Chapter 1

Diels-Alder Reaction, Di-π-methane Rearrangement and Energy Transfer Process in Organic Photochemistry: An Overview

1.1. Abstract

The present chapter outlines the fundamental concepts, based on which our investigations were formulated. The concepts considered here include Diels-Alder reaction, di-π-methane rearrangement and energy transfer process in organic photochemistry.

1.2. Introduction

Organic chemistry is one of the prerequisites of modern science. Through organic synthesis, we are able to synthesise the most complicated natural products, which possess the exact three-dimensional structure of those isolated from nature. The realisation of the most difficult synthetic tasks would be a tremendous accomplishment to the intellectual expertise of the community of synthetic chemists.

Our investigations on the photochemical and photophysical behaviour of a few olefin-appended dibenzobarrelenes and bisdibenzobarrelenes, constitute the core of this thesis. The intention of appending various olefins at the bridgehead position of dibenzobarrelenes, was to assess its efficiency as an intramolecular quencher of triplet excited state of dibenzobarrelenes. The photobehaviour of the novel bisdibenzobarrelenes is yet to be explored. In this chapter an overview of the three basic building blocks of this thesis i.e., Diels-Alder reaction, di-π-methane rearrangement and energy transfer process
in organic photochemistry are presented.

1.3. Diels-Alder Reaction

Diels-Alder reaction is one of the most versatile and useful processes in the repertoire of synthetic chemistry. [2+4] Cycloadditions are called Diels-Alder reactions in honor of Otto Diels and Kurt Alder, the chemists who carried out the first such reaction.¹ This cycloaddition consists of the addition of a "dienophile", which are olefinic and acetylenic compounds to the 1,4-positions of a conjugated diene system with the formation of a six-membered hydroaromatic ring.² Up to four stereocenters may be constructed in one Diels-Alder reaction and the great number of possible substrates gives the reaction great scope.

\[
\text{[Cyclohexene]} + \text{CHO} \rightarrow \text{CHO} \]

\[
\text{[Cyclohexene]} + \text{CO}_2 \text{CH}_3 \rightarrow \text{CO}_2 \text{CH}_3 \]

\[
\text{Scheme 1}
\]

Diels-Alder reaction is one of the most important synthetic routes for six-membered rings and it is one of the most important stereoselective C-C bond-forming reactions in general.³ The additions of various diene systems to dienophiles shown in Scheme 1 are typical examples of Diels-Alder reaction.
The olefinic dienophiles yield cyclohexene derivatives and the acetylenic dienophiles lead to derivatives of 1,4-dihydrobenzene.

**1.3.1. The Diene and the Dienophile**

The diene component in Diels-Alder reaction can be open chain or cyclic and it can have many different kinds of substituents. For the Diels-Alder reaction to occur, the diene must be able to adopt the *s-cis* conformation⁴ (Scheme 2). In butadiene, the *s-trans* conformer 10 is preferred over the *s-cis* conformation 1. But only the *s-cis* conformer is capable of taking part in the Diels-Alder reaction.⁵

\[
\text{\begin{align*}
\text{s-trans} & \quad \text{fast} \quad \text{s-cis} \\
\text{10} & \quad \text{1} \quad \text{11} \quad \text{12}
\end{align*}}
\]

*Scheme 2*

Cyclopentadiene, a cyclic diene that is permanently in the *s-cis* conformation is exceptionally good at Diels-Alder reaction. But cyclic dienes that are permanently in the *s-trans* conformation and cannot adopt *s-cis* conformation, will not undergo Diels-Alder reaction at all.⁶ Furan, cyclohexadiene, cycloheptadiene, anthracene are some examples of dienes that are permanently in the *s-cis* conformation. 1,3-Butadienes with alkyl-, aryl-, alkoxy-, and trimethylsilyloxy substituents are some examples of acyclic dienes.

The dienophiles, active in Diels-Alder reaction can be divided into two main groups: ethylenic and acetylenic.⁷ In the ethylenic compounds, the double bond is usually conjugated with one or more unsaturated groups, but
simple ethylenes have also been found to undergo Diels-Alder reaction. The acetylenic compounds which have been employed contain the triple bond in conjugation with one or more carbonyl or cyanide groups.

**Ethylenic Compounds**

R-CH=CH-Y and Y-CH=CH-Y  
where \( R = H, CH_3, C_6H_5 \)  
\( Y = CHO, CO_2H, CO_2R, COCl, COR, CN, NO_2, SO_2R, \)  
\( CH_2Cl, CH_2OH, CH_2NH_2, CH_2NCS, OCOR, Cl, Br, OR, SR, H \)

**Acetylenic Compounds**

R-\( \equiv \)C-Y and Y-\( \equiv \)C-Y  
where \( R = H, CH_3, C_6H_5 \)  
\( Y = CHO, CO_2H, CO_2R, COCl, COR, CN, NO_2, SO_2R \)

1.3.2. **Stereochemical Course of Diels-Alder Reactions**

Diels-Alder reaction exhibits pronounced stereochemical selectivity. The configuration of the adduct formed conforms to the following general principles commonly known as the "cis" principle and the Alder "endo" rule. In certain special cases, anomeric effect is also prominent.

1.3.2.1. **The "cis" Principle**

The addition of a dienophile to a diene is a purely cis addition. The relative positions of substituents are retained in the adduct. The reliability of the rule is one of the major factors in the importance of the Diels-Alder reaction in synthesis and in stereochemical studies. The almost universal strict cis addition can be readily explained by synchronous formation of the bonds between the two components in a one-step reaction. cis- or trans-Dienophiles react with dienes to give 1:1 adducts in which the cis or trans arrangement of
the substituents in the dienophile is retained, exhibiting the stereoselective nature of the Diels-Alder reaction. An illustrative example is shown for the reactions of the isomeric methyl β-cyanoacrylates 14 and 15 with 9,10-dimethylantracene\(^{10}\) 13 (Scheme 3).

![Scheme 3](image)

Scheme 3

The cis principle applies also to substituents in the diene components, thereby exhibiting its stereospecificity with regard to the diene as shown in Scheme 4. In the 1:1 adduct 19, which can be obtained almost quantitatively from trans,trans-1,4-diphenylbutadiene 18 and maleic anhydride 5 by refluxing in benzene, the phenyl groups are cis to each other.\(^{11}\)

![Scheme 4](image)
1.3.2.2. The Alder "endo" Rule

The title "endo" is derived from the strong propensity of most dienophile substituents to orient in the endo configuration in the bridged bicyclic adducts formed from cyclic dienes. The combination of cyclic dienes with cyclic dienophiles could in principle follow two courses. But in general, only one of these is actually realized. In the reaction of maleic anhydride with cyclopentadiene, two modes of addition are theoretically possible, leading to the formation of an "exo" adduct 21 or an "endo" compound 23 respectively. Actually, the endo configuration is produced exclusively.\(^\text{12}\)

![Scheme 5](image)

After a "sandwich-like" preorientation of the reactants, the dienophile is added in such a way as to give a "maximum concentration" of double bonds\(^8\) in the transition state. The favoured orientation 22 corresponds to the maximum accumulation of double bonds. According to Alder and Stein, this includes not only the \(\pi\) systems directly involved in the reaction, but also those
of the "activating ligands". It has been calculated\textsuperscript{13} that the attractive forces between the two molecules are greater in the \textit{endo} orientation than in the \textit{exo} orientation. The principle of maximum accumulation of unsaturated centers point to the physical reality that electrostatic and electrodynamic attractive forces associated with the mobile electronic systems, not directly involved in the bond-forming processes lower the energy of intermediates such as 23 as compared with the type 21.\textsuperscript{14}

\subsection*{1.3.3. Frontier Orbital Interactions in Diels-Alder Reactions}

Frontier molecular orbital\textsuperscript{15} (FMO) theory as first expressed by Fukui\textsuperscript{16} continues to be used extensively by synthetic organic chemists for the prediction of the reactivity and selectivity of many organic reactions. As pertains to the Diels-Alder reaction, predictions of reactivity and selectivity are normally based on the strength of a single FMO interaction between the diene and the dienophile, the so-called "dominant" interaction. The dominant interaction is usually taken to be the one involving the two frontier orbitals having the smallest energy gap between them.\textsuperscript{17} As shown in Figure 1, when the HOMO\textsubscript{diene} – LUMO\textsubscript{dienophile} energy gap is least, the reaction is called a "normal Diels-Alder cycloaddition" (NDAC), while when the HOMO\textsubscript{dienophile} – LUMO\textsubscript{diene} energy gap is smallest, the reaction is termed as "inverse-electron-demand Diels-Alder cycloaddition" (IEEDAC).

Dienophiles with conjugating groups are usually good for Diels-Alder reactions. Dienes react rapidly with electrophiles because their HOMOs are relatively high in energy, but simple alkenes have relatively high-energy LUMOs and do not react well with nucleophiles. The most effective modification is to lower the alkene LUMO energy by conjugating the double bond with an electron-withdrawing group such as carbonyl or nitro. This type of Diels-Alder reaction, involving an electron-rich diene and an electron-
deficient dienophile are referred to as Diels-Alder reactions with normal electron demand.\textsuperscript{19}

\textbf{Figure 1}. Frontier orbitals in normal and inverse electron-demand Diels-Alder cycloadditions\textsuperscript{18}

Diels-Alder reactions may also occur when the electronic situation of the substrates is completely reversed, that is when electron-rich dienophiles react with electron-poor dienes. \textsuperscript{[4+2]} Cycloadditions of this type are called Diels-Alder reactions with inverse electron demand.\textsuperscript{20,21} 1,3-Dienes that contain heteroatoms such as O and N in the diene backbone are the dienes of choice for this kind of cycloaddition. The reaction of 1,2,4,5-tetrazine-3,6-dicarboxylate 24 with styrene 25 producing 1,4-dihydropyridazines\textsuperscript{22} 27 is an example of inverse electron demand Diels-Alder reaction (Scheme 6).
1.3.4. Regioselectivity of Diels-Alder Reaction

Constitutionally homogeneous cycloadducts are obtained through symmetrically substituted dienes and dienophiles. In contrast, when an unsymmetrical diene and an unsymmetrical dienophile combine in a Diels-Alder reaction, the reaction itself becomes unsymmetrical and it may afford two constitutionally isomeric cycloadducts. The specific regioisomeric behaviour of Diels-Alder reaction was interpreted through the application of simple perturbation theories.\(^\text{23}\) The reaction remains concerted but, in the transition state, bond formation between the largest LCAO coefficients in the closest pair of frontier orbitals, in each partner is more advanced and this determines the regioselectivity of the reaction.\(^\text{24,25}\)

1,3-Butadienes with alkyl substituents in the 2-position favour the formation of the so-called para products in their reactions with acceptor-substituted dienophiles (Scheme 7). The so-called meta product is formed in smaller amounts. This orientation selectivity increases if the dienophile carries two geminal acceptors. 2-Phenyl-1,3-butadiene exhibits a higher "para" selectivity in its reactions with every asymmetric dienophile than any 2-alkyl-1,3-butadiene does.\(^\text{19}\)
Catalysis by Lewis acids can influence the regiochemistry of Diels-Alder reactions. The reaction of but-3-en-2-one 33 with 2-methyl-1,3-butadiene 32 under non-catalytic conditions leads to a mixture of two adducts in the proportion 71:29. Addition of tin tetrachloride, effects almost exclusive formation of the isomer 34 (Scheme 8). The complexing of dienes and dienophiles by Lewis acids changes the energetic position and the structure of the frontier orbitals and thus it affects the regiochemistry (vide infra).

Apart from the dominant HOMO-LUMO interactions, secondary orbital interactions are as additional modifying factors for the regioselectivity of Diels-Alder reaction. They are supposed to enhance the orientation...
behaviour indicated by primary interactions.

1.3.5. **Solvent Effects on Diels-Alder Reaction**

Pericyclic reactions with chargeless transition states, were considered to be insensitive to solvent effects. The pioneering discovery of Rideout and Breslow in 1980, reveals the dramatic acceleration of Diels-Alder reactions in aqueous solutions. The rates of Diels-Alder reactions have been accelerated by factors up to $1.3 \times 10^4$ in aqueous solution as compared to organic solvents. The principal effect was ascribed to hydrophobic association of the diene with the dienophile. Blokzijl and Engberts suggested that "enforced hydrophobic interaction" due to a decrease in the overall hydrophobic surface area during the activation process is a key factor in determining the rate acceleration in water. Other interpretations of the acceleration of Diels-Alder reactions beyond the former two primary effects involve micellar effects, internal pressure, solvophobicity and enhanced hydrogen bonding to the transition state.

![Scheme 9](image)

A striking example is the Diels-Alder reaction of anthracene-9-carbinol 36 with $N$-ethylmaleimide 37 (Scheme 9). The second order rate constant of the reaction, when carried out in water at $45 \, ^\circ\text{C}$ was over 200 times larger than in acetonitrile, showing the expected effects of dissolved salts. With 4.86 M
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lithium chloride the rate in water at 45 °C of the aforementioned reaction, increases by 2.5 fold; lithium chloride is a solute which increases hydrophobic effects, decreasing the solubility of hydrocarbons in water.

1.3.6. Acceleration of Diels-Alder Reactions by Lewis Acid Catalysts

Yates et al. were the first to recognize the significant increase in the reaction rates of Diels-Alder reactions upon the addition of a catalytic amount of AlCl₃. Further studies showed that Lewis acids like BF₃, SnCl₄, TiCl₄ also catalysed the reaction. An additional advantage of Lewis acid catalysed Diels-Alder reaction is that the reaction temperature can be lowered by more than 100 °C with no decrease in rate.

\[ \text{Scheme 10} \]

The catalytic action is due to complex formation between the Lewis acid and the polar groups of the activating substituents in the dienophile (e.g. in maleic anhydride, ethyl maleate etc) or in the diene (reaction of tetraphenyl cyclopentadienone with ethylene). The Lewis acid catalysed Diels-Alder reaction of methyl acrylate 11 with butadiene 1 is \(10^5\) times faster than in the
absence of Lewis acid (Scheme 10). The Lewis acid coordinates at the Lewis base side of the dienophile, for example, at the carbonyl oxygen of methyl acrylate, making the carbonyl group even more electron-withdrawing and thus more reactive.

According to the FMO theory, a Lewis acid that binds to the electron-withdrawing group of the dienophile catalyses the reaction by lowering the LUMO of the dienophile. In the presence of Lewis acids, cis-trans isomeric dienophiles give diastereoisomeric adducts just as in the uncatalysed reaction, revealing that Lewis acid catalysed Diels-Alder reactions also are pure cis additions.38

1.3.7. Effect of Pressure on Diels-Alder Reaction39-41

Pressure exerts an exceptionally large accelerating effect on Diels-Alder reaction42 and this phenomenon has been exploited both for mechanistic43 and for synthetic purposes.44 This effect is particularly important for gaseous reactants, for example, ethylene adds smoothly to dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate at 165 °C/1000 atm.45 The reaction of naphthalene with maleic anhydride at 10⁴ atm gives the 1:1 adduct in 78% yield, whereas at 1 atm and otherwise identical conditions the yield is only 1%.46

1.3.8. Tandem Diels-Alder Reactions

In the context of chemical reactions, "tandem" means two reactions which follow one another. The construction of multiple carbon-carbon bonds in a single chemical step represents an efficient method for the synthesis of complex molecular structures.47 The intramolecular arene-olefin cyclization, applied by Wender48 for the direct synthesis of a series of polycyclic
compounds is an excellent example of the utility of tandem Diels-Alder reaction.

The nature by which the reaction cascades follow one another can be classified into two different ways: Interrupted and Uninterrupted cycloaddition. An example of the interrupted cycloaddition is the extrusion of carbon dioxide from a pyrone Diels-Alder adduct 43 to generate a second diene moiety, 1,3-cyclohexadiene 44, which can undergo a second cycloaddition reaction to give 45 as shown in Scheme 11. The uninterrupted cycloadditions can be further classified into (a) reaction sequences in which both diene-dienophile pairs are present in the starting compounds (Scheme 12) and (b) a sequential pathway in which the first cycloaddition opens up a new diene or dienophile which can then undergo a second cycloaddition reaction (Scheme 13).

Interrupted Biscycloaddition

\[
\begin{align*}
\text{Scheme 11}
\end{align*}
\]

Uninterrupted "Simultaneous"

\[
\begin{align*}
\text{Scheme 12}
\end{align*}
\]
The most important application of this methodology is the Diels-Alder reaction of bicyclic bisdienes, which facilitate the synthesis of a variety of bridged polycyclic ring systems.

Intermolecular Diels-Alder reaction of the bicyclic bisdiene 53 with dimethyl acetylenedicarboxylate 8 leads to the formation of a bimolecular
adduct 54, which can then undergo intramolecular cycloaddition to give the bridged tetracyclic products 55 and 56, in appreciable yield (Scheme 14).\textsuperscript{50} This reaction termed as a "domino" Diels-Alder reaction, served as the cornerstone in the synthesis of dodecahedrane by Paquette.\textsuperscript{51}

1.3.9. Hetero Diels-Alder Reactions

In hetero Diels-Alder reactions, those molecular systems are involved in which one or more atoms of the diene or the dienophile are heteroatoms, leading to the formation of heterocyclic systems. In the production of commercially useful organic intermediates and medicines,\textsuperscript{52} this technique has become an inevitable tool. In hetero Diels-Alder reactions, carbonyl compounds, nitroso compounds, nitrile group, imino group, alkyl azodicarboxylate etc can function as dienophiles, when they are activated by a strong electronegative group in conjugation with the double or triple bond.\textsuperscript{53} The formation of the heterocyclic system 59 from cyclopentadiene 57 and azocarboxylic ester 58 is one of the earliest examples of synthesis by the Hetero Diels-Alder reaction\textsuperscript{54} (Scheme 15).

\begin{equation}
\text{Scheme 15}
\end{equation}

Hetero Diels-Alder reaction is a sharp synthetic tool in the field of natural product total synthesis.\textsuperscript{55} The power of this hetero Diels-Alder based methodology is elegantly illustrated in the total synthesis of agelastatin A\textsuperscript{56} 65 (Scheme 16).
1.3.10. Intramolecular Diels-Alder Reactions

In the intramolecular Diels-Alder reaction,\textsuperscript{57, 58} two rings are formed in one step. In addition to the six-membered ring formed by the [4+2] cycloaddition the product contains a second ring, the size of which depends on the length of the chain connecting diene and dienophile.\textsuperscript{59} When compared to intermolecular Diels-Alder reaction, the two reacting functionalities are part of the same molecule in intramolecular Diels-Alder reaction, thus exhibiting less negative activation entropies and increased reaction rates under mild conditions. The constraints imposed by the connecting chain, together with the lower reaction temperatures, results in pronounced regio- and stereoselectivity. One of the most striking observations in the intramolecular Diels-Alder reaction is the fact that considerable strain can be accommodated in the product. So even substantial ring strain does not deter the reaction.\textsuperscript{60}
Intramolecular Diels-Alder reaction has become a most versatile method for the synthesis of polycyclic structures, particularly natural products. The special interest in it is the selective introduction of stereochemistry. The synthesis of a precursor molecule 67 of the alkaloid, lysergic acid 68 employing intramolecular Diels-Alder reaction\textsuperscript{61} is shown in Scheme 17.

![Scheme 17](image)

1.4. Di-\(\pi\)-methane Rearrangement

Since the discovery of di-\(\pi\)-methane rearrangement by Zimmerman and Grunewald in 1966\textsuperscript{62}, this rearrangement has attracted much attention from organic chemists because of its importance in organic synthesis as well as its interesting mechanistic aspects. In view of the pioneering and extensive contributions of Zimmerman and coworkers to illustrate the generality of di-\(\pi\)-methane rearrangement, this rearrangement is also referred to as the Zimmerman rearrangement. The variants of di-\(\pi\)-methane rearrangement are the oxa-di-\(\pi\)-methane rearrangement\textsuperscript{63}, in which one of the two \(\pi\)-moieties is a carbonyl group and the aza-di-\(\pi\)-methane rearrangement\textsuperscript{64} has a C-N double bond function as one of the \(\pi\) groups.

Di-\(\pi\)-methane rearrangement occurs on photolysis of molecules having two \(\pi\) moieties bonded to a single sp\(^3\)-hybridised carbon atom. The rearrangement leads to a \(\pi\)-substituted cyclopropane. Formally, it involves migration of one \(\pi\) moiety originally bonded to the methane carbon C-3 to C-4.
of the other π moiety with concomitant bonding between C-3 and C-5, resulting in the three-membered ring formation.⁶⁵

Scheme 18

Studies have shown that one basic mechanism⁶⁶, ⁶⁷ describes the skeletal change in the di-π-methane rearrangement. The mechanism is depicted in simple resonance terms in Scheme 19, where two vinyl groups are present. Scheme 20 depicts di-π-methane rearrangement in a molecular system where one of the two π-substituents is a phenyl group. These resonance structures, which have proved useful in describing photochemical mechanisms, are not necessarily intermediates but are approximations of species along the reaction coordinate, simply depicted by points on the energy hypersurface leading from excited state of reactant to ground state of product.⁶⁸

Scheme 19

Scheme 20
The photochemical conversion of barrelene 79 to semibullvalene 83 using acetone sensitisation,\(^6\) prompted Zimmerman \textit{et al.} to the reaction mechanism and to the generality of the di-\(\pi\)-methane rearrangement. The details of the molecular reorganisation occurring were demonstrated using hexadeuteriobarrelene,\(^7\) in which the bridgehead carbons were undeuteriated. The pathway followed during di-\(\pi\)-methane rearrangement is depicted in Scheme 21. Interaction of orbitals at C-2 and C-4 of an electronically excited pentadiene, leads to the stabilization of the excited species, thus accounting for the vinyl-vinyl bonding in the initial steps of di-\(\pi\)-methane rearrangement.\(^7\)

\[
\begin{align*}
79 & \xrightarrow{\text{hv}} \text{Biradical 1} & 80 & \xrightarrow{\text{Conformational Change}} 81 \\
\text{Sens.} & & & \text{Biradical 2} \\
83 & = & 82 \\
\end{align*}
\]

\textbf{Scheme 21}

The reactants with three \(\pi\) groups attached to the central carbon mechanistically are capable of affording both di-\(\pi\)-methane and tri-\(\pi\)-methane photoproducts.\(^7\) Scheme 22 shows the mechanism of the di-\(\pi\)-methane rearrangement and its potential diversion to a tri-\(\pi\)-methane pathway. In this, on excitation of 84, the singlet or triplet bridges to give cyclopropyldicarbinyld diradical 85. Opening of this species tends to give transoid (bond a-b) allylic diradical 86 as consequence of less steric interference. This species closes to
afford π-substituted cyclopropane product 88 characteristic of a di-π-methane rearrangement. In contrast, if cyclopropylidicarbinyl diradical opening were to lead to cisoid allylic diradical 87, closure to tri-π-methane product 89 may compete with 1,3-closure to di-π-methane product 88. Thus tri-π-methane rearrangement exhibits a parallelism with the di-π-methane rearrangement in the initial π-π bridging step with a preference for the more delocalised cyclopropylidicarbinyl diradical.\textsuperscript{73}

1.4.1. Reaction Multiplicity

Di-π-methane rearrangement displays a photochemistry where the excited singlet and triplet states exhibit different intramolecular reactivity. Studies on numerous molecular systems led to the generalisation that acyclic di-π-methane reactants rearrange effectively from their singlet excited states,
whereas bicyclic di-π-methane systems prefer to rearrange via their triplet excited states. Sensitisers used in di-π-methane rearrangement are mainly acetophenone, benzophenone and xanthone, which generate the triplet excited state of the di-π-methane reactant. At times, the singlet excited states produced without a sensitiser, might undergo intersystem crossing to their triplet excited states.

A noteworthy example of di-π-methane rearrangement in acyclic molecular systems is the rearrangement of 3,3-dimethyl-1,1-diphenyl-1,4-hexadiene 90 (Scheme 23).

This diene rearranges on direct irradiation through the singlet excited state to give vinylcyclopropane 91. In contrast, sensitised irradiation through the triplet excited state leads to the cis-trans isomerisation of the diene (Scheme 23). The "free rotor effect" operates in the decay of the triplet excited states of those molecules, in which double bonds are not incorporated in a ring structure or not inhibited from free rotation. 74, 75

Triplet multiplicity is preferred for the di-π-methane rearrangements in rigidly constrained systems i.e., in structures which prohibit free rotation about
Zimmerman and coworkers\textsuperscript{62} have shown that barrelene \textit{79}, which contains \pi moieties within rigidly structured environments, rearranges by the di-\pi-methane pathway to semibullvalene \textit{83} solely by acetone sensitisation. The triplet excited states of bicyclic systems are incapable of "free rotor" energy dissipation due to their rigid structures, thus paving way for the conversion of the triplets to \pi-substituted cyclopropanes. The singlet excited states of many cyclic systems have potentially available facile alternative pericyclic processes which compete with di-\pi-methane rearrangement. Direct irradiation of barrelene \textit{79} leads to cyclooctatetraene \textit{93} by an electrocyclic \([2\pi + 2\pi]\) addition followed by a retro \(2\pi + 2\pi\) fission\textsuperscript{76} (Scheme 24).

\begin{center}
\begin{tikzpicture}
  \node at (0,0) (a) {\includegraphics[width=0.2\textwidth]{scheme24.png}};
  \node at (0,-1.5) {\textbf{Scheme 24}};
\end{tikzpicture}
\end{center}

Dibenzobarrelenes \textit{94} upon direct irradiation produce dibenzocyclooctatetraene \textit{96} through the singlet excited state\textsuperscript{77} and upon sensitised irradiation, the di-\pi-methane photoproduct, dibenzosemibullvalenes \textit{95} are formed through the triplet excited state\textsuperscript{84} (Scheme 25).

\begin{center}
\begin{tikzpicture}
  \node at (0,0) (a) {\includegraphics[width=0.2\textwidth]{scheme25.png}};
  \node at (0,-1.5) {\textbf{Scheme 25}};
\end{tikzpicture}
\end{center}
1.4.2. Regioselectivity of Di-π-methane Rearrangement

Di-π-methane rearrangement exhibits strong regioselectivity in an unsymmetric di-π-methane system i.e., the marked preference for migration of one of the two different π moieties attached to the methane carbon.

An illustrious example is found in the direct irradiation of 3,3,5-trimethyl-1,1-diphenyl-1,4-hexadiene 97 which leads to only one of the two a priori possible products\textsuperscript{74} (Scheme 26). The regioselectivity exhibited in the photoproduct is understood on the basis of "biradical 1" undergoing three-ring opening preferentially by mechanism b rather than a. The cyclopropyldicarbinyl diradical opens up in such a way as to produce the more stable of two alternative 1,3-biradicals, in this case the one with benzhydryl delocalization is retained. The overall process can be summarised as a
preferential formation of that regioisomer which has the less delocalising group on the residual double bond. The regioselectivity of aryl-vinyl di-π-methane systems operate in such a way as to regenerate the aromatic system in the three-membered ring opening process as shown in Scheme 27.

Scheme 27

When heteroatom-bearing substituents are involved, then there is a strong tendency for electron donors to appear on the residual π-bond of the photoproduct and electron-withdrawing groups to be found on the cyclopropane product ring (Scheme 28). This suggests that the carbinyl carbons in the cyclopropylcarbinyl diradicals are electron rich and as the diradical opens its three-membered ring this negative charge is dissipated on the carbon developing π-bond character. Thus, with an electron-donating group present, there is driving force for the carbinyl carbon bearing this donor to be that involved in ring opening and in becoming the π-bonded carbon. Conversely, for electron-withdrawing substituents there is an advantage that the carbinyl carbon retains its electron-rich character and not being the one generating the π bond.
1.4.3. Regioselectivity Exhibited by Barrelene Related Molecules

In barrelene related molecules, we encounter "tri-π-methane" reactants, in which the three π-systems are bonded to a single "methane carbon". Nonequivalence in the three bridges, raises the question of which two π-systems will bond. Zimmerman and coworkers observed a preferential bonding between the two vinyl bridges rather than between benzo and vinyl bridges in the case of benzobarrelene,70,79 2,3-naphthobarrelene80 and related molecules. In the case of benzobarrelene (Scheme 29), the initial interaction between vinyl chromophores leads to a system 113 isoconjugate with triplet butadiene and so of lower triplet energy ($E_T = ca. 58 \text{ kcal/mol}$)71 than the species formed by vinyl-benzo interaction 114 and resembling styrene ($E_T = ca. 64 \text{ kcal/mol}$).12 One exception is that of 1,2-naphthobarrelene where α-naphtho-vinyl bridging is preferred.80
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A different variation in regioselectivity is encountered in systems where the two π-moieties are bonded to "methane carbons" at both ends, opening up two possible sites for the initial π-π bridging. A similar situation occurs in the rearrangement of 2-cyanobarrelene 118 studied by Bender\textsuperscript{81} (Scheme 30). Here the initial bridging occurs between two vinyl groups to leave the cyano group at an odd-electron center. Isotopic labeling ruled out benzo-vinyl bridging. The odd-electron not stabilised by the cyano group is utilised in the three-membered ring opening, leading to the observed photoproduct 120.

Scheme 29

Scheme 30
Paquette\textsuperscript{82,83} has shown that the photochemistry of substituted benzonorbornadienes, follow a similar regioselectivity. Scheme 31 illustrates that in methoxy-benzonorbornadiene, benzo-vinyl bridging occurs distal to the methoxy group while in the cyanobenzonorbornadiene, benzo-vinyl bridging takes place proximate to the cyano group. The regioselectivity is similar to that observed with electron-donating and −withdrawing substituents on acyclic di-π-methane systems, thus drawing the generalisation that electron donors avoid positioning themselves in conjugation with the carbinyl centers of the cyclopropylidcarbinyl biradicals and electron-withdrawing groups lead to stabilisation when so situated.

\begin{center}
\begin{tikzpicture}
\node at (0,0) (121) {121};
\node at (1,1) (122) {122};
\node at (0,-1) (123) {123};
\node at (1,-1) (124) {124};
\draw[->,thick,orange] (121) -- (122);\node at (0.5,0) {$\text{MeO}_{\text{Sens.}}$};
\draw[->,thick,orange] (123) -- (124);\node at (0.5,0) {$\text{NC}_{\text{Sens.}}$};
\end{tikzpicture}
\end{center}

\textbf{Scheme 31}

1.4.4. \textbf{Regioselectivity Exhibited by Dibenzobarrelenes (9,10-Ethenoanthracenes)}

The photochemical studies conducted on several dibenzobarrelenes by Ciganek\textsuperscript{84} and Friedman\textsuperscript{77} indicated that electronic effects are important in determining the course of initial bonding in di-π-methane rearrangement. In fact Ciganek was the first to recognise the modest effect of the bridgehead substituent group on the bridging regioselectivity of di-π-methane systems.
rearrangement. The mechanism\textsuperscript{85} (Scheme 32) in the case of dibenzobarrelene 125 (applicable to all dibenzobarrelenes) is thought to involve (a) initial bonding between positions 9a and 12 ("benzo-vinyl" bridging) to afford the 1,4-biradical 126, (b) cyclopropane ring cleavage to give 1,3-biradical 127 and (c) 1,3-biradical closure to form the dibenzosemibullvalene 128. In Scheme 32, there are three additional pathways (II-IV) for a total mechanistic degeneracy of four, path I and II leading to one enantiomer of 128, and paths III and IV giving the other.

\textbf{Scheme 32}

Path I : Initial 9a-12 bonding  
Path II : Initial 10a-11 bonding  
Path III : Initial 4a-11 bonding  
Path IV : Initial 8a-12 bonding
In Scheme 33, the reactivity seen in the formation of the major dibenzosemibullvalene product 132, from the irradiation of acetone or benzene solution of dibenzobarrelene 129, could be readily explained on the basis of odd-electron stabilisation by the carbomethoxy group.\textsuperscript{71}

![Scheme 33](image)

In the dibenzobarrelene system 133, substituted with methoxycarbonyl at the bridgehead position, unfavourable bridging at the end nearer to the group occurred, which was interpreted as arising from a reluctance to have the electronegative group held by a bond which becomes heavy in s character\textsuperscript{71} (Scheme 34).
Iwamura et al.\textsuperscript{86} has disclosed the effect of a wider range of substituents at the methane position on the bridging selectivity in di-\(\pi\)-methane systems. As depicted in Scheme 35, there are two possible termini capable of competitive vinyl benzo bridging in the excited triplet states (path a and path b). These bridging regioselectivities would be interpreted in terms of the relative stability of the initially formed cyclopropylidicarbinyl diradicals 138 and 139. Experimental and theoretical studies show that \(\pi\)-electron acceptors such as CN, CO\(_2\)CH\(_3\) and CHO at the bridgehead position, should stabilise the cyclopropane ring and thus favours bridging through path a, while \(\pi\)-electron donors such as OCH\(_3\) should destabilise the cyclopropane ring and therefore favour path b.
Richards et al. explained the regioselective rearrangement of the bridgehead hydroxy- and acetoxy- dibenzobarrelene derivatives, through the effect of hydrogen bonding and electronegativity of the bridgehead substituents respectively. Irradiation of the hydroxydibenzobarrelene 142, instead of giving a hydroxysemibullvalene 143, gave almost exclusively keto diester 144 (Scheme 36). The preferred regioselectivity for the formation of the 8b-isomer has been attributed to a decrease in the radical stabilising ability of the ester group due to hydrogen bonding. This would favour radical formation next to the non-hydrogen bonded CO\textsubscript{2}CH\textsubscript{3} group, which leads ultimately to the 8b-hydroxydibenzosemibullvalene.
9-Acetoxydibenzobarrelene 145 upon irradiation in acetone gives the dibenzosemibullvalene 148. Scheme 37 shows that the electronegativity effect will favour the formation of 146 which will have only one electronegative substituent on the incipient cyclopropane ring compared with two in 147.

Scheffer and coworkers were the first to report the tri-π-methane rearrangement pathway for the photoisomerisation of dibenzobarrelenes. They have observed that dimethyl 9,10-dimethyl-9,10-dihydro-9,10-
ethenoanthracene-11,12-dicarboxylate 150, reacts from its singlet state in an unexpected manner to give photoproducts 153 and 154, through the intermediacy of the bis-benzylic diradical 152 (Scheme 38). The involvement of a similar diradical intermediate was postulated in the photoisomerisation of dimethyl 9-chloromethyl-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate.89

\[
\begin{align*}
150 & \rightarrow 151 & \rightarrow 152 & \rightarrow 153 & \rightarrow 154
\end{align*}
\]

Scheme 38

Scheffer et al.90 reported some studies on the influence that vinyl and aryl substituents have on the photochemistry of the dibenzobarrelene system. Disubstituted compounds such as 155 were prepared inorder to analyse the intramolecular competition between two different vinyl substituents (Scheme 39). The photochemical results were in accord with the idea put forward by Zimmerman,91 that the radical termini of the cyclopropyldicarbinyldiradicals (156 and 157) become electron rich during the di-\(\pi\)-methane rearrangement, as
a result both the polar nature as well as the radical-stabilising ability of the substituents are important in determining regioselectivity. As an example, though the radical stabilising abilities of the methyl and ester groups are probably equal, the photoproduct 160 is formed exclusively owing to the preference for the radical to be formed next to the electron-withdrawing ester group rather than the electron-donating methyl substituent.

![Scheme 39](image)

Aryl substituent effects\(^{90}\) were briefly investigated in the 1,5-disubstituted dibenzobarrelene system 162 (Scheme 40). Although photolysis of such compounds can lead to regioisomeric di-\(\pi\)-methane products, results showed the initial benzo-vinyl bridging occurring preferentially ortho to the methoxy substituent.
Scheffer and coworkers have shown that the solid state reactions of dibenzobarrelenes lead to greater regio-, stereo- and enantioselectivity compared to their solution phase reactions. They have shown that the enantioselectivity of several dibenzobarrelenes can be enhanced through the "ionic auxiliary" concept. In this approach, the chromophore is linked to a sensitisir or a heavy atom, followed by the solid state irradiation of the salts, resulting in increased yields of the triplet photoproduct. An example is the irradiation of the salt 171 formed between the dibenzobarrelene ester-acid 169 and the tert-butyl ester of (S)-proline, 170 (Scheme 41). Irradiation of crystals of 171, followed by acidic work-up to remove the ionic chiral auxiliary and the esterification of the resulting carboxylic acid with diazomethane gave exclusively the regioisomer 172. The factors for the preferential enantioselectivity is an intramolecular steric effect in which the substituents on the vinyl group tend to remain far apart during the "benzo-vinyl" bridging.
Chapter 1

Due to the less steric interference, bridging occurs between C(11) and C(4a) as compared to C(11)-C(10a) bridging.

\[ \text{Ihmels and coworkers}^{94} \text{ conducted a recent study showing that the photochemical properties of a chromophore are modified by alkali metal ions through crown ether complexation. The dibenzobarrelene 173, which is annulated with a crown ether, complexes with alkali metals such as sodium, potassium and caesium, on treatment with NaBF}_4, \text{ KBF}_4\text{ and CsBF}_4\text{ respectively. Irradiation of 173 alone or its alkali metal complexes in acetonitrile or benzene, leads preferentially to the dibenzocyclooctatetraene 174 as the photoproduct. In contrast, the solid state irradiation of the alkali metal complexes of 173 leads exclusively to the dibenzosemibullvalene 175, which is attributed to a cation effect (Scheme 42).} \]
George et al.\textsuperscript{95} examined the photoisomerisation of several 9-substituted-11,12-dibenzoyldibenzobarrelenes to understand the factors responsible for the preferred regioselectivity leading to either 4b- or 8b-substituted dibenzosemibullvalenes. Scheme 43 shows that path a involves "benzo-vinyl" bridging [C(12)- C(9a) bridging] leading to the diradical intermediates 177 and 178, which would then be transformed to the 8b-substituted dibenzosemibullvalene 181. Path b depicts [C(11)-C(4a) bridging], involving diradical intermediates 179 and 180, which ultimately lead to the 4b-substituted dibenzosemibullvalene 182. The results summarise that bridgehead substitution by alkyl groups, nitro groups and halogen exclusively afford the 4b-substituted semibullvalenes.\textsuperscript{96-98} Dibenzobarrelenes with substituents such as hydroxy, cyano and aryl groups give the 8b-substituted dibenzosemibullvalenes as intermediates, which then undergo transformation to other products. The conjugative stabilisation of the diradical intermediates by these substituents could be a decisive factor that governs the observed regioselectivity.
Photochemical studies suggest that dibenzocyclooctatetraene formation takes place through the singlet excited states of dibenzobarrelenes, involving an initial intramolecular [2+2] cycloaddition. Although there is a greater propensity for the formation of triplet state mediated products in most of the 11,12-dibenzoyl-substituted dibenzobarrelenes, George and coworkers found that the corresponding dibenzocyclooctatetraenes are also formed. When the bridgehead positions are substituted by isopropyl, cyclopentyl or cyclohexyl groups, substantial amounts of dibenzocyclooctatetraenes are formed. A probable route to the formation of dibenzocyclooctatetraenes are shown in Scheme 44. The reaction is assumed to proceed through the initially formed
[2+2] adduct 184, which rearranges to 185 and ultimately to dibenzocyclooctatetraene 186.

Instances of tri-π-methane rearrangement leading to dibenzocyclooctatetraenes with $C_2$ symmetry, occurred in certain 11,12-dibenzoyl substituted dibenzobarrelenes. Irradiation of 11,12-dibenzoyl-9,10-dimethyl-substituted dibenzobarrelene 187, in benzene and under complete absence of oxygen, gave a mixture of the dibenzocyclooctatetraene 190 and the dibenzopentalene derivative 191 (Scheme 45). The mechanism involves the excitation of 187 leading to the diradical intermediate 188, through a tri-π-methane route. Further transformation of 188 will result in the benzylic 1,4-diradical 189. A Grob type fragmentation of 189, will lead to dibenzocyclooctatetraene 190 whereas rearrangements involving benzooyl group migration would give the dibenzopentalene derivative 191.
1.4.5. Photochemistry of Molecules Possessing Bisbarrelene Moieties

Gray et al.\textsuperscript{103} reported the synthesis of [2.2.2.2](1,2,4,5)cyclophane 192 and its Diels-Alder reaction with dienophiles such as perfluoro-2-butyne 193 and dicyanoacetylene 194 to give the corresponding mono- and bisbarrelene adducts. Irradiation of 196 in THF with a low pressure mercury lamp gave a cyclophane 198 having a cyclooctatetraene moiety for one deck. The irradiation of the bisbarralenes 195 and 197 gave complex mixtures of products, which they were unable to isolate and identify (Scheme 46).
Dehydrojanusene\textsuperscript{104} 199, a molecule possessing two dibenzobarrelene units, upon photosensitisation with benzophenone in methylene chloride using a Hanovia 450-W medium-pressure mercury lamp, gave high yields of the photoproduct 200. (Scheme 47).
With acetone as solvent, an addition product 202, of acetone to photoproduct 200 was also formed (Scheme 48).

\[ \text{hv} \quad \text{CH}_3\text{COCH}_3 \quad \text{hv} \quad \text{CH}_3\text{COCH}_3 \]

Scheme 48

1.5. The Concept of Energy Transfer in Organic Photochemistry

Electronic energy transfer has become a powerful tool for sighting new photochemical reactions, for elucidating mechanisms of photochemical reactions and for obtaining information about molecular excited states. The term energy transfer\(^{105}\) as used in photochemistry, refers to any transfer of energy from an excited molecule to other species. The energy acceptor may itself be promoted to an excited electronic state or the electronic energy may be donated to a host system as vibrational, rotational or translational energy. The energy transfer process may involve two steps with the intermediacy of a photon (radiative transfer) or may be one-step radiationless process requiring some direct interaction of the excited donor with the acceptor.

1.5.1. Radiative Transfer

Radiative transfer of electronic energy involves the possibility of reabsorption of donor emission by an acceptor. The process requires two steps with the intermediacy of a photon (Equations 1 and 2).
No direct interaction of the donor with the acceptor is involved. Only energies corresponding to that part of the emission spectrum of the donor that overlaps with the absorption spectrum of the acceptor can be transferred.

1.5.2. Radiationless Transfer

In this context, the process of electronic energy transfer involves non-radiative transfer of electronic excitation from an excited donor molecule $D^*$ to an acceptor molecule $A$.\textsuperscript{106} The transfer may be an intermolecular process, which can be described in terms of a bimolecular quenching process as in Equation 3.

$$D^* + A ightarrow D + A^* \quad (3)$$

The asterisk denotes an electronic excited state and the bimolecular quenching rate constant $k_q$ is related to an intermolecular energy rate constant $k_{ET}$ by

$$k_{ET} = k_q [A] \quad (4)$$

In most cases $k_{ET}$ is attributed to two possible contributions. The long-range Coulombic contribution was formulated by Galanin\textsuperscript{107} and by Forster\textsuperscript{108} in terms of dipole-dipole interaction. This is particularly suitable for describing inter-electronic energy transfer (inter-EET) in solution whenever conditions for favourable spectroscopic overlap between the emission of $D^*$ and the absorption of $A$ are met.

The second contribution to EET can be realised whenever these condition are not fulfilled. A short range exchange interaction, as formulated by Dexter,\textsuperscript{109} can then facilitate EET.
Intra-EET processes in bichromophoric molecules are usually described in terms of the process

\[ \text{D-B-A} \xrightarrow{k_{ET}} \text{D-B-A}^* \]  \hspace{1cm} (5)

where the excitation energy is transferred from an excited donor D* chromophore moiety to a ground state acceptor moiety A, resulting in quenching of D* fluorescence and sensitisation of A. B denotes a molecular spacer bridge connecting the two chromophores. This bridge may play a role in promoting the transfer process. In all EET processes, a resonance matching between the energy of the initial state of the system and that of its final state is required.

Without electronic energy transfer, the photosynthesis process in plants might not be efficient at all. Excitation transfers are important controlling factors in radiation chemistry and photochemistry of nucleic acids and proteins.

1.5.3. Quenching of Photochemical Reactions

The process of quenching is considered as the transfer of electronic-energy from the substrate to a quencher molecule. Either the excited singlet or the triplet state of the substrate can be quenched. The classical triplet quenching scheme is shown in Figure 2.
1.5.4. Mechanistic Studies

The only way the quencher can interact with the compound of interest is as an acceptor of its triplet excitation energy. The quencher does not compete for the exciting light. If a particular photoproduct is formed in the absence but not in the presence of the triplet quencher, then its formation must involve a triplet state precursor. An easy way to determine whether or not triplet state quenching is occurring is sometimes afforded by the use of quenchers such as olefins and conjugated dienes, which undergo detectable reactions such as isomerisations and dimerisations from their triplet states.

There are cases in which the same product arises by two or more paths, some of which involve a triplet state intermediate. The triplet quencher can block only the paths involving the triplet state intermediate, so the products arising from paths not involving the triplet state will survive.

1.5.5. Ideal Triplet Quencher

The ideal triplet quencher possesses a lowest lying excited singlet state
which lies much higher than that of the substrate and a triplet state which lies lower than the lowest lying triplet state of the substrate. Interaction of the quencher and excited substrate should lead only to electronic energy transfer. The excited quencher should be chemically inert and should be capable of shedding excitation energy very quickly.

Compounds with relatively low-lying triplet states and large singlet-triplet splittings are prime candidates for useful triplet quenchers. Two kinds of compounds, (a) olefins, conjugated dienes and higher polyenes and (b) aromatic hydrocarbons generally fulfill these requirements.

1.5.5.1. An Example of the Use of Quencher

The photolysis of uracil 203 in aqueous solution leads to dimers 204 and the photohydration product 205 (Scheme 49).

\[ \text{HN} \quad \text{hv} \quad \text{HN} \quad \text{O} \quad \text{O} \quad \text{HN} \quad \text{HN} \quad \text{O} \quad \text{O} \quad \text{HN} \quad \text{HN} \quad \text{O} \quad \text{OH} \]

Scheme 49

Addition of 2,4-hexanediol\textsuperscript{110} or oxygen\textsuperscript{111}, which act as triplet quenchers, leads to quenching of dimer production but has no effect on the photohydration. This demonstrates that the dimers arise by way of the uracil triplet state but that the photohydration reaction does not involve the triplet state.
1.6. Outline of Research Problem and its Importance

The exemplary synthetic chemist of all times, Nature has marvelously synthesised its chemical substances with utmost efficiency and remarkable selectivity. Nature puts forth a herculean task to the brand of organic chemists in mimicking her incredible synthetic skills. As a humble venture, we aimed at obtaining selectivity in a selected organic photochemical reaction.

Bicyclo[2.2.2]octa-2,5,7-triene, trivially known as “barrelene”, was the key molecule, which Howard E. Zimmerman used in unlocking the mechanism of the well-known photochemical rearrangement, the di-π-methane rearrangement. Dibenzobarrelenes, similar to the photochemical behaviour of barrelenes, exhibit dissimilar photoreactivity from its singlet and triplet excited states. But the absence of a clear line of demarcation between the singlet and triplet state reactivity of these bicyclic compounds, often results in a mixture of photoproducts from both the excited states.

In an attempt to investigate the conditions for obtaining selectivity in photochemical reactions, we chose dibenzobarrelenes as the precursor molecule. Literature precedences indicate that olefins act as efficient triplet quenchers. In principle, we aimed at introducing a suitable π-system that can act as an intramolecular quencher for the dibenzobarrelene triplet. In order to exploit the true potential of this possibility, it is important to fine-tune the triplet energy of the olefin unit. This entails the synthesis of several alkenylbarrelenes having strategically-positioned olefin units possessing a range of triplet energies for identifying the structural features for efficient intramolecular quenching. Carbomethoxy ester and benzoyl functionalities were appended at the vinylic positions of the dibenzobarrelenes, as they would act as efficient intramolecular intersystem crossing catalysts.
Our research target is outlined in the following scheme (Scheme 50).

Dibenzobarrelenes upon excitation to the singlet excited state, dibenzocyclooctatetraene is formed whereas excitation to the triplet excited state produces dibenzosemibullvalene. With the notion that olefins are efficient triplet quenchers, we intend to quench the triplet excited state of the dibenzobarrelenes from forming triplet mediated photoproducts, through the cis-trans isomerisation of the bridgehead olefin appendages; thereby inducing a selectivity in the photochemical reaction.

Studies have shown that molecular systems with three olefin moieties
bonded to an sp\(^3\) hybridised carbon atom, have the potentiality of undergoing both the di-\(\pi\)-methane and tri-\(\pi\)-methane rearrangement. In this context, our synthesis of bridgehead olefin appended dibenzobarrelenes, opens up the venue for both the rearrangements as well as for hitherto unknown photochemical transformations.

The molecular architecture of the novel bisdibenzobarrelenes is such that they hold tremendous potential to exhibit interesting photochemistry and photophysics. They are ideal molecules for investigating the modes of energy transfer in bichromophoric molecular systems.

1.7. Objectives

1. To synthesise 9-olefin appended anthracenes and bisanthracenes
2. To synthesise bridgehead olefin appended 11,12-dicarbomethoxy substituted dibenzobarrelenes
3. To synthesise bridgehead olefin appended 11,12-dibenzoyl substituted dibenzobarrelenes
4. To synthesise bisdibenzobarrelenes
5. Preliminary fluorescence studies of some synthesised dibenzobarrelenes and bisdibenzobarrelenes employing Time-Correlated Single-Photon Counting (TCSPC) Technique
6. Photochemistry of dibenzobarrelenes to assess the role of the bridgehead olefin moieties and the photochemistry of the novel bisdibenzobarrelenes
References


Chapter 1


