5.1. Abstract

This chapter deals with the photochemical studies of bisdibenzobarrelenes, we have synthesised. Dibenzocyclooctatetraene and dibenzosemibullvalene are the photoproducts obtained respectively through the singlet excited state and triplet excited state of dibenzobarrelenes. Dibenzobarrelene having alkenone appendage at the 9-position are also found to undergo condition-dependent photochemical rearrangements. So, examining the photochemical behavior of novel bisdibenzobarrelenes with alkenone spacer is interesting. Our attempts and results are explained in this chapter. This chapter can also be considered as an extension to our studies on effects on geometry of photochemical and photophysical behaviour of bischromophoric systems having tunable geometry.

5.2. Introduction

The [4+2] cycloaddition between a conjugated diene and a alkene commonly termed the dienophile, to form a cyclohexene system is more commonly known as the Diels-Alder reaction, named after O. Diels and K. Alder, who shared the 1950 Nobel Prize in chemistry for developing this reaction. This reaction occupies a very important place among the tools of the synthetic organic chemist because it provides a method for the construction of six membered rings from acyclic precursors with excellent control of
Chapter 5

stereochemistry. Diels-Alder reaction is one of the major synthetic strategies employed to generate bicyclic compounds. Bicyclic compounds have gained much importance in the recent past since they constitute the basic structural framework of several compounds which are used as potential therapeutic agent against HIV and metastasis, anticancer drugs, anti-thrombotic compounds, therapeutic agents for diseases of the central nervous system, and so on.

Anthracene can undergo both thermal and photochemical Diels–Alder cycloadditions with a variety of dienophiles across the 9 and 10 positions due to the electron rich nature at these positions. The types of dienophile used in the Diels–Alder reactions of anthracene fall broadly into four classes, namely

(i) $\alpha,\beta$ unsaturated carbonyls,
(ii) alkenes attached to a heteroatom or halogen,
(iii) alkenes and alkynes and
(iv) heterodienophiles.

The first reported cycloaddition of a dienophile, the reaction of maleic anhydride 2, to anthracene 1 via a fusion reaction to give 3 at 260 °C was by Diels and Alder in 1931 (Scheme 5.1).

The reaction can proceed even if some of the atoms in the newly-formed ring are not carbon. If diene or dienophile contains one or more heteroatoms, then Diels-Alder adduct formed will be a heterocyclic system. Such Diels-Alder reactions are then called as Hetero-Diels Alder reactions.
(Scheme 5.2). The hetero Diels–Alder reaction of anthracene has been used to ‘trap’ unstable transient compounds as stable cycloadducts.

![Scheme 5.2](image)

Diels-Alder reaction can take place within a molecule if the two reacting functionalities are within the same molecule. Such Diels–Alder reactions are called **intramolecular Diels–Alder (IMDA) cycloadditions**. This exhibits less negative entropies of activation and so reaction rates will be higher under mild conditions. The intramolecular Diels–Alder cycloadditions of the ‘tethered’ alkynes 6 to yield a wide variety of 9,12-bridged ethenoanthracenes 7 has been performed at temperatures ranging from 25 to 220 °C (Scheme 5.3).

![Scheme 5.3](image)

### 5.2.1. Stereochemistry of the Reaction

Diels-Alder reactions can lead to formation of a variety of structural isomers and stereoisomers (enantiomers and diastereomers). Stereochemistry of Diels-Alder adducts depends on “cis principle” or “endo addition rule”.

![Scheme 5.3](image)
5.2.1.1. Cis principle

According to the cis principle or the Alder-Stein rules formulated by Alder and Stein in 1937, the stereochemistry of substituents in the starting material is retained in the product. This means that if a cis-dienophile is reacted, both of the cis-substituents will end up on same side (face) of the product ring. Trans-dienophile will yield a product where both of trans-substituents (that came originally from the dienophile) will be on different sides of the product ring. The same principle applies to dienes. Trans, trans or cis, cis 1,4-substituents will end up on same side of the ring, whereas trans, cis 1,4-substituents will be oriented towards different faces of the ring. An illustrative example is shown for the reactions of the isomeric methyl β-cyanoacrylates 9 and 10 with 9,10-dimethylanthracene 8 (Scheme 5.4).

![Scheme 5.4](image)

5.2.1.2. Endo addition rule

Using the 'cis principle' it is understood that cis-substituents on dienophile, for example, will end up on same side of the molecule. It is not obvious where the substituents on both diene and dienophile will end up
relative to each other. To predict the cis or trans orientation of substituents that are coming from different molecules we have to examine possible transition states. The most stable transition state will lead to the major product. Transition states will also dictate the relative orientation of the diene's and dienophile's substituents on the product ring. In some cases another rule can be applied: the endo addition rule. According to this rule, the most stable transition state results when there is a 'maximum accumulation of double bonds'. This rule is not always followed. It most often applies when dealing with cyclic dienes and dienophiles. For example, the Diels-Alder reaction of cyclopentadiene and maleic anhydride yields over 95% of the endo product. It is important to note that labels "exo" and "endo" relate to the orientation of substituents in the transition state and not to a specific orientation of substituents in the product molecule. In each individual case, the transition state has to be examined to see the most favored relative orientation of substituents. It is not true for the endo transition state that the substituents on dienophile and 1,4-substituents on diene will always point towards the same side of the newly formed ring. "Endo" and "exo" define specific transition states, not orientation of substituents. In the case of maleic anhydride and cyclopentadiene the endo product will have the R groups of the diene and dienophile oriented toward the opposite sides of the newly formed ring. IMDA cyclization of a 9-substituted anthracene derivative reported by Meek and Dann who obtained the cyclic acetal 13 (Figure 5.1) in 2% yield on attempted preparation of 9-anthraldehyde diallyl acetal is an example of endo addition.11

![Figure 5.1](image-url)
5.2.2. Regioselectivity of the Reaction

Synthesis of conformationally constrained bicyclic bisaryl α-amino acids, from 9-substituted anthracenes and 2-acetamidoacrylate is an example for regio-selective Diels–Alder reaction (Scheme 5.5).

\[
\text{R} = \text{CH}_3, \text{Cl, Br etc.} \quad \text{up to > 99/1 meta/ortho ratio}
\]

Scheme 5.5

Thus, a variety of dibenzobarrelenes can be synthesized by the Diels-Alder reaction between suitably substituted anthracenes and reactive acetylenes. IMDA reactions add a whole new dimension to the variety of multicyclic systems that are generated from anthracene derivatives. Our group is actively interested in the generation of barrelene derivatives by Diels Alder reactions. Our primary interest is in examining intramolecular quenching of barrelene excited state and deciphering factors controlling regioselectivity in barrelene-semibullvalene rearrangement. Hence, a brief overview of the diverse photochemistry of barrelenes is deemed appropriate here.

5.3. An Overview on the Photochemistry of Dibenzobarrelenes

Zimmerman and co-workers\textsuperscript{12} have shown that barrelene 18 which contains π moieties within rigidly structured environments, rearranges by the di-π-methane pathway to semibullvalene 18 solely by acetone sensitization. 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 19 leads to cyclooctatetraene 20 by an electrocyclic \([2\pi + 2\pi]\) addition followed by a retro \([2\pi + 2\pi]\) fission (Scheme 5.6).

\[
\begin{align*}
18 \xrightarrow{\text{hv, Sensitised}} 19 \xrightarrow{\text{hv, Direct}} 20
\end{align*}
\]

Scheme 5.6

The solution phase photochemistry of 9,10-ethenoanthracene 21 is multiplicity-dependent. Irradiation of dibenzobarrelenes 22 in the presence of triplet sensitizers leads to dibenzosemibullvalene 21,\(^{13}\) whereas direct irradiation (i.e., irradiation in the absence of triplet sensitizers) affords mainly dibenzocyclooctatetraene 23 (Scheme 5.7)\(^{14}\)

\[
\begin{align*}
21 \xrightarrow{\text{hv, Sensitised}} 22 \xrightarrow{\text{hv, Direct}} 23
\end{align*}
\]

Scheme 5.7

Earlier studies have shown that direct irradiation of 9,10-ethenoanthracene derivatives 24, which have ester substituents attached to vinyl double bond, leads to triplet (di-\( \pi \)–methane or more appropriately tri-\( \pi \)-methane in this case) reactivity, a result that is presumably due to rapid
intersystem crossing of the initially formed singlet excited state (Scheme 5.8).\textsuperscript{15}

![Scheme 5.8](image)

5.3.1. Regioselectivity Exhibited by Dibenzobarrelenes

The photochemical studies conducted on several dibenzobarrelenes by Ciganek\textsuperscript{13} and Friedman\textsuperscript{16} indicated that electronic effects are important in determining the course of initial bonding in di-\(\pi\)-methane (DPM) rearrangement.

Iwamura \textit{et al.} have shown that substituents at the methane position on the bridging position determine the bridging selectivity in di-\(\pi\)-methane systems. There exists two possible competitive vinyl-benzo bridging in the triplet excited states (Scheme 5.9).\textsuperscript{17}

![Scheme 5.9](image)
\[ \text{\(\pi\)-Electron accepting substituents such as CN, CO\textsubscript{2}CH\textsubscript{3} and CHO at the bridgehead position should stabilize the cyclopropane ring, favours bridging through path 1, while \(\pi\)-electron donors such as OCH\textsubscript{3} should destabilize the cyclopropane ring favour path 2.} \]

Richards et al. have shown that bridgehead hydroxy- and acetoxy-dibenzobarrelene have hydrogen bonding and electronegativity effects in forming the product. Irradiation products of hydroxydibenzobarrelene and acetoxy-dibenzobarrelene are given in Scheme 5.10. These results were further supported by the findings by George et al.\textsuperscript{21c} Thus steric effects as well as electronic effect of bridgehead substituents determine the photoproduct of dibenzobarrelene.

\[ \text{Scheme 5.10} \]

Thus steric effects as well as electronic effect of bridgehead substituents determine the photoproduct of dibenzobarrelene.

### 5.3.2. Photochemistry of Enone-appended Barrelenes

On irradiation, dimethyl 9-(1-phenylprop-2-en-1-one)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate, \textbf{36} is found to undergo \textit{cis-trans}
isomerization (*Case I*, Scheme 5.11), while 11,12-dibenzoyl-9-(1-phenylprop-2-en-1-one)-9,10-dihydro-9,10-ethenoanthracene, 38 underwent DPM rearrangement to give dibenzocyclooctatetraene derivative (*Case II*, Scheme 5.11).

\[ \text{H}_3\text{C}O_2\text{C} \quad \text{CO}_2\text{CH}_3 \]

\[ \begin{array}{c}
\text{\text{C}_6\text{H}_5\text{OC} \quad \text{CO}_2\text{CH}_3} \\
\text{\text{C}_6\text{H}_5\text{OC} \quad \text{CO}_2\text{CH}_3}
\end{array} \]

\[ \text{hv, 300nm benzene} \]

\[ \begin{array}{c}
\text{\text{H}_3\text{C}O_2\text{C} \quad \text{CO}_2\text{CH}_3} \\
\text{\text{H}_3\text{C}O_2\text{C} \quad \text{CO}_2\text{CH}_3}
\end{array} \]

\[ \text{36} \quad \text{37} \]

\[ \text{64\%} \]

**Case I**

\[ \text{hv, 300nm benzene} \]

\[ \text{38} \quad \text{39} \]

\[ \text{58\%} \]

**Case II**

\[ \text{hv} \]

\[ \text{Starting material recovered and polymer formation increased as irradiating time increased} \]

\[ \text{40} \]

**Case III**
Irradiation of dimethyl 9-(1-methylprop-2-en-1-one)-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate, 36 gave starting material unchanged (Case III, Scheme 5.11), while barrelene having benzoyl group at the 11,12 positions underwent rearrangement to give an unidentified lactone (Case IV, Scheme 5.11).

All the above interesting photochemistry prompted us for the synthesis of enone appended bisdibenzobarrelenes (Chart 5.I).

### 5.4. Results and Discussion

For the synthesis of dibenzobarrelenes several methods were described in the literature. Paquette et al. synthesized dimethyl 9-deuterio-9,10-dihydro-9,10-ethenoanthracene-11,12-dicarboxylate 44, through neat reaction of anthracene-9-\(d\) 42 and dimethyl acetylenedicarboxylate (DMAD) 43 at 180 °C, in appreciable yield (Scheme 5.12). 19
Richards et al. prepared a series of 9-substituted dimethyl 9,10-dihydro-9,10-ethanoanthracene-11,12-dicarboxylates 46a-f, by refluxing a solution of the appropriate 9-substituted anthracene 45 and dimethyl acetylenedicarboxylate 43 in a suitable solvent \(^ {20} \) (Scheme 5.13).

\[
\begin{align*}
\text{Scheme 5.13} \\
\text{45} + \text{43} & \xrightarrow{180^\circ C} \text{46a-f} \\
X = & \text{ a) Br, b) OCH}_3, \text{ c) OC}_2\text{H}_5, \text{ d) NH}_2, \text{ e) NHAc, f) CH}_3
\end{align*}
\]

George et al. prepared several 11,12-dibenzoyl substituted dibenzobarrelenes, through the Diels-Alder addition of appropriately substituted anthracenes 47 with dibenzoyletylene (DBA) 48, either thermally or in the presence of Lewis acid catalysts such as aluminium chloride. \(^ {21} \) Depending on the substituents and reaction conditions, the reaction yields either 11,12-dibenzoyl-substituted dibenzobarrelene 49 or a mixture of 49 and dibenzoyl-substituted naphthobarrelene 50 (formed through addition across the 1,4 positions of anthracene) \(^ {22} \) (Scheme 5.14).

\[
\begin{align*}
\text{Scheme 5.14} \\
\text{47} + \text{48} & \xrightarrow{180^\circ C} \text{49} + \text{50} \\
R' = & \text{H or CH}_3, \text{ R}_2 = \text{H or CH}_3
\end{align*}
\]

So, by employing Diels–Alder reactions of bisanthracenes as dienes and dimethyl acetylenedicarboxylate (DMAD) and dibenzoyletylene (DBA)
as dienophiles we have synthesized a few bisdibenzobarrelenes, 51a-f. The dibenzobarrelenes synthesized by us are given in Chart 5.1.

5.4.1. Synthesis and Characterization

5.4.1.1. Diels-Alder Reaction of Bisanthracenes (51a-e) with Dimethyl Acetylenedicarboxylate (DMAD)

The bisdibenzobarrelenes 51a-e were synthesized via Diels-Alder reaction of the bisanthracenes 52a-e with the dienophile DMAD (43, excess) in dry xylene under reflux. The bisadducts were formed in appreciable yield accompanied by polymerisation of DMAD (Scheme 5.15).

![Chart 5.1](image-url)
The poor solubility of 51a-d led us to the preparation of potentially more soluble analogues 51e (Scheme 5.16) and 51f (Scheme 5.17).

The structures of the bisbarrelenes 51a-e were established through the comparison of their spectral data with that of monodibenzobarrelenes and via analytical data.
The product 51a was identified as the [4+2] biscycloadduct between bisanthracene 52a and two DMAD units, where the anthracene moieties functioned as the dienes, by spectroscopic methods. The IR spectrum showed strong carbonyl absorption at 1728 cm\(^{-1}\) and a shoulder peak at 1684 cm\(^{-1}\), which were assigned to the ester carbonyls and ring carbonyl respectively. The \(^1\)H NMR spectrum of 51a provided clear indications of the formation of a symmetrical cycloadduct. The salient features of the spectrum pointing towards this were (a) the appearance of aliphatic protons as singlet at \(\delta 2.44\), (b) the methoxy groups of DMAD part as two singlets at \(\delta 3.77\) and 3.83, (c) appearance of bridgehead proton as singlet at \(\delta 5.68\) and (d) appearance of aromatic protons and a vinylic proton as multiplet from \(\delta 7.06\) to \(\delta 7.72\). The salient features of the \(^{13}\)C NMR spectrum include the peaks at (a) \(\delta 27.7\) and 28.8 which were assigned to the bridging methylene carbon and aliphatic carbon, (b) \(\delta 50.9\) due to the quaternary carbons, (c) \(\delta 52.2\) and 52.9 corresponding to the two methoxy carbons, (d) \(\delta 167.2\) and 163.8 due to the two ester carbonyl groups and (e) \(\delta 194.4\) due to the cyclopentanone carbonyl carbon respectively. The proposed structure was further supported by the FAB mass spectrum which showed the [M\(^+\)+1] ion peak at 745.36 and satisfactory elemental analysis.

Similarly, the IR spectrum of 51b showed strong carbonyl absorption at 1729 cm\(^{-1}\) and a shoulder peak at 1683 cm\(^{-1}\), which were assigned to the ester carbonyls and ring carbonyl respectively. In the \(^1\)H NMR spectrum, the multiplet from \(\delta 1.67\) to \(\delta 1.62\) indicates the two geminal hydrogens at the 4-position of cyclohexanone moiety. The four geminal hydrogens at 3 and 5 positions appear as multiplet from \(\delta 2.37\) to \(\delta 2.34\). The singlets at \(\delta 3.76\) and \(\delta 3.90\) depicts the methoxy protons. The bridgehead proton appears as singlet at \(\delta 5.68\). The aromatic protons and a vinylic proton appear as multiplet from \(\delta 7.06\) to \(\delta 7.46\). In the \(^{13}\)C NMR spectrum, the saturated carbons of cyclohexanone moiety appear at \(\delta 28.7\) and at \(\delta 31.3\). The signals of methoxy
carbon appear at \( \delta 51.0 \) and \( \delta 51.9 \). The two bridgehead carbons appear at \( \delta 50.7 \) and \( \delta 59.6 \). The signals from \( \delta 111.4 \) to \( \delta 143.8 \) denote the aromatic and vinylic carbon. The signals of the ester carbonyls appear at \( \delta 162.9 \) and \( \delta 166.2 \). The cyclohexanone carbonyl appears at \( \delta 170.1 \). The peak at \( m/z \) 759.90 (\( M^+ + 1 \)) in the FAB spectrum, ascertains the identity of the molecule.

Similarly, the IR spectrum of \( 51c \) showed strong carbonyl absorption at 1729 cm\(^{-1}\) which is assigned to the ester carbonyl and the stretching frequency of the carbonyl group of cycloheptanone moiety lies embedded in the ester carbonyl region. In the \(^1\)H NMR spectrum, the multiplets from \( \delta 1.74 \) to \( \delta 1.72 \) and from \( \delta 2.42 \) to \( \delta 2.40 \) indicates the four geminal hydrogens at 3 and 6 positions and 4 and 5 positions of cycloheptanone moiety respectively. The singlets at \( \delta 3.76 \) and \( \delta 3.87 \) depicts the methoxy protons. The bridgehead proton appears at \( \delta 5.68 \). The aromatic protons and a vinylic proton appear as multiplet from \( \delta 7.07 \) to \( \delta 7.47 \). In the \(^{13}\)C NMR spectrum, the saturated carbons of cycloheptanone moiety appear at \( \delta 27.6 \), \( \delta 29.2 \), \( \delta 30.2 \) and at \( \delta 30.9 \). The signals of methoxy carbon appear at \( \delta 53.0 \) and \( \delta 53.1 \). The two bridgehead carbons appear at \( \delta 47.5 \) and \( \delta 58.1 \). The signals from \( \delta 123.4 \) to \( \delta 155.6 \) denote the aromatic and vinylic carbon. The signals of the ester carbonyls appear at \( \delta 163.5 \) and \( \delta 166.6 \). The cycloheptanone carbonyl appears at \( \delta 202.7 \). The peak at \( m/z \) 773.20 (\( M^+ + 1 \)) in the FAB spectrum, ascertains the identity of the molecule.

Similarly, the IR spectrum of \( 51d \) showed strong carbonyl absorption at 1732 cm\(^{-1}\) and a shoulder peak at 1688 cm\(^{-1}\), which were assigned to the ester carbonyls and ring carbonyl respectively. In the \(^1\)H NMR spectrum, the multiplets from \( \delta 1.70 \) to \( \delta 1.68 \) indicates the six geminal hydrogens at 4,5 and 6 positions and from \( \delta 2.47 \) to \( 2.45 \) indicates four geminal hydrogens at 3 and 7 positions of cyclooctanone moiety. The singlets at \( \delta 3.75 \) and \( \delta 3.80 \) depicts the methoxy protons. The bridgehead proton appears at \( \delta 5.68 \). The aromatic
protons and a vinylic proton appear as multiplet from \( \delta 7.08 \) to \( \delta 7.52 \). In the \(^{13}\)C NMR spectrum, the saturated carbons of cyclooctanone moiety appear at \( \delta 25.1, 26.4, 28.9, 29.3, 29.6 \). The signals of methoxy carbon appear at \( \delta 52.6 \) and 52.4. The two bridgehead carbons appear at \( \delta 47.5 \) and 60.3. The signals from \( \delta 121.5 \) to 155.9 denote the aromatic and vinylic carbon. The signals of the ester carbonyls appear at \( \delta 163.7 \) and 166.9. The cyclooctanone carbonyl appears at \( \delta 206.3 \). The peak at \( m/z 787.39 \) (M\(^+\) + 1) in the FAB spectrum, ascertains the identity of the molecule.

The IR spectrum of 51e showed strong carbonyl absorption at 1729 cm\(^{-1}\) and a shoulder peak at 1683 cm\(^{-1}\), which were assigned to the ester carbonyls and ring carbonyl respectively. In \(^1\)H NMR spectrum, singlet at \( \delta 0.73 \) corresponds to the \( t \)-butyl protons and multiplet from \( \delta 1.57 \) to \( \delta 1.54 \) denotes the hydrogen at 4-position of \( t \)-butyl cyclohexanone moiety. The geminal hydrogens at position 3 of cyclohexanone appear as multiplet from \( \delta 1.94 \) to 2.41 respectively. The singlets at \( \delta 3.75 \) and \( \delta 3.88 \) depicts the methoxy protons. The bridgehead proton appears at \( \delta 5.68 \). The aromatic protons and a vinylic proton appear as multiplet from \( \delta 7.09 \) to \( \delta 7.46 \). The peak at \( m/z 815.31 \) (M\(^+\) + 1) in the FAB spectrum, ascertains the identity of the molecule.

### 5.4.1.2. Diels-Alder Reaction of Bisanthracenes (51f) with Dibenzoylacetylene (DBA)

The bisdibenzobarrelene 51f were synthesized via Diels-Alder reaction of the bisanthracene 52e with the dienophile DBA (48, excess) in dry xylene under reflux. The bisadducts were formed only in appreciable yield accompanied by polymerisation of DBA (Scheme 5.17).
The spectral analysis of the bisadduct 51f matched with compound 51e, except it showed some extra aromatic peaks in $^1$H NMR.

### 5.4.2. Photochemistry of Bisdibenzobarrelenes

Based on the reports that dibenzobarrelenes undergo interesting phototransformations, we carried out the irradiation experiments on the above bisdibenzobarrelene samples. We anticipated the flowing possibilities here:

1. barrelene-semibullvalene rearrangement
2. barrelene-cyclooctatetraene rearrangement
3. cis-trans isomerization around the enone component
4. hitherto unknown reaction pathways

All irradiations were done in benzene purged with nitrogen at 300 nm using a Rayonet Photochemical Reactor. The criterion for the selection of 300 nm lamps for irradiation was based on a simple Beer-Lambert calculation which reveals that for bulk reactivity, photolysis wavelength near the absorption tail should be used or else the incident radiation will be absorbed near the surface.
Bisdibenzobarrelene posses $S_0 \rightarrow S_1$ transition at 280 nm region. Due to the solubility of the bisdibenzobarrelenes in benzene, and its transparency at the 300 nm region, led us to opt benzene as ideal solvent for photochemical studies. Studies have shown that sensitizers transfer their triplet energy to the acceptor bisdibenzobarrelenes, thereby quenching the singlet excited state of the substrate promoting the triplet mediated pathway. Even after 20 hours no new products were observed, where starting compound remained as such along with some polymeric material. Since bisbarrelenes exhibited strong absorption in the 200-350 nm region, we could not use a suitable sensitizer to examine triplet reactivity of these molecules. The best we could do was to irradiate very dilute solutions of 51a-f in acetone. We fixed the concentration of acetone solution to the level where acetone absorbed most of the light. However, the new product were formed under these sensitized irradiation conditions as well.

5.4.3. Conclusion

The bisdibenzobarrelenes 51a-f was found to be mostly stable under irradiation condition employed by us. The presence of intractable mixture confirms slight photochemical conversion. The UV absorption spectrum of monobarrelene connected to alkenone is having more or less similar in absorption spectra to bisbarrelenes prepared by us. So some radiationless energy dissipations are occurring in the excited state of bisdibenzobarrelenes in the excited state making it different from the reactions of monobarrelene. The vibrational motion of dibenzobarrelene system connected to highly complicated system can dissipate energy, which in turn can prevent the system largely from undergoing reactions in larger amounts. In other words, fast radiationless decay (less fluorescence) from the excited state can prevent it from undergoing reactions.
5.5. Experimental Section

5.5.1. General Techniques

General information about the experiments is given in section 2.5.1 of Chapter 2. Photochemical reactions were carried out in a Rayonet reactor fitted with sixteen lamps.

5.5.2. Starting Materials

Dimethyl acetylenedicarboxylate (DMAD) was purchased from Sigma-Aldrich and was used as received. Solvents were distilled and dried as per requirements.

5.5.2.1. Dibenzoylacetylene (48)

Dibenzoylacetylene was prepared by a known method (72%, mp 109-112 °C).\(^\text{23}\)

5.5.3. Synthesis of Bisdibenzobarrelenes 51a-f

5.5.3.1. Synthesis of Bisdibenzobarrelene 51a

Bisanthracene 52a (1.00 g, 2.2 mmol) was dissolved in dry xylene (8 mL) under inert atmosphere. DMAD 43 (1.39 g, 9.8 mmol) was added to it and stirred under reflux for 12 h. Solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove the excess dienophile using 85:15 hexane-ethyl acetate solvent mixture to afford 51a as a white powder. mp decomposed > 300 °C.
5.5.3.2. Synthesis of Bisdibenzobarrelene 51b

Bisanthracene 52b (1.00 g, 2.1 mmol) was dissolved in dry xylene (8 mL) under inert atmosphere. DMAD 43 (1.35 g, 9.5 mmol) was added to it and stirred under reflux for 12 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove the excess dienophile using 85:15 hexane-ethyl acetate solvent mixture to afford 51b as a white powder. mp decomposed > 300 °C.

Yield 55%;

UV $\lambda_{\text{max}}$ (CH$_2$Cl$_2$) 198 (ε 20,900), 250 (ε 34,900), 300 (ε 2900); IR (KBr) $\nu_{\text{max}}$ 1728, 1684, 1201, 894 cm$^{-1}$; 

$^1$H NMR (300 MHz, CDCl$_3$) : δ 7.72 (s, 2H), 7.47-7.44 (m, 4H), 7.32-7.31 (m, 4H), 7.09-7.06 (m, 8H), 5.68 (s, 2H), 3.83 (s, 6H), 3.77 (s, 6H), 2.44 (s, 4H);

$^{13}$C NMR (75 MHz, CDCl$_3$) : δ 194.4, 167.2, 163.8, 52.9, 52.2, 50.9, 28.8, 27.7;

MS (FAB, [M$^+$+1]): Calcd for C$_{47}$H$_{36}$O$_6$: 744.23; Found: 745.36; 

Elemental analysis calculated for C$_{47}$H$_{36}$O$_6$: C, 75.79; H, 4.87; O, 19.33. Found: C, 75.77; H, 4.77; O, 19.23.
5.5.3.3. Synthesis of Bisdibenzobarrelene 51c

Bisanthracene 52c (1.00 g, 2.0 mmol) was dissolved in dry xylene (8 mL) under inert atmosphere. DMAD 43 (1.31 g, 9.2 mmol) was added to it and stirred under reflux for 12 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove the excess dienophile using 85:15 hexane-ethyl acetate solvent mixture to afford 51c as a white powder. mp decomposed > 300 °C.

Yield 40%;

UV $\lambda_{max}$ (CH$_2$Cl$_2$) 198 ($\varepsilon$ 37,900), 250 ($\varepsilon$ 98,900), 300 ($\varepsilon$ 2800); IR (KBr) $\nu_{max}$ 1729, 1200, 1008, 798 cm$^{-1}$;

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.47-7.37 (m, 10H), 7.09-7.07 (m, 8H), 5.68 (s,2H), 3.87 (s, 6H), 3.76 (s, 6H), 2.42-2.40 (m, 4H), 1.74-1.72 (m, 4H);

$^{13}$C NMR (75 MHz, CDCl$_3$) : 202.7, 166.6, 163.5, 155.6, 123.4, 58.1, 53.1, 53.0, 47.5, 30.9, 30.2, 29.2, 27.6;
**MS** (FAB, [M⁺+1]): Calcd for C₄₉H₄₀O₉: 772.26; Found: 773.20;
Elemental analysis calculated for C₄₉H₄₀O₉: C, 76.15; H, 5.22; O, 18.63. Found: C, 76.25; H, 5.12; O, 18.67.

### 5.5.3.4. Synthesis of Bisdibenzobarrelene 51d

Bisanthracene 52d (1.00 g, 2.0 mmol) was dissolved in dry xylene (8 mL) under inert atmosphere. DMAD 43 (1.27 g, 9.0 mmol) was added to it and stirred under reflux for 12 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove the excess dienophile using 85:15 hexane-ethyl acetate solvent mixture to afford 51d as a white powder. mp decomposed > 300 °C.

Yield 40%;

**UV** λ<sub>max</sub> (CH₂Cl₂) 198 (ε 57,900), 250 (ε 99,900), 300 (ε 2600); **IR** (KBr) ν<sub>max</sub> : 1732, 1688, 1210, 1021,789 cm⁻¹;

**¹H NMR** (300 MHz, CDCl₃) : δ 7.52-7.45 (m, 10H), 7.10-7.08 (m, 8H), 5.68 (s, 2H), 3.80 (s, 6H), 3.75 (s, 6H), 2.47-2.45 (m, 4H), 1.70-1.68 (m, 6H);

**¹³C NMR** (75 MHz, CDCl₃) : δ 206.3, 166.9, 163.7, 155.9, 121.5, 60.3, 52.6, 52.4, 47.5, 29.6, 29.3, 28.9, 26.4, 25.1;

**MS** (FAB, [M⁺+1]): Calcd for C₅₀H₄₂O₉: 786.28; Found: 787.39;
Elemental analysis calculated for C₅₀H₄₂O₉: C, 76.32; H, 5.38; O, 18.30. Found: C, 76.34; H, 5.28; O, 18.40.
5.5.3.5. Synthesis of Bisdibenzobarrelene 51e

Bisanthracene 52e (1.00 g, 1.9 mmol) was dissolved in dry xylene (8 mL) under inert atmosphere. DMAD 43 (1.21 g, 8.5 mmol) was added to it and stirred under reflux for 12 h. The solvent was removed under vacuum and the residue subjected to silica gel column chromatography to remove the excess dienophile using 85:15 hexane-ethyl acetate solvent mixture to afford 51e as a white powder. mp decomposed > 300 °C.

Yield 57%;
UV $\lambda_{\text{max}}$ (CH$_2$Cl$_2$) 198 ($\varepsilon$ 61,900), 250 ($\varepsilon$ 99,900), 300 ($\varepsilon$ 2600); IR (KBr) $\nu_{\text{max}}$: 1729, 1683, 898, 769 cm$^{-1}$;
$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 7.46-7.38 (m, 10H), 7.12-7.09 (m, 8H), 5.68 (s, 2H), 3.88 (s, 6H), 3.75 (s, 6H), 2.41-2.36 (m, 2H), 2.01-1.94 (m, 2H), 1.57-1.54 (m, 1H), 0.73 (s, 9H);
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 195.0, 141.3, 132.7, 129.0, 128.9, 127.3, 124.8, 23.9;
MS (FAB, [M$^+$+1]): Calcd for C$_{52}$H$_{46}$O$_9$: 814.31; Found: 815.31;
Elemental analysis calculated for C$_{52}$H$_{46}$O$_9$: C, 76.64; H, 5.69; O, 17.67. Found: C, 76.54; H, 5.78; O, 17.49.

5.5.3.6. Synthesis of Bisdibenzobarrelene 51f

A sample of bisanthracene 52e (1.00 g, 1.9 mmol) was dissolved in minimum quantity of dry xylene and DBA 48 (1.99 g, 8.5 mmol) was added and the mixture was refluxed for about 12 h under inert atmosphere. The solvent was removed under vacuum and the residue subjected to silica gel
column chromatography to remove the excess dienophile using 85:15 hexane-ethyl acetate solvent mixture to afford 51f as a white powder. mp decomposed > 300 °C.

Yield 50%;

UV λ<sub>max</sub> (CH₂Cl₂) 198 (ε 37,900), 250 (ε 98,900), 300 (ε 2800); IR (KBr) ν<sub>max</sub> : 1729, 1683,1110, 987, 759 cm⁻¹;

¹H NMR (300 MHz, CDCl₃) : δ 7.87-7.48 (m, 10H), 7.42-7.33 (m, 12H), 7.14-6.92 (m, 16H), 5.51 (s, 2H), 2.31-2.26 (m, 4H), 1.56-1.53 (m, 1H), 0.71 (s, 9H);

¹³C NMR (75 MHz, CDCl₃) : δ 195.2, 145.5, 142.3, 141.2, 131.7, 129.8, 127.9, 126.3, 125.8, 23.2;

MS (FAB, [M⁺+1]): Calcd for C₇₂H₅₄O₅: 998.39; Found: 999.43;

Elemental analysis calculated for C₇₂H₅₄O₅: C, 86.55; H, 5.45; O, 8.01. Found: C, 86.54; H, 5.48; O, 8.03.

5.5.4. Irradiation of Bisdibenzobarrelenes 51a-f

5.5.4.1. Irradiation of Bisdibenzobarrelene 51a

A solution of 51a (40 mg, 0.05 mmol) was dissolved in dry benzene (80 mL) and was irradiated in a Rayonet photochemical reactor (RPR) at 300 nm for 12 h after purging with dry N₂ gas. The solvent was removed and the residue was purified by column chromatography on silica gel. Elution with a
mixture (4:1) of hexane and ethyl acetate gave the starting compound 51a (50%) along with some intractable material.

In a repeat run, an acetone solution of 51a was irradiated using RPR (300 nm) for 5h gave the starting compound (50%) along with some intractable mixture.

In another run, an acetone solution of 51a was irradiated using RPR (254 nm) for 5h gave the starting compound (50%) along with some intractable mixture.

### 5.5.4.2. Irradiation of Bisdibenzobarrelene 51b

A solution of 51b (40 mg, 0.05 mmol) was dissolved in dry benzene (80 mL) and was irradiated in a photochemical reactor at 300 nm for 12 h after purging with dry N\textsubscript{2} gas. The solvent was removed and the residue was purified by column chromatography on silica gel. Elution with a mixture (4:1) of hexane and ethyl acetate gave the starting compound 51b (50%) along with some intractable material.

In a repeat run, an acetone solution of 51b was irradiated using RPR (300 nm) for 10h gave the starting compound (50%) along with some intractable mixture.

### 5.5.4.3. Irradiation of Bisdibenzobarrelene 51c

A solution of 51c (40 mg, 0.05 mmol) was dissolved in dry benzene (80 mL) and was irradiated in a photochemical reactor at 300 nm for 12 h after purging with dry N\textsubscript{2} gas. Removal of the solvent under reduced pressure gave a residual solid, which was chromatographed over silica gel. Elution with a mixture (4:1) of hexane and ethyl acetate gave the starting compound 51c (50%). Further elution with a mixture of hexane and ethyl acetate (1:1) gave some intractable mixture.
In a repeat run, an acetone solution of \(51c\) was irradiated using RPR (300 nm) for 10h to get the starting compound (50%) along with some intractable mixture.

### 5.5.4.4. Irradiation of Bisdibenzobarrelene \(51d\)

A solution of \(51d\) (40 mg, 0.05 mmol) was dissolved in dry benzene (80 mL) and was irradiated in a photochemical reactor at 300 nm for 12 h after purging with dry \(N_2\) gas. The solvent was removed and the residue was purified by column chromatography on silica gel. Elution with a mixture (4:1) of hexane and ethyl acetate gave the starting compound \(51d\) (50%) along with some intractable material.

In a repeat run, an acetone solution of \(51d\) was irradiated using RPR (300 nm) for 10h yielding the starting compound (50%) along with some intractable mixture.

### 5.5.4.5. Irradiation of Bisdibenzobarrelene \(51e\)

A solution of \(51e\) (40 mg, 0.04 mmol) was dissolved in dry benzene (80 mL) and was irradiated in a photochemical reactor at 300 nm for 12 h after purging with dry \(N_2\) gas. The solvent was removed and the residue was purified by column chromatography on silica gel. Elution with a mixture (4:1) of hexane and ethyl acetate gave the starting compound \(51e\) (50%) along with some intractable material.

In a repeat run, an acetone solution of \(51e\) was irradiated using RPR (300 nm) for 10h to get the starting compound (50%) along with some intractable mixture.

### 5.5.4.6. Irradiation of Bisdibenzobarrelene \(51f\)

A solution of \(51f\) (40 mg, 0.04 mmol) was dissolved in dry benzene (80 mL) and was irradiated in a photochemical reactor at 300 nm for 12 h after purging with dry \(N_2\) gas. The solvent was removed and the residue was
purified by column chromatography on silica gel. Elution with a mixture (4:1) of hexane and ethyl acetate gave the starting compound 51f (50%) along with some intractable material.

In a repeat run, an acetone solution of 51f was irradiated using RPR (300 nm) for 10h to get the starting compound (50%) along with some intractable mixture.

5.6. References


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