2.1. Abstract

Intramolecular energy transfer is reviewed from several perspectives, such as the generally accepted mechanism and molecular structure dependence. Some unique molecules such as bischromophores linked by rigid bridges were designed to serve as models for studying excited state interaction between constituent chromophore residues. Bischromophoric molecules containing benzene, naphthalene, anthracene and pyrene as donor and acceptor linked by a unique rigid 1,4-dien-3-one linker were synthesized.

2.2. Introduction

In this chapter we describe the effect of structure on photochemical and photophysical properties in a series of conformationally rigid bischromophoric molecules. Our results are discussed vis-à-vis the properties of a flexible bischromophoric molecule reported in literature. Becker and co-workers have shown that irradiation of dianthrylalkenones\(^1\) gave cis-trans isomerization for enone linkage in dianthrylpentenone. In this context, we examined several bischromophoric compounds containing different \(\pi\)-aromatic systems as chromophores connected through cyclopentanone spacer. Dramatic structure-activity relationship could be observed with these molecules. Some of our compounds underwent cis-trans isomerization, while
some others remained inactive. The most probable reasons can be: (a) Insufficient energy for reaction, (b) Exciton coupling and further excited state interaction like excimer formation and (c) Restricted rotation around alkenyl bond. A detailed overview on exciton coupling of bisaromatic systems and the photochemistry of bisanthrylalkenone reported in literature is explained in the following paragraphs.

2.2.1. An Overview on the Photochemistry of Bisarylalkenones

Earlier studies by Becker et al. have shown that upon direct irradiation, \textit{trans,trans}-1,5-bis(9-anthryl)pentadienone 1 is smoothly converted into the \textit{trans,cis} isomer 2. In oxygen saturated solution of dichloromethane with conventional fluorescent "warm white" light tubes, the above \textit{cis,trans} isomer 2 gets converted to \textit{cis,cis} isomer 3\textsuperscript{1} (Scheme 2.1). This result clearly indicates that 1,5-bis(9-anthryl)pentadienones undergo facile photochemical \textit{cis-trans} isomerization. Similar \textit{cis-trans} isomerization reactions can, in principle, be expected in the case of other pentadienones as well.

Scheme 2.1
2.2.2. Interaction between Chromophores in Bisaromatic Systems - Exciton Coupling

Depending upon the orientation of chromophores along molecular axis, interaction takes between chromophore components in these molecules.\textsuperscript{2} The exciton chirality rule advanced by Harada and Nakanishi\textsuperscript{3,4,5} is a powerful method for predicting such interactions. Interactions of conjugated systems have often been discussed in the frame work of molecular exciton theories\textsuperscript{6} based on dipole-dipole interaction models.\textsuperscript{7} Absorption of UV-Vis light causes changes in the distribution of electron density in a molecule (or in a chromophore in the molecule). The movement of electron density due to promoting the molecule from its electronic ground state to an excited state creates momentary dipole, called electronic transition dipole ($\mu$). Consequently, with each electronic transition there is a polarization (electric transition dipole) that has both direction and intensity that vary according to the chromophores and particular excitation. The transition moments of the $\pi-\pi^*$ band of conjugated dienes, enones, etc., are almost parallel to the long axis of chromophores.\textsuperscript{8}

![Diagram](image)

**Figure 2.1:** Diagrammatic representation for a system with two chromophores (X and Y) held together through covalent bonding.\textsuperscript{7}
Suppose two chromophores (represented by X and Y in Figure 2.1) are brought into close proximity, but orbital overlap and electron exchange are negligible. The chromophores may interact through dipole-dipole coupling of their locally excited state to produce a delocalized excitation (called an exciton) and a splitting called exciton coupling of the locally excited states (Figure 2.1).

Orientation-dependence of the exciton coupling forms the basis for the exciton chirality rule. The UV-Vis spectra of the composite system originate not only from the electronic excitation spectral properties of the component chromophores, but they also depend on interchromophoric distance, mutual orientation, and geometry. The spectral shifts and splitting magnitudes can be correlated with the intensity and relative orientation of the electric transition dipole moments associated with the particular UV-Vis absorption band of each chromophore (Figure 2.2).

![Figure 2.2: Diagram for the origin of UV-Vis spectral shifts and splitting due to exciton interaction of two chromophores. Chromophores are represented by ellipses and electric transition dipoles by (→).](image)

In Figure 2.2, for two limiting orientations (a) only excitation into the higher lying exciton state is allowed for the parallel orientation (resulting in a
blue shift), and (b) only excitation into the lower lying exciton state is allowed for the in-line orientation (resulting in a red shift) relative to the isolated chromophore. For orientations lying in between these two limiting cases, (c) a split or broadened band is typically observed. This result arises since dipole-dipole interaction falls off with inverse cube of the separation distance. Consequently, the most useful chromophores for examining exciton coupling phenomena over short and especially over long distances are those with accessible, electric dipole allowed UV-Vis transitions, typically $\pi-\pi^*$, such as aromatic chromophores and polyenes.

The exciton splitting energy for a molecular dimer,\textsuperscript{9,10,11} or a double molecule,\textsuperscript{12} with oblique transition dipoles corresponding to the separation, “$\Delta E$” is given by (Eqn 2.1)\textsuperscript{13}

$$\Delta E = 2 \frac{\left|M\right|^2}{r^3} (\cos \alpha + 3 \cos^2 \Theta)$$

(Equation 2.1)

where $M$ is the transition moment for the singlet-singlet transition in the monomer, $r$ is the centre to centre distance between the chromophores, $\alpha$ is the angle between polarization axes for the component absorbing units and $\Theta$ is the angle made by the polarization axes of the unit molecule with the line of molecular centres.

Anthracene is a good example of a chromophore useful for exciton coupling. It exhibits several $\pi\rightarrow\pi^*$ transitions, including $^1L_a$, short-axis polarized UV absorption near 360 nm ($E \sim 7,500$) and $^1B_b$, a very intense long-axis polarized intense UV absorption near 250 nm ($E \sim 2,00,000$) (Figure 2.3).

In a composite system, where two anthracenes are fused to bicyclo[2.2.2]octane (Figure 2.3), the intense long axis-polarized transition dipoles are oriented neither parallel nor in-line, but intersect at an obtuse angle and lie one in each of the two intersecting planes (dihedral angle of $\sim120^\circ$). Then the two overlapping exciton transitions interact. The result of exciton splitting of excited states in the composite molecule may be the appearance of
strong spectral shifts or splittings (which may be of the order of 2000 cm$^{-1}$) of the absorption bands for the component molecules.$^{14}$

![Figure 2.3: UV spectra of anthracene and ring fused bisanthracene.](image)

At the same time, as a consequence of the exciton splitting of the excited state manifold, an enhancement of triplet state excitation may result. Toluene, diphenylmethane,$^{15}$ and triphenylmethane$^{16}$ offer definite example of the triplet state enhancement through exciton splitting. The experimental results for these shows that the phosphorescence-fluorescence ratio (intersystem crossing ratio) increases conspicuously in this series, while at the same time the phosphorescence mean lifetime remains relatively constant.

To conclude, in bischromophoric molecules the triplet state excitation enhancement depends on the exciton interaction among excited states of the component molecules,$^{17}$ which in turn depends on the alignment of the
bischromophoric system. This is how geometry influences the photochemistry of such systems.

2.2.3. Application of Photochemical \textit{cis-trans} Isomerization of Organic molecule – Optical Molecular Switch

The basic requirement for a molecular switch is bistability, i.e. the occurrence of two stable forms A and B which can be interconverted by external stimuli, \( S_1 \) and \( S_2 \). For an optical molecular switch optical molecular interconversion is effected by means of light. Also the molecular forms must be identified by an external detection method.

Organic compounds can be used for optical information storage.\textsuperscript{18} In those systems switching process occurs through photochemically induced \textit{cis-trans} isomerization or electrocyclization. For example, in the case of azobenzene, \textit{cis-trans} isomerization readily occurs photochemically.\textsuperscript{19} Here the isomers have clearly different UV absorption spectra. Absence of side reactions as well as high energy barrier for thermal \textit{cis-trans} isomerization makes it a good optical molecular switch. From these considerations it is clear that bisaromatic systems with alkene linkage capable of \textit{cis-trans} isomerization can be used as molecular switch.

We synthesized several such systems by employing Claisen-Schmidt reaction.\textsuperscript{20,21} The condensation of aromatic aldehydes (or between ketones and aldehydes lacking \( \alpha \)-hydrogen) with aliphatic or mixed alkyl aryl ketones in the presence of a relatively strong base to form \( \alpha,\beta \)-unsaturated ketones is termed as the Claisen-Schmidt reaction. This reaction is of tremendous value in synthetic organic chemistry\textsuperscript{22,23} and is frequently encountered as a key step in several elegant total synthesis protocols. Claisen-Schmidt condensation can also be catalysed by acid.\textsuperscript{24}
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The first step is a condensation of aldol type, enols or enolates are involved as intermediates in this reaction. This reaction involves the nucleophilic addition of enol or enolate ion derived from methyl ketone to the carbonyl-carbon of the aromatic aldehyde. Dehydration of the hydroxylketone to form the conjugated unsaturated carbonyl compound occurs spontaneously (Scheme 2.3).\textsuperscript{25} There exists a pronounced preference for the formation of a \textit{trans} double bond in the Claisen-Schmidt condensation of methyl ketones.\textsuperscript{26}

\begin{equation}
\text{Scheme 2.3}
\end{equation}

Cycloalkanones such as cyclopentanone and cyclohexanone readily participate in Claisen-Schmidt reaction.\textsuperscript{27} The crossed aldol condensation of cyclopentanone with aldehydes is faster than that of cyclohexanone. This may be due to the removal of the eclipsing effect of the adjacent hydrogen atom in cyclopentanone after the formation of the arylmethylidene derivative.\textsuperscript{28}

2.3. Results and Discussion

To investigate the hypothesis concerning structural control on chromophore-chromophore interaction, we have prepared a set of dimeric arrays (Chart 2.1). The target compounds proposed by us are good models for studying intramolecular chromophore interactions. The common feature of these bisaromatic compounds is that they all contain rigid 2,5-dialkyldiene-cyclopentanone spacer. Compound 12e is an exception and was synthesized to execute a comparative study of bischromophoric systems having flexible linkages vis-à-vis those having rigid linkages.
Chapter 2

2.3.1. Synthesis and Characterization

Cyclopentanone (1 equiv.) on reaction with (2 equiv.) of benzene-carboxaldehyde, 1-naphthalenecarboxaldehyde, 9-anthracenecarboxaldehyde, 1-pyrenecarboxaldehyde in the presence of either acid or base catalyst (2 equiv.) and methanol (10 mL) give the corresponding diarylidene-cyclopentanones 12a-d in very good yield (Scheme 2.4). We selected the base catalyzed Claisen-Schmidt condensation in methanol to prepare desired compounds. The advantages of base catalyzed reaction include simple reaction and work up procedures and relatively mild reaction conditions.

Acid-catalyzed Claisen-Schmidt condensation was utilized for the synthesis of the bispyrene compound 12e. A solution of 1-pyrene-carboxaldehyde 10d and acetone 14 (1:10) in ethyl acetate was saturated with hydrogen chloride gas and stirred for 24 h at room temperature (Scheme 2.5). Bispyrene 12e precipitated from the reaction mixture was purified by soxhlet extraction.

Chart 2.1

![Chart 2.1]
The structures of the bisaromatic compounds 12a-e were established on the basis of analytical results and spectral data. The UV absorption spectra of 12a indicated the presence of extended conjugation in benzene residues. The physical data obtained for 12a was identical to those reported in literature. The α,β-unsaturated keto group in 12a is indicated in the IR spectrum, by the strong peak at 1690 cm⁻¹ and the peak at 1664 cm⁻¹ is indicative of conjugated olefinic bond. The \(^1\)H NMR shows a singlet at δ 2.95 denoting aliphatic proton of cyclopentanone moiety, further proving that 12a is a symmetric molecule. The multiplets appeared from δ 6.99 to δ 7.54 established the aromatic protons of 12a. The proposed structure was further supported by \(^{13}\)C NMR spectrum showing a single carbonyl peak positioned at δ 195.0. The aliphatic carbon of the cyclopentenone part appeared at δ 23.9. Based on
NMR data, we have established that the molecule has a rigid structure with extended conjugation between aryl and dienone components. In the $^{13}$C NMR spectrum of $2E,5E$-dibenzylidene-cyclopentanone, six signals corresponding to aromatic carbons were observed. This suggests partial double bond character and restricted rotation around the bond ‘$a$’ as a direct consequence of efficient extended $\pi$-orbital overlap. The molecular ion peak at $m/z$ 261.39 ($M^+1$) in the FAB mass spectrum, ascertains the structural identity of bisbenzylidene $12a$. Satisfactory elemental analysis data also supported the formation of the adduct.

Absorption spectrum of $12b$ indicated the presence of extended conjugation in naphthalene residues. In the IR spectrum of $12b$, the peak at 1662 cm$^{-1}$ is due to the keto group of the dienone functionality. The $^1$H NMR spectrum showed a singlet at $\delta$ 3.00 denoting aliphatic proton of cyclopentanone moiety, further proving that $12b$ is a symmetric molecule. The appearance of multiplets from $\delta$ 7.47 to $\delta$ 8.37 established the aromatic protons of $12b$. The proposed structure was further supported by $^{13}$C NMR spectrum showing a single carbonyl peak positioned at $\delta$ 195.4. The aliphatic carbon of the cyclopentanone part appeared at $\delta$ 27.1. The molecular ion peak at $m/z$ 361.16 ($M^+1$) in the FAB mass spectrum, ascertains the structural identity of bisnaphthalene $12b$. Satisfactory elemental analysis data also supported the formation of the adduct.

Absorption spectrum of $12c$ indicated the presence of extended conjugation in the anthracene residues. In the IR spectrum of $12c$, the peak at 1634 cm$^{-1}$ symbolizes the keto group of the dienone functionality. The $^1$H NMR spectrum showed a singlet at $\delta$ 2.31 denoting aliphatic proton of cyclopentanone moiety, further proving that $12c$ is a symmetric molecule. The multiplets at $\delta$ 7.46 to $\delta$ 8.57 establish the aromatic protons of $12c$. The proposed structure was further supported by $^{13}$C NMR spectrum showing a single carbonyl peak positioned at $\delta$ 194.1. The aliphatic carbon atom of
cyclopentanone part appeared at $\delta$ 25.7. Furthermore, fourteen signals attributable to the anthracene moiety were observable in the $^{13}$C NMR spectrum. This clearly indicated extended conjugation and concomitant restriction rotation around bond ‘$a$’ in the case of 12c. The molecular ion peak at $m/z$ 461.20 ($M^+ + 1$) in the FAB mass spectrum, ascertains the structural identity of bisanthracene 12c. Satisfactory elemental analysis data also supported the formation of the adduct.

Indisputable evidence for the structure and stereochemistry of the adduct was provided by single crystal X-ray analysis (Figure 2.4).

Crystallographic data authenticated the roof-like geometry of the compound 12c. In this geometry, both long-axes polarized ($^1B_b$) and short-axis polarized ($^1L_a$) transitions are expected to undergo weak exciton coupling. While red shift is expected in the case of $^1B_b$ band, blue shift is expected in the case of $^1L_a$ band. However, extended conjugation and concomitant red shift in anthracene absorption is expected in this case. Structural rigidity imposed by the cyclopentanone spacer is expected to augment the red shift in absorption
maximum of 12c with respect to both an isolated anthracene and conjugated systems such as 1. Comparison of peak position of \( (1L_3) \) band in 12c with that of an isolated anthracene should be quite revealing. If a blue shift is observed, exciton coupling is significant; if a red shift is observed, extended conjugation is more significant. It should be interesting to examine the absorption characteristics and correlate them with the photochemistry and photophysics of compounds such as 12c. Subtle changes in absorption characteristics can have far reaching consequences on the photochemistry and photophysics of bisanthracenes such as 12c.

A strong peak at 1628 cm\(^{-1}\) in the IR spectrum of 12d depicts the presence of \( \alpha,\beta-\)unsaturated keto group. The UV absorption spectra of 12d indicated the presence of extended conjugation in the pyrene residues. Due to the poor solubility of the compound 12d in deuterated CHCl\(_3\), DMSO and in acetone reliable solution phase NMR spectral data could not be collected. So, we recorded its \(^{13}\)C solid state NMR (Figure 2.5a-b) spectrum.

**Figure 2.5a:** Solid-state NMR of the prepared bispyrene compound 12d (5 KHz)
The $^{13}$C solid state NMR is usually collected by means of a technique called CP/MAS (Cross-polarization, magic angle spinning). Unlike solution phase spectrum, the solid state spectrum consists of two types of signals. The isotropic peaks (the actual peaks from the sample) and the spinning side bands, which are equally spaced on either side of the main isotropic bands are observable here. The spinning side bands originate from the Chemical Shift Anisotropy (CSA) of the system, which is a molecular property.

We have taken the spectrum at two different spinning speeds, *i.e.* at 5 KHz and 7.2 KHz, the spinning side bands moved apart with the spinning speed while the isotropic peak remained at the same position. Hence, **12d** sample shows isotropic peaks at 192.4, 133.5, 129.9, 127.6, 122.9 and 27.1. All the other signals are due to spinning side bands. So the data confirmed the presence on one aliphatic carbon with other aromatic carbons, suggesting the identity of compound **12d**.

**Figure 2.5b:** Solid-state NMR of the prepared bispyrene compound **12d** (7.2 KHz)
2.3.2. Photochemical Properties

The photochemistry and photophysics of the above compounds could unravel interesting aspects. We carried out all irradiation experiments with very dilute solutions of 12a-d at 350 nm using a Rayonet Photochemical Reactor. The criterion for the selection of 350 nm lamps for irradiation was based on a simple Beer-Lambert calculation which revealed that for bulk reactivity, photolysis wavelength near the absorption tail should be used or else the incident radiation will be absorbed near the surface. Diarylidene-cyclopentanones 12a-d absorb strongly in the 300-400 nm region. Due to the solubility of the diarylidencyclopentanones in benzene, and its transparency in the 350 nm region, we selected benzene as a suitable solvent for photochemical studies. Extra precaution was taken while handling benzene. All manipulations involving this solvent was carried out in a fume hood provided with powerful exhaust fan.

2.3.2.1. Photochemistry of Compounds 12a-e

Benzene solutions of dibenzylidencyclopentanones 12a-d were degassed by bubbling nitrogen through it and irradiated with UV light of 350 nm wavelength for 10 h. In the irradiation, for the compounds 12a and 12b, new products were formed. Based on prior reports on enone photochemistry, we conclude that cis-trans isomerization is taking place in the case of both 12a and 12b (Scheme 2.7).

![Scheme 2.7](image)

a) Ar = Phenyl
b) Ar = Naphthyl

Scheme: 2.7.
The spectral and analysis data indicated that the products formed were isomers of the starting materials 12a,b. In the IR spectrum of 12a, the \( \alpha,\beta \)-unsaturated carbonyl stretching peak appears at 1663 cm\(^{-1}\). \(^1\)H NMR spectrum of the photoproduct showed that the CH\(_2\) groups in the cyclopentanone unit are not chemical shift equivalent. This is a clear indication that the symmetry available in 12a is lifted in the photoproduct. \(^{13}\)C NMR analysis also confirmed unsymmetrical nature of the molecule. The molecular ion peak at 261.5 (\( M^+ + 1 \)) in the mass spectrum also supported the structure. All the above observations confirmed \textit{cis-trans} isomerization around of the double bond in the molecule.

Similarly, in the IR spectrum of 12b, the \( \alpha,\beta \)-unsaturated carbonyl stretching peak appears at 1643 cm\(^{-1}\). \(^1\)H NMR spectrum of the photoproduct showed that the CH\(_2\) groups in the cyclopentanone unit are not chemical shift equivalent. \(^{13}\)C NMR analysis also confirmed unsymmetrical nature of the molecule. The molecular ion peak at 361.1 (\( M^+ + 1 \)) in the mass spectrum also supported isomerisation upon photolysis. All the above observations confirmed \textit{cis-trans} isomerization around of the double bond in the molecule. However, 12c,d remained unchanged even after prolonged irradiation. This result deserves special attention. Becker et al\(^1\) have reported that compounds such as 1 undergo facile photochemical \textit{cis-trans} isomerization. Though not reported in literature, based on Becker’s findings, 12d also may be expected to undergo \textit{cis-trans} isomerization. The absorption spectra of 12c and 12d are not very different from those of 1 and 12e respectively. In fact, with respect to 12c, bisanthracene 1 exhibits a more red-shifted absorption maximum. Interestingly, irradiation of 12e resulted in the formation of new product/s as evidenced by absorption and emission spectral changes with irradiation. We attribute the observable spectral changes here to photochemical \textit{cis-trans} isomerization reactions. Our attempts to isolate the photoproduct generated
from 12e were not successful and hence our conclusions on the photochemistry of 12e are somewhat speculative in nature.

2.4. Conclusions and Pointers

We have examined the photochemistry of various diarylidene-cycloalkanones. Photochemical studies have shown that cis-trans isomerization takes place in 12a and 12b, while 12c and 12d were unresponsive towards photolysis. These results deserve close scrutiny. Though one can argue that excitation energy is concentrated in anthracene and pyrene components in 12c and 12d, literature survey regarding the photochemistry of dianthrylpentenones such as 1 revealed that cis-trans isomerization is possible for these enones.

Absorption spectra of 12c,d should hold the key to their odd photochemical behavior. The posers here include: a) why photochemistry of 12a and 12b differs from that of 12c and 12d, and b) why photochemistry of 12c differs from that of dianthrylpentenone 1? It may be noted that, thanks to potential exciton coupling in the ground state, roof-like geometry of 12c should result in a slight blue shift in the absorption maximum of the 1La band. However, in reality, while the absorption maximum of compound 1 is located at 410 nm (~69 kcal mole⁻¹), compound 12c and 12d showed absorption maxima at 428 (~66 kcal mole⁻¹) nm and 447 nm (~64 kcal mole⁻¹) respectively. Red-shifted UV spectra of 12c and 12d support efficient conjugation between anthracene and enone components. However, such slight change (~5 kcal mole⁻¹) in excitation energy is unlikely to shut a possible photochemical reaction pathway totally. This points to the effect of other contributing features. A roof-like geometry can also facilitate excimer formation in the excited state for those compounds. This might facilitate an energy wastage pathway and thereby preventing bisaromatic systems from undergoing photochemical reactions. Excimer formation anyway is inefficient with compounds 12a and 12b and hence they are more likely to undergo cis-
trans isomerization. Alternatively, the restricted rotation around vinylic bond or due to adverse steric interaction with cyclopentane methylene hydrogen might have prevented isomerization reaction of 12c and 12d.

Based on the limited substrate set examined in this chapter, we cannot pick the exact reason behind the reluctance of certain compounds to undergo photochemical transformation. At this juncture, excimer formation remains purely speculative. Detailed photophysical investigation including examination of emission spectra and determination of emission lifetime and fluorescent quantum yield ($\phi_F$) are required to establish the role of excimer formation. All these factors are systematically examined and analyzed in the next chapter.

Coming to potential application of bischromophoric systems 12a-d: some of them might find application as optical molecular switch. The starting material and isomeric photoproduct are thermally stable and are interconvertible by a photochemical forward/thermal backward reaction sequence without degradation (side products).

2.5. Experimental Section

2.5.1. General Techniques

All reactions were conducted in oven-dried glasswares under an atmosphere of nitrogen with magnetic stirring unless otherwise noted. The reagents used were purchased from Aldrich Chemical Co. and were used without further purification. Solvents used for experiments were distilled and dried according to procedures given in standard manuals. All reactions were monitored by thin layer chromatography (TLC). Analytical thin layer chromatography was performed on glass plates coated with silica gel containing calcium sulphate as the binder or aluminium sheets coated with silica gel (Merck); visualization was achieved by exposure to iodine vapors or
UV radiation. Solvent removal was done on an IKA-WERKE rotary evaporator. Gravity column was performed using 60-120 mesh silica gel (Qualigens) and mixtures of hexane-dichloromethane were used for elution. Melting points were recorded on a POLMON melting point apparatus and are uncorrected. Infrared spectra were recorded using JASCO 4100 series, FTIR spectrometer. NMR spectra were recorded at 300 ($^1$H) and 75 ($^{13}$C) MHz respectively on a Bruker Avance DPX-300 MHz NMR spectrometer. Chemical shifts are reported in $\delta$ (ppm) relative to TMS ($^1$H) and CDCl$_3$ ($^{13}$C) as the internal standards. Coupling constants ($J$) are reported in Hertz (Hz). Mass spectra were recorded under FAB/LRMS at 5000 resolution using JEOL JMS 600H mass spectrometer. Elemental analyses were performed on Elementar Vario ELIII at Sophisticated Test and Instrumentation Centre (STIC), Kochi. Recrystallization was done by slow evaporation method from chloroform-methanol mixture at room temperature. Photochemical reactions were carried out in a Rayonet reactor fitted with sixteen lamps.

2.5.2. Materials
Cyclopentanone, benzenecarboxaldehyde, 1-naphthalenecarboxaldehyde, 9-anthracenecarboxaldehyde, 1-pyrenecarboxaldehyde were purchased from Sigma-Aldrich and used as received. Solvents were distilled and used in the reaction. Benzene used for photochemical reaction was dried using calcium chloride and distilled over sodium wire.

2.5.3. Preparation of 2,5-Diarylidenecyclopentanones, 12a-d

2.5.3.1. Synthesis of (2E,5E)-2,5-dibenzylidenecyclo-
pentanone (12a)
To a mixture of cyclopentanone (2.10 g, 25 mmol) and benzenecarboxaldehyde (5.31 g, 50 mmol) in methanol (25 mL) taken in a 100 mL conical flask, potassium hydroxide pellets (2.80 g, 50 mmol) was added and
the reaction mixture was stirred at room temperature for 15 min whilst a yellow product precipitated out. The mixture was heated in a hot water bath at 60 °C for 6 h, until an appreciable amount of solid formed. The flask was then cooled in an ice chest and the precipitate that separated out was collected by vacuum filtration. The crude product was washed several times with ice-cold 1 mL portions of ethanol. The product was further purified by recrystallization from a mixture (1:2) of methanol and chloroform to give 12a. The product separated was collected by vacuum filtration and air-dried to yield material of good quality.

Yellow Powder. Yield 90%;

mp = 186-188 °C

UV $\lambda_{\text{max}}$ (CH$_2$Cl$_2$) 300 (ε 2,700), 350 (ε 10,600), 400 (ε 450); IR (KBr) $\nu_{\text{max}}$ : 1690, 1664, 1626, 1610, 1441, 1180, 726 cm$^{-1}$;

$^1$H NMR (300 MHz, CDCl$_3$) : δ 7.54-7.53 (m, 2H), 7.41-7.38 (m, 4H), 7.35-7.32 (m, 2H), 7.29-7.27 (m, 2H), 7.01-6.99 (m, 2H), 2.95 (s, 4H);

$^{13}$C NMR (75 MHz, CDCl$_3$) : δ 195.0, 141.3, 139.8, 136.6, 132.7, 129.0, 128.8, 23.9;

MS (FAB, [M$^+$+1]): Calcd for C$_{19}$H$_{16}$O: 260.40. Found: 261.39;

Elemental analysis calculated for C$_{19}$H$_{16}$O: C, 87.66; H, 6.19; O, 6.15. Found: C, 87.67; H, 6.17; O, 6.16.
2.5.3.2. Synthesis of (2E,5E)-2,5-bis(naphthalen-1-yilmethylene)cyclopentanone (12b)

To a mixture of cyclopentanone (1.08 g, 12.8 mmol) and 1-naphthalene-carboxaldehyde (4.01 g, 25.6 mmol) in methanol (25 mL) taken in a 100 mL conical flask, potassium hydroxide pellets (1.40 g, 25.6 mmol) was added and the reaction mixture was stirred at room temperature for 15 min whilst a yellow product precipitated out. The mixture was heated in a hot water bath at 60 °C for 6 h, until an appreciable amount of solid formed. The flask was then cooled in an ice chest and the precipitate that separated out was collected by vacuum filtration. The crude product was washed several times with ice-cold 1 mL portions of ethanol. The product was further purified by recrystallization from a mixture (1:2) of methanol and chloroform to give 12b. The product separated was collected by vacuum filtration and air-dried to yield material of good quality.

Yield 87%; mp = 183-185 °C
UV $\lambda_{\text{max}}$ (CH$_2$Cl$_2$) 260 (ε 14,900), 350 (ε 15,600), 400 (ε 31,800); IR (KBr) $\nu_{\text{max}}$: 1662, 1630, 1530, 726 cm$^{-1}$;
$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 8.37 (s, 2H), 8.25-8.22 (m, 2H), 7.88-7.85 (m, 4H), 7.65-7.60 (m, 2H), 7.57-7.47 (m, 6H), 3.00 (s, 4H);
$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 195.4, 139.8, 133.7, 132.5, 132.4, 130.5, 129.8, 128.7, 127.1, 126.8, 126.3, 125.1, 124.1, 27.1;
MS (FAB, [M$^+$+1]): Calcd for C$_{27}$H$_{20}$O: 360.15. Found: 361.16;
Elemental analysis calculated for C$_{27}$H$_{20}$O: C, 89.97; H, 5.59; O, 4.44. Found: C, 89.87; H, 5.55; O, 4.54.
2.5.3.3. Synthesis of \((2E,5E)-2,5\text{-bis(anthracen-9-yl-methylene)cyclopentanone}\) (12c)

To a mixture of cyclopentanone (0.81 g, 9.6 mmol) and 9-anthracene-carboxaldehyde (3.97 g, 19.2 mmol) in methanol (25 mL) taken in a 100 mL conical flask, potassium hydroxide pellets (1.08 g, 19.2 mmol) was added and the reaction mixture was stirred at room temperature for 15 min whilst a yellow product precipitated out. The mixture was heated in a hot water bath at 60 °C for 6 h, until an appreciable amount of solid formed. The flask was then cooled in an ice chest and the precipitate that separated out was collected by vacuum filtration. The crude product was washed several times with ice-cold 1 mL portions of ethanol. The product was further purified by recrystallization from a mixture (1:2) of methanol and chloroform to give 12c. The product separated was collected by vacuum filtration and air-dried to yield material of good quality.

Yield 88%; mp > 300 °C

UV \(\lambda_{\text{max}}\) (CH\(_2\)Cl\(_2\)) 260 (\(\varepsilon\) 65,900), 350 (\(\varepsilon\) 14,900), 420 (\(\varepsilon\) 31,600); IR (KBr) \(\nu_{\text{max}}\) : 1634, 1624, 1207, 745 cm\(^{-1}\);

\(^1\)H NMR (300 MHz, CDCl\(_3\)) : \(\delta\) 8.57 (s, 2H), 8.46 (s, 2H), 8.08-8.01 (m, 8H), 7.54-7.46 (m, 8H), 2.31 (s, 4H); \(^13\)C NMR (75 MHz, CDCl\(_3\)) : \(\delta\) 194.1, 144.0, 141.2, 137.1, 132.1, 131.3, 130.0, 129.1, 129.0, 127.9, 126.2, 126.0, 125.8, 125.7, 125.4, 25.7;

MS (FAB, [M\(^+\)+1]): Calcd for C\(_{35}\)H\(_{24}\)O: 460.18. Found: 461.20;

Elemental analysis calculated for C\(_{35}\)H\(_{24}\)O: C, 91.27; H, 5.25; O, 3.47. Found: C, 91.25; H, 5.27; O, 3.48.
2.5.3.4. Synthesis of \((2E,5E)-2,5\text{-bis(pyren-2-ylmethylene)}\) -cyclopentanone (12d)

To a mixture of cyclopentanone (0.36 g, 4.3 mmol) and 1-pyrene carboxaldehyde (2.01 g, 8.6 mmol) in methanol (25 mL) taken in a 100 mL conical flask, potassium hydroxide pellets (0.49 g, 8.6 mmol) was added and the reaction mixture was stirred at room temperature for 15 min whilst a yellow product precipitated out. The mixture was heated in a hot water bath at 60 °C for 6 h, until an appreciable amount of solid formed. The flask was then cooled in an ice chest and the precipitate that separated out was collected by vacuum filtration. The crude product was washed several times with ice-cold 1 mL portions of ethanol. The product was further purified by recrystallization from a mixture (1:2) of methanol and chloroform to give 12d. The product separated was collected by vacuum filtration and air-dried to yield material of good quality.

Yield 89%; mp > 300 °C

UV \(\lambda_{\text{max}}\) (CH\(_2\)Cl\(_2\)) 260 (\(\varepsilon\) 66,900), 350 (\(\varepsilon\) 13,900), 380 (\(\varepsilon\) 25,900), 447 (\(\varepsilon\) 34,600);

IR (KBr) \(\nu_{\text{max}}\) : 1628, 1594, 1349, 1214, 726 cm\(^{-1}\);

NMR: Used solid state NMR for analysis (explained earlier).

Elemental analysis calculated for C\(_{39}\)H\(_{24}\)O: C, 92.10; H, 4.76; O, 3.15. Found: C, 92.30; H, 4.75; O, 3.25.

2.5.3.5. Synthesis of \((1E,4E)-1,5\text{-di(pyren-2-yl)penta-1,4-dien-3-one}\) (12e)

A solution of 1-pyrenecarboxaldehyde 11d (2.01 g, 8.6 mmol) and acetone 14 (1.5 mL) in ethylacetate (50 mL) was saturated with hydrogen
chloride gas and stirred for 24h at room temperature. Bispyrene 12e precipitated from the reaction mixture was purified by soxhlet extraction with dichloromethane. Yield 46%; mp 224-226 °C

IR (KBr) $\nu_{\text{max}}$: 1700, 1210, 789 cm$^{-1}$;

$^1$H NMR: 8.52-8.41 (m, 7H), 8.18-7.91 (m, 4H), 7.87-7.64 (m, 2H), 7.65-7.63 (m, 2H), 7.57-7.42 (m, 5H), 6.78-6.62 (m, 2H);

MS (FAB, [M+1]): Calcd for C$_{37}$H$_{22}$O: 482.16; Found: 483.20.

2.5.4. Photochemical Transformations of Diarylidene Compounds 12a-e

2.5.4.1. Procedure for the Photolysis of 12a

A sample of 12a (0.17 g, 0.7 mmol) was dissolved in a small volume of dry benzene and then made up to 130 mL. The solution was degassed by bubbling dry nitrogen through it and then irradiated at 350 nm. Progress of the reaction was followed by TLC analysis. Starting material was almost completely consumed in 10 h. Solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution of the column with a mixture (2:3) of hexane and dichloromethane gave a new product tentatively identified as the $E,Z$-isomer 13a.

Greenish Yellow crystals. Yield 48%; mp = 216-218 °C

IR (KBr) $\nu_{\text{max}}$: 1663, 1627, 1324, 1107, 722 cm$^{-1}$;

$^1$H NMR (300 MHz, CDCl$_3$): $\delta$ 7.99-7.98 (m, 2H),
7.59-7.58 (m, 2H), 7.52-7.51 (m, 2H), 7.47-7.29 (m, 4H), 6.92 (s, 2H), 3.10-3.07 (m, 2H), 2.99-2.96 (m, 2H);

$^{13}$C NMR (75 MHz, CDCl$_3$) : $\delta$ 194.0, 139.8, 137.8, 137.5, 135.8, 135.0, 133.5, 130.8, 130.7, 130.6, 129.4, 129.3, 129.2, 128.8, 128.7, 128.5, 127.9, 30.8, 26.6;

MS (FAB, [M$^+$+1]): Calcd for C$_{19}$H$_{16}$O: 260.4. Found: 261.2;

Elemental analysis calculated for C$_{19}$H$_{16}$O: C, 87.66; H, 6.19; O, 6.15. Found: C, 87.77; H, 6.18; O, 6.14.

### 2.5.4.2. Procedure for the Photolysis of 12b

A sample of 12b (0.17 g, 0.5 mmol) was dissolved in a small volume of dry benzene and then made up to 130 mL. The solution was degassed by bubbling dry nitrogen through it and then irradiated at 350 nm. Progress of the reaction was followed by TLC analysis. Starting material was almost completely consumed in 10 h. Solvent was removed under reduced pressure and the residue was chromatographed over silica gel. Elution of the column with a mixture (2:3) of hexane and dichloromethane gave a new product tentatively identified as the E,Z-isomer 13b.

Yield 48%; mp = 216-218 °C

IR (KBr) $\nu_{max}$ : 1650, 1623, 1450, 728 cm$^{-1}$;

$^1$H NMR (300 MHz, CDCl$_3$) : $\delta$ 8.03-7.99 (m, 2H), 7.87-7.84 (m, 2H), 7.74-7.70 (m, 4H), 7.49-7.43 (m, 2H), 7.40-7.31 (m, 6H), 2.86 (s, 2H), 2.82 (s, 2H);
\(^{13}\text{C NMR}\) (75 MHz, CDCl\(_3\)) : \(\delta 193.4, 141.3, 139.8, 139.1, 134.7, 133.7, 133.5, 132.5, 132.4, 131.7, 131.6, 130.5, 130.2, 129.9, 129.7, 129.3, 128.8, 128.7, 128.4, 127.0, 126.8, 126.7, 126.2, 125.7, 125.1, 124.3, 124.1, 30.1, 26.8;

\textbf{MS} (FAB, \([M^+1]\)) : \text{Calcd for } C_{27}H_{20}O: 360.2.  
\text{Found: } 361.3; 

Elemental analysis calculated for \(C_{27}H_{20}O\): C, 89.97; H, 5.59; O, 4.44.  
\text{Found: } C, 89.86; H, 5.58; O, 4.46.

\textbf{2.5.4.3. Procedure for the Photolysis of 12c}

A sample of 12c (0.17 g, 0.6 mmol) was dissolved in a small volume of dry benzene and then made up to 130 mL. The solution was degassed by bubbling dry nitrogen through it and then irradiated at 350 nm. Progress of the reaction was monitored by TLC analysis. Even after 12 hours no new products were observed and starting compound was recovered unchanged.

\textbf{2.5.4.4. Procedure for the Photolysis of 12d}

A sample of 12d (0.17 g, 0.4 mmol) was dissolved in a small volume of dry benzene and then made up to 130 mL. The solution was degassed by bubbling dry nitrogen through it and then irradiated at 350 nm. Progress of the reaction was monitored by TLC analysis. Even after 12 hours no new products were observed and starting compound was recovered unchanged.

\textbf{2.5.4.5. Procedure for the Photolysis of 12e}

A sample of 12e (0.17 g, 0.3 mmol) was dissolved in a small volume of dry benzene and then made up to 130 mL. The solution was degassed by bubbling dry nitrogen through it and then irradiated at 350 nm. Progress of the reaction was monitored by TLC analysis. During the course of irradiation
yellow fluorescent solution was changed to blue fluorescent solution with concomitant change in absorption spectrum. Due to poor solubility of the materials, purification and spectral analyses were not feasible.

2.6. References