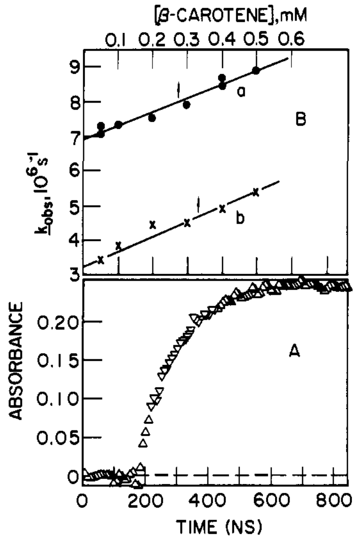
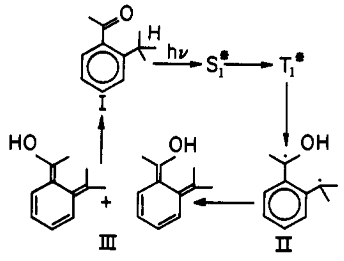


Figure 1. (A) Experimental trace for growth of transient absorbance (at 525 nm) upon 337.1-nm laser flash photolysis of a deaerated solution of 0.05 M *o*-methylacetophenone and 3.0×10^{-4} M β-carotene in toluene. (B) Plots of the observed, first-order rate constant for the growth of β-carotene triplet absorbance vs. β-carotene concentration, with *o*-methylacetophenone, (a) and 2,4,6-trimethylbenzaldehyde (b) as the substrates in toluene.

Scheme I



of 145 and 310 ns for the triplet energy donors derived from OMA and TMB, respectively.

The only possible way in which the relatively slow formation of β-carotene triplet can be explained is the energy transfer from the biradicals II formed via intramolecular hydrogen abstraction in the carbonyl triplets. Note that the lifetime of 145 ns for the triplet precursor in the case of OMA is comparable to that reported[3] for the corresponding biradical enol, 130 ns in cyclohexane. The carbonyl triplets themselves are too short-lived[7] to be identifiable as the donors. More importantly, addition of carbonyl triplet quenchers (short-lived) such as 2,5-dimethyl-2,4-hexadiene and styrene, each up to 0.3–0.4 M, does not make any difference in the observed rate constant for the growth of β-carotene triplet absorption (at a particular [β-carotene]). However, the yield of the carotenoid triplet, measured in terms of plateau absorbance, gradually decreases as the diene or styrene concentration is increased. This proves conclusively that the precursor for the carotene triplet is a product derived from the triplets of carbonyl compounds. The possibility that the observed carotene-related transient could be a reduction product formed by hydrogen or electron transfer from the ketyl sites of biradicals is ruled out by experiments in which *p*-methoxyacetophenone, an electron-rich ketone, is flash photolyzed in the presence of β-carotene and excess of triethylamine; the intense T–T absorption of β-carotene observed in the absence of triethylamine is nearly totally suppressed when the latter is added in sufficiently large concentration to quench the *p*-methoxyacetophenone triplet and thereby generate the (*p*-methoxyphenyl)hydroxymethyl radical.

Using styrene as a carbonyl triplet quencher over a wide range of concentrations (≤35 mM), we have obtained Stern–Volmer plots for the quenching of β-carotene triplet yields (at constant [β-carotene]) with OMA and TMB as substrates. With TMB, the plot is linear with a slope ($k_q^T\tau^T$) of 5.0 M^{-1}, giving a lifetime of 0.6 ns for the TMB triplet (on the basis of $k_q^T = 8.0 \times 10^9$ M^{-1} s^{-1}, measured from benzophenone triplet quenching by styrene). On the other hand, the plot in the case of OMA is bent sublinearly, suggesting the involvement of more than one carbonyl triplets as precursors of biradicals. Analysis[8] of the data in terms of contributions from syn (short-lived) and anti (long-lived) forms of OMA triplets, as proposed by Wagner,[2] gives the corresponding $k_q^T\tau^T$-values as 1.1 and 74 M^{-1}, respectively, with the former contributing to the extent of 75%. Thus, the lifetimes of the two triplets are 0.14 and 9.3 ns, respectively (in toluene). A comparison of the data concerning biradical and carbonyl triplet lifetimes obtained in toluene by the present method to those for the same systems measured in wet acetonitrile by paraquat reduction[7] shows that both biradical and triplet lifetimes in toluene are substantially shorter. Pronounced solvent effect on biradical lifetimes has been documented in previous studies.[3,9]

A few other carotenoids, namely, β-apo-8′-carotenal (a polyenal with 10 double bonds including C=O) and lycopene, are found to accept triplet energy from the biradical derived from TMB, in the same fashion as β-carotene does. The triplet energy of β-carotene has been estimated[10] within the limits of 21 and 25 kcal/mol. Since the rate constant for energy transfer to β-carotene is almost that of diffusion, the biradicals (triplet states of photoenols) must have triplet energies as high as the carotene. In view of this, the results of semiempirical calculations[3] that put the triplet photoenol of OMA ~10 kcal/mol above the ground state become subject to reevaluation.

Acknowledgment. The authors are grateful to Dr. E. J. Land and Hoffman-La Roche for generous gifts of β-apo-8′-carotenal.

Registry No. OMA, 577-16-2; OMB, 529-20-4; TMB, 487-68-3; β-carotene, 7235-40-7; β-apo-8′-carotenal, 1107-26-2; lycopene, 502-65-8.

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(8) The data were fit into an equation of the form

$$\Delta OD_0^T/\Delta OD^T = 1/\sum_{i=1,2} \alpha_i(1 + k_{q,i}^T\tau_i^T[Q]), \qquad \sum_{i=1,2} \alpha_i = 1$$

where ΔOD^T represents the plateau absorbance of β-carotene triplet at a styrene concentration [Q], ΔOD_0^T represents the same in the absence of styrene, and α_i's are fractional contributions of the two triplets.

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Quintet Ground State of a Non-Kekulé Tetraradical, 3,6-Dimethyleneanthracenediyl-1,7-dioxy

David E. Seeger and Jerome A. Berson*

*Department of Chemistry, Yale University
New Haven, Connecticut 06511*

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As a test[1] of theoretical predictions[2h-m] of the total electronic spin of molecules, we have synthesized 3,6-dimethyleneanthracenediyl-1,7-dioxy (**1**), a new type of π-conjugated non-Kekulé system with four unpaired electrons. This species may

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(1) For a related study, see: Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, accompanying article.

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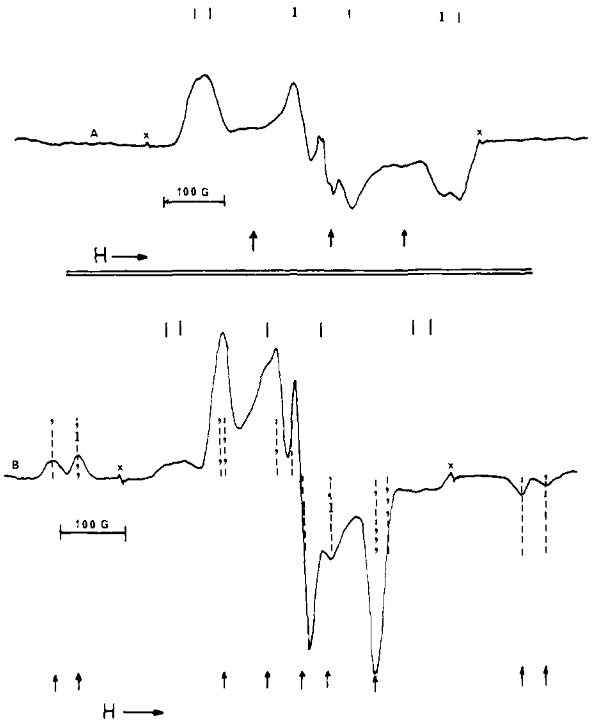
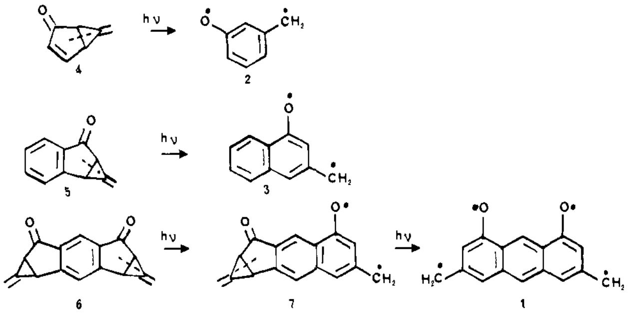


Figure 1. (A) $\Delta m_s = 1$ region of the primary EPR spectrum from photolysis at $305 \le \lambda \ge 525$ nm of a frozen 2-methyltetrahydrofuran solution of **6** after 30 s. The triplet ZFS parameters are $|D|/(hc) \simeq 0.020$ cm^{-1} and $|E|/hc) \simeq 0.005$ cm^{-1}. (B) EPR spectrum from prolonged photolysis at $\lambda \ge 425$ nm of the preparation shown in Figure 1A. The X's mark H atom resonances. For an explanation of the lines and arrows, see text. The quintet ZFS parameters are $|D|/(hc) = 0.01174$ cm^{-1} and $|E|/(hc) = 0.00315$ cm^{-1}.

be looked upon as a primitive prototype of a hypothetical extended array in which an indefinitely large network of electrons with parallel spins displays ferromagnetic properties.[1-3]

The previously reported[4-8] generation of the biradicals **2** and **3** by photolysis of the enone **4** and benzoenone **5** serves as models for the synthesis of **1** from the pentacyclic diketone **6** by sequential photolyses of the two bridge bonds.



The synthesis[8] of the pentacyclic diketone **6** was achieved in six steps from *s*-hyrindacene-1,7-dione, which in turn was prepared by two independent routes from the known substances *m*-benzenedipropionic acid[9] and *s*-hydrindacen-1-one.[10]

Irradiation (305 nm ≤ λ ≤ 525 nm) of a degassed frozen (77 K) solution of either stereoisomer of the pentacyclic diketone **6** at 36 K for 30 s in the microwave cavity of the electron paramagnetic resonance (EPR) spectrometer (Varian E-9) produced an orange color and an EPR spectrum (Figure 1A) very similar to those previously observed[5,6] in the irradiation of the tricyclic model compound **5**. In particular, the "forbidden" $\Delta m_s = 2$ transition diagnostic of a state with $S \ge 1$ was observed at ~1620 G. The total spectral width (approximately $2D$) of the $\Delta m_s = 1$ region was ~450 G, essentially the same as that observed[5,6] for the triplet ground state of the model biradical **3**. The synthetic method and spectroscopic features permit the assignment to the carrier of the main EPR signal, at the primary level of photolysis, of a triplet state of structure **7**, in which one of the two bridge bonds of **6** has been opened.

The $\Delta m_s = 1$ region of the primary spectrum showed some additional resonances (marked by arrows in Figure 1A). These signals almost entirely replaced those of **7** (marked with lines in Figure 1A) when the optical filter was changed to pass $\lambda \ge 425$ nm and irradiation was continued for 180 m. The new spectrum consisted of at least nine discernible, widely spaced lines that spanned a range of nearly 800 G (Figure 1B). It persisted after irradiation was stopped, and the shape was independent of temperature over the range 15–80 K. A search at lower fields for additional absorptions corresponding to $\Delta m_s \ge 2$ was unsuccessful. We assign this secondary spectrum to a quintet state of the tetraradical **1** on the following grounds.

The anisotropic electron spin dipolar interactions of a randomly oriented quintet species with an applied magnetic field can give rise to a maximum of 12 absorptions in the $\Delta m_s = 1$ region (four for each canonical orientation of the molecular axes).[2e,11,12] The nine lines observed here suggest three accidental superpositions of resonant fields. Approximate values for the zero-field splitting (ZFS) parameters D and E were obtained from the positions of the two highest field transitions (H_1 and H_2) combined with the perturbational solution[2a,b] of the quintet Hamiltonian: $D = (H_1 - H_0)/3$ and $H_2 = H_0 + {}^3/_2(D + 3E)$. The spectrum was then simulated by diagonalization of the $S = 2$ approximate Hamiltonian matrix[2e,11,12] for each of the three canonical orientations at regular intervals over the magnetic field range, using as input data the microwave frequency, D, E, and g. Intensities were not calculated, and higher order spin–orbit terms[13] were neglected.

The best fit to the turning points of the spectrum was obtained with $|D|/(hc) = 0.01174$ cm^{-1}, $|E|/(hc) = 0.00315$ cm^{-1}, and $g = 2.0054$. These parameters led to the calculated transitions (dashed lines) shown in Figure 1B, which match all the observed values with an error of 0.1–2.3% of the total spectral width. In particular, the three anticipated coincidences are reproduced by the calculation.

Because the number of spins doubles and because the quintet signal is inherently ${}^6/_5$ as intense per electron as the triplet signal,[14] a quantitative conversion $\mathbf{7} \rightarrow \mathbf{1}$ would have increased the doubly integrated signal intensity by a factor of 2.4. Actually, since **7** was not formed completely free of **1** in the initial photolysis and since the $\mathbf{7} \rightarrow \mathbf{1}$ secondary photolysis reaction did not reach completion because of the internal filter effect as **1** accumulated, the observed increase was only 1.7. This was nevertheless sufficient to demonstrate the net formation of a higher spin (quintet) signal carrier from a lower spin (triplet) paramagnetic precursor.

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(14) (a) The probability of an EPR transition is proportional to ΔN, the population difference between the sublevels of the paramagnetic state. If the g factors for isomeric states of different multiplicity are similar, the ΔN and hence the transition probability for each state will be inversely proportional to the number of sublevels. Four electrons will be spread almost evenly over five or six levels for the quintet and two triplets, respectively. Hence the intensity factor per electron will be ${}^6/_5$. (b) For an earlier discussion, see: Platz, M. S.: Berson, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 2358.

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.

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. Professors R. J. Cross and J. M. McBride and Mr. Ronald Merrill kindly provided some of the computer programs and helpful advice.

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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

David E. Seeger and Jerome A. Berson*

Department of Chemistry, Yale University
New Haven, Connecticut 06511

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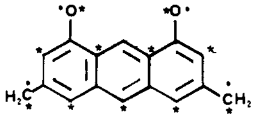
Theory predicts that disjoint biradicals, which have NBMO wave functions confinable to separate spatial domains, are likely to violate Hund's Rule and have low-spin ground states as a consequence of dynamic spin polarization.[1-3] Moreover, semiempirical valence bond considerations[4] suggest that for 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.

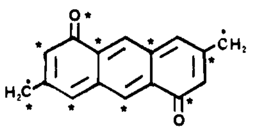
The two non-Kekulé systems **1**[5] and **2** illustrate the contrasting predictions evoked by a seemingly superficial alteration of atomic connectivity.



S = (11-7)/2 = 2

PREDICTED: QUINTET

1



S = (9-9)/2 = 0

PREDICTED: SINGLET

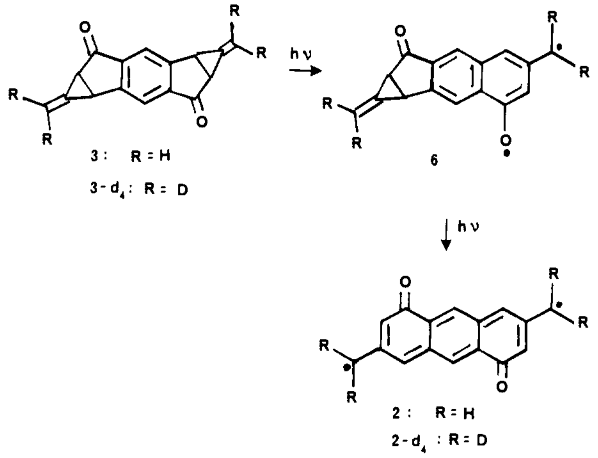
2

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

candidate structure	experiment 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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(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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