

The Biradical, Bis(3,5-di-*tert*-butyl-4-phenoxy)methyleneadamantane, Exhibits Matrix-Dependent EPR Spectra Suggesting Rotamer Bistability with Differential Exchange Coupling

David A. Shultz,* Andrew K. Boal, and Gary T. Farmer

Department of Chemistry
North Carolina State University
Raleigh, North Carolina 27695-8204

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It is now well-documented that large bond torsions in metaphenylene-based biradicals result in antiferromagnetic exchange coupling ($J < 0$),¹ while severe twisting in paraphenylene structures may give ferromagnetic coupling ($J > 0$).^{1g} Since trimethylenemethane (TMM) type coupling fragments are useful for constructing high-spin structures, it is important to test the sensitivity of J to bond torsions in such systems. To this end, we prepared a TMM type biradical (**2**^{••}) and report that the magnitude and probably the sign of J is a function of the solvent matrix, suggesting that in **2**^{••} J is intensely sensitive to bond torsions.

We reasoned that steric repulsion between the “pseudoallylic” hydrogens on the adamantane ring system and the hydrogens on the phenoxy rings will increase phenoxy ring torsion² and thereby attenuate coupling of the phenoxy radicals, making the methyleneadamantane system uniquely suited for studying the effect of bond torsion on J in TMM type biradicals.

The synthesis of **2**^{••} was achieved as shown below.³ Oxidation of **2** with PbO₂ gave blue-violet solutions.⁴ The IR spectrum of the isolated solid is consistent with the proposed oxidation since the spectrum is devoid of OH stretches due to **2** (**2**: 3647 cm⁻¹, sharp) as well as the “normal” phenolic C–O stretches (**2**: 1231 cm⁻¹).

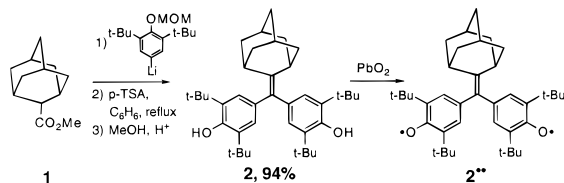


Figure 1a shows the EPR spectrum of **2**^{••} recorded at 77 K in toluene. This spectrum is consistent with a randomly-oriented

(1) For papers discussing the effects of torsion on exchange coupling, see: (a) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180. (b) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847. (c) Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273. (d) Okada, K.; Matsumoto, K.; Oda, M.; Murai, H.; Akiyama, K.; Ikegami, Y. *Tetrahedron Lett.* **1995**, *36*, 6693–4. (e) Adam, W.; van Barneveld, C.; Bottle, S. E.; Engert, H.; Hanson, G. R.; Harrer, H. M.; Heim, C.; Nau, W. M.; Wang, D. *J. Am. Chem. Soc.* **1996**, *118*, 3974–5. (f) Fujita, J.; Tanaka, M.; Suemune, H.; Koga, N.; Matsuda, K.; Iwamura, H. *J. Am. Chem. Soc.* **1996**, *118*, 9347. (g) Okada, K.; Imakura, T.; Oda, M.; Murai, H.; Baumgarten, M. *J. Am. Chem. Soc.* **1996**, *118*, 3047–8. (h) *Ab initio* calculations explain antiferromagnetic coupling in metaphenylene-linked structures, see: Fang, S.; Lee, M.-S.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1995**, *117*, 6727–31.

(2) Diarylmethyleneadamantanes have been used for some time to study reactions of olefins where steric crowding is desirable. See the following and references cited therein: Bosch, E.; Kochi, J. K. *J. Am. Chem. Soc.* **1996**, *118*, 1319–29.

(3) Procedures for the preparation of all compounds, as well as spectral data, are contained in Supporting Information.

(4) Biradical **2**^{••} is stable for at least 1 week if protected from light and oxygen. When a solution of **2**^{••} was irradiated with light of $\lambda > 550$ nm, a decrease in the intensities of both the $\Delta m_s = 1$ and $\Delta m_s = 2$ transitions was observed (rate constants for signal decay: $k_{m=1} = (1.0 \pm 0.1) \times 10^{-4} \text{ s}^{-1}$ and $k_{m=2} = (8.6 \pm 0.9) \times 10^{-5} \text{ s}^{-1}$). This indicates that the blue color of solutions of **2**^{••} is due to **2**^{••} and not due to another species.

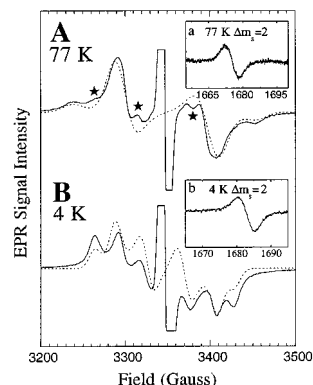


Figure 1. (A) EPR spectrum of **2**^{••} as a solution in toluene at 77 K. The dashed line represents the simulated spectrum using $|D/hc| = 0.01015 \text{ cm}^{-1}$, $|E/hc| = 0.0002 \text{ cm}^{-1}$. Inset (a): $\Delta m_s = 2$ transition at 77 K. (B) EPR spectrum of **2**^{••} at 4 K as a solution in toluene. The dashed line represents the simulated spectrum using $|D/hc| = 0.0077 \text{ cm}^{-1}$, $|E/hc| = 0.0010 \text{ cm}^{-1}$. Inset (b): $\Delta m_s = 2$ transition at 4 K.

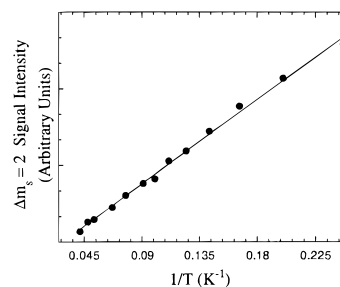


Figure 2. Curie plot for doubly-integrated $\Delta m_s = 2$ signal recorded at $25 \text{ K} \geq T \geq 4 \text{ K}$.

triplet species⁵ along with doublet monoradical impurity. Zero-field splitting parameters obtained from simulation of the spectrum are $|D/hc| = 0.01015 \text{ cm}^{-1}$ and $|E/hc| = 0.0002 \text{ cm}^{-1}$.⁶ The $S = 1$ signature $\Delta m_s = 2$ transition is observed near half-field. In addition to the signals noted in the $\Delta m_s = 1$ region, additional signals exist and are marked with a ★ in Figure 1a.

As the sample is cooled below 77 K the original triplet signal decreases in intensity, consistent with a thermally-populated triplet, $J < 0$. However, the signals marked ★ and associated signals increase in intensity. Below ca. 35 K, the original signal is absent and the new triplet signal continues to grow. The spectrum obtained at 4 K is shown in Figure 1b. Zero-field splitting parameters obtained by spectral simulation are $|D/hc| = 0.0077 \text{ cm}^{-1}$ and $|E/hc| = 0.0010 \text{ cm}^{-1}$. Figure 2 shows a Curie plot for the $\Delta m_s = 2$ region below 25 K (where the original triplet is unpopulated). The temperature-dependence of the doubly-integrated $\Delta m_s = 2$ signal is consistent with either a ground-state triplet species or a singlet/triplet degeneracy.

The picture is quite different if 2-methyltetrahydrofuran (MTHF) is the solvent. The spectrum of **2**^{••} recorded in MTHF at 77 K is shown in Figure 3a. This is the same spectrum as the larger signal in the spectrum in Figure 1a. Note, however, that the signals due to the second triplet are absent. Indeed, as the temperature is lowered, the signal intensity decreases without the concomitant appearance of new signals. The spectrum recorded at 4 K is shown in Figure 3b. Figure 4 shows a Curie

(5) (a) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763. (b) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986. (c) Atherton, N. M. *Principles of Electron Spin Resonance*; Ellis Horwood PTR Prentice Hall: New York, 1993.

(6) Simulations were performed using a routine described previously: Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744 and references cited therein.

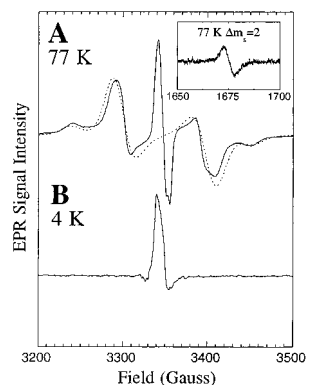


Figure 3. (A) EPR spectrum of $2^{\bullet\bullet}$ as a solution in MTHF at 77 K. Inset: $\Delta m_s = 2$ transition at 77 K. (B) EPR spectrum of $2^{\bullet\bullet}$ as a solution in MTHF at 4 K.

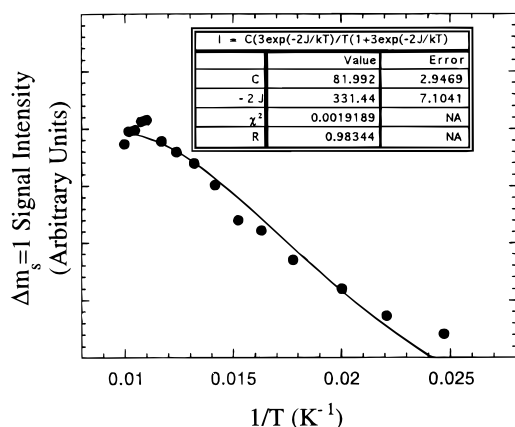


Figure 4. Curie plot for $\Delta m_s = 1$ transition intensity at $100 \text{ K} \geq T \geq 40 \text{ K}$. The solid line represents the fit to the data and gives $J = -165 \pm 4 \text{ cal/mol}$.

plot for the $\Delta m_s = 1$ region. The experimental data were fit to the equation⁷

$$I_{\text{EPR}} = \frac{C}{T} \left[\frac{3 \exp\left(\frac{-2J}{RT}\right)}{1 + 3 \exp\left(\frac{-2J}{RT}\right)} \right]$$

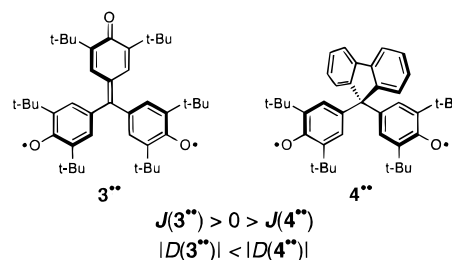
to yield $J = -165 \pm 4 \text{ cal/mol}$. The higher temperatures used in the Curie plot are near the softening point of MTHF, and therefore, the J -value from the fit represents an upper limit. Furthermore, if the MTHF is removed from the sample used to record the spectra shown in Figure 3 and replaced with toluene, spectra identical to those in Figure 1 are observed.

Our observations are consistent with two rotamers (e.g., phenoxy ring rotamers) giving rise to two different $S = 1$ spectra. What is so spectacular is that one rotamer is a singlet ground state ($J \leq -165 \pm 4 \text{ cal/mol}$), while the other rotamer appears to be a triplet ground state ($J \geq 0$), and that the simultaneous presence of these rotamers is dependent on the solvent matrix. We are unaware of another molecule that displays this behavior. There are, however, examples of solvent

(7) For a discussion of the utility of Curie plots, see the following and references cited therein: *The Chemistry of Quinonoid Compounds*; Berson, J. A., Ed.; John Wiley & Sons: New York, 1988; Vol. II, p 482.

affecting a biradical D -value. Luckhurst and co-workers reported EPR spectra for metaphenylene bis(*tert*-butylnitroxide) in toluene ($|D/hc| = 0.0344 \text{ cm}^{-1}$) and ethanol ($|D/hc| = 0.0479 \text{ cm}^{-1}$) and concluded that the two D -values were due to different rotamers.⁸ In view of the observations by Luckhurst et al., the different D -values (0.0077 cm^{-1} vs 0.01015 cm^{-1}) for $2^{\bullet\bullet}$ are in accord with two species that differ in phenoxy ring torsions.

The D -value for the rotamer of $2^{\bullet\bullet}$ that is a singlet ground state is greater than that of the rotamer that appears to be a triplet ground state. For $2^{\bullet\bullet}$, we feel this is reasonable since large phenoxy ring torsions should simultaneously attenuate J and isolate the unpaired electrons in nearby regions of space, thereby decreasing the average interelectronic distance and increasing D ($D \approx 1/r^3$).^{5b,c} There is precedent for our analysis: Kreilick and co-workers showed⁹ that biradicals $3^{\bullet\bullet 10,11}$ and $4^{\bullet\bullet 12,13}$ have the same trend in D and J as we propose for different rotamers of $2^{\bullet\bullet}$.



In conclusion, we have shown that exchange coupling in $2^{\bullet\bullet}$ is dependent on solvent matrix. We propose that in methyleneadamantane type TMM biradicals, J is extremely sensitive to bond torsions, and we feel that our results elaborate on the delicate relationships among geometry, environment, and exchange coupling in general. Further studies along these lines are underway.

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Supporting Information Available: Synthetic details and spectral data (40 pages). See any current masthead page for ordering and Internet access instructions.

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(9) Kopf, P. W.; Kreilick, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 6569.

(10) Kreilick, R. *J. Chem. Phys.* **1965**, *43*, 308.

(11) Yang, N. C.; Castro, A. J. *J. Am. Chem. Soc.* **1960**, *82*, 6208.

(12) Chandross, E. A.; Kreilick, R. *J. Am. Chem. Soc.* **1964**, *86*, 1263.

(13) We are aware of only two references that cite the D -value of $4^{\bullet\bullet}$ alluded to in ref 12 (Kopf, P. W.; Kreilick, R. W. *J. Am. Chem. Soc.* **1969**, *91*, 6569. *Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology*; Hellwege, K.-H., Ed.; *Magnetic Properties of Free Radicals* Vol. 9, Part d2; *Organic Cation Radicals and Polyradicals*; Springer-Verlag: New York, 1980 (this reference notes that the D -value "is not unambiguous"). Several interpretations have led to some ambiguity in the value of D for $4^{\bullet\bullet}$. Nevertheless, all interpretations agree on a value that is at least 0.005 cm^{-1} : a value greater than that of $3^{\bullet\bullet}$. Interestingly, if one uses the outermost peaks of the spectrum of $4^{\bullet\bullet}$, a D -value of ca. 0.012 cm^{-1} is calculated: a value very close to the rotamer of $2^{\bullet\bullet}$ that exhibits antiferromagnetic coupling.