CIEEL path is in competition with a rapid unimolecular decomposition of the key chemiluminescent intermediate.

Experimental Section

General Data. All chemiluminescence measurements were made by the photon-counting technique as previously described.[3] Photoexcited fluorescence spectra were obtained on a Farrand Mark V spectrofluorometer or by photon counting for direct comparison with chemiluminescence emission spectra. UV-VIS absorption spectra were recorded on a Beckman Acta MVI or Cary 14 instrument. Solvents used in the chemiluminescence experiments were purified as previously described.[3]

Cyclic Voltammetry. Cyclic voltammetry was done in argon saturated dichloromethane solution at 23 ± 2 °C with 0.1 M tetra-*m*-butylammonium perchlorate as supporting electrolyte. A three-electrode system, consisting of a platinum working electrode, a counterelectrode, and saturated calomel reference electrode (SCE), was used. Scans were made typically at 0.5 V/s. The E_{ox} values were measured as that potential lying midway between the oxidation and reduction peaks for a given couple.

Peroxides. Dimethyldioxetanone,[3,18] tetramethyldioxetane,[19] and phenoyl peroxide[4b] were prepared and purified as described elsewhere.

Porphyrins. The porphyrin free-bases H_2TPP and H_2TAP were kindly provided by Professor Larry Faulkner. PdTPP was a gift from Professor David Whitten. They were purified by treatment with dichlorodicyanobenzoquinone (DDQ) in refluxing chloroform, as described by Barnett et al.[20] The porphyrins were shown to be chlorin free by visible absorption spectroscopy.[21]

ZnTPP (Sigma) was also purified by treatment with DDQ.

Other metalloporphyrins were prepared by reaction of the appropriate divalent metal salt with the porphyrin free base in refluxing dimethylformamide according to the general procedure of Adler et al.[22] The magnesium porphyrins and CdTPP were recrystallized from benzene-hexane. ZnTAP was purified by dry column chromatography on Al_2O_3, eluting with chloroform, followed by several recrystallizations from chloroform-methanol. CoTPP and AgTPP were purified by dry column chromatography on Florisil, eluting with chloroform, followed by recrystallization from chloroform-methanol.

All porphyrins gave satisfactory elemental analyses and had visible absorption spectra consistent with literature data.[21,23]

Chlorophyll a (Sigma) was used as received.

Acknowledgment. This research was supported by the Office of Naval Research and the National Science Foundation. S.P.S. is a University of Illinois Fellow, 1976-1980.

Supplementary Material Available: Listings of observed rate constants for the porphyrin-catalyzed reaction of **1** (Table III), representative plots of the first-order decay of the chemiluminescence intensity for this reaction (Figure 2), and plots of the effect of activator identity and activator concentration on the observed first-order rate constants (Figure 3) (12 pages). Ordering information is given on any current masthead page.

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(22) A. D. Adler, F. R. Longo, F. Kampas, and J. Kim, *J. Inorg. Nucl. Chem.*, **32**, 2443 (1970).

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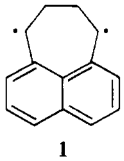
Communications to the Editor

Photolytic Generation of a 1,8-Naphthoquinodimethane Biradical. Time-Resolved and Polarization Electron Spin Resonance Studies

Sir:

The study of biradicals has been quite extensive in the last few years, owing to their real or imagined intermediacy in a large number of thermal and photochemical processes. A wide variety of chemical and physical techniques have been used to characterize the biradicals themselves and the modes of their formation and decay, but despite its obvious suitability time-resolved electron paramagnetic resonance (EPR) has hardly been exploited. To our knowledge, only one study has thus far been reported. Doetschman[1] determined, by a spin-echo method, the initial populations of the spin eigenstates of diphenylmethylene following its formation by photolysis of diphenyldiazomethane in a single-crystal host at 1.2 K.

We report here a study by continuous monitoring of the EPR response at short-time resolution (less than 0.1 μs) of the formation of **1** by photolysis of **2**.[2] In addition, we report the magnetic and optical anisotropy of **1** when it is produced in rigid media by photolysis with plane-polarized light.[3]



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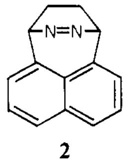

2

The experiments on transient magnetization were performed at 77 K in hexafluorobenzene, octafluorotoluene, or 2-methyltetrahydrofuran. The results are independent of the solvent. Photolysis was accomplished by pulsed irradiation from a nitrogen laser (λ = 337 nm, pulse energy <1 mJ, pulse duration ~6 ns). The experimental methods for detection of the pulses of magnetization have been described.[4] The continuous wave (CW) EPR spectrum of **1** is characteristic of a triplet molecule with axial symmetry of the distribution of the interspin vector ($|D| = 0.018$ cm^{-1}, $|E| < 0.003$ cm^{-1}). Maximum transient magnetization is observed at the positions of the XY peaks (static field perpendicular to symmetry axis). The initial magnetization of the low-field XY peak is absorptive and that of the high-field XY peak emissive[5] (Figure 1). The rise time of the magnetization is of the order of 0.1 μs and that of the decay time on the order of 5 μs.[6]

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(1) Doetschman, D. C.; Botter, B. J.; Schmidt, J.; Van Der Waals, J. H. *Chem. Phys. Lett.* **1976**, *38*, 1. Doetschman, D. C. *J. Phys. Chem.* **1976**, *80*, 2167.

(2) For earlier work on **1**, see: Gisin, M.; Rommel, E.; Wirz, J.; Burnet, M.; Pagni, R. M. *J. Am. Chem. Soc.* **1979**, *101*, 2216, and references cited therein.

(3) Optical dichroism has been noted previously. See ref 2.

(4) Kim, S. S.; Weissman, S. I. *Rev. Chem. Intermed.* **1979**, *3*, 107-120.

(5) The observation of enhanced magnetization in **1** is related to the intersystem crossing (isc) step. The three mechanisms, $^{1}2^{*} \xrightarrow{\text{isc}} {}^{3}\mathbf{1} + N_2$; $^{1}2^{*} \xrightarrow{\text{isc}} {}^{3}2 \rightarrow {}^{3}1 + N_2$; and $^{1}2^{*} \rightarrow N_2 + {}^{1}\mathbf{1} \xrightarrow{\text{isc}} {}^{3}1$, seem reasonable for the formation of triplet **1** (^{3}**1**). Trapping experiments with O_2 demonstrate that the last mechanism does not operate: Pagni, R. M.; Burnett, M. N., unpublished results. Nothing is known at present about the viability of the other two mechanisms.

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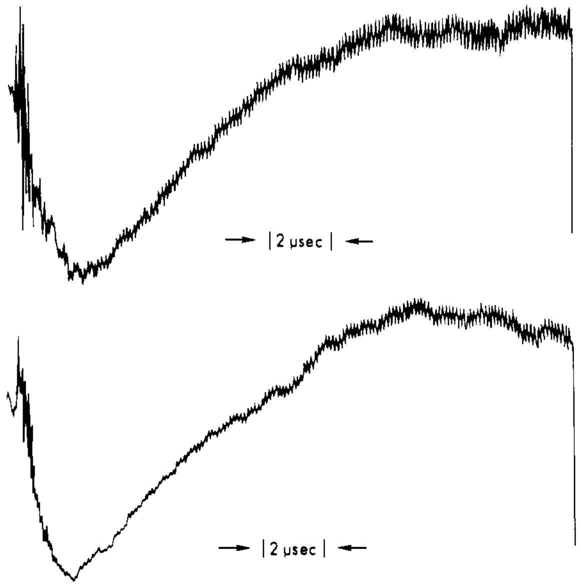

Figure 1. Transient response on formation of **1**. (a) 500 pulses at high-field XY resonance minus 500 pulses off resonance. The low-field transient has the same kinetics but is inverted. (b) 1000 pulses at high-field XY resonance minus 1000 pulses at low-field XY resonance. The signal to noise ratio is enhanced by this procedure. Subtraction removes the field-independent transients which result from the perturbation of the cavity of the laser flash.

The photolyses with plane-polarized light were carried out only in methyltetrahydrofuran glass owing to its superior optical qualities. The optical absorption of the product biradical is dichroic following short photolysis with plane-polarized light in the region 330-380 nm. The peak at 510 nm ($T_0 \leftrightarrow T_1$) is polarized parallel to the polarization of the photolyzing beam, and the peak at 496 nm ($T_0 \leftrightarrow T_2$) is polarized perpendicular to it.[7]

In the observations of the magnetic anisotropy following a short period of photolysis with plane-polarized light, the EPR spectra were recorded with the direction of the photolyzing electric vector, now permanently imprinted in the rigid sample, either parallel to or perpendicular to the static magnetic field. The change is accomplished by rotating the sample tube. The procedure is superior to separate photolyses with the two different polarizations, since the number of biradicals in the cavity is unchanged as the sample is rotated. When the direction of the electric vector of the photolyzing beam is parallel to the static magnetic field, the Z peaks are of low intensity; rotation of the sample by 90° leads to increased intensity of the Z peaks and decreased intensity of the XY peaks (Figure 2).

The experiments on the anisotropies reveal the following relations between steric properties of the parent compound **2** and the biradical **1**: (1) The transition moment of the near-ultraviolet absorption of **2** is parallel to the transition moment of $T_0 \leftrightarrow T_1$ of **1** and perpendicular to the transition moment of $T_0 \leftrightarrow T_2$.[7] (2) The principal axis of the axially summetric spin-spin interaction in **1** is perpendicular to the direction of the near-ultraviolet transition moment of **2**.

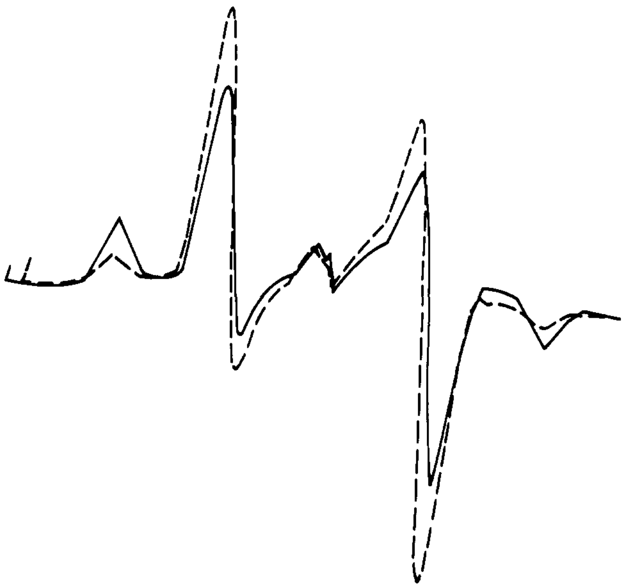

Figure 2. CW EPR spectra of **1** following photolysis by plane-polarized light. (—) Static magnetic field perpendicular to electric vector of light. (- - -) Static magnetic field parallel to electric vector of light.

Although the results described above establish relations between orientations of characteristic vectors of **1** and **2**, they do not fix them in the molecular axis system. The reasonable assumption that the principal axis of the dipole-dipole interaction of **1** is parallel to the axis joining its ·C–C· biradical centers removes part of the uncertainty; the transition moment in **2** is perpendicular to the ·C-C· direction.

Interpretation of the transient experiments reveals with certainty that the biradical is formed within $\sim 10^{-7}$ s of the illumination and that at 77 K it has an effective transverse relaxation time of about 5 μs. But to determine which eigenstates are populated following photolysis requires knowledge of the sign of the spin-spin splitting parameter *D*.

If the spins are predominantly localized on the positions indicated in structure **1**, *D* is negative, and the transient results require that the zero-field eigenstates T_x, T_y (the *z* axis being the interspin axis) are initially populated. It is likely then that the singlet state which is the immediate precursor of the crossing into the triplet manifold has nonvanishing projections on T_x and T_y.

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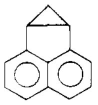
(6) Attempts to perform similar experiments on i and ii failed; the compounds are not photolyzed by light at 337 nm. Continuous irradiation of these materials is known to generate the corresponding 1,8-naphthoquinodimethanes. See: Muller, J.-F.; Muller, D.; Dewy, H.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629. Pagni, R. M.; Burnett, M. N.; Dodd, J. R. *Ibid.* **1977**, *99*, 1972. See also: Platz, M. *Ibid.* **1979**, *101*, 3398.



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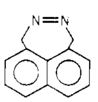

ii

[7] The latter statement also follows from the earlier observation (footnote 2) that the transition moments $T_0 \leftrightarrow T_1$ and $T_0 \leftrightarrow T_2$ are perpendicular to each other.

Enzyme-Catalyzed Organic Synthesis: NADH Regeneration by Using Formate Dehydrogenase[1]

Sir:

Existing methods for regeneration of NADH from NAD^+ for use in organic synthetic procedures based on NADH-dependent enzymes all have disadvantages.[2,3] Here we describe the use of

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(1) Supported by the National Institutes of Health (Grant GM 26543).

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