

# Demonstration of the degeneracy of the singlet and triplet states in 2,3-dimethylenecyclohexane-1,4-diyl by measurement of its magnetic properties †

Kenji Matsuda and Hiizu Iwamura \*

Institute for Fundamental Research in Organic Chemistry, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-81, Japan

Magnetic susceptibility and magnetization of 2,3-dimethylenecyclohexane-1,4-diyl (**1**), a conformationally restricted tetramethyleneethane (TME), have been investigated at 2–20 K and applied fields of 0–5 T. Theoretical curves for a model in which singlet and triplet states are in equilibrium were fitted to the experimental data. In contrast with a previous interpretation of the EPR signal intensities, singlet and triplet states were found to be almost degenerate ( $2|J/k_B| < 1$  K), thus resolving a controversy as to the theoretical and experimental interpretation of the ground state of **1**.

## Introduction

Trimethylenemethane (TMM) and tetramethyleneethane (TME) are the simplest non-Kekulé alternant hydrocarbons (AHs). For such molecules, Longuet–Higgins' rule predicts the occurrence of two non-bonding molecular orbitals (NBMO) that are occupied by a total of two electrons. Therefore, both TMM and TME are diradicals.<sup>1</sup> The two NBMOs have atoms in common in TMM but can be confined to different sets of atoms in TME (Fig. 1). Pointing out this difference, Borden and Davidson predicted in their perturbational MO theory that, while TMM should have a ground triplet state, the singlet and triplet states of TME are nearly degenerate and higher order terms favor a singlet ground state for planar TME.<sup>1f</sup> Ovchinnikov applied valence bond (VB) theory to AHs and concluded that the spin quantum number ( $S$ ) of an AH is 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,<sup>1j</sup> leading again to the prediction of a triplet ground state for TMM but a singlet ground state for planar TME.

The dependence of the singlet–triplet splitting in TME on the dihedral angle  $\varphi$  between the two  $(\text{CH}_2)_2\text{C}$  units has been calculated.<sup>2</sup> Based on the results of large CI calculations, Nachtigall and Jordan predicted that the triplet state becomes more stable than the singlet state at the optimized triplet geometry of  $\varphi = 59^\circ$ ; planar or more twisted structures favor a singlet ground state.<sup>2h</sup>

The triplet ground state of TMM, predicted by theory,<sup>1</sup> has been confirmed by experiments.<sup>3</sup> However, despite the predictions of a singlet ground state for planar TME, even prior to these predictions, triplet EPR spectra had been observed for TME by Dowd<sup>4a</sup> and for 2,3-dimethylenecyclohexane-1,4-diyl (**1**), a conformationally restricted analog, by Roth and Erker.<sup>4b</sup> Nevertheless, it was not clear until 1986 whether the triplet is the ground state or a thermally populated state of TME and of **1**. In that year Dowd *et al.* studied the temperature dependence of the EPR spectra of TME and of **1** and found that the signal intensities obeyed the Curie law in the temperature ranges 16–65<sup>4d</sup> and 15–53 K,<sup>4f</sup> respectively. Although these experiments allow the possibility that the singlet and triplet states are degenerate within 30–40 cal mol<sup>-1</sup> in both molecules, a triplet ground state for each was concluded on the basis that it was clearly less likely that TME and the more conformationally

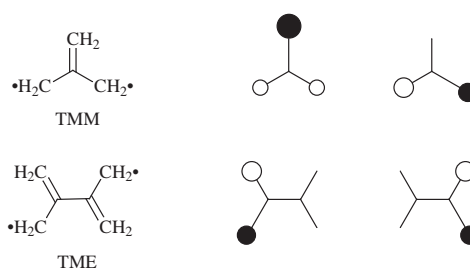


Fig. 1 Schematic presentation of pairs of the NBMOs of trimethylenemethane (TMM) and tetramethyleneethane (TME)

restricted **1** both had nearly degenerate singlet and triplet states.

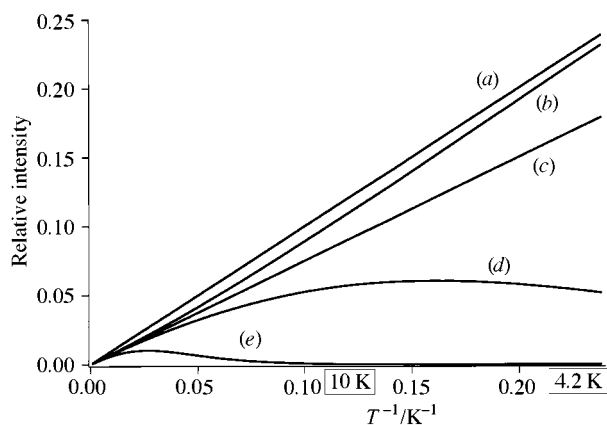
The conclusion that a triplet is the ground state for TME and for **1** is contradictory not only to the above theoretical predictions but also to the singlet ground states, more recently observed for higher vinylogs and benzenologs of TME, which are also disjoint hydrocarbons.<sup>5</sup> A possible resolution is suggested by experiments of Berson and co-workers on *N*-substituted-3,4-dimethylenepyrroles. They found that, while *N*-methyl- and *N*-pivaloyl-3,4-dimethylenepyrroles are singlet diradicals, *N*-tosyl- and *N*-brosyl-3,4-dimethylenepyrroles have both singlet and triplet states that could be observed and between which interconversion was too slow to be detected.<sup>6</sup> This finding at least raises the possibility that singlet and triplet states are both populated in TME and/or **1** but do not interconvert on the timescale of the Curie law studies, thus leading to the observed linear Curie plots.

The question of the energy separation between the singlet and triplet states of TME and of **1** has attracted the interest of theoretical<sup>2</sup> and experimental<sup>4</sup> chemists, evoked much controversy, and therefore should be answered by appropriate methods.<sup>7</sup> Determination of the temperature dependence of the magnetic susceptibility and the magnetic field dependence of the magnetization are the methods of choice for studying the magnitude of the effective magnetic moments and spin quantum numbers of polyradicals.<sup>5,7,8</sup> Here we report a magnetic study directed towards the determination of the energy gap between the singlet and triplet states of **1**.<sup>9</sup>

## Methodology

Diradicals, including carbenes and nitrenes, are often studied by means of EPR spectroscopy. Triplet states are detected by their characteristic fine structure. The resonant microwave frequency, e.g. 9 GHz for a typical X-band spectrometer,

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**Fig. 2** Theoretical curves for the EPR signal intensity vs. reciprocal of temperature (Curie plot) of  $\Delta E/k_B =$  (a)  $+\infty$  K; (b) 5 K; (c) 0 K; (d)  $-5$  K; (e)  $-30$  K. The ordinate was normalized at maximum intensity.

corresponds to a thermal energy,  $kT$ , at 0.4 K. Therefore the EPR transition probability, as measured by the signal intensity, is inversely proportional to temperature at  $>4$  K, where most EPR experiments on diradicals in the condensed phase are carried out. EPR signal intensities of doublet monoradicals and of diradicals with triplet ground states that are energetically well separated from excited singlet states follow this rule.

When both states are populated and in equilibrium, the population is given by the Boltzmann distribution. The EPR signal intensity, due to the triplet species, is expressed in terms of a product of the two factors: transition probability and population [eqn. (1)], where  $C$  is a proportionality constant,

$$\text{Int} = \frac{C \exp(-\Delta E/kT)}{T[1 + 3\exp(-\Delta E/kT)]} \quad (1)$$

and  $\Delta E$  is the potential energy difference between the singlet and triplet states. A positive sign for  $\Delta E$  is defined to correspond to the triplet being the ground state. Some theoretical curves for representative  $\Delta E$  values are drawn in Fig. 2. Note that, unless the absolute intensity is measured, it is impossible to differentiate between the lines for  $\Delta E = +\infty$  and  $\Delta E = 0$ . We also note that it is difficult to differentiate between the values in the range  $-5 \text{ K} < (\Delta E/k_B) < +\infty$  at  $T > 10 \text{ K}$  (Fig. 2); therefore it is highly desirable to perform the experiments at  $T < 10 \text{ K}$ .

With these limitations of Curie studies of EPR signal intensities in mind, we have advocated the usefulness of the determination of the temperature dependence of the paramagnetic susceptibility  $\chi$  and the field dependence of magnetization  $M$  for evaluating the singlet–triplet energy gap  $\Delta E$ . Since an absolute value of the effective magnetic moment [ $\mu_{\text{eff}} = 2.82(\chi T)^{1/2}$ ] of the sample is determined by these methods, it is possible to tell from its temperature independence whether the triplet diradical under question is present to the extent of 100% or 75% of the theoretical value.

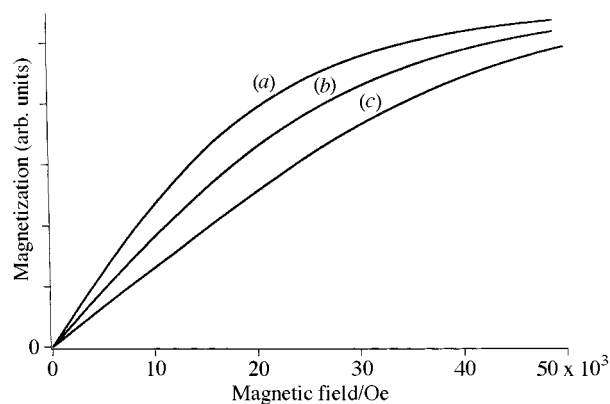
The origin of the energy gap between singlet and triplet states is exchange interaction between two spins, as expressed by the Heisenberg–Dirac–van Vleck Hamiltonian [eqn. (2)], where  $J$  is

$$H = -2J S_1 S_2 \quad (2)$$

the exchange coupling parameter. By introducing this equation the energy difference  $\Delta E$  can be written as  $\Delta E = 2J$ . The Bleaney–Bowers equation for  $\chi T$  is given by eqn. (3).<sup>8</sup>

$$\chi T = \frac{2Ng^2\mu_B^2}{k[3 + \exp(-2J/kT)]} \quad (3)$$

When  $J = 0$  in eqn. (3),  $\chi T$  is only 75% as large as when  $J = \infty$ , because one quarter of the molecules are singlets that do not contribute to  $\chi T$ .



**Fig. 3** Theoretical presentation of the field dependence of magnetization at 2 K with singlet–triplet energy gap  $2J/k =$  (a)  $+\infty$  K; (b) 0 K; (c) 1 K

The measurement of the magnetic field dependence of the magnetization  $M$ , is an even more sensitive method for the determination of the singlet–triplet energy gap. If the energy of the interaction of the spins in a sample with an external magnetic field is not strong, relative to the thermal energy,  $kT$ , the magnetization of the paramagnetic species develops as the applied field is increased and/or the temperature is lowered. The resulting behavior is described by a Brillouin function, which is expanded into eqn. (4) for the magnetization of a diradical with

$$M = Ng\mu_B \frac{\exp(g\mu_B H/kT) - \exp(-g\mu_B H/kT)}{\exp(g\mu_B H/kT) + 1 + \exp(-g\mu_B H/kT) + \exp(-2J/kT)} \quad (4)$$

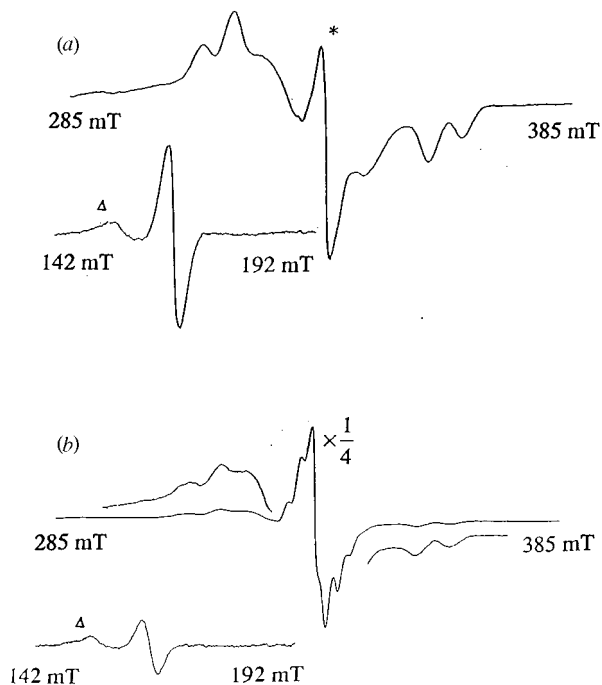
a small singlet–triplet energy gap ( $2J$ ) that is comparable to the Zeeman splitting. Sample theoretical curves for the dependence of magnetization on the strength of the magnetic field are shown in Fig. 3. Such a plot is a very sensitive method of differentiating between cases  $2J \gg 0$  and  $2J \approx 0$ . Fig. 3 also shows that the curvature is perturbed even by as small an energy gap as  $2J/k \approx 1 \text{ K}$ .

The magnetic susceptibility  $\chi$ , in eqn. (3) is  $(\partial M/\partial H)_{H=0}$ . Since  $\chi T$  only corresponds to the slope of eqn. (4) at very small applied magnetic fields,  $\chi T$  utilizes only a part of the information that is available by plotting the magnetization against the magnetic field strength.

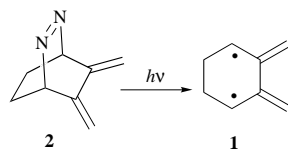
## Results and discussion

### Generation of diradical 1

Diradical **1** was obtained by the photolysis of 5,6-dimethylene-2,3-diazabicyclo[2.2.2]oct-2-ene (**2**) [eqn. (5)], which was the method for generating **1** employed by Dowd *et al.* (Scheme 1).<sup>4f</sup> Precursor **2** was synthesized from 1,2-dihydrophthalic acid, according to the method of Roth *et al.*,<sup>10</sup> and obtained as pale yellow crystals [UV–VIS absorption maxima at 274 nm ( $\epsilon$  4990) and 379 nm ( $\epsilon$  112)]. Since the magnetic measurements are not spectroscopic and depend on all the photoproducts, it was necessary to minimize any side reactions that give paramagnetic impurities.<sup>7</sup> We therefore optimized the reaction conditions for the formation of **1** from **2** in a 2-methyltetrahydrofuran (MTHF) glass. The photolysis was carried out in the cavity of the EPR spectrometer by using light from a high-pressure mercury lamp and a set of Kenko band-pass filters. While light of  $\lambda > 340 \text{ nm}$  was not effective in forming the photoproduct, light of  $\lambda > 320 \text{ nm}$  gave  $g = 2$  signals ( $|D/hc| = 0.024 \text{ cm}^{-1}$  and  $|E/hc| = 0.0039 \text{ cm}^{-1}$ ) as well as forbidden lines at  $g = 4$  [Fig. 4(a)]. The  $D$  and  $E$  values corresponded nicely to those



**Fig. 4** (a) A 9.428 GHz EPR 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 marked with \* appeared only when irradiated with the light of  $\lambda > 300$  nm. the  $\Delta m_s = \pm 2$  region is also presented. (b) An EPR spectrum obtained after continued irradiation at  $\lambda > 300$  nm at 9.5 K. The signal marked  $\Delta$  was due to an impurity in the cavity.



**Scheme 1**

observed previously,<sup>4f</sup> as well as to the theoretical values.<sup>†</sup><sup>11</sup>  $D$  gave a distance of 4.77 Å between the two spins using a simple point-dipole approximation,<sup>§</sup> corresponding to the distance between two spin centers of allyl radical moieties.<sup>11</sup> We conclude this species is the desired diradical **1**.

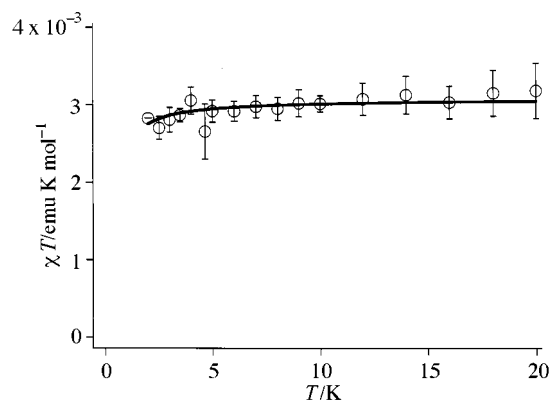
Continued irradiation of **1** with the light of  $\lambda > 300$  nm gave another set of EPR signals [Fig. 4(b)]. The signals from the second photoproduct grew at the expense of those from **1**. No forbidden transition was observed at  $g = 4$ ; the signal at  $g = 4$  just decreased. If the outer-to-inner peaks and shoulders of the signals from the second photoproduct are assumed to be the  $\pm z$ ,  $\pm y$  and  $\pm x$  transitions of a triplet species,  $|D/hc| = 0.0059$  cm<sup>-1</sup> and  $|E/hc| = 0.00067$  cm<sup>-1</sup> are obtained. The small  $D$  and  $E$  values, which correspond to a distance between the two spins of 7.61 Å using a point-dipole approximation, may be assigned to a hydrogen migration product. However, the splitting between the peaks for this second product also corresponded to the hyperfine splitting in the allyl radical. Therefore there is another possibility that the EPR spectrum of this second product originated from a mono-allyl radical or di-allyl radical with very weak interallylic interaction. The EPR spectrum reported by Dowd *et al.*<sup>4f</sup> is reproduced by the sum of those due to the first and second photoproduct.

#### Magnetic measurements

Magnetic measurements were performed on a SQUID susceptometer/magnetometer for samples of **1** obtained under similar

<sup>†</sup>  $|D/hc| = 0.0329$  cm<sup>-1</sup> and  $|E/hc| = 0.0180$  cm<sup>-1</sup> for **1** were obtained at B3LYP(6-311++G\*\*) geometry ( $\varphi = 23^\circ$ ) by CASSCF(6,6)/6-31G\* calculations in reference 11(c).

<sup>§</sup>  $2D$  (G) =  $3g\mu_B r^{-3}$ . The 'factor' of 2 used in reference 11(a) was not employed.



**Fig. 5**  $\chi T$  vs.  $T$  plots for **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 [eqn. (3)].

conditions as those described above. A solution of 0.33 mg of **2** in 10 ml of MTHF was placed in a quartz cell. Light ( $\lambda > 320$  nm) was allowed into the SQUID susceptometer through an optical fiber introduced into the sample probe and the photolysis of **2** in MTHF was performed at 4–10 K for 14 h. The data before irradiation were subtracted as background data.

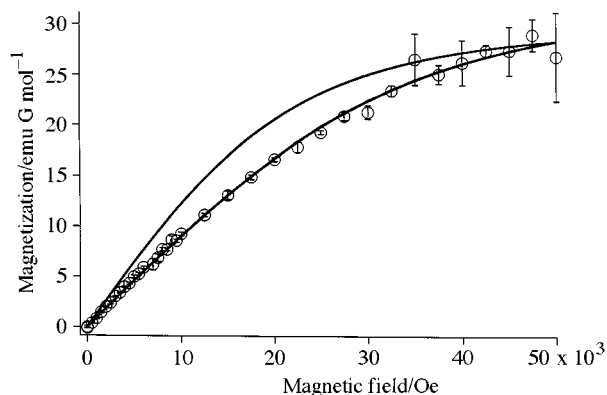
The paramagnetic susceptibility  $\chi$ , obtained at the field of 5000 G in the temperature range 2–20 K, is presented as a  $\chi T$  vs.  $T$  plot (Fig. 5). The nearly horizontal line is consistent with Dowd's finding that the EPR signal intensity of **1** obeys the Curie law. However, the apparent decrease in the  $\chi T$  values in 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. Although the effect is too small to model accurately by a ground singlet state that is in equilibrium with a triplet separated from it by a small gap ( $2J$ ), nevertheless, a theoretical curve [eqn. (3)] for  $2J/k_B = -0.76$  K, which is derived from the field dependence of the magnetization (*vide infra*), is also given in Fig. 5.

The field-dependence of the magnetization ( $M$ ) of **1** is shown in Fig. 6. The fitting of eqn. (4) to the observed data by a least-squares method gave  $2J/k_B = -0.76 \pm 0.16$  K ( $= -1.5 \pm 0.3$  cal mol<sup>-1</sup> =  $-6.3 \pm 1.3$  J mol<sup>-1</sup>), indicating that the singlet and triplet states are nearly degenerate in **1**. For a triplet ( $S = 1$ ) ground state and  $J \gg 0$ , the last term in the denominator of eqn. (4) vanishes, and the corresponding theoretical curve does not fit the observed data at all. For  $J \approx 0$ , this term is equal to one, and therefore, the initial slope of the curve for  $J \approx 0$  is 3/4 that of the curve for  $J \gg 0$ . As discussed above, the physical reason is that, with  $J = 0$ , 25% of the diradical molecules are in the singlet state and hence give no magnetization. Because the theoretical  $S = 1$  curve is normalized at 50 kOe rather than at low fields, the initial slope of this curve is almost, but not quite, 4/3 of the slope of the curve for  $2J/k_B = -0.76$  K.

#### Conclusions

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. This finding resolves the ambiguity inherent in the EPR results, as to whether the triplet is the ground state of **1** or whether the singlet and triplet states have nearly the same energy. Our experimental results are in excellent accord with the computational prediction of Nash, Dowd, and Jordan that the singlet–triplet gap in **1** is almost exactly zero.<sup>2f</sup>

The experimental data now available are consistent with the qualitative prediction<sup>1i</sup> that so-called disjoint hydrocarbons, such as higher vinyls and benzenologs of TME and even the



**Fig. 6** Field dependence of magnetization of **1** measured at 2.0 K. Two solid curves are a theoretical  $S = 1$  curve (top) and a best-fit curve (bottom) with a singlet-triplet gap of  $2J/k_B = -0.76$  K [eqn. (4)].

corresponding heteroatom analogs, have nearly degenerate singlet and triplet states, with the former usually slightly more stable than the latter.<sup>5</sup> Disjoint dinitrenes also have singlet ground states, with low-lying excited quintet states.<sup>5</sup>

### Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a JEOL EX-270 instrument. UV-VIS spectra were obtained on a Hitachi U-3300 spectrophotometer. 2-Methyltetrahydrofuran (MTHF) used in the magnetic measurements was purified by successive distillation from lithium aluminium hydride and from sodium-benzophenone ketyl under a dry nitrogen atmosphere.

#### Preparation of 5,6-dimethylene-2,3-diazabicyclo[2.2.2]oct-2-ene (**2**)

Compound **2** was obtained from 1,2-dihydrophthalic acid according to the method of Roth *et al.*<sup>10</sup> and obtained as pale yellow crystals: mp 37.5–39.5 °C (lit.,<sup>10</sup> 40 °C);  $\delta_{\text{H}}$ (270 MHz; CDCl<sub>3</sub>) 1.4–1.7 (AB system, 4 H), 5.03 (s, 2 H), 5.34 (s, 2 H), 5.66 (s, 2 H);  $\delta_{\text{C}}$ (67.8 MHz; CDCl<sub>3</sub>) 21.8, 71.5, 107.1, 137.7;  $\lambda_{\text{max}}$ (CH<sub>2</sub>Cl<sub>2</sub>)/nm ( $\epsilon/M^{-1} \text{ cm}^{-1}$ ) 274 (4990), 379 (112) nm [Found: MH<sup>+</sup>, 135.0920. Calc. for C<sub>8</sub>H<sub>11</sub>N<sub>2</sub> (MH<sup>+</sup>): 135.0922] [lit.,<sup>10</sup> Found:  $M - N_2$ , 106.0771. Calc. for C<sub>8</sub>H<sub>10</sub> ( $M - N_2$ ): 106.0782].

#### EPR measurements

Photolysis of the azoalkane precursor was carried out in MTHF matrices at 9 K in the EPR cavity. Light was obtained from a high-pressure mercury lamp with a Kenko sharp-cut filter. A Bruker ESP 300 spectrometer was used to obtain X-band EPR spectra. Temperatures were controlled by an Air Products LTD-3-110 cryogenic temperature controller. The cryostat was maintained at high vacuum by a diffusion/rotary pump set.

**Magnetic measurements.** Magnetic measurements were performed on a Quantum Design MPMS-5S SQUID susceptometer. Blank data due to sample holder, a quartz cell, and light guide were subtracted from the data after irradiation. This technique is found to be very sensitive because the blank data originate from the same sample. A solution of 0.33 mg of **2** in 10 ml of MTHF was placed in a quartz cell. Light ( $\lambda > 320$  nm), obtained from a Xenon lamp in combination with a Kenko sharp-cut filter and an OCLI B cold mirror, was introduced into the SQUID susceptometer through an optical fiber inserted into the sample probe and the photolysis of **2** in MTHF was performed at 4–10 K for 14 h. The paramagnetic susceptibility  $\chi$  was obtained at a field of 5000 G in the temperature range 2–20 K. The field-dependence of magnetization ( $M$ ) of **1** was obtained at 2.0 K.

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