Singlet Biradical → Singlet Zwitterion Optical Transition in a Twisted Olefin

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We report the first direct observation of the singlet biradical → singlet zwitterion transition in a twisted olefin, biphenanthrenylidene (Scheme 1). Biphenanthrenylidene (full name, bi-4*H*-cyclopenta[*def*]phenanthren-4-ylidene, abbreviated as BPH) is an analogue of tetraphenylethylene (TPE) and stilbene, both of which are the favorite models of photoisomerization reactions.[1] The investigations have been focusing on the dynamics of the twisting motion of the double bond which leads to decoupling of the two halves of the olefin and results in the formation of the D_{2d} 90°-twisted zwitterionic or biradical excited state.[2]

Thanks to the rigidity of the chromophores of BPH its isomerization coordinate is limited to the pure rotation around the double bond, and it is considerably simpler than in the case of stilbene and TPE.[3] In this regard it resembles biindanylidene in which the reaction coordinate is essentially one-dimensional.[4] Of additional importance is the large, ~30° twist of the central $>C{=}C<$ bond in the ground state of BPH caused by the severe steric interaction of the 1,1′-hydrogens of the opposing chromophores.[5] The twist weakens the central bond, as evidenced by the red shift of the $>C{=}C<$ stretch Raman frequency from 1595 cm^{-1} in TPE to 1561 cm^{-1} in BPH. As a result of the nonplanarity, the π-delocalization is not complete in this molecule. This is reflected in the absorption spectrum which contains a strong delocalized band in the visible (the compound is deep red, $\lambda_{max} = 506$ nm, $\epsilon_{506} = 15000$, $\mu_{trans} = 5.6$ D) and a localized, "monomeric" band in the UV (Figure 1). The emission spectrum of BPH is broad and featureless (Figure 1), and the fluorescence quantum yield Φ_f is $<1\%$ in most solvents. Both the λ_{max} and Φ_f are independent of the solvent polarity; however, the quantum yield does depend on the solvent viscosity and the relaxation times, τ_{sol} (Table 1). As in the case of *cis*-stilbene and *cis*-biindanylidene, the relative weakness of the viscosity dependence suggests that due to the steepness of the potential the relaxation of the emissive Franck−Condon state of BPH is very rapid and weakly coupled to the solvent reorganization.[6]

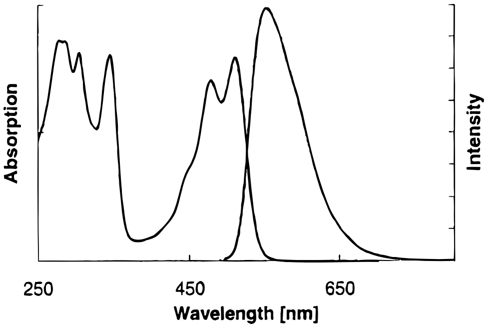

Figure 1. Absorption and emission spectra of BPH in benzene (arbitrary scaling).

Table 1. Fluorescence Quantum Yield Φ_f of Biphenanthrenylidene in Solvents of Various Viscosity, η, and Dielectric Constant, ϵ^a

solvent	ϵ^b	η^b [cP]	$\tau_{sol}{}^c$ [ps]	$10^3\Phi_f$	λ_{max} [nm]
hexane	1.89	0.30		6.1	545
hexadecane		3.34		11.2	543
dioxane	2.2	1.18	0.92	5.3	548
acetonitrile	36.6	0.37	0.15	2.4	545
DMSO	47.2	1.99	0.91	4.4	555

[a] 1.00×10^{-5} M BPH, excited at 480 nm, room temperature, tetracene as a reference. [b] From the following: 1990−1991 *CRC Handbook of Chemistry and Physics*; Chemical Rubber Publishing Co.: Cleveland, OH, 1990−91. Lide, D. R. *Handbook of Organic Solvents*; CRC: Boca Raton, 1995. [c] From: Horng, M. L.; Gardecki, J. A.; Papazyan, A.; Maroncelli, M. *J. Phys. Chem.* **1995**, *99*, 17311.

Excitation of BPH in benzene, toluene or 3-methylpentane either into the visible or the UV band[7] leads to observation of a NIR singlet transient absorption with $\lambda_{max} \approx 1050$ nm, $\tau < 2$ ns, and a much longer lived triplet component consisting of a prominent bleach of the ground state absorption and a new band with $\lambda_{max} = 700$ nm, $\tau > 1$ μs (Figure 2). The long lived transient has been reproduced by sensitization with benzophenone. It is important to note that, when corrected for its short lifetime, the excited singlet spectrum is much more intense than the triplet one. The measurements were repeated in a rigid 3-methylpentane glass at −100 °C, in which the large amplitude $D_2 \rightarrow D_{2d}$ twist is not possible. As expected, no transients were detected under these conditions. Spectra collected in −20 °C toluene were qualitatively identical with the room temperature spectra, with the intensity increasing at low temperatures. These results confirm that both the singlet and the triplet spectra belong to a 90°-twisted species.

The assignment of the biradical $>C^{\bullet}-{}^{\bullet}C<$ *vs* zwitterion $>C^{+}-{}^{-}C<$ nature of the excited states of BPH was accomplished through dc and microwave time resolved conductivity measurements.[9] Similar experiments were used recently in order to conclusively demonstrate that the lowest excited singlet state of TPE is zwitterionic, with $\mu = 7.5$ D.[10] In the case of BPH the conductivity measurements indicate that neither the fast, nor the slow optically detected transient originates from a

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[1] (a) Waldeck, D. H. *Chem. Rev.* **1991**, *91*, 415. (b) Saltiel, J.; Sun, Y.-P. *Cis−Trans Isomerization of C═C Double Bonds*; Dürr, H., Bouas-Laurent, H., Eds.; Elsevier: Amsterdam, 1990; pp 64−164 and references therein.

[2] (a) Sumitami, M.; Nakashima, N.; Yoshihara, K.; Nagakura, S. *Chem. Phys. Lett.* **1977**, *51*, 183. (b) Greene, B. I. *Chem. Phys. Lett.* **1981**, *79*, 5153. (c) Barbara, P. F.; Rand, S. D.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1981**, *103*, 2156. (d) Pedersen, S.; Bañares, L.; Zewail, A. H. *J. Chem. Phys.* **1992**, *97*, 8801.

[3] (a) Lenderink, E.; Duppen, K.; Wiersma, D. A. *J. Phys. Chem.* **1995**, *99*, 8972. (b) Ma, J.; Dutt, G. B.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **1994**, *116*, 10619. (c) Piotrowiak, P. *Chem. Phys. Lett.* **1995**, *241*, 387.

[4] (a) Saltiel, J.; D'Agostino, J. T. *J. Am. Chem. Soc.* **1972**, *94*, 6445. (b) Rothenberger, G.; Negus, D. K.; Hochstrasser, R. M. *J. Chem. Phys.* **1983**, *79*, 5360. (c) Doany, F. E.; Heilweil, E. J.; Moore, R.; Hochstrasser, R. M. *J. Chem. Phys.* **1984**, *80*, 201.

[5] The twist angle is 31° from the X-ray data of Stezowski et al. (Stezowski, J. J.; Hildebrand,T.; Suissa, M. R.; Agranat, I. *Struct. Chem.* **1989**, *1*, 123) and 27° predicted by AM1.

[6] (a) Abrash, S.; Repinec, S.; Hochstrasser, R. M. *J. Chem. Phys.* **1990**, *93*, 1041; (b) Todd, D. C.; Jean, J. M.; Rosenthal, S. J.; Ruggiero, A. J.; Yang, D.; Fleming, G. R. *J. Chem. Phys.* **1990**, *93*, 8658.

[7] Nd:YAG, 532 nm, 7 ns fwhm, 100 mJ or Nd:YAG, 355 nm, 5 ns fwhm, 30 mJ. No photodegradation of the sample was observed.

[8] Upper limit estimated from the reconvolution of the 7 ns instrument response function.

[9] 308 nm XeCl excitation (microwave conductivity), 355 nm Nd:YAG excitation (dc conductivity).

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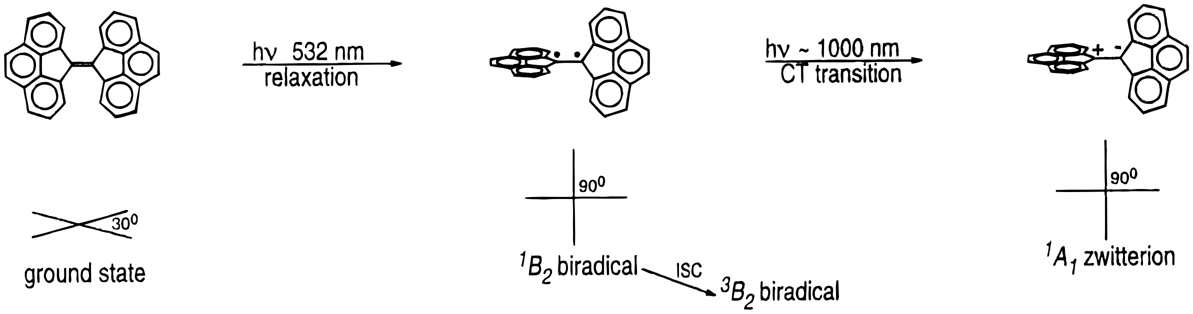
Scheme 1



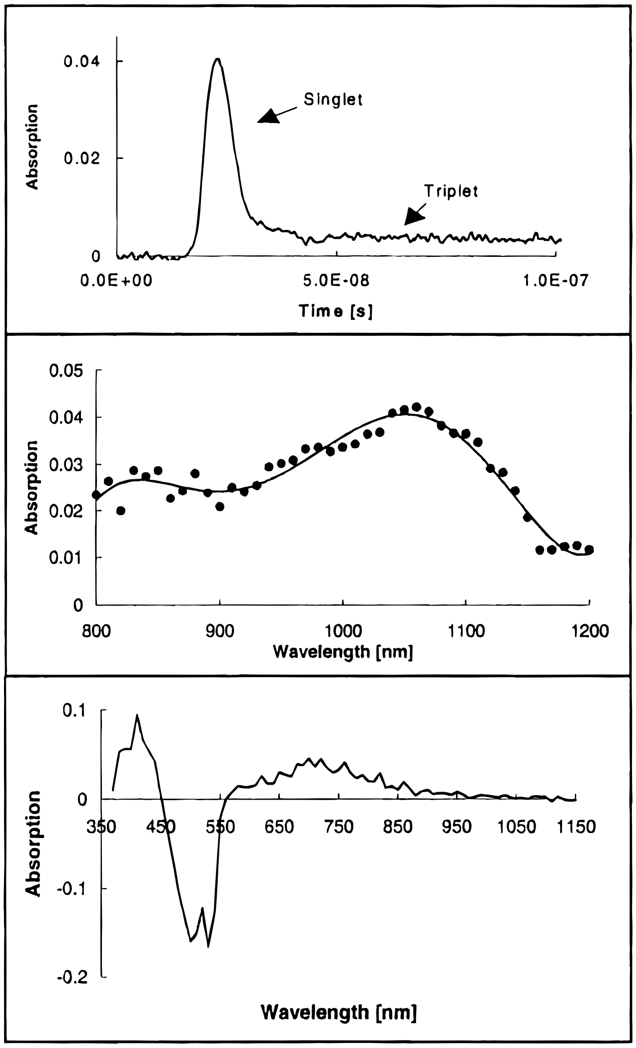


Figure 2. Transient absorption spectra of BPH in benzene, 532 nm excitation: (a) the transient profile at 1000 nm; (b) the $^1A_1 \leftarrow {}^1B_2$ singlet spectrum at 0 ns delay; and (c) the $^3B_2$ triplet spectrum at 430 ns delay.

species with a large dipole moment characteristic of a zwitterion.[11] Therefore, we conclude that both the lowest excited singlet and triplet state of BPH are the $\mu = 0$, 90°-twisted biradicals. This behavior is in contrast with most olefins in which the lowest excited singlet state is zwitterionic;[1] however, it fulfills the long held expectation that the increased aromaticity of the chromophores should stabilize the aryl radicals resulting from the 90° twist more than the corresponding radical anion and cation.[12]

On the basis of the above findings we assign the NIR excited singlet absorption (Figure 2b) to the *z*-polarized charge transfer transition between the $^1B_2$ biradical singlet state and the $^1A_1$ zwitterion singlet state of BPH. The transition is symmetry allowed in the D_{2d} geometry of the 90°-twisted BPH and, in agreement with the observation, it should be intense due to the large transition dipole and favorable Franck–Condon factors. To our knowledge, this is the first direct observation of such a CT transition in a twisted olefin.[13]

The preliminary measurements indicate that the appearance of the $^1A_1 \leftarrow {}^1B_2$ singlet spectrum does not change significantly when the polarity of the solvent is increased. This behavior is consistent with an electronic transition in which the initial state is not polar. However, the low energy of the transition (1.2 eV) implies that the energy gap between the $^1A_1$ state and the $^1B_2$ state is modest and it is reasonable to anticipate that in a sufficiently polar medium the increasing solvent stabilization of the zwitterion could reverse the order of the $^1A_1$ and $^1B_2$ states. This interesting possibility is being investigated.

The ~30% triplet yield of BPH is exceptionally high for a stilbene-like molecule, however, it is fully consistent with the biradical character of the lowest excited singlet state, which leads to efficient mixing and intersystem crossing between the $^1B_2$ and $^3B_2$ states. The triplet spectrum is tentatively assigned to the transverse transition localized at either "radical half" of the 90°-twisted BPH.

The investigation of the excited state dynamics of BPH, in particular the formation of the $^1B_2$ biradical state (Is the $^1A_1$ zwitterion an intermediate in the relaxation of the original Franck–Condon state?) and its disappearance (the competition between the ISC to the $^3B_2$ state and the decay to the ground state), is continuing at a higher time resolution.

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(10) Schuddeboom, W.; Jonker, S. A.; Warman, J. M.; Haas, M. P. d.; Vermeulen, M. J. W.; Jager,W. F.; Lange, B. d.; Feringa, B. L.; Fessenden, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 3286.

(11) The dipole moment of the fully charge separated state of BPH estimated on the basis of AM1 calculations of the charge distribution in the cyclopentaphenanthryl radical anion and radical cation is 21 D.

(12) Orlandi, G.; Palmieri, P.; Poggi, G. *J. Am. Chem. Soc.* **1979**, *101*, 3492.

(13) The two-photon $2^1A_1 \leftarrow 1^1A_1$ ground state-to-zwitterion state transition in a binuclear Mo complex, which in terms of electronic symmetry is closely related to our system, was first observed in the elegant experiment of Engebretson et al. (Engebretson, D. S.; Zaleski, J. M.; Leroi, G. E.; Nocera, D. G. *Science* **1994**, *265*, 759).