

Intramolecular Antiferromagnetic vs Ferromagnetic Spin Coupling through the Biphenyl Unit

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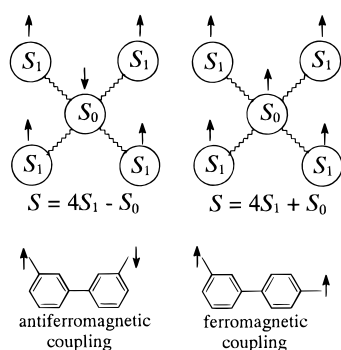
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Abstract: Two isomeric triarylmethyl-based diradicals, with 3,3'- and 3,4'-biphenyl as the spin coupling units, were prepared and studied in frozen solutions by ESR spectroscopy and SQUID magnetometry. The 3,3'-isomer was found to be the singlet ground state, with a singlet–triplet energy gap of -0.1 kcal/mol. The 3,4'-isomer was found to be the triplet ground state. This dependence of intramolecular spin coupling (antiferromagnetic vs ferromagnetic) on topology is in agreement with simple theoretical models. The singlet ground state for the 3,3'-isomer, which has two half-filled nonbonding orbitals, is in formal violation of Hund's rule, as applied to molecules.

Introduction

Design of mesoscopic-size very-high-spin organic molecules is an important aspect of organic magnetism.¹ Recently, versatile synthetic methods for preparation of macrocyclic polyarylmethyl defect-resilient polyradicals with $S \leq 4$ (S is total spin) were reported.^{2,3} One of the possible designs to construct very-high-spin molecules may rely on such macrocyclic polyradicals as modules with spin values, $S_0, S_1 \gg 1/2$, coupled either antiferromagnetically or ferromagnetically via coupling units. Therefore, it is important to identify coupling units, which are readily accessible by efficient synthetic methodologies, possess suitable strengths of spin coupling, and will stabilize radicals.



Sterically unencumbered 3,3'- and 3,4'-biphenyls may provide the desired properties.^{4–6} From the synthetic point of view,

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(1) Recent reviews on spin-coupled organic molecules: Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, 26, 179. Dougherty, D. A. *Acc. Chem. Res.* **1991**, 24, 88. Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, 26, 346. Rajca, A. *Chem. Rev.* **1994**, 94, 871. Miller, J. S.; Epstein, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 385. Yoshizawa, K.; Hoffmann, R. *Chem. Eur. J.* **1995**, 1, 403.

(2) Rajca, A.; Rajca, S.; Padmakumar *Angew. Chem., Int. Ed. Engl.* **1994**, 33, 2091. Rajca, A.; Rajca, S.; Desai, S. R. *J. Am. Chem. Soc.* **1995**, 117, 806.

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(4) Borden, W. T.; Iwamura, H.; Berson, J. A. *Acc. Chem. Res.* **1994**, 27, 109.

(5) Hhckel, E. *Z. Phys. Chem. Abt. B* **1936**, 34, 339.

straightforward C(aryl)–C(aryl) bond forming reactions can be used to make the coupling units and assemble large molecules without subsequent need for extensive functionalization. 3,4'-Biphenyl moiety should also stabilize the radical, without introduction of severe steric congestion. The most straightforward models to assess these coupling units are the related diradicals.

In 1915, Schlenk and Brauns reported preparation of diradicals **1** and **2**.⁷ While di- and polyradicals related to **1** were intensively studied, **2** received much less attention.^{1,8–10} The past studies of **2** were hampered by its thermal instability, which lead to formation of complex mixtures.⁹ When triarylmethyl sites were screened with bulky substituents, stability was improved dramatically and pure diradicals, such as **3** and **4**, were prepared. However, **3** and **4** are undoubtedly highly nonplanar, especially around their biphenyl moieties, therefore it is not obvious whether very weak spin couplings found in **3** and **4**, may even be pertinent to the sterically unencumbered 3,3'-biphenyl-based coupling unit or diradical **2**.¹⁰ In related isomeric dicarbenes **5** (3,3'-isomer) and **6** (3,4'-isomer) which are less sterically hindered than **3** and **4**, the expected antiferromagnetic and ferromagnetic spin couplings were found.¹¹ Similar results were obtained for dinitrenes, analogous to **5** and **6**, with an important exception; i.e., for the 3,3'-isomer, the reported experimental data are compatible with either very strong antiferromagnetic coupling or very weak spin coupling.¹²

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(7) Schlenk, W.; Brauns, M. *Ber.* **1915**, 48, 661, 716.

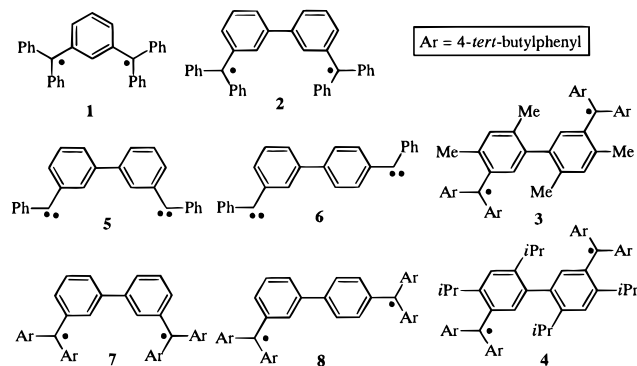
(8) (a) Lockhurst, G. R.; Pedulli, G. F. *J. Chem. Soc. B* **1971**, 329. (b) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Engl.* **1970**, 9, 906. (c) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, 113, 2552. (d) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, 113, 9235. (e) Rajca, A.; Utamapanya, S. *J. Org. Chem.* **1992**, 57, 1760.

(9) Schmidt, R.; Brauer, H.-D. *Angew. Chem., Int. Ed. Engl.* **1971**, 10, 506. Schmidt, R.; Brauer, H.-D. *Z. Naturforsch.* **1972**, B27, 1363.

(10) Rajca, A.; Utamapanya, S.; Smithhisler, D. J. *J. Org. Chem.* **1993**, 58, 5650.

(11) Itoh, K. *Pure Appl. Chem.* **1978**, 50, 1251. Okamoto, M.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *Chem. Phys. Lett.* **1990**, 173, 265. Teki, Y.; Fujita, I.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1994**, 116, 11499.

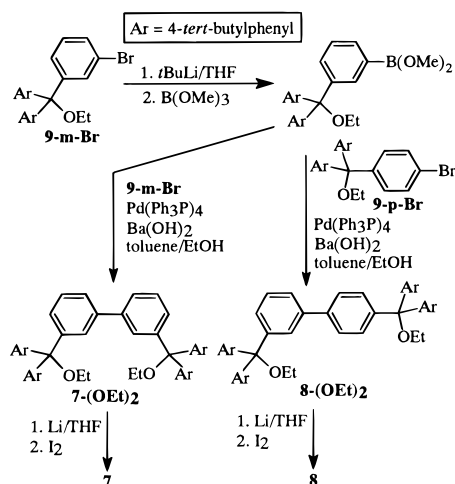
(12) Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1993**, 115, 4532.



Now we report preparation and study of diradicals **7** and **8**, which possess sterically unencumbered 3,3'- and 3,4'-biphenyls as their coupling units. It will be of some historical interest if **7** is the singlet ground state, in agreement with MO and VB theories, but in formal violation of Hund's rule,¹³ as applied to a molecule with two half-filled nonbonding orbitals.¹⁴

Results and Discussion

Diethers **7**-(OEt)₂ and **8**-(OEt)₂ are obtained by Suzuki couplings of aryl bromides **9-m-Br** and **9-p-Br**.¹⁵



The diethers are converted to dianions and, then, to diradicals, using the procedure analogous to that already reported for similar diradicals.^{10,16} Dianion $7^{2-} \cdot 2Li^+$ in THF-*d*₈ is studied by NMR spectroscopy; both ¹H and ¹³C NMR spectra are interpreted in terms of a single two-fold symmetric structure on the NMR time scale at ambient temperature.

Both diradicals are studied in frozen solutions by SQUID magnetometry and ESR spectroscopy. For SQUID magnetometry, $\sim 3 \times 10^{-2}$ M diradicals in THF are used and, for selected samples, ESR spectra at ~ 80 K are obtained, following the SQUID studies. For ESR spectroscopy at variable temperatures, $\sim 3 \times 10^{-2}$ M diradicals in THF are several-fold diluted with either 2-methyltetrahydrofuran (2-MeTHF) or toluene.

7 and **8** in frozen solutions at ~ 80 K give intense ESR spectra. In the $\Delta m_s = 1$ region, a spectral pattern, consistent with a triplet state ($S = 1$), is observed for both diradicals; the center peaks are assigned to monoradical ($S = 1/2$) impurities (Figure 1).¹⁷ Detection of a weak transition in the $\Delta m_s = 2$ region further

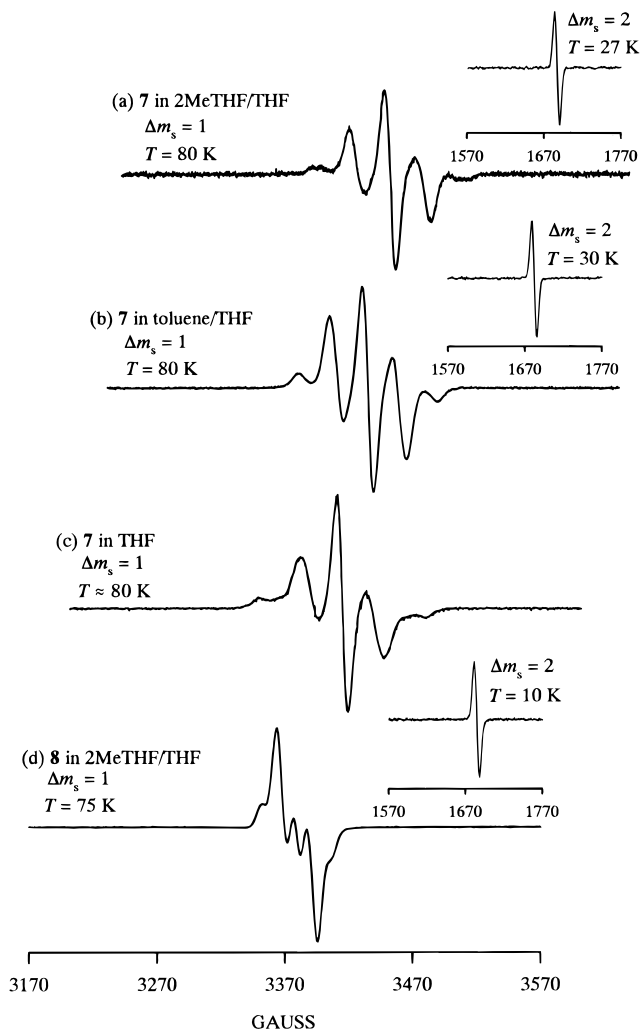


Figure 1. ESR spectra of diradicals **7** and **8** (for all spectra, $|E/hc| \approx 0 \text{ cm}^{-1}$): (a) **7** in 2-MeTHF/THF, $|D/hc| \approx 0.005 \text{ cm}^{-1}$, (b) **7** in toluene/THF, $|D/hc| = 0.0050 \text{ cm}^{-1}$, (c) **7** in THF, $|D/hc| = 0.0060 \text{ cm}^{-1}$ (the same sample as shown in the main plot of Figure 4, following SQUID magnetometry), (d) **8** in 2-MeTHF/THF, $|D/hc| = 0.0025 \text{ cm}^{-1}$.

confirms the presence of a triplet state ($S = 1$) for both diradicals. The spectral width of the $\Delta m_s = 1$ region in these diradicals equals $2|D/hc|$, where $|D/hc|$ is a zero field splitting (zfs) parameter. In the ESR spectra for **7**, both the spectral width and the line width show solvent dependence.¹⁸ Even larger differences in spectral widths are found between the diradicals; i.e., $|D/hc|$ increases in this order: **8** (0.0025 cm^{-1}), **3** \approx **4** (0.0041 cm^{-1}), **7** ($\sim 0.005 \text{ cm}^{-1}$).¹⁹⁻²¹

The ground states for diradicals **7** and **8** are determined by variable-temperature ESR spectroscopy and SQUID magnetometry.

Diradical 7. Upon lowering the temperature from ~ 80 to ~ 4 K, the ESR spectra in both the $\Delta m_s = 1$ and 2 regions become very weak for diradical **7**, suggesting that the observed

(17) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman and Hall: New York, 1986; Chapter 10. For the samples of the present diradicals in frozen solutions, the observed resonances in the $\Delta m_s = 1$ region of the triplet ESR spectra arise from the relatively few molecules that are appropriately oriented with respect to the external magnetic field: Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(18) The variation of the line width in the triplet spectrum for the randomly oriented molecule depending on a rigid matrix is well-known; see: ref 17. Such variations may arise from slightly different conformations and their distribution, and their relative orientation with the respect to the external magnetic field.

(19) In ref 10, the reported values of $|D/hc|$ for diradicals **3** and **4** should be divided by a factor of 2.

(13) Hund, F. *Z. Phys.* **1928**, *51*, 759.

(14) Longuet-Higgins, H. C. *J. Chem. Phys.* **1950**, *18*, 265.

(15) For a recent review, see: Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. For the use of barium hydroxide and the *in situ* procedure, see: Suzuki, A. *Pure Appl. Chem.* **1994**, *66*, 213. Maddaford, S. P.; Keay, B. A. *J. Org. Chem.* **1994**, *59*, 6501.

(16) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 2396.

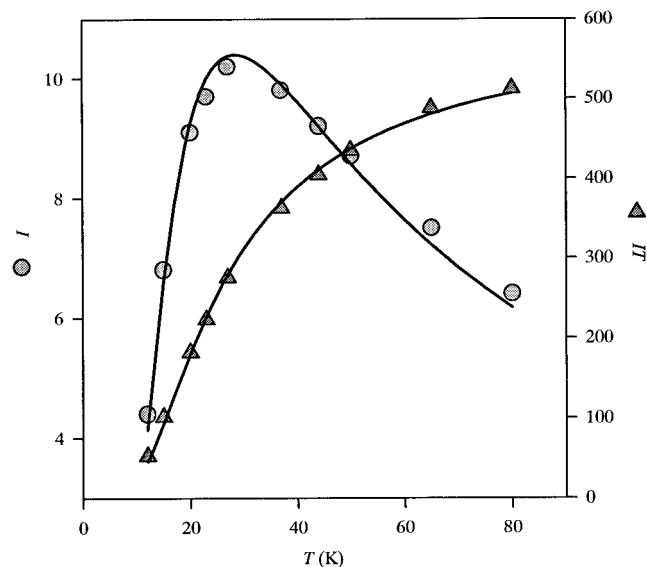


Figure 2. ESR spectroscopy ($T = 12\text{--}80\text{ K}$) for diradical **7** in 2-MeTHF/THF. Plot of the ESR intensity (I) for the $\Delta m_s = 2$ signal vs temperature (T) and plot of the product (IT) of I and T vs T . The solid lines correspond to a fits, using eq 1 of the Experimental Section. The fitting parameters are the normalization factor and J/k . For I vs T , $J/k = -22.8\text{ K}$ and the parameter dependence is 0.662. For IT vs T , $J/k = -23.5\text{ K}$ and the parameter dependence is 0.605.

triplet state is thermally populated and the singlet state is the ground state. Quantitative determination of the singlet–triplet energy gap is carried out by measuring the ESR signal intensity of the triplet state as a function of temperature; typically, microwave saturation for organic diradicals limits the available temperature range to $T \geq 10\text{ K}$. For diradical **7** in 2-MeTHF/THF, the plot of the intensity (I) for the $\Delta m_s = 2$ signal versus the temperature ($T = 12\text{--}80\text{ K}$) shows a maximum at $T \approx 30\text{ K}$,²² fitting these data as I vs T and IT vs T to a simple model based upon the two-site Heisenberg Hamiltonian, $H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$, gives $J/k = -23 \pm 1\text{ K}$ (Figure 2, eq 1 in the Experimental Section).^{10,23–25} A similar procedure for **7** in toluene/THF gives $J/k = -22 \pm 2\text{ K}$. These results establish that the singlet state is the ground state and the triplet state, observed in the ESR spectra, is the thermally populated excited state; the energy gap between the two states is $\Delta E_{ST} = 2J \approx -0.1\text{ kcal/mol}$.

(20) Application of the simplest model for interpreting relative values of triplet $|D/hc|$, assuming only dipolar contributions to $|D/hc|$ and localized “unpaired” electrons, where $|D/hc| \propto 1/r^3$ (r = distance between “unpaired” electrons), suggest that diradical **7** may possess a “syn” conformation around the biphenyl moiety (most likely with the somewhat twisted biphenyl moiety). Dreiding models and molecular mechanics calculations (ref 21) for conformations of **7** around the biphenyl moiety indicate that r would increase in the following order: “syn”, “perpendicular”, and “anti”. Thus, out-of-plane twisting, which may be achieved by introducing steric hindrance (e.g., **3** vs **7**) in “syn” and “anti” conformation should decrease and increase $|D/hc|$, respectively. Eaton, S. S.; More, K. M.; Sawant, B. M.; Eaton, G. R. *J. Am. Chem. Soc.* **1983**, *105*, 6560.

(21) Molecular mechanics (MM2) strain energy in **2** and **7** is calculated to be somewhat smaller (2–5 kcal/mol) for “syn” compared to “anti” conformation. In **3**, the out-of-plane distortion around the biphenyl moiety increases, compared to **2** and **7**, and the MM2 strain energy for the “anti” conformer is less than that for the “syn” conformer ($\sim 1\text{ kcal/mol}$). In the “syn” conformation for **2** and **7**, benzene rings of the “endo” phenyl and 4-*tert*-butylphenyl define nearly parallel planes and the closest contacts, C(para)–C(para), between the adjacent rings are only 3.4 and 4.9 Å, respectively; such contacts may contribute to non-negligible through-space antiferromagnetic interactions, especially in **2**.

(22) (a) The spectral width of the $\Delta m_s = 1$ region, $2|D/hc|$, is constant throughout this temperature range. (b) For smaller $|D/hc|$, intensity of the $\Delta m_s = 2$ resonance, relative to the $\Delta m_s = 1$ region, is expected to decrease; e.g.: Weissman, S. I.; Kothe, G. *J. Am. Chem. Soc.* **1975**, *97*, 2537.

(23) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London A* **1952**, 214.

(24) Heisenberg, W. *Z. Phys.* **1928**, *49*, 619.

(25) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.

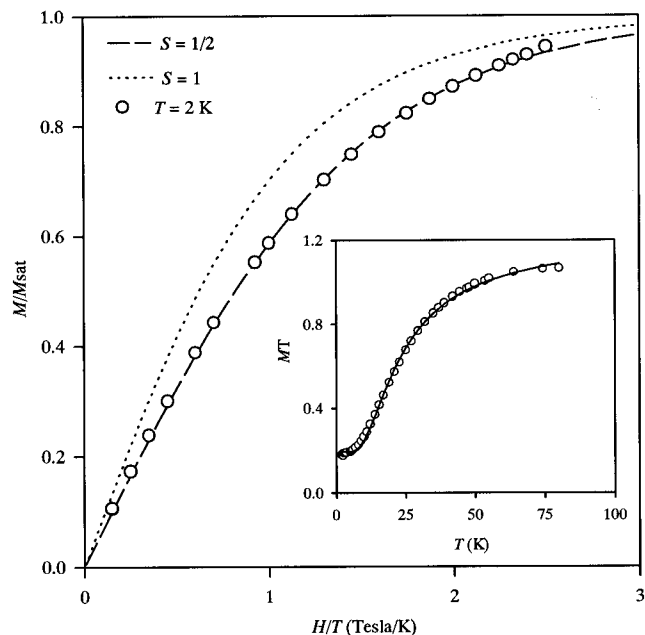


Figure 3. SQUID magnetometry ($H = 0\text{--}5.0\text{ T}$) for diradical **7** in THF. Inset: Plot of the product (MT) of magnetization (M) and T vs T . Open circles correspond to experimental points at $H = 0.5\text{ T}$. The solid line corresponds to a fit, using eq 3 of the Experimental Section; the fitting parameters (parameter dependence) are $n_1 = 5.20 \times 10^{-8}$ (0.755), $n_2 = 2.81 \times 10^{-7}$ (0.977), $J/k = -21.5\text{ K}$ (0.811), and correction for residual diamagnetism, where $2n_1$ = number of moles of monoradical, n_2 = number of moles of diradical with a spin coupling constant of J/k . Main plot: M/M_{sat} vs H/T ; the experimental points at $T = 2\text{ K}$ are indicated with open circles and the plots of Brillouin functions with $S = 1/2$ and 1 are shown as lines. The fitting parameters are $S = 0.506$ and $M_{\text{sat}} = 0.0005183$ with the parameter dependence 0.771.

Magnetization (M) is measured as a function of magnetic field ($H = 0\text{--}5.5\text{ T}$) and temperature ($T = 2\text{--}120\text{ K}$) (Figure 3). The M vs T data ($T = 2\text{--}80$ or $2\text{--}120\text{ K}$) are fit as MT vs T , employing the model analogous to that for the ESR data, IT vs T , except for an additional term, which is used to account for “monoradical impurities” ($S = 1/2$) (eq 3 in the Experimental Section). The 4-parameter fit (residual diamagnetism, J/k , number of moles of diradical, number of moles of monoradical) gives $J/k = -21 \pm 2\text{ K}$, in agreement with the ESR data; for the three samples studied, the fitted number of moles suggest the following contents of monoradical is 27%, 28%, and 32%. For such high monoradical content ($\sim 30\%$), at $T = 2\text{ K}$, contribution to magnetization from the diradical with $J/k = -21\text{ K}$ should be negligible; i.e., M vs H/T should follow the $S = 1/2$ Brillouin curve.²⁵ The M vs H data at $T = 2\text{ K}$ and $H = 0\text{--}5.0\text{ T}$ are fit to a Brillouin function with two variable parameters, S and magnetization at saturation, M_{sat} .² The MT vs T fit gives $S = 0.51$ but M_{sat} is $\sim 10\%$ less than the calculated value from the number of moles of monoradical in MT vs T fit (Figure 3).

Interpretation of ESR spectra in the lowest temperature range (4–10 K) and magnetization data at higher magnetic fields suggest the presence of a few percent of a “diradical” with a small value of J/k ($J/k \approx -5\text{ K}$). However, numerical fitting of the data with such a “diradical” leads to overparametrized fits (Figure 4). Furthermore, in the 4–10 K range, ESR intensities are difficult to measure and $|D/hc|$ is decreasing.^{22b} Thus, the value of J/k and the content of this “diradical” impurity are very approximate. Whether this “diradical” with a small $|J/k|$ corresponds to another conformation for diradical **7** cannot be ascertained at this time.^{20,21,26}

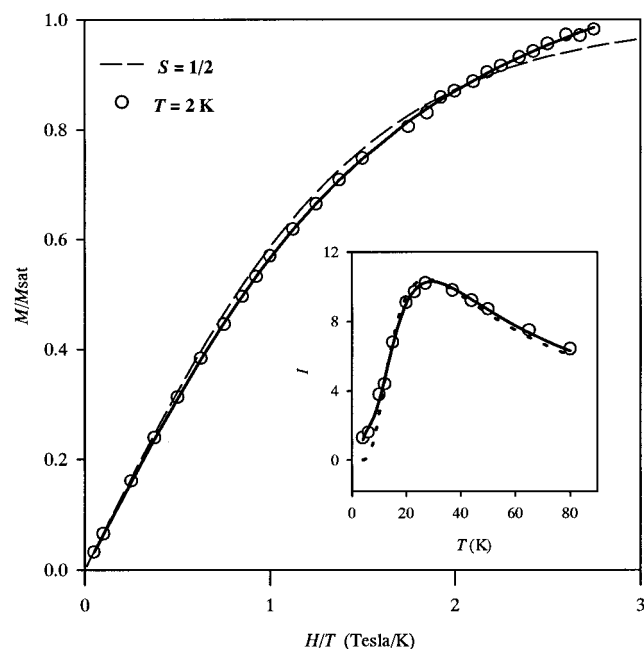


Figure 4. ESR spectroscopy ($T = 4\text{--}80\text{ K}$) and SQUID magnetometry ($H = 0\text{--}5.5\text{ T}$) for diradical **7**. Inset: Plot of the ESR intensity (I) for the $\Delta m_s = 2$ signal vs T . Open circles correspond to the experimental points at $T = 4\text{--}80\text{ K}$. The intercepted line corresponds to the identical fit as in the Figure 2 (eq 1 of the Experimental Section); the fitting parameters are the normalization factor and $J/k = -22.1\text{ K}$. The parameter dependence is 0.638. The solid line corresponds to a fit, using eq 2 of the Experimental Section; the fitting parameters (parameter dependence) are normalization factor for the first diradical, 4.8×10^3 (0.669), normalization factor for the second diradical, 2.4×10^2 (0.948), and the corresponding spin coupling constants, $J_1/k = -24.6\text{ K}$ (0.900), $J_2/k = -6.2\text{ K}$ (0.856). Main plot: M/M_{sat} vs H/T . Open circles correspond to experimental points at $T = 2\text{ K}$; M_{sat} is obtained from the one-parameter fit to the Brillouin function with $S = 1/2$ (the intercepted line). The solid line corresponds to a fit, using eq 4 of the Experimental Section; the variable fitting parameters (parameter dependence) are $n_1 = 1.28 \times 10^{-7}$ (0.978), $n_2 = 2.41 \times 10^{-8}$ (0.986), $J/k = -3.6\text{ K}$ (0.995); where $2n_1 =$ number of moles of monoradical, $n_2 =$ number of moles of diradical with a spin coupling constant of J/k . (The parameters for diradical with $J/k \sim -20\text{ K}$ are fixed; its contribution its negligible.)

In summary for **7** in 2-MeTHF/THF, toluene/THF, and THF, the ESR and magnetization data establish the singlet ground state ($S = 0$) with $J/k \approx -20\text{ K}$ ($\Delta E_{\text{ST}} \approx -0.1\text{ kcal/mol}$).

Diradical 8. For this diradical, the T dependence of the ESR spectra and T and H dependencies of the magnetization are dramatically different compared to those for the 3,3'-isomer. For **8**, in 2-MeTHF/THF at $\sim 4\text{ K}$, the ESR spectra in both the $\Delta m_s = 1$ and 2 regions are very intense. The plots of the product (IT) of the intensity (I) for the $\Delta m_s = 2$ signal and temperature (T) versus T are shown in the $T = 10\text{--}75\text{ K}$ range (Figure 5).^{22a} Because of the microwave saturation and low signal to noise (relatively small $|D/hc|$)^{22b} for the $\Delta m_s = 2$ signal, determination whether IT vs T is constant (and in what temperature range) can only be very approximate. Within these experimental constraints, the change in population of the triplet state is not detectable in the studied temperature range; that is, the triplet is the ground state with $\Delta E_{\text{ST}} > RT$ or the triplet and singlet states are near-degenerate with $\Delta E_{\text{ST}} < RT$ ($T = 10\text{--}40\text{ K}$). This ambivalence may be resolved by magnetization studies.

(26) Another candidate for a "diradical" with small antiferromagnetic $|J/k|$ is a dimer of diradicals **7**; in ref 2, an analogous dimer of triradicals was shown to possess a small antiferromagnetic interaction.

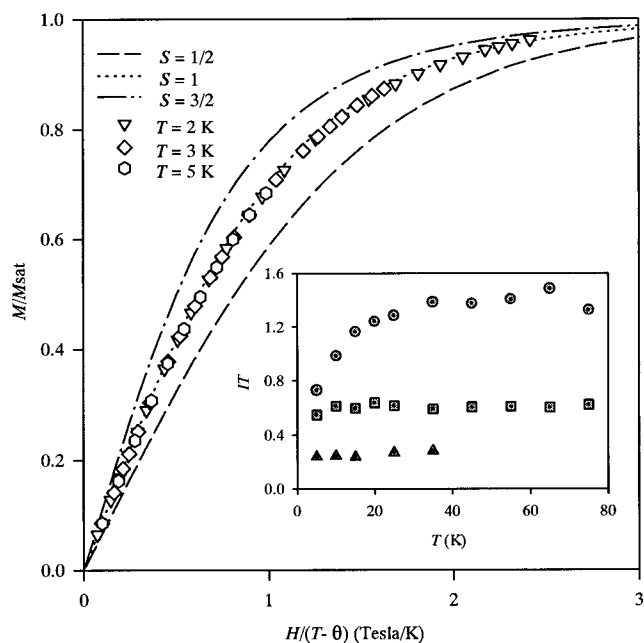
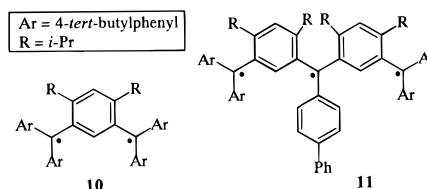


Figure 5. ESR spectroscopy and SQUID magnetometry for diradical **8**. Inset: For diradical **8** in 2-MeTHF/THF. Full circles, squares, and triangles correspond to experimental points at microwave power attenuations of 10, 20, and 30 dB, respectively; the data at 10 dB show significant microwave saturation at low T . Main plot: For diradical **8** in THF, M/M_{sat} vs $H/(T - \theta)$, $\theta = -0.07\text{ K}$; the experimental points at $T = 2, 3, 5\text{ K}$ are indicated with symbols and the plots of Brillouin functions with $S = 1/2, 1,$ and $3/2$ are shown as lines. The fitting parameters at $T = 2, 3, 5\text{ K}$ are $S = 0.956, 0.957, 0.957$, and the corresponding $M_{\text{sat}} = 0.001486, 0.001482, 0.001477$; the parameter dependence is 0.63, 0.85, and 0.97, respectively.

The M vs H ($H = 0\text{--}5.0\text{ T}$) data at $T = 2, 3, 5\text{ K}$ are corrected for intermolecular antiferromagnetic interactions with a mean-field parameter, $\theta = -0.07\text{ K}$, and, then, fit as M vs $H/(T - \theta)$ to Brillouin functions with two variable parameters, S and M_{sat} . $S = 0.96$ is obtained (Figure 5). Therefore, diradical **8** is the triplet ground state with a significant ΔE_{ST} .²⁷

Unlike diradical **7**, which has to be handled at low temperature in solution, diradical **8** is quite stable at ambient temperature; it can be isolated as a red-brown solid and stored under argon. Solid **8** is dissolved in either 2-MeTHF or THF for studies by ESR spectroscopy, UV-vis spectroscopy, and SQUID magnetometry. The ESR spectrum in 2-MeTHF at $T \approx 80\text{ K}$ is similar to that in Figure 1, except for the relatively greater intensity of the center peak. $S \approx 0.9$ is obtained from the fits to the Brillouin functions for the magnetization data ($H = 0\text{--}5.0\text{ T}$) in THF at $T = 1.8, 3,$ and 5 K . The UV-vis spectrum in THF shows two intense bands at $\lambda_{\text{max}} \approx 350$ and 380 nm . (Additional, relatively weak, bands are also found in the $\lambda = 400\text{--}900\text{ nm}$ range.) These two intense bands can be compared to the $\lambda_{\text{max}} \approx 350\text{ nm}$ band in diradical **10** and the $\lambda_{\text{max}} \approx 350\text{ nm}$ band with a shoulder at $\lambda_{\text{max}} \approx 370\text{ nm}$ in biphenyl-substituted triradical **11**.^{8de,28}



(27) Determination of ferromagnetic couplings in a series of polyradicals related to **8** is in progress.

Conclusion

Diradicals **7** and **8** are found singlet and triplet ground states, respectively; the singlet–triplet energy gap is approximately -0.1 kcal/mol in **7**. These findings are in agreement with recent theoretical models relating molecular connectivities to the ground states for planar π -conjugated diradicals and, for **7**, in formal violation of Hund's rule, as applied to molecules.

Biphenyl linkages are potential coupling units for very-high-spin molecules. Formation of biphenyl linkage via C(aryl)–C(aryl) bond forming steps allows for connections of already functionalized and sterically unencumbered modules. This simplification in organic synthesis is an important step toward highly functionalized mesoscopic-size molecules. Thermal stability of diradical **8** makes 3,4'-biphenyl linkage especially promising.²⁹

Experimental Section

Materials. Ether and tetrahydrofuran (THF) for use on a vacuum line were distilled from sodium/benzophenone in a nitrogen atmosphere. Iodine (99.999%, resublimed crystals) was obtained from Johnson-Mathey. THF-*d*₈, which was obtained from Cambridge Isotope Labs, was doubly vacuum transferred from sodium/benzophenone prior to the use. Preparation of aryl bromide **9-*m*-Br** was reported,³⁰ **9-*p*-Br** was prepared using an analogous procedure, similar to that reported by Hellwinkel.³¹ Other major chemicals are obtained from Aldrich.

Special Procedures. Solutions of carboxypolyanions in THF were prepared in a Vacuum Atmospheres glovebox; outside the glovebox, carboxypolyanions were handled on a 10^{-3} Torr vacuum line.¹⁶ Similar vacuum lines were used for all air-sensitive synthetic procedures.

NMR Spectroscopy and Other Analyses. NMR spectra were obtained using an Omega spectrometer (¹H, 500 MHz) in CDCl₃, benzene-*d*₆, and THF-*d*₈; the chemical shift references were ¹H, TMS, 0.0 ppm, benzene-*d*₅, 7.15 ppm, THF-*d*₇, 3.48 ppm, and ¹³C, CDCl₃, 77.0 ppm, THF-*d*₈, 67.45 ppm. For ¹³C NMR spectra in CDCl₃, exponential multiplication (EM) of 1.0 Hz, prior to Fourier transform, was used. For ¹H NMR spectrum of **8-(OEt)₂** in benzene-*d*₆, resolution enhancement was applied via EM and Gaussian broadening (GB). UV–vis spectra for diradical **8** were obtained using a Perkin-Elmer Lambda 6 spectrophotometer attached to the Vacuum Atmospheres glovebox, as described elsewhere.²⁸ Elemental analyses were completed by M-H-W Laboratories, P.O. Box 15149, Phoenix, AZ 85060.

Diethers 7-(OEt)₂ and 8-(OEt)₂. *t*-BuLi (2.0 equiv, 1.7 M in pentane) was added to **9-*m*-Br** (1.0 equiv, 0.1 M in THF) at -78 °C. After 1 h at -78 °C, the reaction mixture was placed in a -25 °C cooling bath for 10 min and, then, cooled back to -78 °C. Subsequently, B(OMe)₃ (1.2 equiv) was added and the reaction mixture was allowed to slowly warm up over 24 h. After the solvents were removed (stream of nitrogen, followed by vacuum), the reaction flask was loaded with the other aryl bromides (1 equiv, **9-*m*-Br** or **9-*p*-Br**), Ba(OH)₂·8H₂O (~1 equiv), Pd(Ph₃P)₄ (0.06 equiv), and toluene/EtOH (1:1, saturated with nitrogen). After 48 h of reflux under nitrogen, the usual aqueous workup (extraction with ether) followed. Filtration through a silica bed (hexane/benzene, 1:1), recrystallization/precipitation (100% EtOH), and drying under vacuum (10^{-3} Torr, 70 °C) overnight gave analytically pure products as white solids.

Diether 7-(OEt)₂. From **9-*m*-Br** (0.250 g) and **9-*m*-Br** (0.252 g), using toluene/EtOH (5 + 5 mL), 0.312 g (75%) of the product was obtained. No well-defined mp (glassy). Anal. Calcd for C₅₈H₇₀O₂: C, 87.17; H, 8.83. Found: C, 86.89; H, 8.25. ¹H NMR (500 MHz, CDCl₃): 7.71 (bs, 2 H), 7.40–7.25 (m, 24 H), 3.10 (q, *J* = 7, 4 H), 1.30 (s, 36 H), 1.22 (t, *J* = 7, 6 H). NMR (500 MHz, benzene-*d*₆): 8.20 (t, *J* = 2, 2 H), 7.60 (d, *J* = 9, 8 H), 7.56 (bd, *J* ≈ 8, 2 H), 7.40 (bd, *J* ≈ 8, 2 H), 7.23 (d, *J* = 9, 8 H), 7.12 (t, *J* = 8, 2 H), 3.21 (q, *J*

= 7, 4 H), 1.19 (s, 36 H), 1.18 (t, *J* = 7, 6 H). ¹³C NMR (¹H) and { $\theta = 135^\circ$ }DEPT, 125 MHz, CDCl₃): 149.5 (q), 145.9 (q), 141.4 (q), 140.6 (q), 128.5, 127.9, 127.3, 127.1, 125.3, 124.5, 86.3 (q), 59.3 (CH₂), 34.4 (q), 31.4, 13.5. FABMS (3-NBA), cluster: *m/z* (percent relative peak height in the *m/z* 100–1500 range) at (M – OC₂H₅)⁺, 753.6 (100), 754.6 (65), 755.6 (20), 756.6 (5).

Diether 8-(OEt)₂. From **9-*m*-Br** (0.491 g) and **9-*p*-Br** (0.504 g), using toluene/EtOH (10 + 10 mL), 0.491 g (60%) of the product was obtained. Mp 174–176 °C. Anal. calcd for C₅₈H₇₀O₂: C, 87.17; H, 8.83. Found: C, 87.52; H, 8.76. ¹H NMR (500 MHz, benzene-*d*₆, EM = -1.8 Hz, GB = $+1.2$ Hz): 8.18 (t, *J* = 2, 1 H), 7.65–7.57 (m, 11 H), 7.49 (d, *J* = 9, 2 H), 7.37 (bd, *J* ≈ 8, 1 H), 7.26 (d, *J* = 9, 4 H), 7.24 (d, *J* = 9, 4 H), 7.17 (t, *J* = 8, 1 H), 3.24 (q, *J* = 7, 2 H), 3.20 (q, *J* = 7, 2 H), 1.20 (s, 18 H), 1.18 (t, *J* = 7, 3 H), 1.17 (s, 18 H), 1.17 (t, *J* = 7, 3 H). ¹³C NMR (¹H) and { $\theta = 135^\circ$ }DEPT, 125 MHz, CDCl₃): 149.5 (q, overlap), 145.9 (q), 144.3 (q), 141.4 (q, overlap), 140.0 (q), 139.4 (q), 128.8, 128.5, 128.4, 128.0, 127.3, 127.0, 126.3, 125.2, 124.5 (overlap), 86.3 (q), 86.1 (q), 59.35 (CH₂), 59.32 (CH₂), 34.4 (q, overlap), 31.4 (overlap), 15.38, 15.35. FABMS (3-NBA), cluster: *m/z* (percent relative peak height in the *m/z* 100–960 range) at (M – OC₂H₅)⁺, 753.4 (100), 754.4 (60), 755.4 (20), 756.4 (5); calcd for C₅₈H₆₈O, 753.5 (100), 754.5 (63), 755.5 (20), 756.5 (4).

Dianion 7²⁻·2Li⁺. A 5-mm NMR tube equipped with a high-vacuum PTFE stopcock (Kontes) was heated under vacuum and, then, loaded with diether **7-(OEt)₂** (~15 mg). A piece of Li metal was added in the Ar-filled glovebox. THF-*d*₈ (~0.4 mL) was vacuum transferred to the tube and the tube was flame sealed. The reaction was followed with NMR spectroscopy over several hours, until complete conversion to EtOLi was attained and a sharp ¹H NMR spectrum was obtained. ¹H NMR (500 MHz, THF-*d*₈): 7.52 (bs, 2 H), 7.29 (bd, *J* ≈ 8, 8 H), 7.11 (bd, *J* ≈ 7, 2 H), 6.59 (d, *J* ≈ 8, 8 H), 6.43 (t, *J* ≈ 7, 2 H), 1.19 (s, 36 H); EtOLi, 3.76–3.68 (m, 4 H), 1.15–1.05 (m, 6 H). ¹³C NMR (¹H) and { $\theta = 135^\circ$ }DEPT, 125 MHz, THF-*d*₈, EM = 5.0 Hz): 149.4 (q), 148.0 (q), 144.1 (q), 134.7 (q), 127.8, 124.6, 124.3, 122.0, 121.2, 111.7, 88.2 (q), 34.2 (q), 32.3; EtOLi, 59.4 (CH₂), 59.1 (CH₂), 23.4, 23.3.

Diradicals 7 and 8. Techniques for preparation of similar radicals were previously described.^{2,10} Following stirring of the diether (~15 mg) in THF (0.5 mL) with Li metal (multimolar excess) in an Ar-filled glovebox for ~1 day, the reaction mixture is transferred (and separated from Li) to another vessel and treated with iodine (1 equiv) at -95 °C on a vacuum line. The resultant solutions of diradicals contain LiI and EtOLi as side products.

In order to obtain solid **8**, the oxidation with I₂ was carried out at -78 °C, THF was removed, and the remaining solid residue was repeatedly washed with degassed MeOH, and, then, dried under high vacuum at ambient temperature.^{8a,c} Diradical **8** is isolated as red-brown solid (0.057 g from 0.074 g of **8-(OEt)₂**).

ESR Spectroscopy. Preparation of triarylmethyl-based di- and polyradicals for ESR spectroscopy was previously described.^{2,16} ESR spectra are acquired with a Bruker 200D instrument, equipped with an Oxford Instruments ESR900 liquid helium cryostat or liquid nitrogen insert dewar, as described elsewhere.² The intensities used for the *I* vs *T* and *IT* vs *T* plots were checked for the microwave saturation by using 2 or 3 power settings different by at least 10 dB throughout the studied temperature range; temperatures were stepped up and down in each experiment. Modulation amplitude was kept at or below 1/5 of the estimated peak-to-peak width for all spectra. Numerical values of *I* were taken either as peak-to-peak heights or via numerical double integration (Gramms386 software package).

SQUID Magnetometry. The samples for magnetometry were prepared as described previously.¹⁶ Quantum Design (San Diego, CA) instruments MPMS5 and MPMS5S were used.

Numerical Curve Fitting. 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: $dependence = 1 - ((variance\ of\ the\ parameter,\ other\ parameter\ constant)/(variance\ of\ the\ parameter,\ other\ parameters\ changing))$. Values close to 1 indicate overparametrized fit.

For fitting ESR and SQUID data for diradical **7**, all equations are based upon the Heisenberg Hamiltonian, $H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$, where, $S_1 = S_2 = 1/2$ and $\Delta E_{ST} = 2J$. The equations for magnetization (*M*) per

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(29) A series of high-spin polyradicals, based upon 3,4'-biphenyl linkage, including a hexadecaradical (*S* = 8), was reported by A. Rajca at the symposium on Molecular Based Magnetic Materials; Pacificchem '95, Honolulu, Hawaii.

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mole as a function of temperature (T) and magnetic field (H) are of the following form:

$$M = 2Ng\mu_B \sum_i \sinh(g\mu_B H/kT) / [\exp(-2J_i/kT) + 1 + 2 \cosh(g\mu_B H/kT)]$$

Each “ i ”-term in the sum corresponds to a “diradical”; variable (or fixed) parameters for each “ i ”-term are coupling constant (J_i) and number of moles of “diradical” (n_i). For $i = 1$ and $H/T \approx 0$, the above equation reduces to the Bleaney–Bowers equation.²² The following equations are used in the fitting:

$$i = 1, \text{ i.e., “one diradical”, two variable parameters } (J \text{ and } n) \quad (1)$$

$$i = 1, 2, \text{ i.e., “two diradicals”,} \\ \text{four variable parameters } (J_1, n_1, J_2, n_2) \quad (2)$$

$$i = 1, 2, \text{ and } J_1 = 0, \text{ i.e., “one diradical plus monoradical”,} \\ \text{three variable parameters } (n_1, n_2, J_2) \quad (3)$$

$$i = 1, 2, 3, \text{ and } J_1 = 0, J_3 = \text{fixed, } n_3 = \text{fixed,} \\ \text{i.e., “two diradicals plus monoradical”,} \\ \text{three variable parameters } (n_1, n_2, J_2) \quad (4)$$

A typical procedure for magnetization data involves fitting MT vs T with one of the above equations, using an additional variable parameter

(M_{dia}) to account for residual diamagnetism. Using this value of M_{dia} , M vs H data are corrected for diamagnetism before numerical fitting with the above equations.

The above equations are used for fitting of X-band ESR intensities (I) in the $\Delta m_s = 2$ region; i.e., M is replaced with I , H is set to 0.16 T, and $2Ng\mu_B$ and number of moles are lumped into a “normalization factor” to account for arbitrary units of I . As far as diradical **8** is concerned, the previously described fitting procedures to Brillouin functions are used.²

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