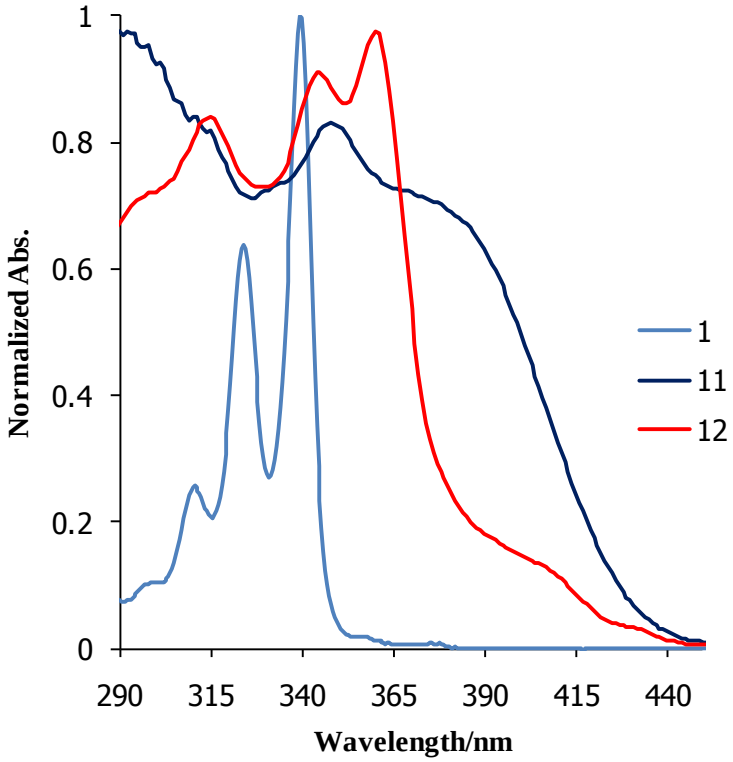


Fig 6.7 Normalized UV-vis absorption spectra of **11**(before cyclization) and **12**(after cyclization) recorded in dichloromethane at ~10^{-5} M concentration at 25°C, compared with that of 2,7-di-*tert*-butylpyrene **1.**

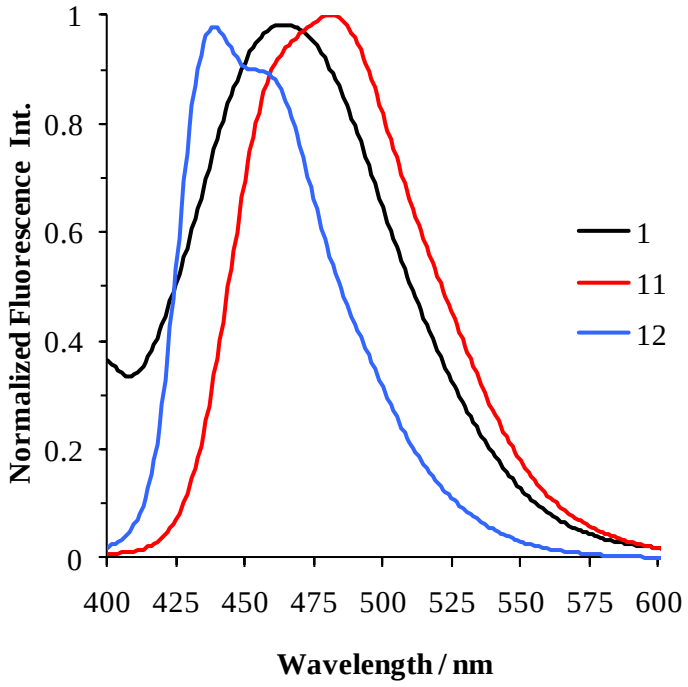


Fig 6.8 Normalized fluorescence spectra of **11** (before cyclization) and **12** (after cyclization) recorded at ~10^{-7} M concentration at 25°C, compared with that of 2,7-di-tert-butyl-pyrene **1.**

at room temperature shows broad band blue emission (Figure: 6. 8). Compared with the lower energy emission band of 2,7-di-*tert*-butyl pyrene, the lower emission band of **11** was found to be bathochromically red shifted at 477 nm. The fluorescence emission band is broad and the only one emission band that observed in visible pure-blue region indicates that the emission occurred from the lower excited state with the largest oscillator strength.

Similarly the maximum emission spectra of **12** (after cyclization) in CH_2Cl_2 are shown in Figure: 6.8. Compared with the lower energy band of 2,7-di-*tert*-butyl pyrene, lower energy band of **12** was found to be hypsochromically blue shifted at 436 nm with small shoulder at 454 nm. The emission band is sharper and narrower than the corresponding starting compound **11** and was observed in visible pure-indigo regions. The larger stock shifts of the compound even more than the series of **7** and **9** (Chapter 4) is ascribed to be because of extended aromatic rings leading to the more distortion of the aromatic core caused of [5]helicenes architectures which was even enhanced by bulky *tert*-butyl groups at the terminals of helicenes.

Table: 6. 1 Optical absorption and emission spectroscopic data for **11** and **12** in CH_2Cl_2 (~ 10^{-6}-10^{-7}M) at room temperature, compared with that of 1 [a]

Compd	Absorption [b] λ_{abs} [nm]	Fluorescence[c] λ_{max}[nm] (λ_{ex})[d]	Stokes-shifts [nm]	F.Q.Y Φ_f[e]
1	339	460 (240)	121	0.10
12	35, 387	477 (293)	126	0.64
13	38, 362,	**436**, 454 (276)	49	0.20

[a] all measurements were perfomed under degassed conditions. [b] ~10^{-6} M in CH_2Cl_2, λ_{abs} is absorption band appearing at the longest wavelength. [c] ~ 10^{-6} M in CH_2Cl_2, λ_{ex} fluorescence band appearing at the shorest wavelength. [d] wavelength of excitation.[e]absolute quantum yields (± 0.01- 0.03) in dichloromethane.

On the other hand, compounds **11** showed considerable extent of higher quantum yield than the cyclized compound **12** (Table: 6.1). The higher quantum yield of compounds was ascribed to be because of extended π-conjugation. However the quantum yield of the compounds was observed as lower values compared to that of phenylethenyl incorporated compounds to the one or both ends, which is because of electron accepting pyrenes incorporated to the both ends with the electron accepting pyrene core at the centers in **11**.

The molecules because of bulky *tert*-butyl groups enhanced the lost of co-planarity has also contributed in the lesser values of quantum yields.

After Cyclization, because of extended aromatic rings, extended helicene nature of compound there is a considerable extend of decrease of aromaticity[24]and as a result lesser extent of π-electron delocalization leading to the hypsochromically shifted emission bands and low quantum yield.[13] However the quantum yield of the compound **12** was observed to be enhanced by 50% with respect to the compound 2,7-di-*tert*-butyl pyrene.

6.3 Conclusion

Using the improved Wittig reaction , we have concluded that Wittig reaction of 2,7-di-*tert*-butyl-4,9-diformylpyrene with benzyl (2,7-di-*tert*-butyl-pyrene-4-yl)triphenylphosphonium chloride salt in the present of *n*-BuLi should be useful for the preparation of 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene. Photo induced cyclization of 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene in the presence of iodine and propylene oxide led to the novel expanded π-conjugated systems 2,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg, op*]dipyreno[*a,j*]tetracene, in which the new class of [5]helicene structure are contained. Study of characteristic splitting of ^{1}H NMR picks and the study of energy minimized, optimized geometry (MM2) of the compound 2,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg,op*]dipyreno[*a,j*]tetracene, suggested that this was also synthesized in the conformation in which both helicenes rotate in opposite sense. However the primary observation in energy minimized structure shows both of the double cyclization have occurred in a same direction with respect to the central pyrene core resulting in the formation of left handed (M) helicene in both of the sides, quite different mode of cyclization as compared to that of 2,11-di-*tert*-butyl-tetrabenzo[*a,fg,j,op*]tetracene and its derivatives (Chapter: 4), which is induced by the bulky *tert*-butyl group presence in the all of the pyrene motifs and non concerted photo induced cyclization.

The result obtained through inspecting the absorption and emission spectra of these compounds serves to shift the wavelength to pure blue regions for 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene. The UV-Vis absorption shows even broader, less well resolved bands than that of all the previously synthesized compounds in former chapters. The absorption band was found to be bathochromically red-shifted by 48 nm arising from the introduced 2', 7'-di-*tert*-butyl-pyrenylethenyl units at 4 and 9 positions of central pyrene core as compared with 2,7-di-*tert*-butylpyrene. Despite being longer conjugation the

absorption maxima of the compounds are found slight lesser values because of two electron accepting pyrene units incorporated to the both ends with the electron accepting pyrene core. Even though the absorption bands observed as more bathochromically red shifted than that of previously synthesized compounds proved the longer extended π-conjugation in the system. Rapid decrease of π-conjugation because of extended helicene structure that lead to the structural distortion was clearly observed from UV-Vis as hypsochromically blue shifted absorption band after cyclization.

Upon excitation, 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene shows broad band blue emission which is found to be bathochromically red shifted as compared with the 2,7-di-*tert*-butylpyrene. However maximum emission spectra after cyclization in CH_2Cl_2 found to be hypsochromically blue shifted at 436 nm with small shoulder at 454 nm. Because of electron accepting pyrenes incorporated to both ends with the electron accepting pyrene core at the center of 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene, the quantum yield of compound was observed with lesser values as compared to the phenylethenyl incorporated compounds. Similarly the lower values of quantum yields of cyclized compounds shows the existence of lower aromaticity, lesser extent of π-electron delocalization. However the quantum yield of cyclized compound was observed to be enhanced by 50% with respect to the compound 2,7-di-*tert*-butylpyrene.

6.4 Experimental

All melting points are uncorrected. The ^{1}H NMR spectra were recorded at 300 MHz on a Nippon Denshi JEOL FT-300 NMR spectrometer in deuteriochloroform with TMS as an internal reference. The IR spectra were obtained as KBr pellets on a Nippon Denshi JIR-AQ2OM spectrometer. UV/Vis spectra were obtained with a Perkin Elmer Lambda 19 UV/VIS/NIR spectrometer in various organic solvents. Fluorescence spectroscopic studies were performed in various organic solvents in a semi micro fluorescence cell (Hellma®, 104F-QS, 10 × 4 mm, 1400 μL) with a Varian Cary Eclipse spectrophotometer. Fluorescence quantum yields were measured using absolute methods. Mass spectra were obtained on a Nippon Denshi JMS-HX110A Ultrahigh Performance Mass Spectrometer at 75 eV using a direct-inlet system. Elemental analyses were performed with a Yanaco MT-5 analyzer.

Materials

Preparation of 2,7-di-*tert*-butylpyrene (**1**) was previously described[25,26]

Synthesis of 2,7-di-*tert*-butylpyrene-4-carboaldehyde **6** and 2,7-di-*tert*-butylpyrene-4,9-biscarbaldehyde **10** was described in chapter 4.

Synthesis of 2,7-di-*tert*-butylpyren-4-yl)methanol 7: To the solution of compound **6** (500mg, 1.46 mmol) and methanol (25mL) was slowly added sodium borohydride (220mg, 5.84mmmol) at room temperature. The mixture was stirred 3h at room temperature and refluxed 10 hours at 70^{o}c under argon. The mixture was quenched by large amount of ice-water, extracted with dichloromethane (2 × 50mL), washed with water, followed by brine solution and finally dried over anhydrous $MgSO_4$ and concentrated. The residue obtained was finally washed with hexane and recrystallized in dichloromethane to obtain 2,7-di-*tert*-butylpyren-4-yl)methanol 7 (400mg, 80%) as pale yellow solids; m.p = 137-138, ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.57 (9H, s *t*Bu), 1.59 (9H, s *t*Bu), 1.70 (1H, s, -OH), 5.36 (2H, s, -CH_2-), 8.01 (2H, s, $H_{9,10}$), 8.08 (1H, s, H_5), 8.17 (1H, d *J* = 2.1Hz,H_8), 8.19 (1H, d, *J* = 1.8Hz, H_1), 8.20 (1H, d, *J* = 1.8Hz,H_3), 8.41 (1H,d, *J* = 1.5 Hz, H_6); MS (EI): *m*/*z*: 344.3 (M^+). Elemental Analysis for $C_{25}H_{28}O$ (344.49): C, 86.16; H, 8.19; Found: C: 87.00; H: 8.17

2,7-di-*tert*-butyl-4-(chloromethyl)pyrene 8: To the solution of compound **7** (346.51mg, 1.0 mmol) and toluene (30mL) was slowly added mixture of $SOCl_2$ (0.9mL,12.47mmol) and pyridine (0.1mL) at room temperature. The mixture was stirred 3h at room temperature and refluxed 3 h at 110^{o}C. The reaction mixture is than stirred at room temperature for 2hrs. The mixture was quenched by large amount of ice-water, extracted with ethyl acetate (2 × 50mL), washed with 10% $NaHCO_3$, water, brine solution and finally followed by dried over anhydrous $MgSO_4$ and concentrated. The residue obtained was washed with MeOH to get white solid compound and recrystallized in dichloromethane and hexane to obtain 2,7-di-*tert*-butyl-4-(chloromethyl)pyrene **8** as white crystalline solid (357mg, 98.0%). The compound was confirmed by ^{1}H NMR spectra and Gas Chromatography and subjected directly for further reaction. m.p = 140-142°C; ^{1}H-NMR (300MHz, $CDCl_3$): δ(ppm): 1.57 (9H, s, tBu), 1.60 (9H, s, tBu), 1.52 (2H ,s, -CH_2-), 8.17 (1H, s, -H_5), 8.18 (1H, d, *J* = 1.8 Hz), 8.20 (1H, d, *J* =1.8Hz, H_1), 8.22 (1H, d, *J* = 1.5 Hz, H_3), 8.47 (1H, d, J = 1.8 Hz H_6); MS (EI): *m*/*z*: 362.18 (M^+). Elemental Analysis for $C_{25}H_{27}Cl$ (362.93): C, 82.73; H, 7.5; Found: C: 82.46; H: 8.17

(2,7-di-*tert*-butylpyren-4-yl-)triphenyl phosphonium chloride 9: To a solution of triphenyl phosphine (1.049 gm, 4mmol) in benzene(30mL) was added 2,7-di-*tert*-butyl-4-(chloromethyl)pyrene **8** (730mg, 2 mmol) and the mixture was refluxed for 12 h. The ppt obtained was washed with hot hexane and benzene to obtain white solids (97%). The structure of compound was confirmed by ^{1}H NMR and directly used for the Wittig reaction. ^{1}H NMR (300 MHz, $CDCl_3$): δ(ppm): 1.27 (9H, s *t*Bu), 1.51 (9H, s *t*Bu), 6.30 (2H, d, *J* = 14.4Hz), 7.27-8.17 (40H, m, Ar-H),

Preparation of 2,7-di*tert*butyl-4,9-bis(2',7'-di*tert*butylpyrenylethenyl)pyrene 11: To a solution of phosphorous ylide (1gm, 1.6mmol) in dry THF (15mL) was slowly added *n*-butyllithium in hexane (1mL, 1.6 mmol) at 0^{o}C under argon. The mixture was stirring for 10 minutes and a solution of 2,7-di-*tert*-butylpyrene-4-carboaldehyde **6** (250 mg, 0.67 mmol) in dry THF (15mL) was injected under same conditions. After this addition, the mixture was warmed to room temperature stirring for 10h under argon. The mixture was quenched by large amount of ice-water, extracted with ethyl acetate (2 ×100mL). Pale yellow solid obtained during extraction was filtered and the filtrate obtained was further washed with water followed by drying with brine and dried over anhydrous $MgSO_4$ and concentrated. The residue was adsorbed in silica gel and chromatographed over silica (Wako C-300, 200 g) with hexane-dichloromethane (40%) as eluent to give mixture of (***E,E***), (***E,Z***) (***Z,Z***)-isomers (NMR analysis) as light-yellow solids. Recrystallization from chloroform / methanol and finally washed with hexane afforded (341.26 mg, 51.3%) pure yellowish solid. m.p = 165-166 °C; For *E*-isomer: ^{1}H-NMR (300MHz, $CDCl_3$): δ(ppm): 1.604 (36H, s *t*Bu-outside), 1.626 (9H, s *t*Bu-Inner), 1.633 (9H, s *t*Bu-Inner), 7.975 (2H, d *J* = 16.5Hz, -CHb=CH-), 8.228 (2H, d, *J* = 16.5Hz, -CH=CHa-), 7.700-8.698 (Py-H). For *Z*-isomer: δ 7.99 (2H, d, *J* = 7.7 Hz,) MS (EI): m/z: 990.7 (M^+). Elemental Analysis for $C_{76}H_{78}$ (990.62): C, 92.07; H, 7.93; Found: C: 91.05, H: 7.15

General procedure for photocyclization

Photo reactor was a cylindrical glass vessel with an immersion well and two tapered joints, one vertical attached with condenser to which argon source was fitted. Another angled for withdrawal and addition of samples. The vessel was flat bottom to allow a magnetic stirring bar to rotate. The immersion well was a double walled Pyrex tube cooled by water and containing high pressure quartz Hg-vapor lamp. Argon gas was bubbled through benzene for 20-30 min and used to dissolved sample and iodine. The dissolved solutions of sample, iodine and propylene oxide were added to the reaction vessel through angled joint and the

lamp was turned on. The reaction was carried out under argon atmosphere. Photo reactions were monitored by ^{1}H NMR and iodine color change. After complete irradiation, work included washing with 15% $Na_2S_2O_3 \cdot H_2O$ and saturated brime, drying with anhydrous $MgSO_4$, filtering and concentrated to dryness on a rotary evaporator. The residue obtained was washed either through a short column of silica gel or different solvent systems were used to obtain the pure compounds.

Synthesis of 2,7,12,15,20,25-hexa*tert*butyl-dibenzo[*fg,op]*-dipyreno[*a,j]*tetracene 12 : A solution of 2,7-di*tert*butyl-4,9-bis(2',7'-di*tert*butylpyrenylethenyl)pyrene **11** (50.0 mg, 0.05 mmol) in 360 mL of benzene was irradiated in presence of I_2 (32.0 mg, 0.12 mmol) and propylene oxide(1.5 mL, 22.16 mmol) for 10 hrs. Worked up and the residue obtained was washed in column chromatogram using Hexane/chloroform (20%) as eluent. The compound obtained was further recrystallized in chloroform /Methanol system to obtain 2,7,12,15,20,25-hexa*tert*butyl-dibenzo[*fg,op]*-dipyreno[*a,j]*tetracene **12** 21mg (44%) as yellowish solid. m.p = 264-265 °C (decomposed),^{1}H-NMR (300MHz, $CDCl_3$): δ(ppm): 1.19 (18H,s, t-Bu-outside), 1.12 (18H,s, t-Bu-outside), 1.70 (18H,s, *t*-Bu-inside), 8.07(4H,d, *J* = 2.1Hz, Ar-$H_{9,10,22,23}$), 8,26 (2H, d, *J* = 1.2Hz, Ar-$H_{13,26}$), 8.56 (2H, d, *J* = 1.8Hz, Ar-$H_{8,21}$), 8.70 (2H, d, Hz, Ar-$H_{1,4}$), 8.79 (2H, d, *J* = 2.1Hz, Ar-$H_{6,19}$), 8.903 (4H,d, *J* = 6.9,Hz, Ar-$H_{4,15,17,18}$), ^{13}C NMR (300 MHz, CDCl3): δ (ppm): 29.70 (C), 31.23 (Me), 231.48 (Me), 35.53(C), Pyr-C = 114.6, 117.88, 119.46, 122.19, 122.51,122.98, 125.98, 126.90, 127.83, 128.56, 128.60, 129.06, 129.22, 129.48, 129.64, 130.90, 131.05, 131.11, 146.47(C), 146.47(C),.MS (EI): m/z: 986.5 $[M-1]^+$, for $C_{76}H_{74}$ (986.58): C, 92.45; H, 7.55; Found : C 91.05 , H:7.15

6.5 References

[1] S. Pogodin, I. Agrant, *Org. Lett*. **1999**, 1(9), 1387-1390.

[2] a) W. C. Herdon, D. A. Connor, P. Lin, *Pure. Appl. Chem*. **1990**, 62, 435-444. b) W. C. Herndon, P. C. Nowak, D. a. Connor, P. Lin, *J. Am. Chem. Soc*. **1992**, 114, 41-47.

[3] A. R. Murphy, J.-M, Frechet, Chem. Rev. 2007, 107, 1066-1096.

[4] A. dadvand, F. Rosei, V. G. Nenajdenko, D. F. Perepichka, *Chem. Commun*. **2008**, 5354-5356.

[5] a) J. S. Seigel, T. Sieders, *J. Chem. Br*. **1995**, 31, 313-316. b) P.W. Rabideau, A. Sygula, Acc. Chem. Res. **1995**, 34, 1429-1432.

[6] a) Jr. R.A. Pascal, Pure Appl. Chem. **1993**, 65, 105-110. b) X. Qiao, D. M. Ho, Jr. R. A. Pascal, *Angew. Chem. Int. Ed. Engl*. **1997**, 36, 1531-1532.

[7] a) R. H. Martin, Angew. Chem. Int. Ed. Engl. **1974**, 13, 649-660. b) W. H. Laarhoven, W. J. C. Prinsen, In *Topics in Current Chemistry,* Boschke, F. L., Ed., Springer-Verlag, Berline, **1984**, 125, 65-127. c) S. Grimme, J. Harren, A. sobanski, F. Vogtle, *Eur. J. Org. Chem.* **1998**, 1491-1509.

[8] a) L. Ammerer, A. Zinke, *Monatsh. Chem*. **1953**, 84, 25-31. b) A. J. Fatiadi, *J. Org. Chem*. **1967**, 32, 2903-2904. b) A. J. Fatiadi, *J. Org. Chem*. **1967**, 32, 2903-2904. c) T. von der Haar, A. Hebecker, Yu. V. Il_ichev, Y.-B. Jiang,W. _hnle, K. A. Zachariasse, *Recl. Trav. Chim. Pays-Bas* **1995**, 114, 430-442. d) M. Baumgarten, L. herghel, J. Friedrich, M. Jurczok, W.Rettig, *J. Phys. Chem. A* **2000**, 104, 1130-1140. e) C.-H. Yang, T.-F. Guo, I.-W. Sun, *J. Lumin*. **2007**, 124, 93 - 98.

[9] a) J. Bargon, S. Mohmand, R. J.Waltman, *IBM J. Res. Dev.* **1983**, 27, 330-341. b) S. Hino, K. Iwasaki, K. Matsumoto, *Synth. Met*. **1994**, 64, 259-264. c) L. Qu, G. Shi, *Chem. Commun.* **2004,** 2800-2801.

[10] T. M. Figueira-Duarte, S. C. Simon, M. Wagner, S. I. Druzhinin, K. a. Zachariasse, K. Mullen, *Angew. Chem*. **2008**, 120, 1-5.

[11] J-Y. Hu, M. Era, M. R. J. Elsegood, T. Yamato, *Eur. J. Org. Chem*. **2010**, 72-79.

[12] Z. Tomovic, M. D. Watson, K. Mullen, *Angew. Chem. Int. Ed*. **2004**, 43,755-758.

[13] D. Wasserfallen, M. Kastler, W. Pisula, W. A. Hofer, Y. Fogel, Z. H. Wang, K. Mullen, *J. Am. Chem. Soc*. **2006**, 128, 1334-1339.

[14] W. Pisula, M. Kastler, D. Wasserfallen, M. Mondeshki, J. Piris, I. Schnell, K. Mullen, *Chem. Mater.* **2006**, 126, 3634-3640.

[15] a) R. El Abed, B. B. Hassine, J.-P. GenÞt, M. Gorsane, A. Marinetti, *Eur. J. Org. Chem*. **2004**, 1517-1522. b) H. Meier, M. Schwertel, D. Schollmeyer, *Angew. Ch*em. **1998**, 110, 2224-2226, *Angew. Chem. Int. Ed*. **1998**, 37, 2110-2113. c) A. M. Gilbert, T. J. Katz, W. E. Geiger, M. P. Robben, A. L. Rheingold, *J. Am. Chem. Soc*. **1993**, 115, 3199-3211. d) C. A. Liberko, L. L. Miller, T. J. Katz, L. Liu, *J. Am. Chem. Soc*. **1993**, 115, 2478-2482. e) B. Yang, L. Liu, T. J. Katz, C. A. Liberko, L. L. Miller, *J. Am. Chem. Soc.* **1991**, 113, 8993-8994. f) L. Liu, B. Yang, T. J. Katz, M. K. Poindexter, *J. Org. Chem.* **1991**, 56, 3769-3775.

[16] a) K. Yano, M. Osatani, K. Tani, T. Adachi, K. Yamamoto, H. Matsubara, *Bull. Chem. Soc. Jpn.* **2000**, 73, 185-189. b) C. Stammel, R. Froehlich, C. Wolff, H.

Wenck, A. de Meijere, J. Mattay, *Eur. J. Org. Chem*. **1999**, 1709-1718. c) A. Terfort, H. Goerls, H. Brunner, *Synthesis* **1997**, 79-86. d) L. Liu, T. J. Katz, *Tetrahedron Lett*. **1991**, 32, 6831-6834. e) W. H. Laarhoven, W. J. C. Prinsen, *Top. Curr. Chem.* **1984**, 125, 63-130.

[17] A. Urbano, *Angew. Chem*. **2003**, 115, 4116-4119, *Angew. Chem. Int. Ed*. **2003**, 42, 3986-3989. b) R. H. Martin, *Angew. Chem*. **1974**, 86, 727-738.

[18] a) K. Nakano, Y. Hidehira, K. Takahashi, T. Hiyama, K. Nozaki, *Angew. Chem*. **2005**, 117, 7298-7300, *Angew. Chem. Int. Ed.* **2005**, 44, 7136-7138. b) Y. Ogawa, M. Toyama, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahedron Lett*. **200**3, 44, 2167-2170. c) D. PePa, A. Cobas, D. PGrez, E. GuitiQn, L. Castedo, *Org. Lett*. **2003**, 5, 1863-1866. d) Y. Ogawa, T. Ueno, M. Karikomi, K. Seki, K. Haga, T. Uyehara, *Tetrahedron Lett*. **2002**, 43, 7827 - 7829.

[19] F. Dubois, M. Gingras, Tetrahedron Lett. **1998**, 39, 5039-5040.

[20] a) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett*. **2002**, 43, 7345-7347. b) D. C. Harrowven, M. I. T. Nunn, D. R. Fenwick, *Tetrahedron Lett*. **2002**, 43, 3189-3191.

[21] a) I. G. Stara, I. Stary, A. Kollarovic, F. Teply, D. Saman, P. Fiedler, *Collect. Czech. Chem. Commun.* **2003**, 68, 917-930. b) F. Teply, I. G. StarQ, I. Stary, A. KollQrovic, D. Saman, L. RulRsek, P. Fiedler, *J. Am. Chem. Soc*. **200**2, 124, 9175 - 9180.

[22] P.P. Meurer, F. Voltle, Helical Molecules in Organic Chemistry, *Top Curr. Chem*. **1997**, 62, 1274-1285.

[23] K. shiraishi, A. Rajca, M. Pink, S. Rajca, *J. Am. Chem. Soc.* **2005**. 127, 9312-9313.

[24] E. Clar, The aromatic Sextet, John Wiely & Sons, London, **1972**.

[25] T. Yamato, A. Miyazawa and M. Tashiro, *J. Chem. Soc., Perkin Trans. 1*, **1993**, 3127-3137.

[26] T. Yamato and J. Hu, *J. Chem. Research*, **2006**, 12, 762-765.

Summary

Polycyclic aromatic hydrocarbons have proven their potential active components as advance materials in present time. On the other hand helical compounds currently provide an active field of research in supramolecurlar chemistry, related to their self assembly and physicochemical properties. Also their unique chiral array can provide functionalized helicenes for use as ligands and auxiliaries in asymmetric syntheses. However the development of helicene chemistry was long hampered by the lack of convenient synthetic methods and despite much recent progress, the preparation of helicenes still requires improvements. The most classical helicene synthesis, Martin's photochemically mediated cyclization of stilbenes derivatives, has been optimized and widely applied. In modern contest, the key improvement over previous efforts includes production of helicenes compounds via photochemical process in presence of iodine oxidant and propylene oxide with Hg-lamp radiation source having Wittig ylide, a common intermediate to the helicenes.

Although pyrene and its derivatives have extensively been used in the synthesis of various organic advanced materials and applied in huge practical areas, syntheses of helicene compounds based on pyrene core have not yet reported. Based on this assumptions, present research was focused on the synthesis and characterization of pyrene cored single and double [4] and [5] helicene compounds using improved photochemical methods. All these developed materials are novel helicene compounds and thus new class of polycyclic aromatic hydrocarbons.

In chapter 1, the general introduction of pyrene and pyrene cored materials with respect to their applications are presented and a brief introductory outline of present thesis are discussed.

In chapter 2, recent literature concerning synthesis and development of polycyclic aromatic hydrocarbons, helicenes and present proposed of study are presented.

In chapter 3, the more efficient synthesis routes to substituted and unsubstituted pyrene based [4] helicene compounds with their optoelectronic properties are presented. Wittig reaction of 2,7-di-*tert*-butylpyrene-4-carboaldehyde with benzyltriphenylphosphonium salt in the presence of n-BuLi to afford 2,7-di-*tert*-butyl-4-(phenylethenyl)pyrenes, from which naphthalene condensed aromatic compounds, 2,7-di-*tert*-butyl-dibenzo[ij,no]tetraphenes derivatives were obtained by photo-induced cyclization in the presence of iodine and propylene oxide. On the other hand, studies on the electronic

absorption and fluorescence emission properties for these new helicenes are fully presented by using UV-Vis absorption and photo luminescence spectroscopy techniques.

In Chapter 4, the Wittig reaction of 2,7-di-*tert*-butylpyrene-4,9-biscarboaldehyde and 2,7-di-*tert*-butylpyrene-4,10-biscarboaldehyde with benzyl triphenylphosphonium salt in the present of n-BuLi should be useful for the preparation of 2,7-di-*tert*-butyl-4,9-bis(phenylethenyl)pyrenes and 2,7-di-*tert*-butyl-4,10-bis(phenylethenyl)pyrene and their derivatives were presented. Photo induced cyclization of these compounds afforded the novel expanded π-conjugated systems tetrabenzo[*a,fg,j,op*]tetracene, and tetrabenzo[*a,de,h,mn*]tetracene derivatives, in which the first member of new class of bis[4]helicene structure are contained. Similarly the UV-Vis spectra of compounds show considerably bathochromically red shifted absorption maxima. These compounds exhibited higher quantum yields because of phenylethenyl units incorporated to both ends with the electron accepting pyrene core. However the cyclized compounds exhibited hypochromic absorption in UV-Vis and pronounced hypsochromically blue shifted emission maximum bands. The quantum yields of the cyclized compounds are less because of distorted structure of compounds caused by bis[4]helicene structure patterns. The single X-ray crystal study revealed inhibition to face π-π stacking interactions between neighboring pyrene units and revealed herringbone array of molecules in crystal lattice.

In chapter 5, more efficient synthesis routes to substituted and unsubstituted 7-*tert*-butyl-1,3-dimethylpyrene based[4]helicene compounds with their optoelectronic properties are presented. Photo induced cyclization of corresponding Wittig products in presence of iodine and propylene oxide lead to the corresponding novel expanded π-conjugated dibenzo[*ij,no*]*tert*aphene derivatives containing methyl group at fjord regions. Introduction of two methyl groups at fjord region of [4]helicene was found to be responsible for enhanced distorted structure of compounds. On the other hand, studies on the electronic absorption and fluorescence emission properties for these new helicenes are fully presented by using UV-Vis absorption and photo luminescence spectroscopy techniques.

In chapter 6, Synthesis, spectral and photo physical properties of pyrene cored new class of polycyclic aromatic hydrocarbons derivatives containing double [5] helicene motifs are reported in this chapter. These compounds features bearing of phenanthrene condensed pyrene cored polycyclic aromatic hydrocarbons having bis [5]helicene structural patterns. We have adopted the similar reaction strategies of Wittig reaction to obtain 2,7-di-*tert*-

butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene and its photo induced cyclization reaction to get in ,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg,op*]-dipyreno[*a,j*]tetracene a bis[5]helicene compound. Study of characteristic splitting of ^{1}H NMR picks and the study of energy minimized, optimized geometry (MM2) of the compound ,7,12,15,20,25-hexa-*tert*-butyl-dibenzo[*fg,op*]dipyreno[*a,j*]tetracene, suggested different mode of cyclization giving left handed [M] bis[5] helicenes in both of the sides.

Similarly the UV- Vis absorption and emission spectra of the compounds were studied. Because of electron accepting pyrenes incorporated to both ends with the electron accepting pyrene core at the center of 2,7-di-*tert*-butyl-4,9-bis-(2',7'-di-*tert*-butylpyrenylethenyl)pyrene, the quantum yield of compound was observed less as compared to the phenylethenyl incorporated compounds. Similarly the lower values of quantum yields of cyclized compounds shows the existence of lower aromaticity, lesser extent of π-electron delocalization because of highly distorted [5] helicene structure.

Therefore, various types pyrene cored novel PAHs having unique helicene structure patterns were selectively synthesized. The design and synthetic methods for all the compounds were fully presented. Chemical structure and photophysical properties for these compounds were determined by modern techniques and demonstrated. The results revels that the synthesized compounds are unique in their structural patterns and opened a new area in the synthesis of polycyclic aromatic hydrocarbons. On the other hand, we have demonstrated that the use of PAH core for the synthesis of helicene compounds with unique molecular architecture and the best way to overcomes the problem of obtaining complex side product during photo induced reaction.