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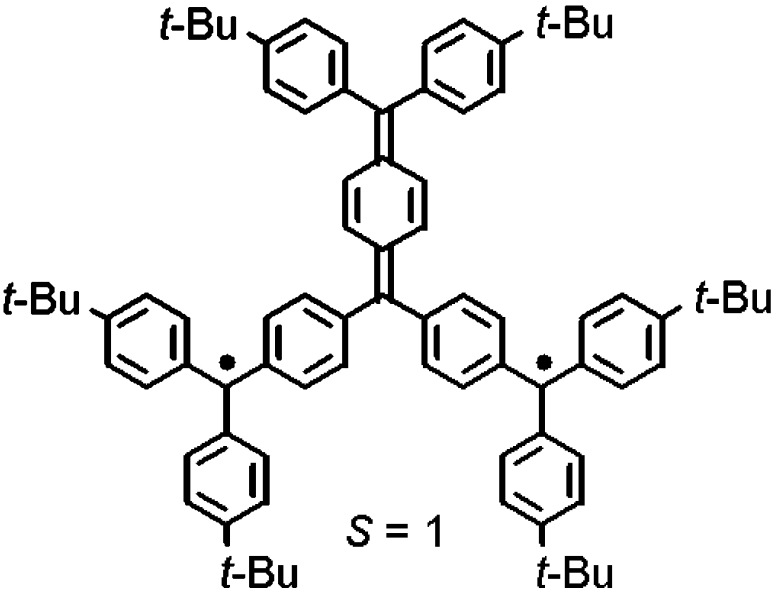

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Stable Hydrocarbon Diradical, An Analogue of Trimethylenemethane

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Abstract: Hydrocarbon diradical **1**, a new stable, 3-fold symmetric analogue of trimethylenemethane (TMM) with no heteroatom perturbation, is prepared and studied. Such diradicals should provide new building blocks for high-spin hydrocarbon polyradicals with very strong net ferromagnetic coupling. Magnetic studies (SQUID) and EPR spectroscopy indicate that **1** in tetrahydrofuran-d_8 (THF-d_8) possesses a triplet ($S = 1$) ground state, with strong ferromagnetic coupling. After annealing at room temperature, the EPR spectra of **1** ($\sim$0.02 M in frozen THF-d_8) consist of a single narrow resonance ($\Delta H_{\mathrm{pp}} < 1$ G), and intermolecular antiferromagnetic coupling is increased by 1 order of magnitude. This behavior is consistent with the presence of exchange narrowing, thus suggesting aggregation of **1** in THF-d_8. Blue solutions of **1** in THF-d_8 possess a strong UV−vis absorption band at $\lambda_{\max} \approx 640$ nm. Diradical **1** in THF-d_8 is stable (or persistent) at room temperature, with no detectable decomposition for at least 2 days.

Introduction

Trimethylenemethane (TMM) diradical was first detected in an inert matrix at cryogenic temperatures by Dowd in 1966.[1] Since then, both the parent TMM structure and its derivatives have been among the most studied reactive organic intermediates,[2] with current relevance spanning a wide range of areas, such as theory of molecular structure and bonding,[3−6] gas-phase chemistry,[7,8] organometallic chemistry,[9] organic synthesis,[10] and organic magnetism.[11−16] The significant and diverse impact of TMM has resulted from the synthesis and studies of TMM derivatives, modified to improve stability (or persistence) and tailored to the desired properties. In this context, the minimally perturbed and stable derivatives of TMM are of general interest.

TMM is the triplet ground state diradical with an extraordinary large singlet−triplet energy gap, $\Delta E_{\mathrm{ST}} = 13{-}16$ kcal mol^{-1}, as estimated by the photoelectron spectroscopy of the radical anion of TMM.[7] This estimate is within the range predicted by computational models.[4a,b,5a] The large ΔE_{ST} implies extraordinary strong ferromagnetic coupling between the spins of unpaired electrons in TMM. Therefore, TMM and its derivatives provide excellent structural templates for study of pairwise exchange coupling, and they are attractive building blocks for high-spin polyradicals.[11−15]

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(1) (a) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587−2589. (b) Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242−248. (c) Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726−5727. (d) Cramer, C. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1007−1013.

(2) (a) Berson, J. A. In *Reactive Intermediate Chemistry*; Moss, R. A., Platz, M. S., Jones, M., Jr., Eds.; Wiley: Hoboken, NJ, 2004; Chapter 5, pp 165−203. (b) Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446−453. (c) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725−5726.

(3) (a) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587−4594. (b) Borden, W. T. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 1.

(4) (a) Ma, B.; Schaefer, H. F. *Chem. Phys.* **1996**, *207*, 31−41. (b) Cramer, C. J.; Smith, B. A. *J. Phys. Chem.* **1996**, *100*, 9664−9670. (c) Li, J.; Worthington, S. E.; Cramer, C. J. *J. Chem. Soc., Perkin Trans. 2* **1998**, 1045−1051.

(5) (a) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2002**, *117*, 4694−4708. (b) Slipchenko, L. V.; Krylov, A. I. *J. Chem. Phys.* **2003**, *118*, 6874−6883.

(6) Baily, T.; Maltsev, A.; Gerson, F.; Frank, D.; de Meijere, A. *J. Am. Chem. Soc.* **2005**, *127*, 1983−1988.

(7) (a) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1996**, *118*, 475−476. (b) Wenthold, P. G.; Hu, J.; Squires, R. R.; Lineberger, W. C. *J. Am. Soc. Mass. Spectrom.* **1999**, *10*, 800−809.

(8) Radical cations of TMM in the gas phase: Chou, P. K.; Gao, L.; Tichy, S. E.; Painter, S. L.; Blackstock, S. C.; Kenttämaa, H. I. *J. Phys. Chem. A* **2000**, *104*, 5530−5534.

(9) (a) Evans, W. J.; Perotti, J. M.; Ziller, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 1068−1069. (b) Kissounko, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2004**, *126*, 5946−5947.

(10) (a) Maiti, A.; Gerken, J. B.; Masjedizadeh, M. R.; Mimieux, Y. S.; Little, R. D. *J. Org. Chem.* **2004**, *69*, 8574−8582. (b) Lee, H.-Y.; Kim, Y. *J. Am. Chem. Soc.* **2003**, *125*, 10156−10157. (c) Nakamura, E.; Yamago, S. *Acc. Chem. Res.* **2002**, *35*, 867−877. (d) Trost, B. M.; Crawley, M. L. *J. Am. Chem. Soc.* **2002**, *124*, 9328−9329.

(11) Reviews on high-spin polyradicals: (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346−351. (b) Rajca, A. *Chem. Rev.* **1994**, *94*, 871−893. (c) Lahti, P. M. *Magnetic Properties of Organic Materials*; Marcel Dekker: New York, 1999; pp 1−713. (d) Itoh, K., Kinoshita, M., Eds. *Molecular Magnetism*; Gordon and Breach: Kodansha, 2000; pp 1−337. (e) Crayston, J. A.; Devine, J. N.; Walton, J. C. *Tetrahedron* **2000**, *56*, 7829−7857. (f) Rajca, A. *Chem.−Eur. J.* **2002**, *8*, 4834−4841.

(12) Bis-TMM tetraradicals: (a) Jacobs, S. J.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744−1753. (b) Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273−13283. (c) West, A. P., Jr.; Silverman, S. K.; Dougherty, D. A. *J. Am. Chem. Soc.* **1996**, *118*, 1452−1463.

(13) (a) Tanaka, M.; Matsuda, K.; Itoh, T.; Iwamura, H. *J. Am. Chem. Soc.* **1998**, *120*, 7168−7173. (b) Sakurai, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **2000**, *122*, 9723−9734. (c) Shultz, D. A.; Fico, R. M., Jr.; Bodnar, S. H.; Kumar, K.; Vostrikova, K. E.; Kampf, J. W.; Boyle, P. D. *J. Am. Chem. Soc.* **2003**, *125*, 11761−11771. (d) Shultz, D. A.; Fico, R. M., Jr.; Lee, H.; Kampf, J. W.; Kirschbaum, K.; Pinkerton, A. A.; Boyle, P. D. *J. Am. Chem. Soc.* **2003**, *125*, 15426−15432.

(14) Michinobu, T.; Inui, J.; Nishide, H. *Org. Lett.* **2003**, *5*, 2165−2168.

(15) (a) Rajca, S.; Rajca, A.; Wongsriratanakul, J.; Butler, P.; Choi, S. *J. Am. Chem. Soc.* **2004**, *126*, 6972−6986. (b) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *J. Am. Chem. Soc.* **2004**, *126*, 6608−6626. (c) Rajca, A.; Wongsriratanakul, J.; Rajca, S.; Cerny, R. L. *Chem.−Eur. J.* **2004**, *10*, 3144−3157.

(16) (a) Rajca, A.; Wongsriratanakul, J.; Rajca, S. *Science*, **2001**, *294*, 1503−1505. (b) Rajca, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **1999**, *121*, 6308−6309.

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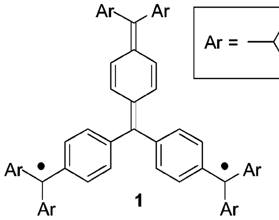
TMM



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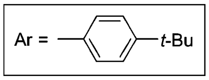

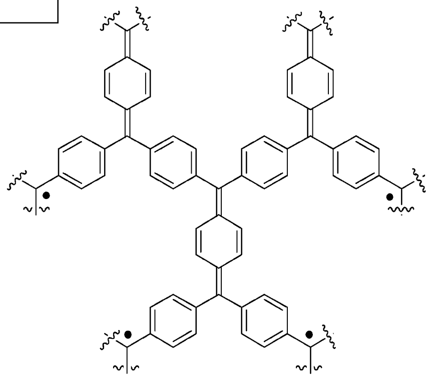

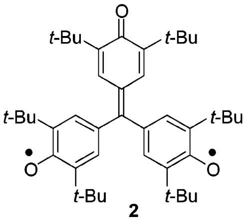

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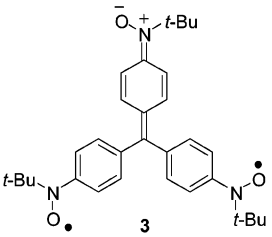

3

Diradicals with strong ferromagnetic coupling are prerequisites for the design of organic polymers with improved magnetic ordering temperatures.[11f,16a] Thermal stability (or long-term persistence) at room temperature is one of the desired properties. Furthermore, the structures of diradicals have to be adequate for incorporation in the extended π-conjugated system of the polymer, such that the strong ferromagnetic coupling and thermal stability are maintained. The design and synthesis of such diradical building blocks remains a challenge.[11f,15,16]

Diradical **1**, which is the 1,4-phenylene analogue of TMM, may provide a building block for organic magnetic materials. Moreover, the structure of **1** is suitable for homologation to extended π-systems with high-spin and minimally perturbed ferromagnetic coupling. The heteroatom analogues of **1**, such as diradicals **2** ("Young's biradical") and **3**, are well-known, stable, triplet ground state diradicals, though the extension to high-spin polyradicals with strong ferromagnetic coupling is inherently limited by their structures.[17−21]

We now report efficient synthesis and magnetic characterization of hydrocarbon diradical **1**. We find that diradical **1** is stable (or long-term persistent) at room temperature and possesses a triplet ground state with strong ferromagnetic coupling. Thus, **1** is one of the very few hydrocarbon diradicals combining strong ferromagnetic coupling with stability at room temperature.[22]

Results and Discussion

1. Carbotetraanion $\mathbf{1^{4-},4Li^{+}}$: Synthesis, Quenching Studies, and Cyclic Voltammetry. Carbotetraanion $\mathbf{1^{4-},4Li^{+}}$ (Scheme 1) is the key intermediate in preparation of diradical **1**. In addition, $\mathbf{1^{4-},4Li^{+}}$ may be viewed as an analogue of the unknown TMM tetraanion.

Tetraether $\mathbf{1\text{-}(OEt)_4}$ is prepared via a convergent route, in which 3-fold addition of aryllithium to dimethyl carbonate is followed by etherification with ethyl chloroformate in the presence of trace amounts of ethanol (Scheme 1).[23] Treatment of $\mathbf{1\text{-}(OEt)_4}$ with Li (1% Na) metal in tetrahydrofuran (THF) for 4 days at room temperature gives a suspension of purple−red carbotetraanion $\mathbf{1^{4-},4Li^{+}}$. Addition of MeOH or MeOD to $\mathbf{1^{4-},4Li^{+}}$ gives hydrocarbon $\mathbf{1\text{-}(H)_4}$ and its tetradeuterated isotopomer $\mathbf{1\text{-}(D)_4}$ (96% D). Thus, carbotetraanion $\mathbf{1^{4-},4Li^{+}}$ is persistent (or stable) in THF.

Cyclic voltammetry (CV) of $\mathbf{1^{4-},4Li^{+}}$ in THF/TBAPF$_6$ (tetrabutylammonium hexafluorophosphate), carried out at room temperature, shows only a single quasi-reversible wave at half-peak potential ($E_{p/2}$) of −1.39 V and an irreversible wave at peak potential (E_p) of +0.27 V. This cyclic voltammogram is similar to that reported for the tris(4-*tert*-butylphenyl)methyl carbanion.[24] As more CV waves are expected for a carbotetraanion such as $\mathbf{1^{4-},4Li^{+}}$, this result suggests the possibility of quenching of $\mathbf{1^{4-},4Li^{+}}$ by the electrolyte solution at room temperature. Therefore, following the electrochemical study, the solution is quenched with MeOD; only two quenching products, $\mathbf{1\text{-}(D)_3(H)_1}$ and $\mathbf{1\text{-}(D)_3(Bu)_1}$ are isolated (Scheme 1). This implies that carbotrianions, which are derived from $\mathbf{1^{4-},4Li^{+}}$ by either protonation or butylation at its center triarylmethyl carbanion, are responsible for the CV wave at $E_{p/2} = -1.39$ V.

Quenching of $\mathbf{1^{4-},4Li^{+}}$ by TBAPF$_6$ can be suppressed at low temperature, as indicated by the experiment carried out at −78 °C, in which TBAPF$_6$ is added to $\mathbf{1^{4-},4Li^{+}}$ in THF, and then, after 2 h, followed by MeOD, to give exclusively $\mathbf{1\text{-}(D)_4}$ (93% D). Therefore, the electrolyte solution, containing $\mathbf{1^{4-},4Li^{+}}$, is prepared and handled strictly below −70 °C in the subsequent electrochemical study, in which several CV waves in the −0.2 to −3.0 V range at −73 to −76 °C are observed. Four major CV waves at $E_{p/2} = -2.32$, -2.11, -1.15, and -0.94 V are assigned to the consecutive four one-electron oxidations from tetraanion-to-(trianion radical)-to-dianion-to-(radical anion)-to-diradical (Figure 1s in the Supporting Information). This assignment may only be tentative as the electrode processes are complex.[25] At slow scanning rates, the peak cathodic (return) current becomes greater than the peak anodic (forward) current

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

(18) EPR spectroscopy and X-ray crystallography of **2**: (a) Mukai, K.; Ishizu, K.; Kakahara, M.; Deguchi, Y. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 3363−3364. (b) Willigen, H.; Kirste, B.; Kurreck, H.; Plato, M. *Tetrahedron* **1982**, *38*, 759−764. (c) Bock, H.; John, A.; Havlas, Z.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 416−418.

(19) Tris[*p*-(*N*-oxyl-*N*-*tert*-butylamino)phenyl]methyl, diradical **3**: (a) Itoh, T.; Matsuda, K.; Iwamura, H.; Hori, K. *J. Am. Chem. Soc.* **2000**, *122*, 2567−2576. (b) Oniciu, D. C.; Matsuda, K.; Iwamura, H. *J. Chem. Soc., Perkin 2* **1996**, 907−913.

(20) Although extended high-spin structures can be drawn for analogues of **3**, in which *t*-Bu groups are replaced with 1,3-phenylene-like coupling units, such oligonitroxides would be unprecedented. For example, no successful extension from diarylnitroxide to high-spin π-conjugated bis(diarylnitroxides) was reported to date.

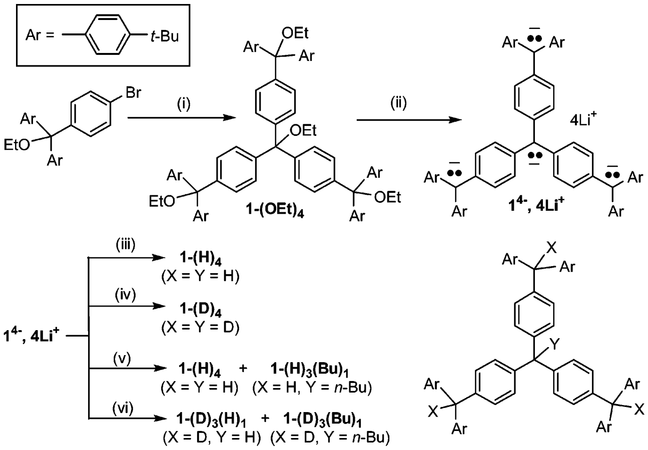
(21) The diradical, which is formally derived from **2** via replacement of one of the phenoxyls with the triarylmethyl, was difficult to prepare, and neither its ground state nor strength of the exchange coupling could be determined: Fukuzaki, E.; Takahashi, N.; Imai, S.; Nishide, H.; Rajca, A. *Polym. J.* **2005**, *37*, 284−293.

(22) Rajca, A.; Utamapanya, S. *J. Org. Chem.* **1992**, *57*, 1760−1767.

(23) Rajca, A. *J. Org. Chem.* **1991**, *56*, 2557−2563.

(24) Utamapanya, S.; Rajca, A. *J. Am. Chem. Soc.* **1991**, *113*, 9242−9251.

Scheme 1. Synthesis and Quenching Studies of Carbotetraanion ($\mathbf{1^{4-},4Li^{+}}$) [a]



[a] Conditions: (i) BuLi (1.0 equiv), diethyl ether, −10 °C for 0.5 h, then dimethyl carbonate, −10 °C to room temperature for 2 h, then ethyl chloroformate, 0 °C to room temperature for 12 h; (ii) Li (1% Na), THF, rt for 4 days; (iii) MeOH at −78 °C; (iv) either MeOD at −78 °C or TBAPF$_6$ at −78 °C, then MeOD at −78 °C; (v) rt with TBAPF$_6$, then MeOH at −78 °C; (vi) rt with TBAPF$_6$, then MeOD at −78 °C.

for the wave at $E_{p/2} = -1.15$ V (dianion−radical anion couple). Two additional shoulders are found, with $E_{p/2} = -1.8$ to -1.9 V and $E_{p/2} = -1.2$ to -1.3 V.[26] This is in contrast to 1,3-phenylene-based polyarylmethyl carbotetraanions at low temperatures, for which well-defined reversible CVs for the oxidation tetraanion to tetraradical in the $E_{p/2} = -1.2$ to -1.9 V potential range, with the relative peak currents 1:2:1 (or 1:1:2), were obtained.[27] Upon warming the solution to room temperature, a single reversible wave at $E_{p/2} = -1.39$ V is obtained (Figure 1s in the Supporting Information); after quenching with MeOH, **1-(H)$_4$** and **1-(H)$_3$(Bu)$_1$** are isolated (Scheme 1).[28]

Significant potential differences between the four one-electron redox couples between the tetraanion and the diradical suggest that all intermediate redox species may be prepared without significant disproportionation.[29] The large potential difference of nearly 1 V between the (trianion radical)−dianion and dianion−(radical anion) couples is consistent with increased stability of the dianion. The corresponding TMM dianion, in which both nonbonding and degenerate π-HOMOs are occupied, may be formally considered as a six-electron Y-aromatic species.[30] Although the (radical anion)−diradical couple possesses significantly less negative potential, compared to those for the corresponding 1,3-phenylene-based polyradicals, iodine should still be a suitable reagent for oxidation of $\mathbf{1^{4-},4Li^{+}}$ to **1**.[31]

2. Generation of Diradical 1 for Magnetic and EPR Studies. Tetraether **1-(OEt)$_4$** (1.2−1.5 mg) was treated with Li metal (1% Na) in THF-d_8 (~0.06 mL) for 2−4 days at room temperature. The resultant purple−red carbotetraanion $\mathbf{1^{4-},4Li^{+}}$ was filtered into a SQUID sample container. Due to low solubility of $\mathbf{1^{4-},4Li^{+}}$ and its strong affinity for the quartz surface, it is difficult to ensure complete mass transfer of the sample. Upon addition of iodine in small portions at the temperatures near the freezing point of the reaction mixture, the following sequence of color changes is observed: purple, blue, blue−green, and green. The studies, described in the following section, established that the blue color corresponds to diradical **1**, and subsequent color changes are associated with the admixture of iodine (yellow color in THF-d_8). Therefore, three types of samples corresponding to distinct titration points, that is, identified by their color as “blue” (diradical **1**), “blue−green” (diradical **1** with slight excess of iodine), and “green” (diradical **1** with large excess of iodine), were studied (Table 1).

3. Magnetic Studies, EPR Spectroscopy, and UV−Vis Spectroscopy of Diradical 1. Magnetic studies and EPR spectroscopy were carried out using identical samples of diradical **1** in THF-d_8. The samples for magnetic studies were contained in specially designed flame-sealed 5 mm o.d. quartz tubes with false bottoms to provide more uniform diamagnetic background, as described elsewhere.[15] Such tubes were accommodated by the nitrogen gas flow system of the X-band EPR instrument, allowing EPR spectra of **1** to be obtained before and after each SQUID run. In addition, samples of **1** in such tubes are used to obtain UV−vis spectra of thin layers of **1** in THF-d_8 at room temperature. Another set of samples of relatively dilute **1** in 2-methyltetrahydrofuran/THF (2-MeTHF/THF) was studied only by EPR spectroscopy.

For the initial set of measurements, each sample of diradical **1** in THF-d_8 was prepared and handled strictly near the freezing point of the solvent (~170 K), using procedures described elsewhere.[15] Magnetization (M) was measured as a function of magnetic field ($H = 0{-}5 \times 10^4$ Oe and $T = 1.8$, 3, and 5 K) and temperature ($T = 1.8{-}150$ K at $H = 5000$ Oe and, for selected samples, 500 Oe). For most samples, following the initial sequence of magnetic measurements, EPR spectra were obtained at 140 K. The next sequence of the SQUID/EPR measurements was carried out after annealing diradical **1** in THF-d_8 at room temperature. Those samples of **1**, which contained a large excess of iodine (green color), became effectively diamagnetic, even after relatively brief (30 min) exposure to ambient temperature, thus allowing for point-by-point background correction for diamagnetism.[15]

The results of magnetic and EPR spectroscopic studies are summarized in Table 1 and illustrated in Figures 1−6.

3.1. Studies of 1 Before Annealing at Room Temperature. Initial studies involved the samples of ~0.02 M diradical **1** in THF-d_8, which were prepared and handled strictly at low temperature. The samples are annealed at 170 K (or 90 K) prior to magnetic studies (Table 1).

The magnetization (M) versus magnetic field (H) data at low temperatures ($T = 1.8$, 3, 5 K) provide excellent fits to the Brillouin functions with a mean-field parameter ($\theta < 0$), that is, M versus $H/(T - \theta)$. Such fits have two variable parameters, that is, total spin (S) and magnetization at saturation (M_{sat}); the mean-field parameter θ is adjusted until the M/M_{sat} versus $H/(T - \theta)$ plots overlap at all temperatures. The values of $S \approx 1$

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(25) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980; Chapters 3, 11, and 12.

(26) In addition to complex electrode processes (e.g., slow electron transfer, follow-up reaction, or adsorption), the shoulders in CVs obtained at low temperatures may be caused by the presence of impurity carbotrianions derived from the reaction of $\mathbf{1^{4-},\ 4Li^{+}}$ with TBAPF$_6$ (or inadvertent protic impurities).

(27) (a) Rajca, S.; Rajca, A. *J. Am. Chem. Soc.* **1995**, *117*, 9172−9179. (b) Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, *117*, 806−816.

(28) Atomic connectivity in **1-(H)$_3$(Bu)$_1$** is confirmed, using partially refined X-ray crystallographic data (Figure 2s, Supporting Information).

(29) Rajca, A.; Safronov, A.; Rajca, S.; Wongsriratanakul, J. *J. Am. Chem. Soc.* **2000**, *122*, 3351−3357.

(30) Sommerfeld, T. *J. Am. Chem. Soc.* **2002**, *124*, 1119−1124.

(31) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877−910.

Table 1. Summary of Magnetic Data and Numerical Fits to the Brillouin Functions for Diradical **1**[a]

sample number	mass[a] (mg)	color	anneal temp (K)	anneal time (h)	S	$-\theta$ (K)	M_{sat}[b] (μ_B)	χT[c] (emu K mol^{-1})	$\chi T/M_{sat}$
1	1.37	blue	170		1.00	0.07	0.64	0.68	1.06
			rt[d]	1	0.98	0.5	0.77	0.78	1.01
			rt[d]	57	0.98	0.5	0.76	0.77	1.01
2	1.45	blue/ green	170		0.97	0.06	0.70	0.72	1.01
			rt[d]	1	0.98	0.5	0.62	0.60	0.98
			rt[d]	600	0.98	0.5	0.51	0.49	0.96
3	1.40	green	170		~1.0	0.05	0.65		
			rt[d]	1	dia	dia	dia	dia	dia
4	1.21	green	90		0.92	0	0.49	0.49	1.00
			rt[d]	0.5	dia	dia	dia	dia	dia
5	1.18	green	170		0.95	0.05	0.59	0.60	1.02

[a] Mass of tetraether **1-(OEt)$_4$**. [b] M_{sat} per mol of arylmethyl diether, i.e., per mol of expected radical. [c] χT_{max} per mol of tetraether **1-(OEt)$_4$** measured at 5000 Oe. [d] Room temperature, 293−298 K.

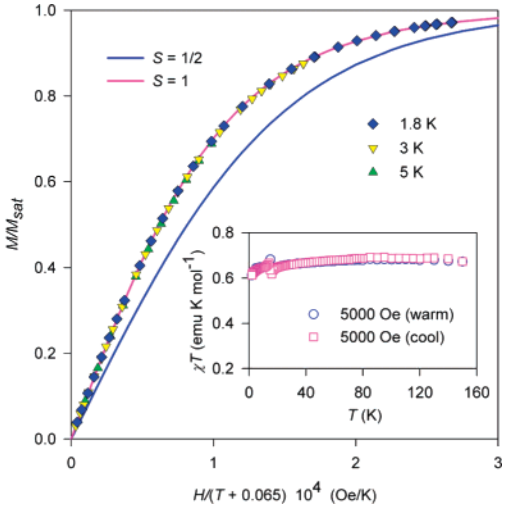

Figure 1. SQUID magnetometry for diradical **1** in THF-d_8 after annealing at 170 K (sample 1, Table 1). Main plot corresponds to M/M_{sat} versus $H/(T - \theta)$, with solid lines showing plots of Brillouin functions with $S = {}^1/_2$ and $S = 1$; inset plot corresponds to χT versus T in both cooling and warming modes.

(0.92−1.00), determined from the curvature of the Brillouin plots, indicate the triplet ($S = 1$) ground state for diradical **1** (Figure 2). The values of $\theta < 0$ and $|\theta| \approx 0$ imply nearly negligible, and almost certainly intermolecular, antiferromagnetic coupling.

M_{sat} measures the number of unpaired electron spin (or spin concentration) in the limit of low temperature and high magnetic field. For an $S = 1$ diradical, M_{sat} should be 1.00 in the units of Bohr magneton (μ_B) per radical site. The measured values for **1** are $M_{sat} = 0.49-0.70$ μ_B (Table 1). Unlike the values of S, values of M_{sat} are dependent on the mass of the starting tetraether, **1-(OEt)$_4$**. Therefore, values of M_{sat} would be lower if mass transfers during preparation of **1** are incomplete. This may include transfers of **1-(OEt)$_4$**, which is an electrostatic powder, to the reaction vessel, mass losses in filtration of **1^{4-},4Li$^+$**, or formation of defects in the process of radical generation.[15]

The value of χT (product of magnetic susceptibility and temperature) and its temperature dependence measure both the ground state and the strength of exchange coupling in **1** (Figure 1). For an $S = 1$ diradical, with strong ferromagnetic coupling, a value of χT should be 1.00 emu K mol^{-1} (per mol of precursor of diradical, such as **1-(OEt)$_4$**). The measured values, $\chi T = 0.49-0.72$ emu K mol^{-1}, are nearly identical to the numerical values of M_{sat} (in the unit of μ_B) for each sample of **1** (Table 1). Therefore, $\chi T \approx 1$ is found for all samples of **1**, after values of χT are corrected by spin concentration (M_{sat}). Although the χT versus T plots are nearly flat (Figure 1), small errors in correction for diamagnetism may have significant impact on such plots, especially at higher temperatures. Because accurate point-by-point correction for diamagnetism for samples of **1** could not be attained, only a lower limit of more than 100 K (0.05 kcal mol^{-1}) for the singlet−triplet energy gap may be estimated. This is consistent with a strong ferromagnetic coupling.

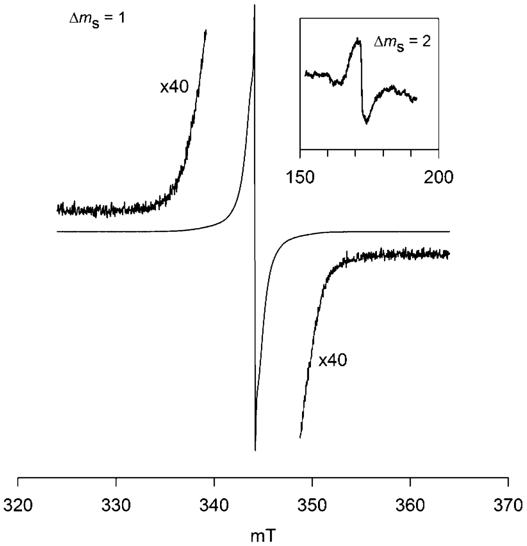

Figure 2. EPR spectra for diradical **1** in THF-d_8, following SQUID magnetometry (sample 1, Table 1). The sample was maintained at all times below 170 K. Main and inset plots show $\Delta m_s = 1$ and $\Delta m_s = 2$ regions, respectively, at 140 K.

Following the magnetic studies, diradical **1** in THF-d_8 is studied by EPR spectroscopy at 140 K. The $\Delta m_s = 1$ spectra consist of a narrow center line (peak-to-peak width, $\Delta H_{pp} \approx 0.09$ mT = 0.9 G) and broad shoulders with a spectral width on the order of 10 mT (Figure 2).[32] Similar spectral widths have been reported for diradicals **2** and **3**.[18,33] In the $\Delta m_s = 2$ region, a weak singlet is observed at high microwave power and high gain; this signal is observed in both perpendicular and parallel modes.[34] These results indicate the presence of triplet state.

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(32) The g value for **1** is approximately 2.003.

(33) The EPR spectrum for diradical **3** in 2-methyltetrahydrofuran matrix at cryogenic temperatures has been described as "broad and little-structured signal" with spectral width of 140 G and $g = 2.0043$; no $\Delta m_s = 2$ transition has been observed.[19b]

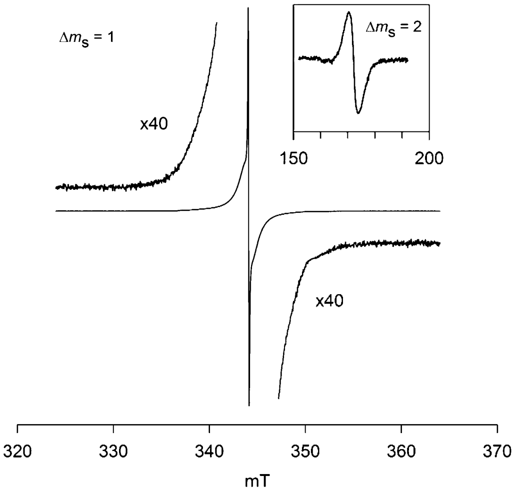

Figure 3. EPR spectroscopy for a dilute sample of diradical **1** in THF-d_8 after annealing at 170 K (sample 3, Table 1). Main and inset plots show $\Delta m_s = 1$ and $\Delta m_s = 2$ regions, respectively, at 140 K.

EPR spectra of a dilute sample of **1** in THF-d_8 is shown in Figure 3; the most outer shoulders for diradical **1** may be discerned, and the center line is relatively narrow ($\Delta H_{pp} \approx 0.03$ mT = 0.3 G).[35]

3.2. Studies of 1 After Annealing at Room Temperature. Selected samples of diradical **1** are annealed for at least 0.5 h at room temperature. It should be emphasized that those samples prepared with a large excess of iodine (green color) become diamagnetic (Table 1). After annealing for 1 h at room temperature, the sample prepared with a slight excess of iodine (blue−green color) retained its paramagnetism, with somewhat lowered values of M_{sat} and χT (Table 1); after 25 days at room temperature, the values of M_{sat} and χT are decreased to 0.5 μ_B (i.e., spin concentration of 50%) and 0.5 emu K mol^{-1}, respectively. After annealing for 1 h at room temperature, the sample prepared with an adequate amount of iodine (blue color) retained paramagnetism and its blue color, and its values of M_{sat} and χT are modestly increased from 0.64 to 0.77 μ_B and from 0.68 to 0.78 emu K mol^{-1}, respectively (Figures 1 and 4); after 2 days at room temperature, the values of M_{sat} and χT are unchanged (Table 1). UV−vis absorption spectrum for such blue-colored **1** in THF-d_8 possesses an intense band at $\lambda_{max} \approx$ 640 nm (Figure 3s in the Supporting Information).

These results indicate that diradical **1** is persistent at room temperature in THF-d_8. The behavior of the samples after annealing at room temperature may be rationalized by increased reactivity of iodine at higher temperatures. For the green and green−blue samples, an excess amount of iodine reacts with diradical at elevated temperatures, leading to diamagnetic products and/or decreased paramagnetism.[36] Increase in paramagnetism of the blue sample after annealing at room temperature may indicate that the oxidation process was incomplete at low temperature; that is, at elevated temperatures, unreacted iodine further oxidizes carbanionic intermediates, increasing the amount of diradical.

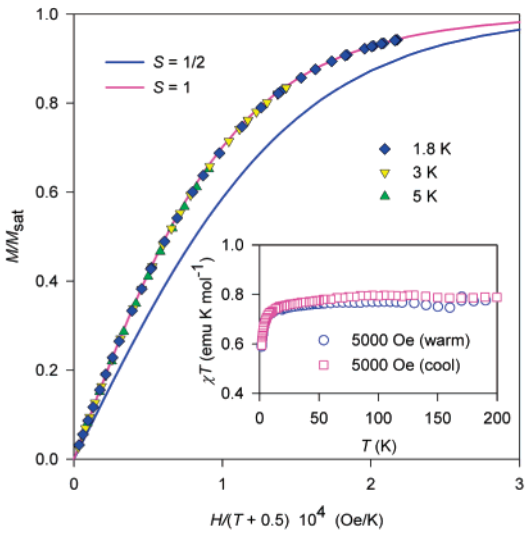

Figure 4. SQUID magnetometry for diradical **1** in THF-d_8 after annealing at room temperature for 1 h (sample 1, Table 1). Main plot corresponds to M/M_{sat} versus $H/(T - \theta)$, with solid lines showing plots of Brillouin functions with $S = {}^1/_2$ and $S = 1$; inset plot corresponds to χT versus T in both cooling and warming modes.

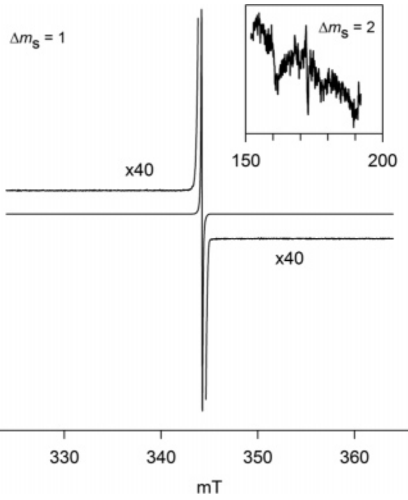

Figure 5. EPR spectroscopy for diradical **1** in THF-d_8 after annealing at room temperature for 1 h (sample 1, Table 1) and following SQUID magnetometry. Main and inset plots show $\Delta m_s = 1$ and $\Delta m_s = 2$ regions, respectively, at 140 K.

Notably, the samples of diradical **1** in THF-d_8, which remain strongly paramagnetic after annealing at room temperature, show only a narrow center line with $\Delta H_{pp} \approx 0.08$ mT = 0.8 G and the spectral width at the baseline (e.g., 2^{11} vertical expansion) of <2 mT at 140 K. Consequently, the $\Delta m_s = 2$ signal is almost undetectable at 140 K (Figure 5). Because the magnetic data for such samples indicate the $S = 1$ ground state, the apparent absence the electron dipole−dipole spectroscopic pattern may be associated with the exchange narrowing via intermolecular exchange coupling.[37] Although samples of diradical **1** in THF-d_8 appear homogeneous at room temperature, either aggregation or precipitation of diradical **1** upon cooling to 140 K may not be excluded. Indirect support for the exchange narrowing is

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(34) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986; Chapter 10, pp 242−244.

(35) Because the samples are relatively short (~5 mm height), the spectra are dependent on the position of the sample tube in the X-band cavity; that is, a relatively more intense center line is obtained when the upper part of the sample tube (especially just above the sample) is inside the cavity. This part of the sample tube is more likely to contain "impurities" (e.g., monoradicals, precipitated diradical) and also diradical, which could have been inadvertently warmed during the preparation.

(36) For 1,3-phenylene-based polyarylmethyls, reaction with an excess amount of iodine leads to rapid loss of paramagnetism upon annealing at room temperature.[15]

(37) Anderson, P. W.; Weiss, P. R. *Rev. Mod. Phys.* **1953**, *25*, 269−276.

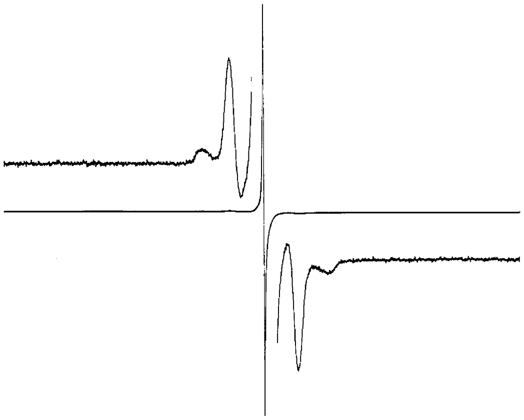

Figure 6. EPR spectrum ($\Delta m_s = 1$) for 0.002 M diradical **1** in 2-MeTHF/THF at ~100 K, after annealing at room temperature. The 64-fold vertical expansions clearly show four side peaks for the $S = 1$ state. The spectral sweep and the center field are 40 and 330 mT, respectively. Modulation of 0.03 mT (0.3 G) is used.

provided by the magnetic studies; that is, after annealing at room temperature, the absolute values of the mean-field parameter $|\theta|$ are increased 10-fold, from $|\theta| \approx 0.05$ to $|\theta| \approx 0.5$ K (Table 1).

For a very dilute, 0.002 M, **1** in 2-MeTHF/THF (7:1), EPR spectra at ~100 K show both the narrow center line ($\Delta H_{pp} \approx 0.09$ mT = 0.9 G) and the well-resolved four side lines in the $\Delta m_s = 1$ region (Figure 6).[38] The four side lines, spanning the spectral width of 10.1 mT (101 G), indicate the presence of the $S = 1$ state and allow for determination of its zero-field-splitting parameters (zfs) (i.e., $|D/hc| \approx 0.004$ cm^{-1} and $|E/hc| = 0$ cm^{-1}). The corresponding values for TMM are $|D/hc| = 0.025$ cm^{-1} and $|E/hc| = 0$ cm^{-1}.[1] These values of zfs parameters are consistent with the 3-fold symmetry for both diradicals.[39] Because the value of $|D/hc|$ in **1** is only modestly decreased compared to that in TMM, this suggests a significant delocalization (and/or polarization) of spin density into the center triarylmethyl moiety of **1**.[40]

Conclusion

1,4-Phenylene-based diradical **1** is stable (or long-term persistent) at room temperature, and it possesses the triplet ground state with relatively strong ferromagnetic coupling. These properties provide an impetus for synthesis of higher homologues of **1** that may lead to high-spin building blocks for organic polymers that order magnetically at higher temperatures and possess improved thermal stability.

Hydrocarbon diradical **1** is a new stable, 3-fold symmetric analogue of TMM with no heteroatom perturbation, thus allowing for a convenient access to study fundamental aspects of TMM-related electronic structure.

Experimental Section

Procedures Involving Lithium and its Organometallic Derivatives were carried out under vacuum (≤1 mTorr) or strictly inert atmosphere of argon or nitrogen gas (≤1 ppm of O_2 and H_2O). However, lithium metal was handled under argon or vacuum only to avoid the reaction with N_2. Excess of lithium metal was typically quenched with ethanol under argon atmosphere.

Electrochemistry. Cyclic voltammetry was carried out in a Vacuum Atmospheres glovebox under an argon gas atmosphere. The glovebox was grounded to minimize electromagnetic interference. The homemade electrochemical cell, solid reagents, syringes, needles, etc. were thoroughly evacuated in Schlenk vessels on the vacuum line, prior to the transfer to the glovebox. Solvent (THF) was doubly vacuum transferred from Na/K alloy benzophenone. Ferrocene, which was sublimed under vacuum, was used as a reference (0.510 V vs SCE). PARC Model 270 potentiostat/galvanostat was used. Three electrodes were used: quasi-reference (Ag-wire), counter (Pt-foil), and working (100-μ Pt-disk supplied by BAS). The concentration of an electroactive solute was about 0.005 M and of the supporting electrolyte (tetrabutylammonium hexafluorophosphate), it was about 0.16 M. The solution volume was about 2.5 mL. The temperature of the solution/electrolyte in the cell was continuously monitored using a thermocouple sensor, placed in a thin-wall glass capillary, partially filled with THF. The cell was placed in a tight-fitting, heavy copper block, which was positioned at the bottom of the well, extending through the floor of the glovebox. Indium metal was used to facilitate good thermal contact between the well and the copper block. The low temperatures were attained by cooling the well with liquid nitrogen.

EPR Spectroscopy. CW X-band EPR spectra for **1** in THF-d_8 were acquired on Bruker EMX instrument, equipped with a frequency counter and nitrogen flow temperature control (130−300 K). The samples, which were contained in the SQUID sample tubes as described in the procedure for preparation of **1**, were typically inserted to the pre-cooled cavity at 140 K. All spectra were obtained using dual mode cavity, with the oscillating magnetic field either perpendicular (TE_{102}) or parallel (TE_{012}) to the swept magnetic field. Most of the spectra were obtained in perpendicular mode. The g values were referenced using DPPH ($g = 2.0037$, powder, Aldrich).

For EPR spectra of **1** in 2-MeTHF/THF (samples in 4 mm o.d. EPR quartz tubes), Bruker 200D SRC instrument, equipped with a Varian nitrogen flow temperature control (100−300 K), was used.

SQUID Magnetometry. Quantum Design (San Diego, CA) MPMS5S (with continuous temperature control) was used. The SQUID sample tubes, kept in liquid nitrogen, were rapidly inserted (<15 s) to the magnetometer at low temperature (typically 10 K) under a helium atmosphere and, then, evacuated and purged with helium in the sample chamber at 90 K. Following the sequence of magnetic measurements, the samples were rapidly withdrawn from the sample chamber of the magnetometer, without melting the THF-d_8 matrix. Following the SQUID and EPR studies at low temperatures, the samples were allowed to attain room temperature for a specified period of time (Table 1). Such samples were carefully reinserted to the magnetometer, with the sample chamber at 300 K. The sequence of measurements started with a cooling mode from 300 to 2 K, and then followed the identical set of measurements as that of the original sample. For the samples, which become diamagnetic due to the excess of iodine, the resultant data were used for the point-by-point correction for diamagnetism. For the remaining samples, correction for diamagnetism was carried out by extrapolation of the χ versus $1/T$ plots from the 70−140 or 70−200 K range (cooling mode with 60 s delay after equilibrium is reached at each temperature).

Numerical Curve Fitting for Magnetic Data. The SigmaPlot for Windows software package was used for numerical curve fitting. The reliability of a fit is measured by the parameter dependence, which is defined as follows: *dependence = 1 − ((variance of the parameter,*

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(38) Blue solutions of **1** in 2-MeTHF/THF are prepared via oxidation of the carbotetraanion in THF at −78 °C, followed by dilution with 2-MeTHF and annealing at room temperature; the EPR spectra, such as in Figure 6, were obtained as early as in 1991. However, at that time, the techniques for SQUID sample preparation were not developed to allow for quantitative magnetic measurements of air-sensitive liquid samples, as reported in this work.

(39) Approximately zero value $|E/hc|$ may also be found by accident, for example, ref 2c.

(40) In a simple point dipole approximation, not applicable in the presence of delocalization, spectral width $|D/hc|$ is related to $1/r^3$, where r is the distance between point dipoles: Rohde, O.; Van, S. P.; Kester, W. R.; Griffith, O. H. *J. Am. Chem. Soc.* **1974**, *96*, 5311−5318.

other parameters constant)/(variance of the parameter, other parameters changing)). Values close to 1 indicate overparametrized fit.

M versus *H* data at low temperatures ($T = 1.8, 3, 5$ K) were analyzed with Brillouin functions (with mean-field parameters) as described in the text (Table 1). Values of parameter dependence were 0.47−0.64, 0.81−0.88, and 0.97−0.98 at 1.8, 3, and 5 K, respectively.

Diradical 1 for SQUID Magnetic Studies and EPR Spectroscopy. All samples of diradical **1** were prepared using a modified low-temperature procedure.[15] Tetraether **1-(OEt)$_4$** (1.18−1.45 mg) was placed in a glass reaction vessel, equipped with a 5 mm o.d. quartz tube with thin bottom 6 cm from the end of the tube.[15a] The vessel containing **1-(OEt)$_4$** was heated overnight under vacuum; that is, part of vessel containing tetraether was immersed in an oil bath at 60 °C, and the rest of the vessel was heated at 200 °C using heating tape. Subsequently, the vessel was transferred to a glovebox and a small piece of Li (1% Na) metal was added. Following attachment of the vessel to vacuum line, Li was allowed to come in contact with **1-(OEt)$_4$** and THF-d_8 (0.05−0.07 mL, 99.95% D) was immediately vacuum-transferred from sodium/benzophenone. After 2−4 days of stirring at ambient temperature, the reaction mixture was filtered under temperature gradient into the quartz tube. Multiple sequences of solvent transfers and filtrations were carried out to ensure as complete as possible mass transfer of suspension of tetraanion **1^{4-},4Li^{+}**. Iodine (99.999%, ultra dry, Alfa) was vacuum-transferred in small portions to the reaction mixture at −103 to −106 °C, until the final color of **1** (blue, blue−green, or green) appeared. The tube was flame-sealed (total length of ∼20 cm) and stored in liquid nitrogen prior to insertion to SQUID magnetometer or EPR spectrometer.

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Supporting Information Available: General procedures and materials, experimental details of the synthesis of **1-(OEt)$_4$**, quenching experiments and cyclic voltammetry studies for the corresponding carbotetraanion, and UV−vis spectra of **1**. This material is available free of charge via the Internet at http://pubs.acs.org.

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