

2,2-Dimethyl-2H-dibenzo[cd,k]fluoranthene, the First Kekulé Hydrocarbon with a Triplet Ground State

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Pioneering theoretical work of Hückel, Longuet-Higgins, Ovchinnikov, and Borden and Davidson, *inter alia*, has addressed the question of the applicability of Hund's first rule to molecules.¹ Experimental results have established that non-Kekulé biradicals may have a triplet or singlet ground state, depending on whether the topology leads to a large exchange interaction between the nonbonding electrons, as well as whether the nonbonding orbitals are sufficiently perturbed from degeneracy.²

On the other hand, the question of whether Kekulé molecules might forego maximum bonding and exist as ground-state triplet species has been less thoroughly examined. The well-known pseudo-Jahn-Teller distortion of cyclobutadiene,² along with the recently predicted low-symmetry singlet ground state of acenaphthalene,³ calls into question the proposition of a stable triplet ground state for a neutral Kekulé species with topology-imposed orbital degeneracy.⁴

For Kekulé species with a sufficiently small HOMO–LUMO gap, the exchange interaction should allow promotion of an electron to give a triplet ground state, but just how small a gap is necessary for such behavior is unknown.⁵ One can favor the biradical valence structures of a Kekulé π -system by "aromatic" stabilization, not available to the canonical structure. Heilbronner and co-workers have proposed cyclohepta[def]fluorene as a model of such a strategy,⁶ but numerous attempts at its synthesis have failed. We chose instead to investigate 2,2-dimethyl-2H-benzo[cd]fluoranthene (**1**) and 2,2-dimethyl-2H-dibenzo[cd,k]fluoranthene (**2**). These molecules compensate the formal loss of a double bond with the aromatic resonance energy of fluoranthene and benzo[k]fluoranthene, respectively, in the biradical [triplet] resonance form (Scheme 1).

In terms of molecular orbital theory, these biradicaloids combine exceptionally small HOMO–LUMO splittings, 0.17β for **1** and 0.11β for **2** at the Hückel level, with large local overlap of the HOMO and LUMO, ensuring a large exchange interaction

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(1) Hückel, E. *Z. Phys. Chem. B* **1936**, *34*, 339–347. Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265–274. Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 297–304. Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587–4594.

(2) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, *27*, 109–116.

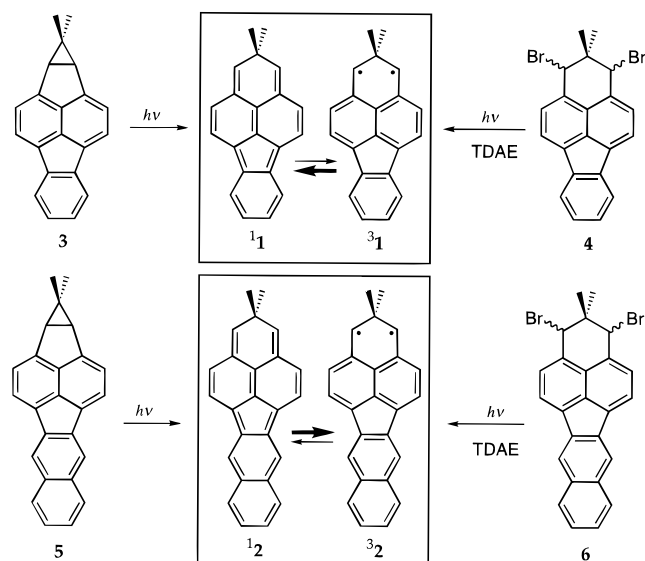
(3) Haag, R.; Schröder, D.; Zywiets, T.; Jiao, H.; Schwarz, H.; von Ragué Schleyer, P.; de Meijere, A. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1317–1319.

(4) O₂ and S₂, of course, are unable to "break symmetry" and have triplet ground states.

(5) An estimate has been made, but this did not consider the dependence of the exchange interaction on the "nondisjointedness" of the MOs: Hoffmann, R. *J. Am. Chem. Soc.* **1968**, *90*, 1475–1485.

(6) Baumgartner, P.; Weltin, E.; Wagnière, G.; Heilbronner, E. *Helv. Chim. Acta* **1965**, *48*, 751–764.

Scheme 1



($K_{HO,LU}$). The AO coefficients of these frontier MOs are in fact very similar to those of 1,8-naphthoquinodimethane, a robust ground-state triplet non-Kekulé biradical.⁷

Biradicals **1** and **2** were generated photochemically in rigid organic glasses from two separate precursors each (Scheme 1), cyclopropanes **3** and **5** as well as dibromides **4** and **6**,⁸ and investigated by optical and EPR spectroscopies. Platz, Migirdicyan, and co-workers⁹ have demonstrated that dihalides can be photo-dehalogenated to the corresponding biradicals in the presence of tetrakis(dimethylamino)ethene (TDAE).

Hydrocarbon **1** displays electronic transitions throughout the visible and well into the near infrared. Figure 1 shows the spectrum obtained after irradiation of cyclopropane **3** in a methyltetrahydrofuran (MTHF) glass at 81 K with a 200 W medium-pressure Hg arc lamp filtered with a 365 nm bandpass filter. The 0–0 band of the longest-wavelength transition has its maximum at 1284 nm. On the basis of loss of starting material, the molar absorption coefficients are estimated at $\log \epsilon \approx 3.0$ for the bands at 1284 and 750 nm, $\log \epsilon \approx 3.9$ for the band at 528 nm, responsible for orange-red color of **1**, and $\log \epsilon \approx 4.7$ for the band at 380 nm. Compound **1** proved to be photochemically stable: prolonged irradiation with the unfiltered output of the Hg arc lamp caused no change in the spectrum. On the other hand, **1** was found to decay rapidly and irreversibly upon thawing the matrix. The same spectral features were obtained by irradiation of a mixture of dibromide **4** and TDAE in a dibutyl phthalate glass at 165 K.

Markedly different results were obtained for hydrocarbon **2**, as shown in Figure 2. Irradiation of cyclopropane **5** in MTHF at 81 K caused the formation of new peaks in the visible and UV only. The longest-wavelength absorption was observed at 665 nm, ($\log \epsilon \approx 3.0$); no transitions of lower energy were discernible out to 2200 nm,

(7) Platz, M. S.; Carrol, G.; Pierrat, F.; Zayas, J.; Auster, S. *Tetrahedron* **1982**, *38*, 777–785. Hasler, E.; Gassmann, E.; Wirz, J. *Helv. Chim. Acta* **1985**, *68*, 777–788. Burnett, M. N.; Boothe, R.; Clark, E.; Gisin, M.; Hassaneen, H. M.; Pagni, R. M.; Persy, G.; Smith, R. J.; Wirz, J. *J. Am. Chem. Soc.* **1988**, *110*, 2527–2538. Hasler, E.; Hörmann, A.; Persy, G.; Platsch, H.; Wirz, J. *J. Am. Chem. Soc.* **1993**, *115*, 5400–5409.

(8) Synthesis involved Friedel–Crafts acylation of fluoranthene (or benzo[k]fluoranthene) with dimethylmalonyl chloride, followed by LAH reduction and bromination with PBr₃, to form **4** (**6**). Dehalogenation of **4** (**6**) with Zn dust in DMF yielded **3** (**5**). Experimental details will be published elsewhere.

(9) Haider, K.; Platz, M. S.; Després, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318–2320. Biewer, M. C.; Biehn, C. R.; Platz, M. S.; Després, A.; Migirdicyan, E. *J. Am. Chem. Soc.* **1991**, *113*, 616–620.

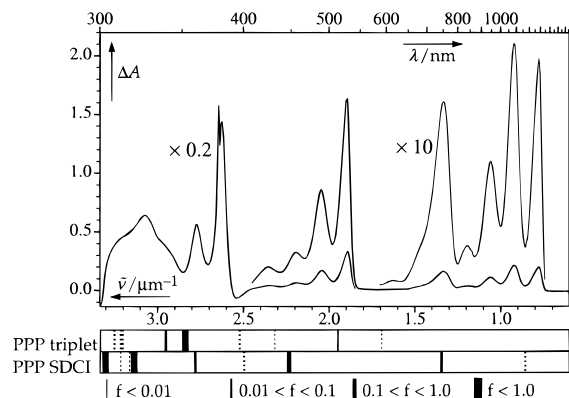


Figure 1. Difference spectrum obtained by 365 nm irradiation of cyclopropane **3** in MTHF glass at 81 K and results of PPP calculations on **1** (see text). The UV region was determined in a separate experiment at lower concentration. Calculated polarizations are indicated by a solid (long in-plane axis) or dotted (short in-plane axis) line.

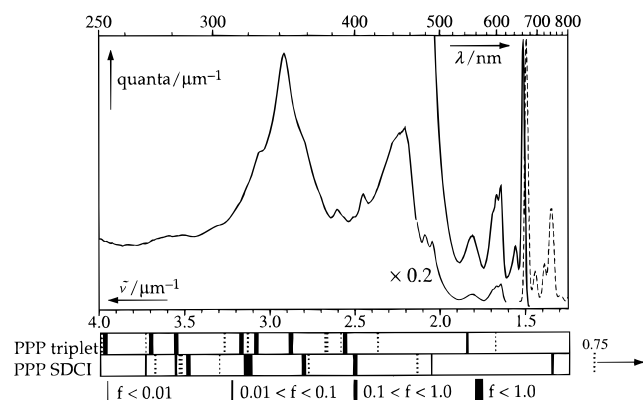


Figure 2. Fluorescence excitation (solid) and emission (dashed) spectra of **2** generated by 405 nm irradiation of cyclopropane **5** in MTHF glass at 77 K and results of PPP calculations on **2** (see text). The excitation spectrum was obtained in two separate experiments at different concentrations.

above which wavelength MTHF is opaque due to vibrational overtones. There was also a very strong absorption at 346 nm ($\log \epsilon \approx 4.8$). Like **1**, biradical **2** also proved photostable: no decomposition of **2** was observed even upon irradiation with the unfiltered Hg arc lamp, and numerous isosbestic points were retained during its formation. Hydrocarbon **2** is somewhat more thermally labile than **1**, decaying slowly in a rigid dibutyl phthalate matrix between 130 and 150 K.

The visible absorption of **2** was accompanied by a strong red emission which has a sharp 0–0 peak at 670 nm and vibrational structure tailing into the near infrared (Figure 2). All features of the absorption spectrum were reproduced in the excitation spectrum. The emission was also observed upon excitation with a 351 nm pulse from a XeF excimer laser with a pulse width of *ca.* 25 ns, and its decay followed the temporal shape of the laser pulse. It is, therefore, a fluorescence with a lifetime of less than 25 ns.

Generation of **1** from either the cyclopropane **3** or the dibromide **4** by irradiation in MTHF glasses at 89 K in the cavity of an EPR spectrometer gave no signals assignable to a persistent triplet species under conditions where the orange-red color characteristic of **1** was present. Irradiation of cyclopropane **5** in an MTHF glass at 89 K with 405 nm light, on the other hand, rapidly produced a species whose EPR spectrum, persistent for hours in the dark, is diagnostic for a randomly-oriented triplet. It is characterized by zero-field splitting parameters $|D/hc| = 0.0210 \text{ cm}^{-1}$ and $|E/hc| = 0.0034 \text{ cm}^{-1}$ and a signal at half field. The same spectral features were obtained upon irradiation of a glassy matrix containing dibromide **6** and TDAE.

The electronic transitions of **1** and **2** were calculated using PPP SCF CI methods for both the singlet¹⁰ and triplet¹¹ manifolds. Reasonable agreement with experiment for **1** (Figure 1) was achieved only for the singlet and only by inclusion of doubly excited configurations in the configuration interaction matrix. Of particular interest are the first and second transitions, which are to states of primarily HOMO–LUMO singly and doubly excited character, respectively. Such states have no counterpart in the triplet manifold, and the location, intensity and polarization¹² of the corresponding transitions are in excellent agreement with the calculation. This indicates that **1** has a singlet ground state, ¹**1**, consistent with the lack of an EPR signal.

The longest-wavelength band observed for compound **2** occurs at much *shorter* wavelength than in the smaller system **1** and also than the first two transitions calculated for ¹**2** [1338 and 759 nm]. While the longest-wavelength band might be obscured by solvent vibrational absorption, the stronger transition to the S₂ state, correctly predicted for ¹**1**, should have been easily visible. Moreover, the observation of strong fluorescence emission corresponding to the transition at 665 nm indicates that there are no longer-wavelength bands (Kasha's rule). Although the agreement between the experimental spectrum and the calculated triplet spectrum is only mediocre, the experimental spectrum is strongly reminiscent of those of triplet 1,8-naphthoquinodimethanes, which show sharp, highly structured, relatively weak bands ($\log \epsilon \approx 2-3$) around 500 nm and a strong ($\log \epsilon \approx 4.5$) peak around 330–340 nm.⁷ This already suggests that **2** was observed in its lowest triplet state, ³**2**, and this is strongly supported by the observed EPR spectrum, which displayed a linear Curie plot in the range of 8–75 K, indicating a triplet ground state.¹³ The *D*-value obtained, 0.0210 cm^{-1} , is similar to those found for various 1,8-naphthoquinodimethanes, which range from 0.018 to 0.029 cm^{-1} .⁷

The remarkable differences in the spectroscopic properties of **1** and **2** are the result of the different ordering of the lowest singlet and triplet states for the two compounds. In the case of **1**, the ground state is of singlet multiplicity; **2** is a ground-state triplet. Compound **2** is the first representative of a fundamentally new class of high-spin molecules.

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(10) We thank Prof. J. Waluk, Institute of Physical Chemistry, Warsaw, for making available a PPP SDCI program, which includes all singly and doubly excited configurations within a 5×5 orbital space. C_{2v} symmetry was assumed, and all bond lengths set to 140 pm. Standard parameters: $I_u = 11.42 \text{ eV}$, $A_u = 0.58 \text{ eV}$, $\gamma_{uu} = 8.89 \text{ eV}$, and $\beta_{uv} = -2.6 \text{ eV}$.

(11) Gisin, M.; Wirz, J. *Helv. Chim. Acta* **1983**, *66*, 1556–1568. All singly excited configurations were included up to a 10×10 orbital space. The geometry used was the same as for the singlet manifold (ref 10). Standard parameters: $\gamma_{uu} = 10.84 \text{ eV}$ and $\beta_{uv} = -2.318 \text{ eV}$.

(12) Determined in stretched polyethylene. Michl (Michl, J.; Thulstrup, E. W. *Spectroscopy with Polarized Light*; VCH Publishers: New York, 1986) offers an excellent introduction to this technique.

(13) Two conceivable yet unlikely alternative explanations can be formulated: (1) a linear Curie plot is consistent not only with a triplet ground state but also with very nearly degenerate lowest singlet and triplet states ($E_T - E_S \leq 0.02 \text{ kcal/mol}$); (2) the Berson group recently reported a case of long-lived spin isomerism (ref 14), for which a Curie plot is meaningless. However, the fact that all absorption features are reproduced in the fluorescence excitation spectrum of **2**, along with the observed persistence of the EPR spectrum down to 5 K, corroborates the case for a triplet ground state of **2**. Finally, the factors believed to be responsible for spin isomerism in Berson's case are unlikely to apply to **1** or **2**, which have little conformational freedom.

(14) Bush, L. C.; Maksimovic, L.; Feng, X. W.; Lu, H. S. M.; Berson, J. A. *J. Am. Chem. Soc.* **1997**, *119*, 1416–1427.