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Excited state behavior of twisted olefins with rigidly linked and rotationally free chromophores

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Abstract

The stilbene analogues tetraphenylethylene and bi-4H-cyclopenta[def]phenanthren-4-ylidene (BPH) prove to be useful models for studying photoisomerization reactions in olefins with freely rotating and rigid chromophores. In the former, the rotation of the phenyl rings follows a complex isomerization pathway from one of the two isoenergetic enantiomers to the 90° twisted conformer. The isomerization pathway for BPH is much simpler since only idealized rotation about the double bond is possible. © 1997 Elsevier Science S.A.

Keywords: Photoisomerization; Tetraphenylethylene; Olefins; Biradical

1. Introduction

There has been considerable interest in understanding *cis* → *trans* photo-isomerization reactions with an abundance of the research focusing on the barrierless isomerization of *cis*-stilbene. Photoisomerization reactions are important in many biological systems, notably in the primary event in vision involving the retinal chromophore in rhodopsin [1–3].

Photoexcitation of olefins prompts a twisting about the ethylenic bond with relaxation to a 90° geometry breaking the π-bond. This motion results in the formation of either a biradicaloid or a charge separated (CS) excited state [4]. Stilbene, tetraphenylethylene (TPE) and their analogues adopt this twisted geometry with the formation of a CS excited singlet state dubbed the "phantom state", $^1p*$ [5,6]. The phantom state of stilbene lives for < 200 fs [7], however, the lifetime is solvent dependent [8].

In a recently published paper [9], we explored the triplet state surface of TPE. The photoisomerization pathway, from a *cis*-arrangement to a *trans*-arrangement of the phenyl rings, depends not only on the photo-assisted twist of the ethylenic bond, but also on the correlated rotation of the phenyl rings. The approximate calculations were used to describe qualitatively the isomerization pathway. Although the triplet surface was explored, it is evident that the important factors are steric interactions not electronic factors thus making it possible to relate these calculations to a description of the singlet surface.

The calculations generated a complex triplet isomerization pathway described by two activation barriers and three minima. Geometry optimization yields three conformers: two enantiomers designated ΔD_2 and ΛD_2 for the right-handed and left-handed propeller arrangement of the phenyl groups, and a C_{2h} conformer ascribed to the 90° twisted state. The activation barrier associated with going from one enantiomer to the C_{2h} conformer is ~3.1 kcal/mol which is reasonably close to the spectroscopically determined value of 2.4 kcal/mol obtained by Ma et al. [10].

The minima corresponding to the ΔD_2 and ΛD_2 enantiomers lie at 81.0° and 99.0° respectively. These isoenergetic enantiomers can not be differentiated spectroscopically and are believed to correspond to the relaxed emissive state of TPE ($\tau = 250$ fs) [11]. The 90° C_{2h} conformer corresponds to the phantom state previously discussed. The lifetime of this state is longer (~3 ns) [12] than the lifetime of the emissive state due to conformational trapping of TPE along this reaction coordinate.

The driving force in going from either D_2 enantiomer to the C_{2h} conformer is the strain of the phenyl carbon attached to the carbon of the ethylenic bond as the rings "lag" behind the twist of the $>C{=}C<$ [11]. The photoinduced twist of the double bond forces the phenyl groups to rotate, due to the steric hindrance of the ortho-H's, in a gearing motion.

The complexity of the excited state dynamics of TPE points to the need for model compounds in which there is no other motion but the twisting of the ethylenic bond thus reduc-

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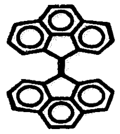
ing the photoisomerization reaction coordinate to one important torsional motion. The remainder of this paper will deal with a study of an analogue of stilbene and TPE, bi-4H-cyclopenta[def]phenanthren-4-ylidene (BPH) in which rigid cyclopentaphenanthrene chromophores are linked through a double bond.



BPH

There have been other such models, dubbed the "stiff-stilbenes" [13–15] in which rotation of the phenyl rings was impossible. One such model, biindanylidene, follows a similar *cis* → *trans* isomerization pathway as stilbene and was useful in determining isomerization intermediates [16].

In the ground state geometry of BPH, there is already a twist of ~30° [17] of the >C=C< in contrast with the stilbenes and TPE in which the ground state geometry is planar or nearly planar. Also, we will show that unlike most known stilbene analogues, BPH possesses a biradicaloid lowest excited singlet state.

2. Experimental

BPH was prepared by first brominating cyclopentaphenanthrene (Aldrich) to 9-bromocyclopentaphenanthrene followed by coupling in dry THF with NaOH. The compound was isolated via a column and recrystalized from ethanol.

The transient absorption spectra were obtained using a Continuum NY61-10 Nd:YAG laser with a pulse energy of approximately 30 mJ and a pulse length of 5 ns for the third harmonic (355 nm) and a pulse energy of 100 mJ, 7 ns pulse length, for the second harmonic (532 nm) as the excitation source. The analyzing light source was a Hamamatsu Super-Quiet Xe flash lamp. Isolation of the detected wavelengths was achieved with an Oriel 77250 monochromator with resolutions of ~5 nm in the visible region and ~13 nm in the near IR. The transients were detected with a Si photodiode (Thorlabs FDS100) in the visible range and a germanium photodiode (EG and G Judson J-16-R01M-Hs) in the near-IR and subsequently processed with a Tektronix SCD1000 ultrafast digitizer.

The low temperature measurements were performed using the above instrumentation as well as a thermocouple to record the temperature. The samples were cooled in an optical dewar with temperature control provided by flowing cooled N_2.

The solutions for the low temperature study were prepared in spectrophotometric grade toluene (Aldrich) and 99% methylpentane (Aldrich) further purified by distillation and stored over Na. All other solutions for transient absorption were prepared in spectrophotometric grade benzene (Aldrich). The samples were deaerated 5 times via the freeze-pump-thaw method prior to photoexcitation.

The UV-Vis spectra of BPH in spectrophotometric grade hexane, dioxane, benzene, acetonitrile and DMSO as well as high purity, anhydrous hexadecane (all from Aldrich) were recorded using a Perkin-Elmer Lambda 6 spectrometer. Fluorescence spectra in the same solvents were collected on a Perkin-Elmer LS-5B fluorimeter with excitation at 480 nm.

The Raman spectrum of BPH was obtained with a Perkin Elmer 2000 FT-IR with Raman attachment at a resolution of 2 cm^{-1}. Excitation of the solid sample, uniformly packed in a capillary, was achieved with the fundamental (1064 nm) of a Nd:YAG laser (Spectron Laser Systems) operated with a power of 100 mW.

Descriptions of the transient microwave and dc conductivity setups can be found elsewhere [18,19].

Calculations were performed using the SPARTAN package by Wavefunction running on an IBM 25T.

3. Results and discussion

The cross-sections of the ground state singlet and triplet surfaces of BPH, shown in Fig. 1, were generated at the AM1 level (with 3 × 3 CI for the singlet surface) and describe the isomerization pathway involving rotation of the ethylenic bond. The value of the S_0-T_1 energy gap is most likely underestimated by this level of calculation and the cross sections should be regarded as qualitative descriptions only. The ground state singlet cross-section has two minima at 27° and 153° and a maximum at 90° where the strain on the double bond is greatest. The minimum on the cross-section of the triplet surface corresponds to the 90° twisted biradical state. The triplet surface is much simpler in the case of BPH than TPE since rotation of the phenyl rings is impossible.

The 30° twisted geometry of the ground state of BPH prevents full π-delocalization which is reflected in the ground state absorption spectrum. The spectrum contains a band in the near UV corresponding to a localized absorption of the cyclopentaphenanthrene "monomer" as well as a delocalized band in the visible (Fig. 2). The vibronic structure of the bands in the visible region of the absorption spectrum corresponds to an excited state frequency of the central >C=C< of 1306 cm^{-1}, a difference of ~255 cm^{-1} with

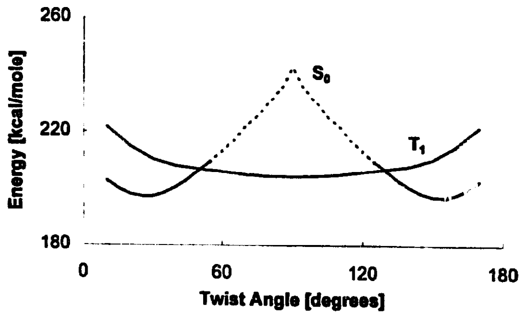


Fig. 1. Cross sections of the ground state singlet and triplet surfaces of BPH (AM1 semiempirical calculations) as a function of the double bond twist.

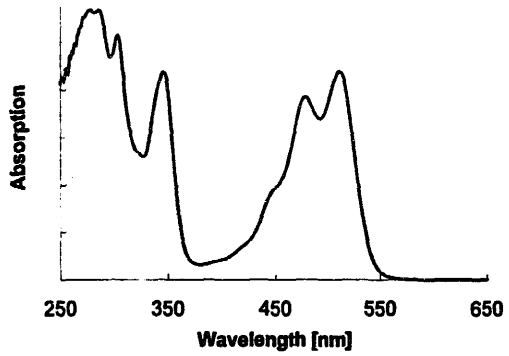


Fig. 2. Ground state absorption spectrum of BPH (0.1 mM in benzene).

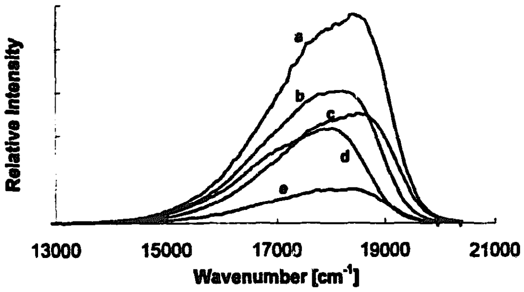


Fig. 3. Emission spectra of BPH in (a) hexadecane (b) dioxane (c) hexane (d) dimethylsulfoxide (e) acetonitrile (all solutions 0.01 mM).

the Raman stretching frequency of >C=C< in the ground state (1561 cm^{-1}) indicating that already in the vertical Franck-Condon state, the central bond is 30% weaker than in the ground state.

The transition dipole associated with the above transition is ~6 D. The highly symmetric BPH molecule has no dipole moment in its ground state suggesting that the initially created Franck-Condon state possesses some CS character. The fluorescence occurs from the Franck-Condon state relaxing to the twisted excited state. The relaxation is believed to be activationless and is limited only by the solvent friction. The effect of solvent friction on the fluorescence of stilbene analogues was discussed in detail in the review by Saltiel and Sun. [5].

The influence of the medium on the shape and position of the emission band was explored in solvents of varying polarity and viscosity (Fig. 3). Despite the likely CT character of the emissive state, the fluorescence band appears to be only slightly polarity dependent. However, the polarity of the solvent is only one factor influencing the spectral appearance. The response time of the solvent (τ), i.e. the solvent's ability to reorient around the molecule upon photoexcitation, also influences the emission spectra. The solvent response time is crucial in BPH not only due to the rearrangement of charge in the molecule upon photexcitation, but also due to the geometric changes. In acetonitrile, a "fast" solvent (τ=0.15 ps) [20], the emission of BPH is only slightly shifted from the position in hexane but the broadening of the band and lowering of the quantum yield suggest that the lifetime of the emissive state is of the same order as this solvents response time.

Table 1
Fluorescence quantum yields of BPH in a variety of solvents

Solvent	Φ_{fl}	Viscosity (cP) [a]
Hexadecane	0.011	3.34
Hexane	0.006	0.326
Dioxane	0.005	1.087 [b]
DMSO	0.004	1.996 [b]
Acetonitrile	0.002	0.345

[a] R.C. Weast et al., CRC Handbook of Chemistry and Physics, 66th Edition,. CRC, Florida, 1985, p. F-40.

[b] J.A. Riddick, W.B. Bunger, Organic Solvents, Wiley-Interscience, USA, 1970, p. 222, 446.

The fluorescence quantum yield of BPH (Φ_{fl}) is viscosity dependent, ranging from 0.0061 in hexane to 0.011 in hexadecane, as listed in Table 1. The more viscous solvents extend the lifetime of the Franck-Condon state by impeding the rotation about the central double bond. However, the slope of the viscosity dependence is considerably less than 1, suggesting a weak coupling between the twisting motion of BPH and the surrounding medium. Similar solvent effects were explored in detail in the case of *cis*-stilbene by Todd et al. [21].

BPH can be excited into either band of the ground state absorption spectrum, creating identical transient spectra. Transient absorption is observed from the UV region well into the near-IR. Below 750 nm, the transient decays can be fit with a single exponential yielding lifetimes >2 µs. This absorption, which can be reproduced via sensitization, is assigned to triplet state absorption and extends from 350 nm to 1150 nm, with a maximum at ~700 nm, and a prominent bleach centered at 550 nm corresponding to ground state absorption (Fig. 4).

The transient profiles in the near-IR have two characteristic components (Fig. 5). There is a fast (t<2 ns), intense component corresponding to singlet absorption and a longer-lived (t>2 µs), weaker component corresponding to the triplet absorption discussed previously. The singlet absorption spectrum (Fig. 6) in the near-IR is characterized by a broad band extending from ~750 nm to ~1200 nm with a maximum at ~1050 nm.

Transient conductivity experiments in collaboration with Warman and Smirnov have determined that the lowest

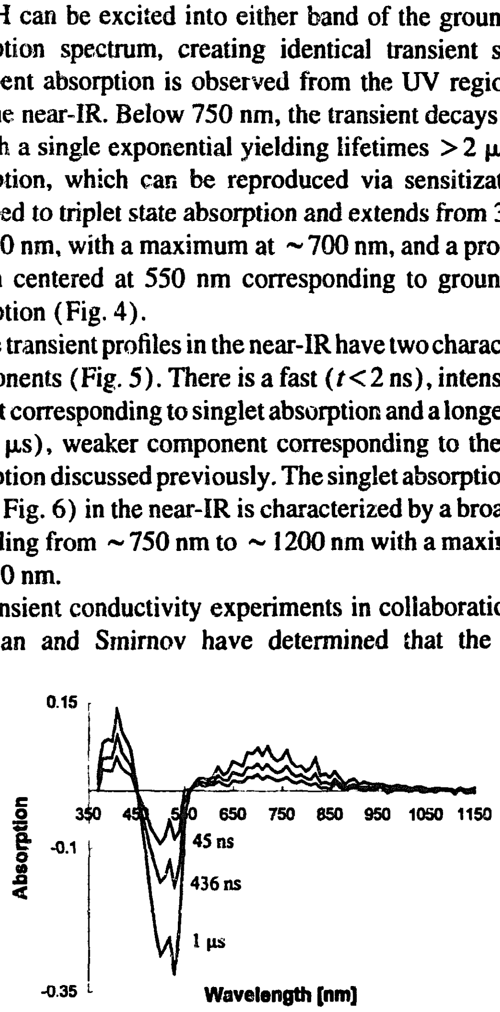


Fig. 4. Triplet absorption spectrum of BPH at different time delays after excitation.

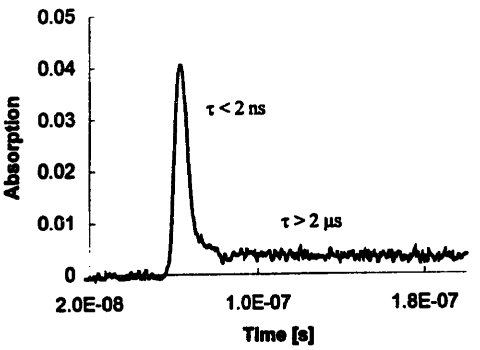


Fig. 5. Transient profile of BPH at 1000 nm.

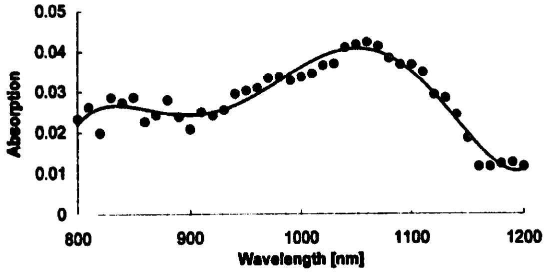


Fig. 6. Singlet absorption spectrum of BPH.

excited singlet state of BPH is a biradical as opposed to the zwitterionic character associated with the "phantom states" of stilbene and TPE. A biradicaloid excited singlet state is more favorable in BPH due to the added aromaticity of the fused ring system of the chromophores and the subsequent ability to delocalize the radical.

Since the lowest excited singlet state is biradical, the singlet absorption is attributed to the delocalized CT transition from the $^1B_2$ biradical state to the higher lying $^1A_1$ zwitterionic state. The lower limit of the transition dipole associated with this delocalized transition is estimated at ~ 15 D, which is in a reasonable agreement with the maximum dipole moment of the fully charge separated species (~21 D) [2].

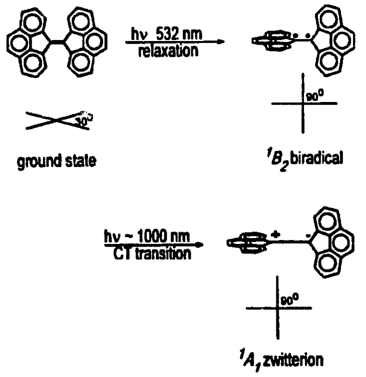
The triplet absorption spectrum is assigned at this time to a transition localized on one cyclopentaphenanthrenyl radical unit, but has not as yet been confirmed. [3]

No transients were observed in low temperature 2-methylpentane glass due to the inability of the molecule to freely rotate about the ethylenic bond upon photoexcitation, however, transients were recorded in low temperature solvents down to −90 °C and appeared identical to room temperature transients.

4. Conclusions

The isomerization pathway of TPE follows a complex motion involving the twist of the olefinic bond, as well as the large amplitude correlated rotation of the phenyl rings. The restricted motion of BPH provides insight into the idealized rotation about the ethylenic bond, creating a much simplified reaction coordinate.

Unlike the other stilbene analogues, BPH is a rare example of an olefin possessing a biradicaloid lowest excited singlet state with a lifetime <2 ns. The delocalized transition from this biradical state to the higher lying zwitterionic state is accompanied by a large transition dipole moment. The following sequence has been proposed:



The short lifetime of the singlet state requires increased time resolution for full exploration of the dynamics.

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[2] PM3 calculation performed using the spartan package by Wavefunction Inc.

[3] Confirmation of this assignment will be accomplished by the generation and subsequent photoexcitation of the cyclopentaphenanthrenylidene radical.

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