Evidence for a Planar Cyclically Conjugated 8π System in the Excited State: Large Stokes Shift Observed for Dibenz[*b,f*]oxepin Fluorescence

Deepak Shukla and Peter Wan*

Department of Chemistry, Box 3055
University of Victoria
Victoria, British Columbia, Canada V8W 3P6

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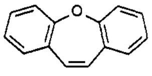
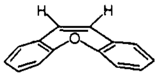
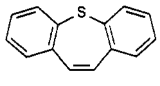
Recent studies from our laboratory[1] have shown that the driving force inherent in a number of photochemical reactions (photosolvolysis,[1c,f] photodecarboxylation,[1a] excited-state carbon acidity[1b,d,e]) involving dibenzannelated systems may be interpreted as being derived from attainment of a cyclically conjugated $4n\pi$ system on photoreaction. This has in turn led to the proposal that such systems have inherent stability on the excited-state surface, akin to the driving force associated with the formation of an aromatic product in ground-state reactions.[1a,f] We report here that the observed photophysical and associated photochemical behavior of dibenz[*b,f*]oxepin (**1**) indicate (i) the equilibrium geometry of this molecule is planar in S_1, in contrast to its highly nonplanar (bent) structure in S_0; (ii) the S_1 state shows very little photochemical reactivity, unlike related molecules lacking the 8π cyclic array; and (iii) there is an enhanced driving force for photochemical formation of this ring system. These observations indicate that the equilibrium geometry of photoexcited dibenz[*b,f*]oxepin (**1**) exhibits properties often associated with that of an aromatic molecule.


1 (planar)



1 (bent)

Interest in the photochemistry of xanthene and related compounds[2] prompted us to study the photochemistry of 10,11-dihydrodibenz[*b,f*]oxepin[3] (**3**). Photolysis of **3** in aqueous solution resulted in the formation of a spiro adduct which is believed to arise via initial aryl–oxygen bond homolysis, followed by coupling of the biradical by ipso attack of the phenyl radical to the alkyl position of the phenoxyl ring.[5] However, dibenz[*b,f*]oxepin[3] (**1**) was found to be photochemically inert. Although the extended conjugation inherent in **1** (*cis*-stilbene-like chromophore) lowers the singlet energy relative to **3**, the complete lack of homolysis of the aryl-oxygen bond was unexpected. Fluorescence emission studies of these compounds proved to be informative. Whereas the structureless fluorescence emission (λ_{max} = 300 nm) of **3** was found to be weak ($\Phi < 0.03$) and with no significant Stokes shift, the emission of **1** (λ_{max} = 478 nm in cyclohexane; 485 nm in H_2O; 10^{-5}–10^{-6} M) was highly Stokes-shifted (4720 cm^{-1} [6]; cf. 3310 cm^{-1} for biphenyl in cyclohexane[7]) with well-defined vibrational fine structure (progression ≈ 1500 cm^{-1}; assignable to aromatic ring stretching modes) (Figure 1) and relatively high quantum efficiency ($\Phi_f = 0.14 \pm 0.02$; $\tau = 10.4 \pm 0.2$ ns (cyclohexane); excitation spectrum identical to its absorption spectrum). Samples of **1** that were repeatedly purified by recrystallization (>99% purity by GC) gave identical results. The emission spectrum of dibenz[*b,f*]thiepin (**2**) also displayed a similarly large Stokes shift although its emission yield was considerably lower, most probably due to its enhanced intersystem crossing yield. Suberene (**4**) also possesses the *cis*-stilbene chromophore but lacks possible conjugation through the methylene carbon. Its emission spectrum did not exhibit the anomalous Stokes shift or enhanced vibrational fine structure. However, **4** was found to be highly fluorescent ($\Phi_f = 0.86 \pm 0.05$; $\tau = 5.04 \pm 0.04$ ns (CH_3CN)),[1b] which is a general characteristic of "locked" stilbenes.[8]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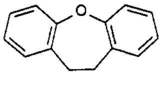
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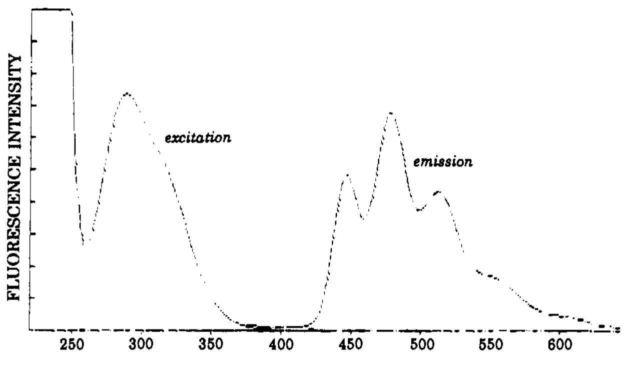
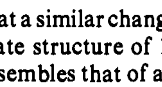


Figure 1. Fluorescence excitation and emission spectra of **1** in cyclohexane (uncorrected; λ_{ex} = 280 nm; λ_{em} = 480 nm; 23 °C).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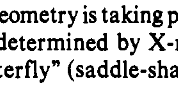

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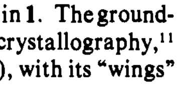

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A change from a nonpolar ground state to a more planar fluorescent excited singlet state has been well-documented for biphenyl and related compounds.[7,9] The rationale commonly accepted for this behavior of biphenyl is that there is enhanced double character in the bond joining the two phenyl rings in the excited state which is absent in the ground state.[10] We propose that a similar change in geometry is taking place in **1**. The ground-state structure of **1**, as determined by X-ray crystallography,[11] resembles that of a "butterfly" (saddle-shaped), with its "wings" highly bent backwards. The high degree of nonplanarity of the ground state is not surprising since simple Hückel-type arguments would predict that a planar structure would be highly unfavorable due to the antiaromatic nature of a planar 8π array in the internal ring. More sophisticated MO calculations confirm this.[12] The equilibrium excited-state geometry of **1** is that of a rigid planar

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[1] (a) Krogh, E.; Wan, P. *J. Am. Chem. Soc.* **1992**, *114*, 705. (b) Budac, D.; Wan, P. *J. Org. Chem.* **1992**, *57*, 887. (c) Krogh, E.; Wan, P. *Can. J. Chem.* **1990**, *68*, 1725. (d) Wan, P.; Budac, D.; Earle, M.; Shukla, D. *J. Am. Chem. Soc.* **1990**, *112*, 8048. (e) Wan, P.; Budac, D.; Krogh, E. *J. Chem. Soc., Chem. Commun.* **1990**, 255. (f) Wan, P.; Krogh, E. *J. Am. Chem. Soc.* **1989**, *111*, 4887.

[2] Huang, C.-G.; Shukla, D.; Wan, P. *J. Org. Chem.* **1991**, *56*, 5437.

[3] Prepared according to Boekelheide et al.[4]

[4] Hess, B. A., Jr.; Bailey, A. S.; Bartusek, B.; Beokelheide, V. *J. Am. Chem. Soc.* **1969**, *91*, 1665.

[5] The exact structure of the photoproduct has still to be finalized: Shukla, D.; Wan, P., unpublished results.

[6] The Stokes shift was calculated according to the definition given by Berlman.[7]

[7] Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*, 2nd ed.; Academic Press: New York, 1971.

[8] Turro, N. J. *Modern Molecular Photochemistry*; University Science Books: Mill Valley, CA, 1991.

[9] (a) Werner, T. C. In *Modern Fluorescence Spectroscopy*; Wehry, E. L., Ed.; Plenum Press: New York, 1976; Vol. 2. (b) Berlman, I. B. *J. Phys. Chem.* **1970**, *74*, 3085.

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[11] Drake, J. A. G.; Jones, D. W. *Acta Crystallogr.* **1982**, *B38*, 200.

[12] (a) Dewar, M. J. S.; Trinajstic, N. *Tetrahedron* **1970**, *26*, 4269. (b) Hess, B. A., Jr.; Schaad, L. J.; Holyoke, C. W., Jr. *Tetrahedron* **1972**, *28*, 3657.

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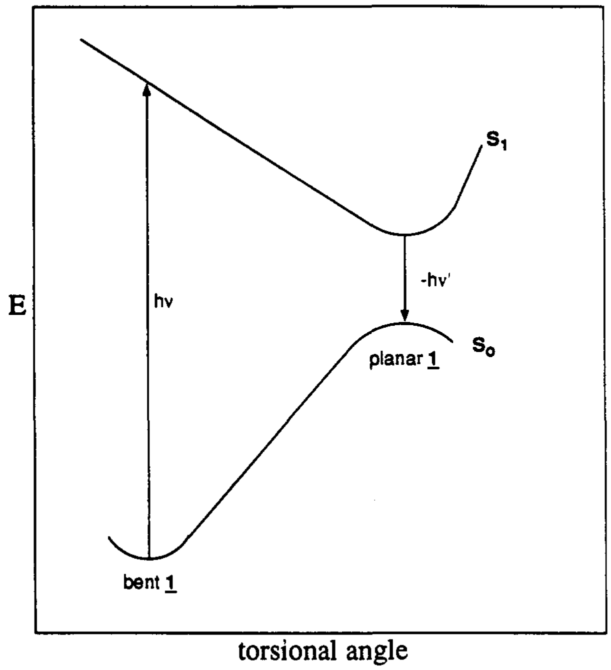

Figure 2. Potential energy surface plotted vs torsional angle for the ground and excited singlet states of **1** (energies not drawn to scale).

system, allowing for complete conjugation of the internal cyclic array. Indeed, the emission of **1**, with its associated fine structure, could be mistaken for the fluorescence emission of anthracene (which has similar overall appearance but is about 80 nm blue-shifted), a classic example of a strongly fluorescent rigidly planar (in both S_0 and S_1) aromatic molecule.[7-9,13]

Corroborating chemical evidence for the above proposal of a "stabilized" planar geometry of **1** in S_1 comes from the following reactivity data. Photolysis of **4** in the presence of Et_3N resulted in efficient photoreduction of the alkene moiety. The same reaction using **1** was much more sluggish. Photolysis of **4** in aqueous acid (≈10% H_2SO_4) resulted in significant photohydration of the alkene (overall addition of water), whereas **1** showed no reaction. Thermal acid-catalyzed dehydration of **5** was readily achievable (to give **4**), whereas **6** was inert to dehydration even in refluxing aqueous acid. On the other hand, *photodehydration* of **6** to give **1** in 1:1 H_2O–MeOH was observable even in dilute acid (pH 1–3), whereas **5** gave only the corresponding methyl ether, indicating that there is an enhanced driving force for forming **1** from **6** in the excited state which is absent in **5**.

In summary, evidence was presented supporting the proposal that on photoexcitation, nonplanar ground-state **1** undergoes fast torsional twisting to give a planar fluorescent state. The energetics of the process plotted as a function of torsional angle are illustrated in Figure 2. The driving force for this geometry change is the attainment of a cyclically conjugated system of 8π electrons in the central ring,[14] which is believed to have inherent stability on the excited-state surface, akin to "driving force" arguments used in ground-state reactions giving rise to products having $(4n + 2)\pi$ electrons in a cyclically conjugated array.[14,15]

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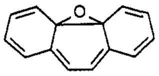
(13) A mechanism which was considered but ruled out involves initial electrocyclic 6π ring closure in the central ring, to give an oxygen-bridged valence isomer of **1**:



Adiabatic extrusion of the oxygen atom in a second step gives phenanthrene in S_1. However, the known fluorescence emission of phenanthrene[7] is ≈110 nm *blue-shifted* from that observed in this work. An alternative is that the emission is due to the oxygen-bridged valence isomer itself. This is unlikely since the mechanism would be equally favorable for suberene (**4**), for which no such long wavelength emission was observed. The long wavelength emission with the same Stokes shift is also observed for **1** at 77 K in a 2-propanol/ether glass (without the appearance of any new blue-shifted emission assignable to nonplanar **1**). This indicates that the torsional motion has a very low activational barrier.

(14) We have carried out π-SCF PPP calculations of planar **1** in both S_0 and S_1. The results show a greater degree of delocalization of the oxygen electron pair to the rest of the π system in S_1 than in S_0. Moreover, the electron density from the oxygen is distributed more in the central ring in S_1 than in S_0, consistent with our initial hypothesis that there is inherent driving force for this ring to achieve complete delocalization of the 8π electrons. Thus, it would be fair to think of this planarization as driven by formation of a cyclically conjugated 8π system in the internal ring rather than a 16π $(4n)$ system based on an electron count using the whole periphery of the molecule. Additional calculations indicate that, in general, dibenzannelation has only a minor effect on the electronic behavior of the internal ring system.

(15) A referee queried whether the triplet states of **1** and **2** would display a similar change in geometry. The techniques used to probe changes in S_1 geometry relative to S_0 are not useful for T_1 because of intrinsic differences in obtaining spectra. Our work on photogeneration of related cyclically conjugated systems[1] has shown that the corresponding triplet states behave differently. Based on these results and the fact that electron correlation would be different for T_1, we predict that the triplet state would probably not be planar.