

Singlet and Triplet States Are Degenerate in 2,3-Dimethylenecyclohexane-1,4-diyl

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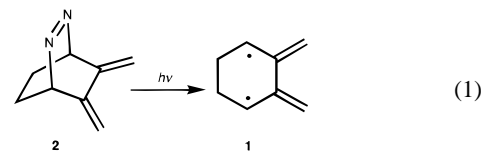
Trimethylenemethane (TMM) and tetramethyleneethane (TME) are the simplest non-Kekulé alternant hydrocarbons (AHs) for which the Longuet-Higgins rule dictates the occurrence of two nonbonding molecular orbitals (NBMO) that have zero π -bond energy.¹ The two NBMOs have atoms in common in TMM and can be confined to different sets of atoms in TME, and Hund's rule can not therefore be applicable in a straightforward manner to the latter. Pointing out this difference, Borden and Davidson predicted in their perturbational MO theory that while TMM should have a ground triplet state, singlet and triplet states are nearly degenerate and higher order terms favor the singlet ground state for TME.² Ovchinnikov adopted valence bond (VB) theory for AHs to conclude that the spin quantum number (S) of the AHs can be given by $S = (n^* - n)/2$, where n^* and n are the numbers of starred and unstarred carbon atoms in AHs, respectively. The S values of TMM and TME are predicted by this rule to be 1 and 0, respectively.³

While the triplet ground state of TMM was accepted unanimously,⁴ it was only in 1986 when the ground spin state of TME was tested experimentally by Dowd *et al.* They studied the ESR spectra of TME and 2,3-dimethylenecyclohexane-1,4-diyl (**1**), a conformationally restricted analog, to find that their signal intensities obeyed Curie law in the temperature ranges of 16–65^d and 15–53 K,^{5f} respectively. While the possibility that the singlet and triplet states are degenerate within 30–40 cal mol⁻¹ was mentioned, their triplet ground states were concluded on the basis that it was clearly less likely that both TME and **1** of different planarity showed similar degeneracy. This conclusion was contradictory to the above theoretical predictions and the observed singlet ground states of higher

vinyls and benzenologs of TME.⁶ Recently Berson *et al.* investigated *N*-substituted-3,4-dimethylenepyrroles extensively and reported that while *N*-methyl- or *N*-pivaloyl-3,4-dimethylenepyrroles were characterized as singlet biradicals, *N*-tosyl- or *N*-brosyl-3,4-dimethylenepyrroles existed as both singlet and triplet biradicals and intersystem crossing between the two spin states could not be observed. They concluded substitution by an electron-withdrawing group at the nitrogen of the pyrrole ring can tune the singlet–triplet energy gap.⁷

A question how the singlet and triplet ground states of TME are separated evoked much controversy and should be answered by proper methods.⁸ Determination of temperature dependence of the magnetic susceptibility and magnetic field dependence of the magnetization is a method of choice for studying the magnitude of the effective magnetic moments and spin quantum numbers of polyradicals.^{6,9} In this paper, we report a magnetic study directed to determine the energy gap of the singlet and triplet states of **1**.

Diradical **1** was obtained by the photolysis of 5,6-dimethylene-2,3-diazabicyclo[2.2.2]oct-2-ene (**2**) (eq 1) as employed by Dowd *et al.*⁴ Precursor **2** was synthesized from 1,2-dihydrophthalic acid according to the method of Roth *et al.*¹⁰ and obtained as pale yellow crystals {UV–vis absorption maxima at 274 nm (ϵ 4990) and 379 nm (ϵ 112)}. Since the magnetic



measurement is not spectroscopic and treats the photoproducts as a whole, it is necessary to minimize any side reaction giving paramagnetic impurities.⁹ We therefore optimized the reaction conditions for the formation of **1** from **2** in 2-methyltetrahydrofuran (MTHF) frozen solution. The photolysis was carried out in an ESR cavity by using light from a high-pressure mercury lamp and a set of Kenko band-pass filters. While the light $\lambda > 340$ nm was not effective in giving any ESR active product, the light ($\lambda > 320$ nm) gave $g = 2$ signals ($|D/hc| = 0.024$ cm⁻¹ and $|E/hc| = 0.0039$ cm⁻¹) as well as forbidden lines at $g = 4$ (Figure 1a). The D and E values correspond to the theoretical values^{11,12} for **1** and are in good agreement with a distance of 4.77 Å between the two spins by a point-dipole approximation. We conclude this species as the desired diradical **1**.

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(12) A CASSCF(6,6)/6-31G* calculation for **1** at the B3LYP(6-311++G**) geometry (23° twist) has been performed by Havlas and Michl to yield $|D/hc| = 0.0329$ cm⁻¹ and $|E/hc| = 0.0180$ cm⁻¹. We thank Prof. Josef Michl for the information prior to the publication.

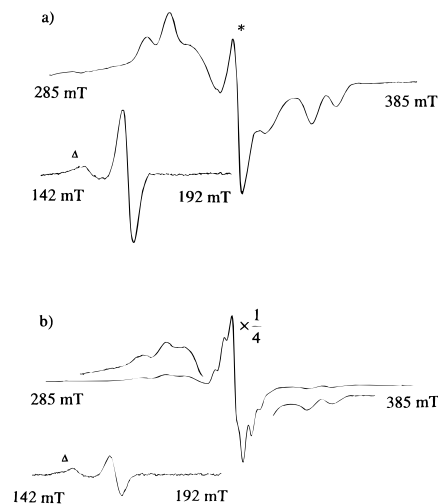


Figure 1. (a) A 9.428 GHz ESR spectrum of a solid solution of **2** in MTHF (0.1 M) after irradiation with light ($\lambda > 320$ nm) measured at 9.4 K. The signal denoted with an asterisk (*) appeared only when irradiated with light ($\lambda > 300$ nm). The $\Delta m_s = \pm 2$ region is also presented. (b) An ESR spectrum obtained by continued irradiation at $\lambda > 300$ nm at 9.5 K. The signal denoted with Δ was due to the impurity in the cavity.

hotolysis of **2** or continued irradiation of **1** with the light $\lambda > 300$ nm gave another set of ESR signals (Figure 1b). The second photoproduct appeared at the expense of the signal from the first product. If the outer-to-inner peaks and shoulders of these signals are assumed to be the $\pm z$, $\pm y$, and $\pm x$ transitions of a triplet species, $|D/hc| = 0.0059$ cm^{-1} and $|E/hc| = 0.00067$ cm^{-1} are obtained. However, no forbidden transition is observed at $g = 4$, proven by the decrease of the signal at $g = 4$. The small D and E values, corresponding to the distance between the two spins of 7.61 Å by a point-dipole approximation, may be assigned to a hydrogen migration product. The ESR spectrum reported by Dowd *et al.*^{5f} is reproduced by a sum of the two species.

The wavelength-dependence of the photoproduct has been reported by Berson *et al.* in the *N*-(arenesulfonyl)-3,4-dimethylenepyrrole system.⁷ The irradiation at 370 nm afforded the ESR inactive singlet biradical, but irradiation at 265 nm afforded a triplet species. With irradiation at 343 nm, a different triplet species (smaller D and E values) was produced. Both triplet species exhibited a forbidden line at $g = 4$. The triplet species with larger D and E values was assigned to a triplet biradical, and the triplet species with the smaller D and E values was assigned to the triplet diazenyl biradical.

Magnetic measurements were performed on a SQUID susceptometer/magnetometer for samples of **1** obtained under similar conditions as those described above. A solution of 0.33 mg of **2** in 10 μL of MTHF was placed in a quartz cell. The light ($\lambda > 320$ nm) was introduced to the SQUID susceptometer through an optical fiber introduced into a sample probe and the photolysis of **2** in MTHF was performed at 4–10 K. The data before irradiation was subtracted as background data.

The paramagnetic susceptibility χ obtained at a field of 5000 G in the temperature range 2–20 K is presented as a χT vs T plot (Figure 2). The nearly horizontal line is consistent with Dowd's finding that the EPR signal intensity of **1** obeys the Curie law. The slightly decrease in the χT values at the low-temperature region ($T < 4$ K) suggests a singlet–triplet equilibrium in which the singlet is very slightly lower in energy, rather than a triplet ground state. The effect is, however, too small to apply a model in which a ground singlet state is in equilibrium with a triplet separated by a small gap ($2J$). Nevertheless, this theoretical curve for $2J/k_B = -0.76$ K derived from the field dependence of magnetization (*vide infra*) is also given in Figure 2.

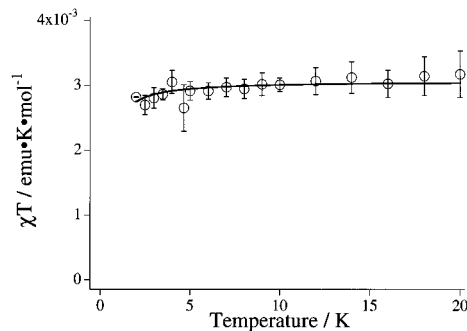


Figure 2. χT vs T plots of **1** measured at 5000 G. The ordinate is based on the amount of **2** placed in a sample cell and not normalized on the basis of the amount of **1** produced. The solid curve is a theoretical one for a singlet–triplet model with a gap of $2J/k_B = -0.76$ K.

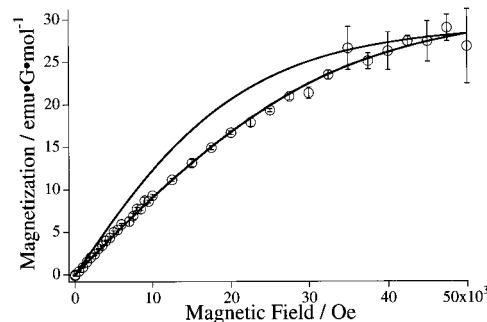


Figure 3. Field dependence of the magnetization of **1** measured at 2.0 K. The two solid curves represent a theoretical $S = 1$ curve (top) and a best-fit curve (bottom) with a singlet–triplet gap of $2J/k_B = -0.76$ K (eq 2).

Field-dependence of the magnetization (M) of **1** is shown in Figure 3. A theoretical formula for the magnetization of a diradical with a small singlet and triplet energy gap ($2J$) comparable to the Zeeman splitting is given by eq 2. The fitting

$$M = Ng\mu_B \frac{\exp\left(\frac{g\mu_B H_0}{k_B T}\right) - \exp\left(\frac{-g\mu_B H_0}{k_B T}\right)}{\exp\left(\frac{g\mu_B H_0}{k_B T}\right) + 1 + \exp\left(\frac{-g\mu_B H_0}{k_B T}\right) + \exp\left(\frac{-2J}{k_B T}\right)} \quad (2)$$

of eq 2 to the observed data gave $2J/k_B = -0.76 \pm 0.16$ K, indicating that the singlet and triplet states are nearly degenerate in **1**. For a triplet ($S = 1$) ground state ($J \gg 0$), the last term in the denominator vanishes and the corresponding theoretical curve did not fit the observed data at all. For $J \approx 0$, this term is 1 and, therefore, the initial slope of the curve for $J \approx 0$ is three-fourths that of the curve for $J \gg 0$, indicating that 25% of the diradical molecules are in the singlet state and hence give no magnetization.¹³

These experimental results are in excellent accord with some of the computational results that the singlet–triplet gap in **1** is almost exactly zero.⁸

In conclusion, we have been able to demonstrate experimentally that the singlet and triplet states of **1**, a conformationally fixed analog of TME, are almost degenerate, terminating a controversy as to theoretical and experimental interpretation of the ground state of **1**.

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(13) The theoretical $S = 1$ curve is normalized at 50 kOe. The initial slope of the curve is therefore nearly but not quite as high as four-thirds that of the curve for $2J/k_B = -0.76$ K.