

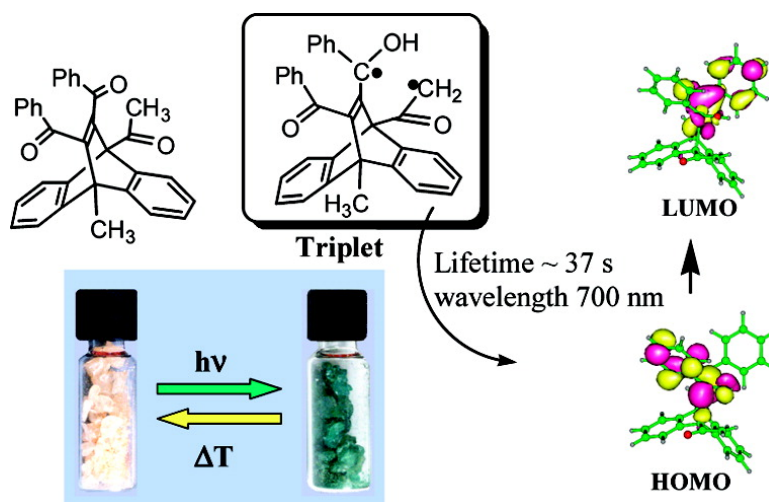
Article

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Meledathu C. Sajimon, Danaboyina Ramaiah, Cherumuttathu H. Suresh,
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Photochromic Dibenzobarrenes: Long-Lived Triplet Biradical Intermediates

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Abstract: Upon exposure to UV light, the disubstituted dibenzobarrelene derivative **1a** turns green in the solid phase and reverts back to its original pale-yellow color within several hours in the dark. The lifetime of the colored species in degassed benzene at room temperature is 37 ± 2 s (E_a for decoloration is 14.5 ± 0.7 kcal mol⁻¹ and log A is 8.92 ± 0.5 s⁻¹) and highly sensitive to molecular oxygen; the Stern–Volmer quenching constant is $6.9 \pm 0.2 \times 10^8$ M⁻¹ s⁻¹. Similarly, the disubstituted dibenzobarrenes **1b** and **1c** exhibited pink coloration when exposed to UV light in the solid phase. On the basis of combined experimental and theoretical evidence, it is proposed that upon photoexcitation the excited singlet state of **1a** undergoes rapid intersystem crossing to its triplet state, followed by intramolecular δ -H abstraction, to yield the triplet biradical intermediate ³**2**. Upon prolonged irradiation, **2** undergoes cyclization to the alcohol **3**, which affords the enone **4** as the final photoproduct. The δ -H abstraction on the triplet-state potential energy surface, calculated at the B3LYP/6-31G* level of density functional theory (DFT), has an activation energy of 18.5 kcal/mol. Further, the absorption spectrum of the triplet biradical ³**2**, obtained from time-dependent DFT calculations, displays an intense absorption maximum at 670 nm, which is in good agreement with the observed absorption peak at 700 nm. The molecular-orbital analysis of the triplet diradical ³**2** suggests that its long-wavelength absorption involves the transition of the unpaired electron from the comparatively localized benzyl-type HOMO to the extensively conjugated benzoyl-type LUMO. The present experimental and theoretical results strongly support the intervention of a long-lived triplet biradical ³**2** in the photochromism of appropriately substituted dibenzobarrenes.

Introduction

The phototransformations of dibenzobarrenes have been investigated in detail by several workers. The most commonly observed processes are photorearrangements leading to dibenzocyclooctatetraenes and dibenzosemibullvalenes.¹ It has been shown that dibenzocyclooctatetraenes are formed through a singlet-state pathway, whereas the dibenzosemibullvalenes are

derived from the triplet-state di- π -methane rearrangement.² In recent years, we have investigated the photoisomerization of several dibenzobarrelene derivatives with dibenzoylalkene functionality in order to understand the role of bridgehead substituents on the observed regioselectivity of these rearrangements.³ In this context, we have observed that certain bridgehead-disubstituted dibenzobarrenes exhibit a novel photochromic behavior, of which the 9-acetyl-10-methyl-ethenoanthracene derivative **1a** is an illustrative example.

Photochromic materials continue to attract considerable attention due to their applications in holography and three-dimensional memory information storage devices.⁴ Most photochromic reactions involve either pericyclic reactions or *cis*–*trans* photoisomerization processes. For example, the diarylethenes,

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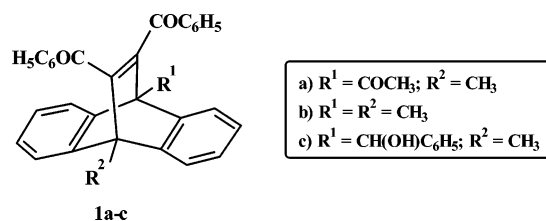
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[⊥] Jawaharlal Nehru Centre for Advanced Scientific Research.

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Chart 1



a well-studied photochromic system, undergo reversible intramolecular cyclization.^{4b,c} Likewise, the photochromic fulgides^{5a} and spiroopyrans^{5b} proceed through related electrocyclic transformations, whereas azobenzene utilizes the *cis-trans* isomerization of the N=N double bond.⁶

Photochromic systems that are based on hydrogen-abstraction reactions as in the case of 2-methylbenzophenone and related systems have been reported in the literature.⁷ In this report, we show that the photochromism displayed by the appropriately disubstituted 9,10-ethenoanthracene derivatives **1a-c** (also known as dibenzobarrelene derivatives) in the solid state as well as in benzene solution (Chart 1) rests on intramolecular hydrogen abstraction. Thus, in contrast to the known photochromic systems, a reversibly formed persistent triplet biradical intermediate is proposed as the photochromic species. We describe herein the photophysical and photochemical studies, which have been used for the detection, characterization, and the elucidation of the mechanism of this novel photochromic case. Further, with the help of density functional theory computations, the absorption properties of the photochromic species and the reaction mechanism have been evaluated.

Results and Discussion

On sunlight or UV irradiation of the 9,10-disubstituted-9,10-dibenzobarrelene **1a** in the solid state (also in benzene solution), we observed a green color, which disappeared within several hours in the dark (Figure 1). This process may be repeated several times, but prolonged irradiation results in the irreversible formation of a mixture of products, namely the ketone **4** and the corresponding dibenzosemibullvalene derivative, as has been observed in solution photolysis.^{3g} Remarkably, this photochromic behavior occurs only with bridgehead-disubstituted ethenoanthracenes that carry substituents with an abstractable hydrogen atom. Thus, for example, 9,10-dimethyl-9,10-dihydroethenoanthracene, **1b**, and 9-methyl-10-(α -hy-

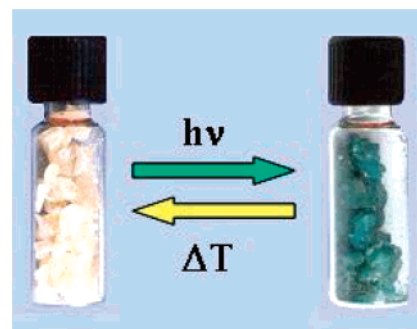


Figure 1. Photochromism displayed by the disubstituted 9,10-ethenoanthracene **1a** before and after irradiation at 350 nm in the crystalline state.

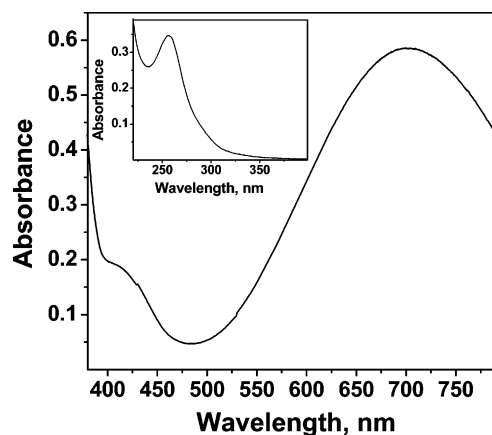


Figure 2. Absorption spectrum of the irradiated 9,10-ethenoanthracene **1a** in degassed benzene solution, recorded immediately after irradiation at 350 nm. (Inset) Absorption spectrum of the starting ethenoanthracene derivative **1a**.

droxybenzyl)-9,10-dihydroethenoanthracene, **1c**, exhibited a pink color when exposed to UV light or sunlight in the solid phase. This pink color reverted back to the original pale-yellow color of the starting material, when irradiated samples were kept in the dark for several hours; however, no coloration was observed in the solution phase. It should be mentioned in this context that Scheffer and co-workers⁸ have observed that certain 9,10-dialkyl-substituted triptycene quinones gave rise on irradiation intensely colored (broad absorption centered around 570 nm) norcaradiene derivatives in addition to the expected di- π -methane photorearrangement products. The color in these products has been attributed to charge-transfer interaction between the norcaradiene and quinone chromophore.

In order to understand the photochromism of disubstituted ethenoanthracenes and also to characterize the transient intermediates involved, we have examined the photophysical properties of **1a** under various conditions. Figure 2 shows the absorption spectrum of **1a** in degassed benzene solution, recorded immediately after irradiation at 350 nm. Its spectrum reveals a weak absorption (shoulder) around 415 nm and a strong maximum around 700 nm. The inset displays the absorption spectrum of the starting ethenoanthracene derivative **1a**, which has an absorption maximum at 252 nm.

The colored intermediate persisted for considerable time in solution, which permitted the use of conventional UV spectroscopy to determine its lifetime. The decay of the transient

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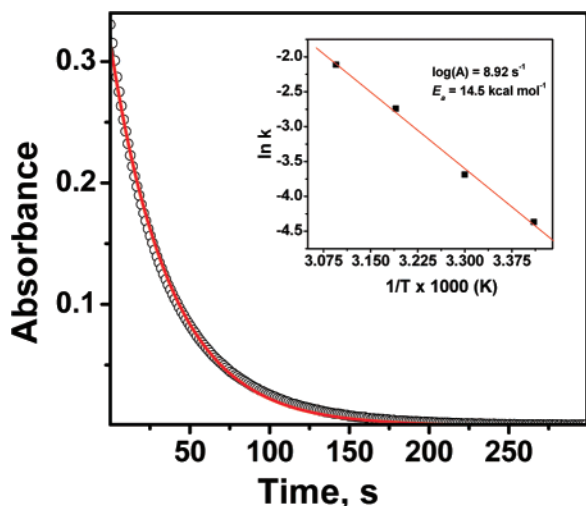
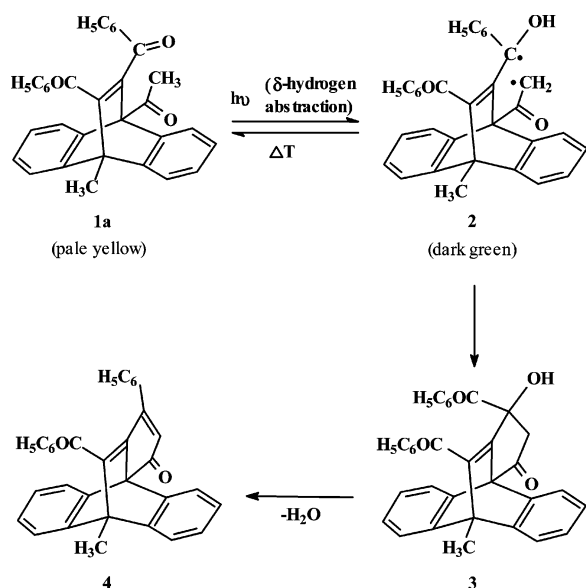


Figure 3. Time profile of the transient intermediate generated from the 9,10-ethenoanthracene **1a** in benzene solution and monitored at 700 nm. (Inset) Arrhenius plot for the decay of the transient.

Scheme 1. Phototransformation of **1a** and Formation of the Enone **4** via the Biradical **2**



was monitored at the absorption maximum of 700 nm, and the lifetime was found to be 37 ± 2 s under ambient conditions (Figure 3, see Tables S1 and S2 in the Supporting Information for the kinetic data). It may be noted that the lifetimes of triplet biradicals similar to **2** (Scheme 1) fall in the nanosecond to microsecond time domain;⁹ thus, the exceedingly long lifetime (~ 37 s) for the triplet biradical **2** is certainly surprising. Arrhenius activation parameters for the decoloration of the green-colored species were determined in solution by monitoring the decay rates between 20 and 50 °C (Figure 3). The activation energy (E_a) for the decay of the transient was found to be 14.5 ± 0.7 kcal mol⁻¹, and the frequency factor ($\log A$) was 8.9 ± 0.5 s⁻¹. Although the E_a value is quite high for ISC,¹⁰ the relatively low frequency factor (~ 8.9) is indicative of a spin-forbidden process and, thus, characteristic of the triplet biradicals.^{3g,11}

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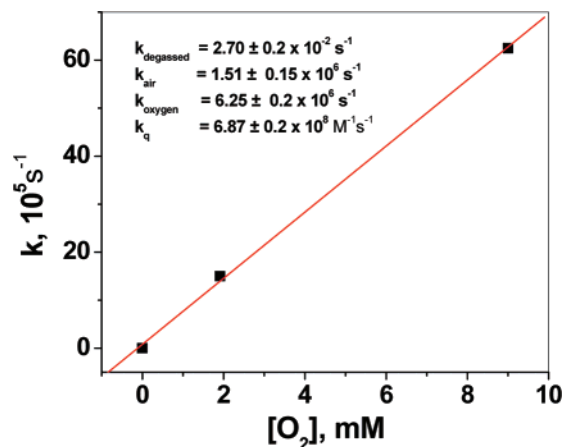
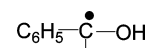


Figure 4. Stern–Volmer oxygen-quenching plot of the transient generated from **1a** upon irradiation at 350 nm in benzene solution.

It is mechanistically significant to mention that the color was not observed in air- and oxygen-saturated solutions. When the colored transient was generated in degassed benzene and subsequently oxygen gas was introduced into the green solution, immediate decoloration ensued. The observation of oxygen quenching is consistent with the formation of the triplet biradical **2**,¹² generated by intramolecular δ -hydrogen abstraction from the acetyl group by the proximate benzoyl oxygen atom in **1a** (Scheme 1). The weak band at 415 nm (shoulder) in the absorption spectrum of the intermediate (Figure 2) is characteristic of similar Norrish-type II biradicals;^{9,13} however, the long-wavelength absorption at 700 nm needs justification. It has been reported recently that the substituted cyclopentane-1,3-diyl biradicals also show strong absorption in the long-wavelength region (~ 580 nm), which has been attributed to the benzyl-radical chromophore.^{11,14} Therefore, the benzyl-type radical site



in the triplet biradical **2** may be further delocalized by the nearby benzoylalkene functionality to result in the longer-wavelength absorption (Scheme 1).¹⁵

To confirm that a triplet biradical **2** is formed in the irradiation of the 9,10-ethenoanthracene **1a**, as suggested by the ³O₂ quenching, the influence of molecular oxygen was examined since effective quenching of triplet biradicals by ³O₂ is well documented in the literature.¹⁶ The Stern–Volmer quenching constant (k_q) of the transient **2** for ³O₂ was determined by monitoring the decay rates at various oxygen concentrations (Figure 4), and the quenching constant (k_q) was found to be 6.9

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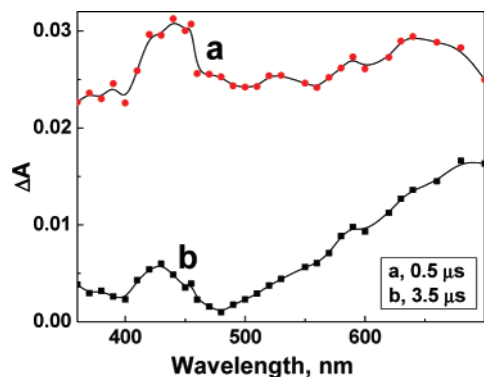


Figure 5. Transient absorption spectra recorded after (a) 0.5- μ s and (b) 3.5- μ s laser excitation (355 nm) of **1a** in benzene solution.

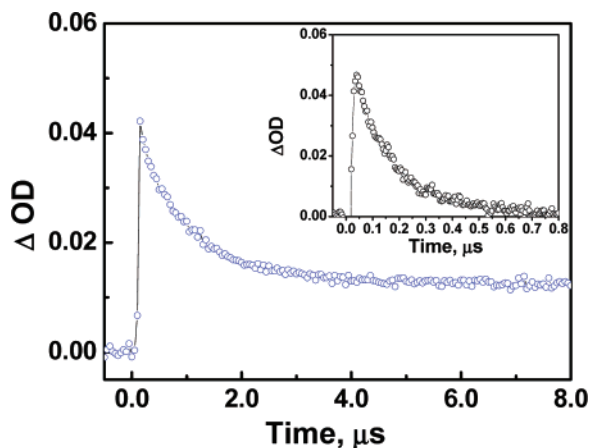


Figure 6. Decay profile of the transients generated from **1a** and monitored at 640 nm in degassed and oxygen-saturated (inset) benzene solutions.

$\pm 0.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, which is in good agreement with the values reported for similar conjugated biradicals.¹⁷

In order to probe for any short-lived intermediates generated from **1a** on irradiation, laser-flash photolysis was carried out ($\lambda_{\text{exc}} = 355 \text{ nm}$) under a variety of conditions. The transient absorption spectra obtained after 0.5 and 3.5 μ s laser excitation of **1a** are shown in Figure 5, and the transient decay monitored at 640 nm is shown in Figure 6. The transient absorption spectrum exhibited a biexponential behavior, in which the lifetime of the short-lived component is around 1 μ s, whereas for the long-lived component it is a few seconds. The latter is attributed to the green-colored triplet biradical intermediate **2** (Scheme 1). This assignment is supported by the good match of the transient absorption spectrum of **1a**, recorded after 3.5 μ s (Figure 5b), with the absorption spectrum of the irradiated solution of **1a** (Figure 2). In addition, this long-lived species is highly sensitive to molecular oxygen, and its lifetime is decreased to nanoseconds in an oxygen-saturated solution (inset of Figure 6). The short-lived component ($\sim 1 \mu$ s) is assigned to the triplet excited-state of the ethenoanthracene derivative **1a** on the basis of standard quenching studies, as reported for similar 9,10-ethenoanthracene derivatives.^{3a-c}

The intermediacy of the biradical **2** is further supported by the isolation of the ketone **4** from the steady-state photolysis of the 9,10-ethenoanthracene **1a**.^{3g} The formation of ketone **4** arises from the excited **1a**, a process that is proposed to take place

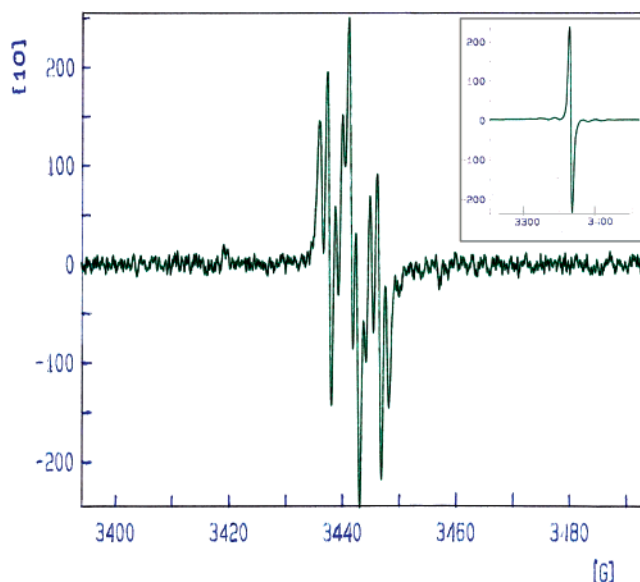


Figure 7. EPR spectrum of **1a** in degassed benzene solution at 25 °C, recorded immediately after irradiation with a 351-nm laser source. (Inset) EPR spectrum of **1a** recorded after 2 min irradiation in MTHF glass at 77 K.

along the pathway shown in Scheme 1. The excited state of **1a** first abstracts a δ -hydrogen atom from the methyl group of the acetyl substituent to give the 1,5-biradical intermediate **2**, which subsequently cyclizes to the alcohol derivative **3**. Elimination of water from **3** generates the observed product **4**. The structure of **4** was confirmed through X-ray crystallographic analysis (Figures S1 and S2, Supporting Information). The shortest intramolecular distance between the acetyl hydrogen atom and the adjacent benzoyl oxygen atom in the starting 9,10-ethenoanthracene **1a** is 2.75 Å, which is close enough for hydrogen abstraction to generate the biradical intermediate **2**.^{9,18}

Evidence for the presence of a paramagnetic biradical species was furnished by EPR-spectral studies. As expected, the irradiated green-colored solution of **1a** in degassed benzene at room temperature and at 77 K exhibited an EPR signal centered around 3340 G (Figure 7). Instead of a characteristic triplet EPR spectrum expected for the biradical **2**, a benzyl-type monoradical species was registered, which resembles closely the EPR spectrum of the benzyl radical reported in the literature (see the inset in Figure 7).¹⁹ The EPR spectrum of the irradiated (77 K) **1a** in MTHF glass showed a similar EPR signal centered around 3370 G. Control experiments on nonphotochromic model systems such as the unsubstituted and monosubstituted 9,10-ethenoanthracene derivatives showed no EPR-active species on irradiation under analogous conditions.

To substantiate the mechanism of formation of the biradical intermediate **2** proposed in Scheme 1 and to corroborate its absorption properties, we have carried out a detailed theoretical study. The widely used B3LYP/6-31G* level density functional theory (DFT) method,^{20,21} as implemented in Gaussian 03 suite

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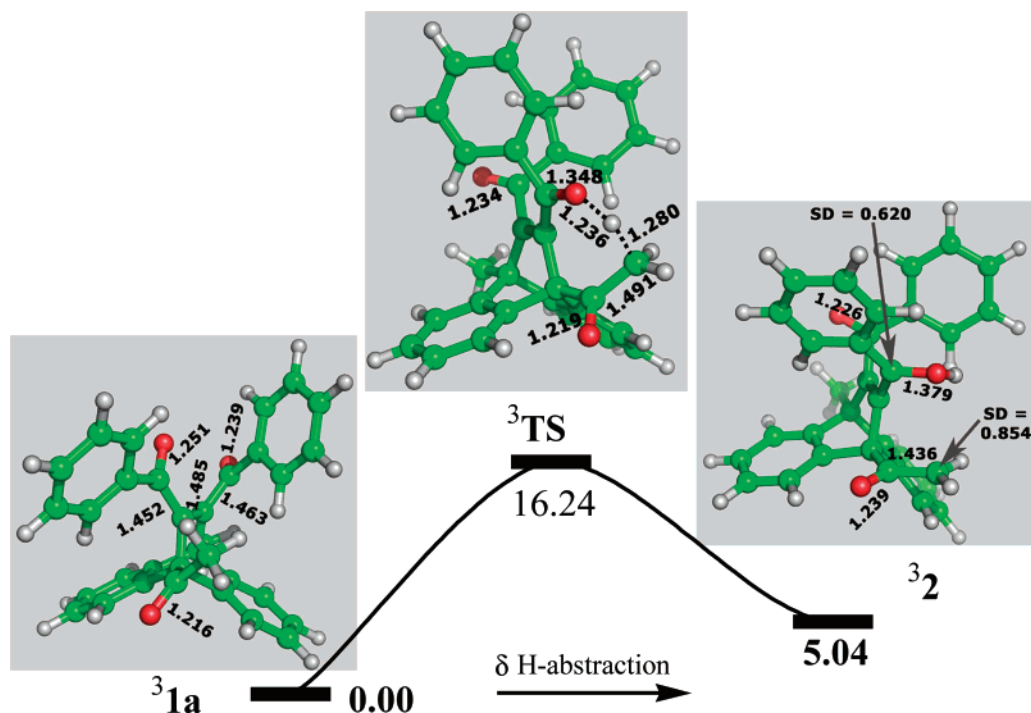


Figure 8. Computed triplet-state potential energy surface for the δ -H abstraction with the spin density (SD) values for $^3\mathbf{2}$. All bond lengths are in Å, and the relative energies are in kcal/mol.

of programs, was used for this purpose.²² Since ketones in general undergo fast intersystem crossing,²³ it is reasonable to assume that the δ -H abstraction occurs from the triplet state $^3\mathbf{1a}$. The computed triplet-state potential energy surface is given in Figure 8. It may be seen that $^3\mathbf{1a}$ has a significantly long (1.25 Å) benzoyl C=O bond (typical C=O distance is 1.22 Å), which implies photoexcitation of the carbonyl group. Subsequently, the excited carbonyl group abstracts the δ -H atom from the proximate acetyl group. In the transition state, $^3\mathbf{TS}$, the abstractable H atom is seen nearly equidistant from the carbonyl oxygen atom and the methylene group, a feature commonly observed in similar photoreactions.²⁴ An activation energy of 16.2 kcal/mol was calculated at the unrestricted B3LYP level [the large 6-311++G(d,p) basis set was used] for the formation of the triplet biradical $^3\mathbf{2}$ from $^3\mathbf{TS}$, which is considered reasonable for such a hydrogen-abstraction process. The spin density (SD) analysis reveals that one of the unpaired electrons (SD = 0.854) in $^3\mathbf{2}$ is essentially localized at the methylene carbon atom, whereas the second unpaired electron (SD = 0.620) is centered at the benzyl-type carbon atom and is significantly delocalized (Figure 8). This result is in accordance with the previously mentioned interpretation on the EPR-spectral findings. Intersystem crossing of the triplet biradical $^3\mathbf{2}$ to the singlet biradical $^1\mathbf{2}$, followed by cyclization, affords the product $\mathbf{3}$, as shown in Scheme 1.

The cyclization of the biradical results from triplet–singlet spin-state change, followed by the formation of a new bond on the singlet potential energy surface. To locate the triplet–singlet crossing point is quite difficult, as it requires multireference theory such as the CASSCF or CI method. In the present case,

the system contains 62 atoms and is quite large for such calculations. A qualitative estimate of the barrier height has, however, been obtained by assuming that the geometry of the triplet–singlet crossing point is not much different from that of the triplet biradical intermediate. Therefore, the energy obtained from a single-point “singlet” energy calculation with triplet biradical geometry is considered to be an adequate estimate of the energy for the triplet–singlet crossing point. With such a calculation, the estimated barrier height is found to be 10.6 kcal/mol, which is in qualitative agreement with the experimental barrier height of 14.5 ± 0.7 kcal/mol.

In order to compute the absorption spectrum of the triplet biradical intermediate $^3\mathbf{2}$, the time-dependent DFT calculation was carried out at the UB3LYP/6-31G* level.^{25–27} The computed spectrum is shown in Figure 9, along with the HOMO and LUMO for the most intense electronic transition. The calculated value of 677 nm for the absorption peak is in good agreement with the experimental value around 700 nm. The 677 nm absorption peak corresponds to the transition of the electron from the comparatively localized benzyl-type HOMO to the benzoyl-type LUMO, which is extensively conjugated with the adjacent carbonyl group. This offers a reasonable rationale for the unusual long-wavelength absorption observed herein experimentally for the triplet biradical $^3\mathbf{2}$.

Conclusions

We have shown that appropriately disubstituted 9,10-ethenoanthracenes display intriguing photochromic behavior, with the novel feature that a long-wavelength absorbing (ca. 700 nm) and long-lived (seconds in solution, hours in the solid

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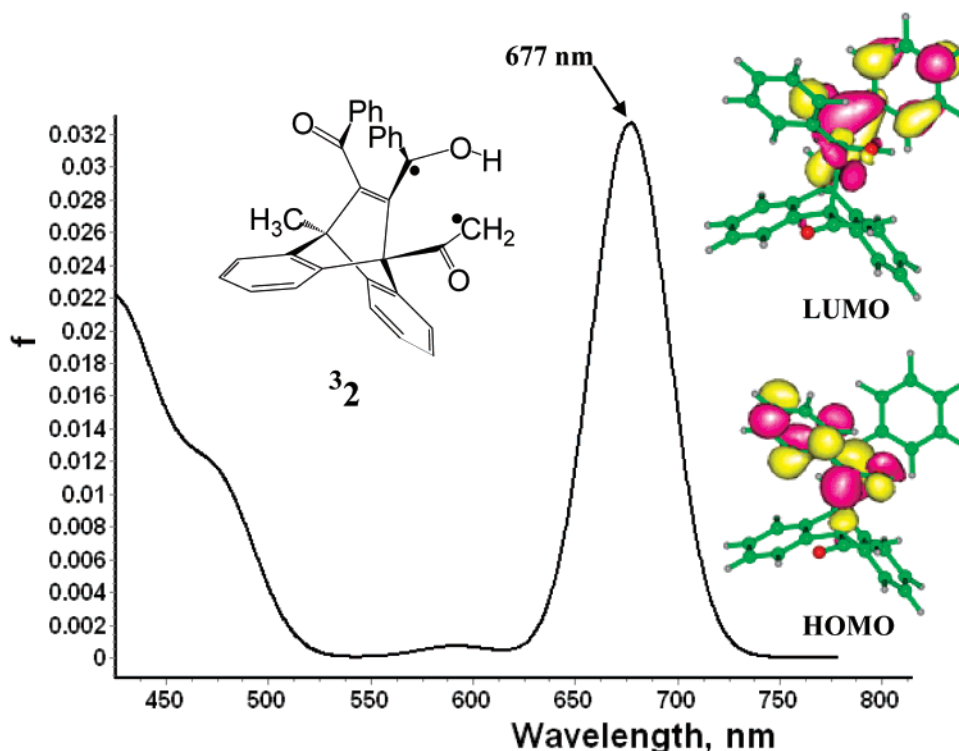


Figure 9. The oscillator strength (f) versus wavelength plot for the computed absorption spectrum of the triplet biradical 3_2 .

phase) triplet biradical intervenes as the reversible color-bearing species. The long-wavelength absorption of the triplet biradical is attributed to the extensive π delocalization between the benzyl and benzoyl groups, which are connected by the conjugating alkenyl double bond. Persistence (long life time) is provided by the rigidity of the ethenoanthracene skeleton in the triplet biradical 3_2 , which encumbers the cyclization ($E_a = 14.5 \pm 0.7$ kcal mol⁻¹) to the strained alcohol derivative **3**.

Experimental Section

The equipment and procedure for melting point determination and spectral recordings are described in earlier publications.^{3h,28} All steady-state irradiation experiments were carried out in a Srinivasan-Griffin Rayonet Photochemical Reactor (RPR 300 nm) or by using Pyrex-filtered light from a Hanovia 450-W, medium-pressure mercury lamp as described elsewhere.^{3g} Solvents for the photolysis experiments were purified and distilled before use. As petroleum ether, the fraction with bp 60–80 °C was used.

Starting Materials. 9-Acetyl-11,12-dibenzoyl-9,10-dihydro-10-methyl-9,10-ethenoanthracene (**1a**),^{3g} mp 226–227 °C, 11,12-dibenzoyl-9,10-dihydro-9,10-dimethyl-9,10-ethenoanthracene (**1b**),^{3a} mp 261–262 °C, and 11,12-dibenzoyl-9,10-dihydro-9-(α -hydroxybenzyl)-10-methyl-9,10-ethenoanthracene (**1c**),^{3e} mp 218–219 °C, were prepared by reported procedures. The structures of **1a** and the photoproduct **4** (mp 211–212 °C)^{3g} were unambiguously established by X-ray crystallographic analysis.

Laser-Flash Photolysis Studies. The laser-flash photolysis studies were performed on a Laser Photonics PRA/model UV-24 nitrogen laser system (337.1 nm, 2-ns pulse width, 2–4 mJ/pulse) and/or by the third harmonic laser pulse from a Nd:YAG laser GCR-12 series, Quanta Ray (355 nm, 10-ns pulse width, ~70 mJ/pulse). A kinetic absorption spectrometer (LKS-20 Applied Photophysics) was used to detect the

changes in optical density after the laser excitation. Typical experiment consisted of several replicate shots per single measurement. The intrinsic lifetimes were measured in benzene at 25 °C, after purging with argon gas for 30 min. Oxygen-quenching constants were determined by monitoring the decay rates of the respective substrates in air and in oxygen-saturated benzene solutions. The transient absorption spectra were recorded in degassed benzene by using a flow cell. The optical density of the solution was in the range 0.4–0.8 at 355 nm.

UV-Spectroscopic Studies. The UV-visible spectra were recorded on a Shimadzu UV-3101PC UV-vis-NIR scanning spectrophotometer. The absorption spectra of the transients were recorded immediately after irradiation of a degassed solution by the use of a 300-nm band-pass filter on an Oriel Optical bench, in a quartz cell (6 mm \times 6 mm), at a distance of 30 cm from the light source. The kinetics of the transient decay was studied over the temperature range of 20–50 °C, and the desired temperature was adjusted by means of a Shimadzu TCC controller (error limit is ± 0.2 °C). The Arrhenius activation energy (E_a) and frequency factor ($\log A$) were evaluated by using the linear regression method.

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Supporting Information Available: Complete reference 22, details of photolysis and kinetic parameters of **1a**, single-crystal X-ray ORTEP diagrams of **1a** and **4**, and the Cartesian

coordinates for the optimized geometries of ³**1a**, ³**2**, and ³**TS** at B3LYP/6-31G* level. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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