Significantly, prolonged irradiation of the model triplet species **3** at λ 425 nm produced no change in EPR signal intensity or line shape.

The signal intensity of the quintet spectrum was linear (r = 0.988) with reciprocal temperature over the range 15–70 K. At least part of the curvature observed at the lowest temperatures was caused by saturation, as was demonstrated by a saturation plot.

Although a thorough discussion[8b] of alternatives must be deferred to a full paper, these data are most reasonably interpreted to mean that the ground state of **1** is quintet and that no nearby state is thermally populated within the experimental temperature range. Strictly, Hund's Rule does not apply here, because the double heteroatom perturbation of the π-electron[15] system of **1** prevents degeneracies of half-occupied orbitals at the single-electron theoretical level. That the state of highest multiplicity nevertheless is favored demonstrates the powerful influence of electron repulsion effects in non-Kekulé molecules.

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(15) For evidence that **2**, **3**, and hence probably **1** are π- rather than σ-radicals, see: Hilinski, E F.; Seeger, D. E.; Matlin, A. R. *J. Am. Chem. Soc.*, submitted for publication.

2,6-Dimethyleneanthracenediyl-4,8-dioxy. High-Spin Ground State of a Disjoint Biradical That Has No Hückel NBMO Degeneracy

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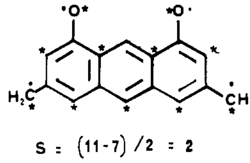
Theory predicts that disjoint biradicals, which have NBMO wave functions confinable to separate spatial domains, are likely to violate Hund's Rule and have low-spin ground states as a consequence of dynamic spin polarization.[1-3] Moreover, semiempirical valence bond considerations[4] suggest that for alternant π-systems, the total spin of the ground state will be given by $S = (n^* - n)/2$, where n^* and n are the numbers of starred and unstarred π-centers. Non-Kekulé molecules with $n^* = n$ can be shown[1] to be disjoint, so that both lines of argument favor a singlet ground state in such cases. The present paper describes a test of these theories.

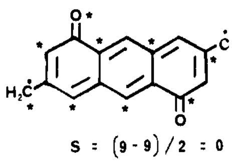
The two non-Kekulé systems **1**[5] and **2** illustrate the contrasting



S = (11-7)/2 = 2

PREDICTED: QUINTET

1



S = (9-9)/2 = 0

PREDICTED: SINGLET

2

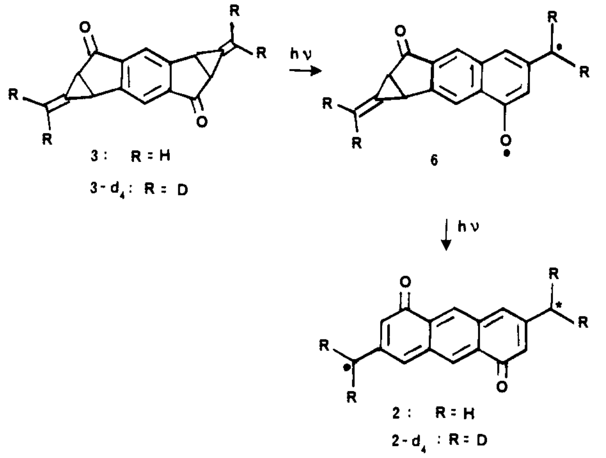
predictions evoked by a seemingly superficial alteration of atomic connectivity.

Table I. Experimental Refutations of Candidate Structures for the Carrier of the Secondary EPR Signal[a]

	experiment		
candidate structure	1 (solv.)	2 (label)	3 (intensity)
a [^{2}**2**-H· + ^{2}R·]	*X*	*X*	*X*(?)
b ^{3}[**2**-H· R·]	*X*	*X*	
c ^{2}[**2**-H·]			*X*
d ^{2}[R′·]	*X*	*X*	*X*
e ^{3}[**2**]			

[a] A matrix element X_{ij} indicates refutation of structure i by experiment j.

Methods similar to those employed in the companion paper[5] led to two independent syntheses of a separable mixture of two stereoisomers of the pentacyclic diketone **3**, which is a precursor of **2**. Irradiation (high-pressure Hg arc) of a degassed, glassy solution of either stereoisomer of **3** in 2-methyltetrahydrofuran (2-MTHF) at 77 K in the cavity of the electron paramagnetic resonance (EPR) spectrometer (microwave frequency 9.181 GHz) for 30 s produced a persistent spectrum (Figure 1A) and a red-orange color. The visual color, the magnitude of the zero-field splitting, and the $\Delta m_s = 2$ transition near 1630 G were very similar to those of 3-methylenenaphthalenyl-1-oxy[6] and suggest that the signal carrier is the triplet biradical **6**. Further irradiation at λ ≥ 425 nm caused the primary triplet signal to disappear and be replaced by a narrow intense secondary pattern (Figure 1B). We assign the secondary pattern to a triplet state of the tricyclic biradical **2** for the following reasons:



(1) The spectra observed in ethanol and perdeuterioethanol glasses were identical with those in 2-MTHF. This suggests that no part of the signal carrier is derived from the solvent.

(2) When the experiment was repeated with deuterium-labeled diketone, **3**-d_4, the secondary pattern was markedly simplified (Figure 1C) by the elimination of the hyperfine interaction. The signal carrier thus must be structurally derived from **3**.

(3) The doubly integrated intensities of the secondary and primary spectra were the same within experimental error (±8%). This is consistent with preservation of the total number of spins during the photoconversion of the primary to the secondary signal carrier.

The conceivable candidates for the carrier of the secondary spectrum are (a) two doublet radicals, **2**-H· and R·, formed, for example, by hydrogen transfer from solvent RH to **2**, (b) a triplet radical pair, formed as in a, (c) a doublet derived from the **2**-H· portion of the pair a or b, (d) a doublet derived from the solvent portion R· of the pair a or b, and (e) the triplet biradical **2**. The predicted changes in signal intensities[5,7a] for quantitative con-

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(1) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(2) See also: Hückel, E. *Z. Phys. Chem., Abt. B* **1936**, *34*, 339.

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(4) (a) Ovchinnikov, A. A. *Theor. Chem. Acta.* **1978**, *47*, 297. (b) Misurkin, I. A.; Ovchinnikov, A. A. *Russ. Chem. Rev.* (*Engl. Transl.*) **1977**, *46*, 967. (c) Klein, D. J. *Pure Appl. Chem.* **1983**, *55*, 299. (d) Klein, D. J.; Nelin, C. J.; Alexander, S.; Matsen, F. A. *J. Chem. Phys.* **1982**, *77*, 3101.

(5) For the synthesis of the tetraradical **1**, see: Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, preceding article.

(6) Seeger, D. E.; Hilinski, E. F.; Berson, J. A. *J. Am. Chem. Soc.* **1981**, *103*, 720.

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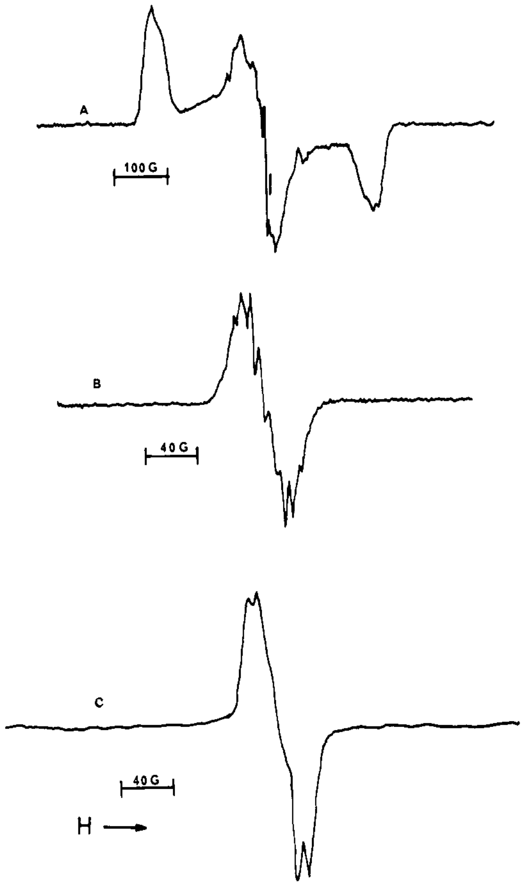


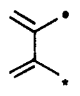
Figure 1. (A) $\Delta m_s = 1$ region of the primary EPR spectrum obtained by brief irradiation of a 2-MTHF glass of **3**. The vertical bar marks 3260 G. The $\Delta m_s = 2$ transition near 1630 G was also observed but is not shown here. The triplet ZFS parameters are $|D|/(hc) = 0.020$ cm^{-1} and $|E|/(hc) = 0.007$ cm^{-1}. (B) Secondary spectrum (at reduced amplitude) obtained after prolonged irradiation of the preparation of A ($\lambda > 425$ nm). (C) Spectrum obtained by processing **3**-d_4 through the same steps used to obtain B. The triplet ZFS parameters are $|D|/(hc) = 0.0025$ cm^{-1} and $|E|/(hc) = 0.0009$ cm^{-1}.

versions of **6** are to a, a decrease of 25%, to c or d, a decrease of 62.5%, and to b or e, no change. Experiment 3 probably is not quite sensitive enough to rule out a, but it clearly eliminates c and d and is consistent with b and e.

Table I displays a truth matrix that tests the compatibility of the candidates with the experimental facts. The only candidate to survive this scrutiny is the triplet biradical **2**.[7b]

A Curie study of a 2-MTHF glass of the secondary signal carrier showed the intensity to be linear with $1/T$ between 15 and 90 K ($r = 0.991$). If the slight convexity at the low-temperature end of the plot is assigned, for the sake of argument, entirely to thermal population of a triplet state from a lower energy singlet, the singlet cannot lie more than 0.024 kcal/mol below the triplet. Thus, either the singlet and triplet are almost exactly degenerate, or more plausibly, the triplet is the ground state of biradical **2**.

Triplet states of the simpler disjoint biradical system tetramethyleneethane have been observed in the parent compound[10] **7** and a derivative[11] **8**. Unfortunately, it is not known whether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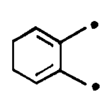
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these triplet species are the ground states and, if so, whether they are planar. The biradical **2** therefore represents a rare experimental test of the energetic consequences of disjoint character in a non-Kekulé compound.[12,13] Apparently in the present case, this property is insufficient to produce a low-spin ground state. Although a generalization of this finding clearly would be premature, one cannot suppress completely the conjecture that even in the absence of the degeneracy that forms the basis of the atomic Hund's Rule, a quasi-Hund's Rule may operate in non-Kekulé molecules.

Acknowledgment. We thank the Dox Foundation for a graduate fellowship and the National Science Foundation for support of this work and the NSF Northeast Regional NMR Facility at Yale University.

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(7) (a) Cf: Platz, M. S.; Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358. (b) That no $\Delta m_s = 2$ transition could be observed for this species is not surprising, since the ZFS is very small, and the two-quantum transition is strongly forbidden even at low field. The total spectral width of about 40 G for the secondary signal excludes the previously discussed[8] type of triplet structure resulting from "wrong bond" photolysis, i.e., cleavage of a side bond of **3** rather than a bridge bond. This would lead to a vinyl radical, whose hyperfine splitting alone would be larger than the observed total width.[9]

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(12) For an excellent review of recent results on cyclobutadiene, a disjoint Kekulé compound, see: Borden, W. T. "Diradicals"; Wiley: New York, 1982; p 46.

(13) The assignment of a triplet ground state to the Schlenk-Brauns hydrocarbon, a non-Kekulé compound which, *if planar*, would be disjoint, rests on a Curie plot covering a narrow, high-temperature region in which curvature is difficult to detect: Schmidt, R.; Brauer, H.-D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 506.

Electric Field Gradient at Iron in Dicarbonyl Complexes of (Tetraphenylporphyrinato)- and (Octamethyltetrabenzoporphyrinato)iron(II)

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In diamagnetic $Fe(P)L_2$ complexes[1] the electric field gradient (EFG) at iron is due primarily to an imbalance of electron densities in the iron 3d valence orbitals,[2] and in all such species for which the sign of V_{zz}, the principal component of the EFG tensor, is known, it is positive.[3-8] This oblate charge distribution leads one to expect V_{zz} to increase with increasing π acceptance or decreasing

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(1) Abbreviations: P = dianion of a porphyrin or phthalocyanine; L = nitrogen- oxygen-, or sulfur-donor ligand; TPP, OMBP, Pc = the dianions of tetraphenylporphyrin, octamethyltetrabenzoporphyrin, and phthalocyanine, respectively; pip = piperidine; py = pyridine; diox = anion of a dioxime ligand.

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