Near-Degeneracy between the Low- and High-Spin States in an Alternant Hydrocarbon Diradical: Topology and Geometry

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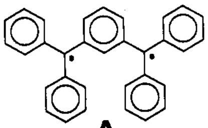
Treatment of polyarylmethyl diethers with lithium metal in THF gave the corresponding carbodianions; subsequent oxidation with iodine at 180 K produced diradicals, which were studied in frozen THF solutions by SQUID magnetometry in the 2–100 K temperature and 0–5.5 T magnetic field ranges. Magnetization dependence on both the temperature and magnetic field was compared to the model based upon the Heisenberg Hamiltonian plus mean field. Small intramolecular magnetic interactions were found; both diradicals are triplet ground states.

Introduction

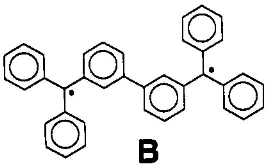
The interdisciplinary frontier of organic magnetism holds the promise of translating very strong ferromagnetic coupling between two "unpaired" electrons in an organic diradical to a magnetic order in a mesoscopic polyradical or molecular solid.[1–4] Strong ferromagnetic coupling in a diradical implies a large energy gap (ΔE_{ST}) between the triplet ground state (both electron spin are parallel) and the lowest singlet excited state; in some organic diradicals, $|\Delta E_{ST}| \approx 10$ kcal/mol; i.e., the magnetic coupling may be stronger than in transition metal dimers.[5]

Topology is thought to control magnetic coupling (ferro- vs antiferro-) in planar π-conjugated diradicals;[6] however, planar diradicals are rare. From a materials perspective, nonplanarity is almost a rule because the radical centers in a diradical should be screened by bulky substituents in order to prevent bond formation between the molecules (as transition metal centers are screened with complexing ligands to prevent clustering). Therefore, how the geometry of diradical affects the magnetic coupling is an important question.

In 1936, Huckel implied that diradicals such as **A** and **B**, which have been earlier prepared by Schlenk and Brauns, should possess the triplet and singlet ground states because of their topologies;[7,8] that is, **B** should violate Hund's rule.[9] Thermal instability of **A** and **B** prevented their thorough characterization.[10] Recently, stable and highly sterically-hindered derivatives of **A** have been prepared and found to possess a triplet ground state with strong ferromagnetic coupling between "unpaired" electrons in spite of inevitable geometric distortion of the π-conjugated sytems.[11] Now we report synthesis and magnetic studies of sterically-hindered derivatives of **B**, i.e., diradicals 1 and 2.



A



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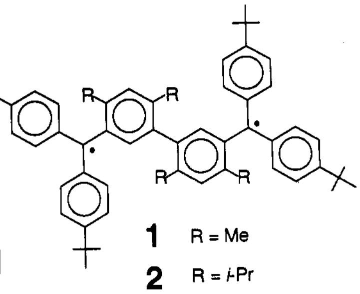

1 R = Me

2 R = *i*-Pr

Results and Discussion

Diradicals 1 and 2 are prepared according to eq 1 using tetrahydrofuran (THF) as a solvent: (i) copper-mediated symmetrical aryl–aryl coupling gives the biphenyl-containing diethers,[12,13] and (ii) treatment of the diethers with excess lithium metal, which gives the corresponding carbodianions, is followed by oxidation with 1 equiv of I_2 at 180 K.[2a,14] Solutions of the diradicals must be handled at low temperature; solid 2, which is stable at ambient temperature, is obtained by removal of THF at 250 K,

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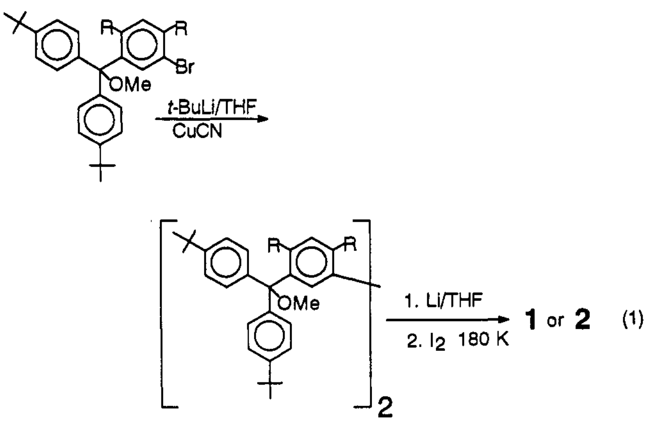

thorough washing with methanol, and drying under vacuum.[11a,e]

1 and **2** in frozen THF or 2-MeTHF at 77 K give intense ESR spectra, including a weak $\Delta m_s = 2$ transition, characteristic of a triplet state ($S = 1$); zero field splitting (zfs) parameters are $|D/hc| = 0.0081$ cm^{-1} and $|E/hc| \approx 0$ (Figure 1).

Because triplet $|D/hc|$ can be related to a distance between "unpaired" electrons,[15] similarity of $|D/hc|$ for both diradicals suggests that their conformations are comparable, i.e., presumably highly twisted about the CC biphenyl bond.[16] The center peak in the $\Delta m_s = 1$ region of the ESR spectrum in Figure 1 corresponds to a monoradical impurity at the level of ~1% according to ^{1}H NMR spectroscopic studies.[17] This ESR spectrum detects the triplet state for the diradical as either a ground state or thermally populated excited state.

The ground state of a diradical may be determined by examining the thermal population of the lowest excited state via variable-temperature (T) measurements in the range where the thermal energy (kT) is comparable to the energy gap (ΔE_{ST}) between the two states. A typical method relies on ESR relative intensities, which are measured over a wide range of T, to determine population of the $S = 1$ state; however, accurate measurement and interpretation of ESR intensities at cryogenic T is extremely difficult.[2f,18] The alternative method is detection of the $S = 1$ population (and other $S > 0$ species present) by measuring bulk magnetization (M, average magnetic moment of the sample) using a sensitive magnetometer such as SQUID. In addition to T, the magnetic field (H) can perturb population of states with different S;[19] because the energies corresponding to large laboratory H are small (e.g., at $H = 3$ T, Zeeman energy, $g\mu_B H$, is equivalent to kT at $T = 4$ K), the study of M vs H at very low T provides an especially sensitive probe for small ΔE_{ST}.

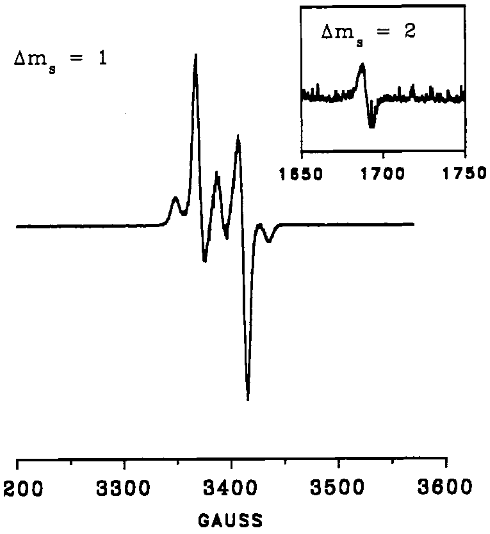

Figure 1. ESR spectrum of diradical **2** in 2-MeTHF at 77 K. (Solid **2** is dissolved in 2-MeTHF.) The zero-field splitting parameters for the $\Delta m_s = 1$ region are in the text. The insert shows $\Delta m_s = 2$ region.

Interpretation of the magnetic data requires that both intra- and intermolecular magnetic interactions are accounted for. The former may be described using a model based upon the Heisenberg Hamiltonian, $H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$; for a diradical, $S_1 = S_2 = 1/2$ and $\Delta E_{ST} = 2J$, an equation for magnetization (M) per mole of diradical as a function of T and H is straightforward to derive.[20] This equation is corrected for intermolecular interactions using mean-field replacement of T by $T - \theta$ in the arguments of the hyperbolic functions to give the following:[21]

$$M = 2Ng\mu_B \sinh\,(g\mu_B H/k(T-\theta))/[\exp(-2J/kT) + 1 + 2\cosh\,(g\mu_B H/k(T-\theta))] \quad (2)$$

Diradicals in THF are characterized by two types of measurements:[22a] (1) MT vs T for $T = 2$–100 K at constant $H = 0.5$ or 1.0 T and (2) M vs H for $H = 0$–5.5 T at constant $T = 2$ K.[2a] Both measurements are fit to eq 2 using fixed values of "J". First, the MT vs T data are fit to obtain correction for residual diamagnetism,[22c] number of moles (n) of diradical, and "θ". Second, the M vs H data are corrected for diamagnetism and fit to eq 2 to obtain "n" and "θ". The "J" is varied until values for "θ" and, especially, "n" are within two standard deviations (<5% and <2%, respectively) for the MT vs T and M vs H fits (Figure 2).[23]

Qualitative interpretation of the M vs H curves such as in Figure 2 rules out intramolecular antiferromagnetic interactions, $J < 0$, with $|J/k| > 1$ K; that is, sigmoidal shape (upward curvature) in the M vs H curves is not observed at $T = 2$ K.

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(22) (a) SQUID samples contain diradicals either with 2 equiv of LiI in THF or in pure THF; in the last case, samples are obtained by dissolution of solid **2**. (b) **1** (LiI/THF) $\theta = -3.8$ K (0.030 mmol/mL) and $\theta = -2.9$ K (0.0035 mmol/mL); **2** (THF) $\theta = -1.9$ K (0.015 mmol/mL) and $\theta = -1.6$ K (0.0021 mmol/mL). (c) The SQUID samples, which are prepared according to ref 2a, possess approximately uniform diamagnetic background; a small correction is still required for quantitative fitting.

(23) Typical SQUID sample possesses less than 4% monoradical impurity according to ^{1}H NMR and ESR spectroscopies, which is comparable to two standard deviations of the fit parameters (ref 17). Therefore, monoradical impurities are not included in the fitting procedures.

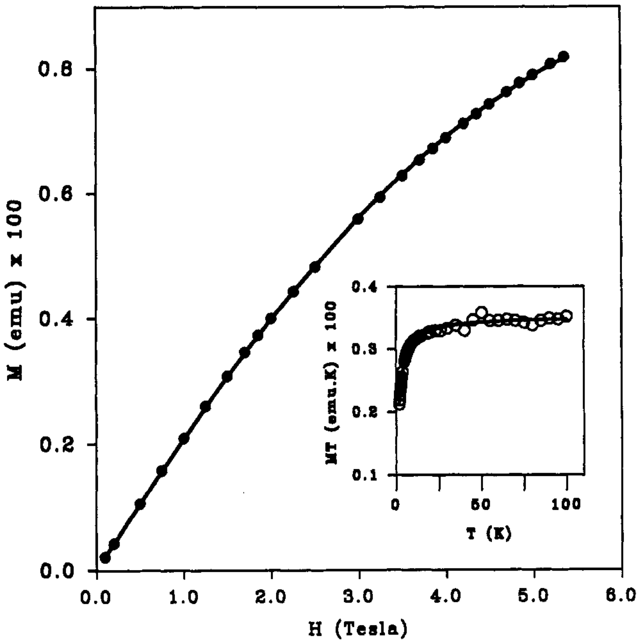

Figure 2. Diradical 2 (0.026 mmol/mL) with 2 equiv of LiI in THF. Circles are the experimental points, and the solid lines are the fits with $J/k = 1$ K to eq 2. Main plot: magnetization (M) vs applied magnetic field (H) at temperature, $T = 2$ K ($n = 9.38 \times 10^{-7}$ mol, $\theta = -1.96$ K). Insert plot: MT vs T at $H = 0.5$ T ($n = 9.40 \times 10^{-7}$ mol, $\theta = -1.87$ K).

Quantitative fitting, which gives $J > 0$ and $\theta < 0$, implies intramolecular ferromagnetic interactions (triplet ground state) and intermolecular antiferromagnetic interactions, respectively. As expected for intermolecular interactions, $|\theta|$ decreases upon dilution.[22a,b] Small ferromagnetic interactions are very difficult to measure;[19] the intermolecular antiferromagnetic interactions, which effectively raise the measurement temperature from T to $T - \theta$, flatten the M vs H curves and further add to the difficulty. Thus, the values of $J/k \approx 10$ K (1) and $J/k \approx 1$ K (2) should be viewed as tentative.

Notably, dicarbene, which is related to diradical **B**, has been assigned a singlet ground state using ESR spectroscopy.[24] Other topologically-related diradicals, tetramethylenebenzene and tetramethyleneethane, have been found to have singlet and triplet ground states, respectively.[25]

Experimental Section

Major chemicals were obtained from Aldrich. Tetrahydrofuran (THF) and tetramethylethylenediamine (TMEDA) were distilled from sodium/benzophenone solution and sodium/potassium alloy, respectively. [(3-Bromo-4,6-dimethylphenyl)bis(4-*tert*-butylphenyl)methoxy]methane and [(3-bromo-4,6-di-isopropylphenyl)bis(4-*tert*-butylphenyl)methoxy]methane, which are referred to as "bromo ethers", were prepared previously.[13] ^{1}H and ^{13}C NMR spectra were obtained using Omega spectrometers (300 and 500 MHz for ^{1}H).

Precursors for Diradicals 1 and 2 (eq 1). *t*-BuLi (4 mmol of 1.7 M solution in pentane) was added to a solution of bromo ether (2 mmol) in THF (10 mL) at −78 °C. After 50 min at −78 °C and a brief warming period (2 min), CuCN (1 mmol) was added under nitrogen at −78 °C and followed by TMEDA 10 min later. After an additional 10 min, O_2 was passed through the reaction mixture for 1 h. The reaction mixture was warmed to ambient temperature, and addition of water and usual aqueous workup gave a crude product.

Diether (R = Me). Column chromatography (20 psi, flash silica, ether/hexane, 1/20), 0.32 g (39 %). After treatment with boiling MeOH, 0.15 g of white powder was obtained (mp 222–224 °C). ^{1}H NMR ($CDCl_3$): 7.32–7.22 (m, 18 H), 7.00 (s, 2 H), 3.08 (s, 6 H), 2.08 (s, 6 H), 1.95 (s, 6 H), 1.27 (s, 36 H). ^{13}C NMR ({^{1}H} and {$\theta = 135°$} DEPT, $CDCl_3$):148.9 (q), 137.8 (q), 137.7 (q), 137.5 (q), 135.0 (q), 133.9, 132.4, 127.7 (broad), 127.4 (broad), 124.5 (intense), 87.6 (q), 52.6, 34.3 (q), 31.4, 21.3, 19.3. FABMS (3-NBA), cluster: *m/z* (peak height) at M^+, 824.6 (3), 825.6 (10), 826.6 (10), 827.6 (5), 828.6 (2); $(M - OCH_3)^+$, 795 (200); M^+ calcd for $C_{60}H_{74}O_2$ 826.56888, found 826.5659 and 826.5655.

Diether (R = *i*-Pr). After treatment with boiling MeOH, 0.65 g (30%) of white powder was obtained (mp 262–264 °C). ^{1}H NMR ($CDCl_3$): 7.35–7.23 (m, 18 H), 7.19 (s, 2 H), 3.08 (s, m, 8 H), 2.85 (sept, $J = 7$, 2 H), 1.26 (s, 36 H), 1.16 (d, $J = 7$, 6 H), 1.05 (d, $J = 7$, 6 H), 0.79 (d, $J = 7$, 6 H), 0.75 (d, $J = 7$, 6 H). ^{13}C NMR ({^{1}H} and {$\theta = 135°$} DEPT, $CDCl_3$): 148.94 (q), 148.85 (q), 148.1 (q), 145.8 (q), 142.2 (q), 141.8 (q), 136.27 (q), 136.22 (q), 131.4, 128.0, 127.9, 124.34, 124.31, 124.19, 87.4 (q), 53.0, 34.3 (q), 31.3, 29.5, 29.2, 24.8, 24.0, 23.7, 23.2. FABMS (3-NBA), cluster: *m/z* (peak height) at $(M - OCH_3)^+$, 906.6 (4), 907.6 (10), 908.6 (8), 909.6 (4); $(M - OCH_3)^+$ calcd for $C_{67}H_{87}O$ 907.675690, found 907.6718 and 907.6723.

Diradicals 1 and 2. Techniques for preparation of similar radicals and handling of ESR and SQUID samples were previously described.[2a,11e] The purity of the SQUID samples was estimated by ESR spectroscopy after SQUID measurements. For each independently prepared sample of solid 2, a set of ^{1}H NMR and ESR spectra in THF-d_8 was obtained. ^{1}H NMR spectra were integrated including the broad peak between +20 ppm and −10 ppm, solvent peaks, and a relatively sharp impurity peak(s) at 1.3 ppm; integrations of the impurity peaks in the NMR spectra were related to the center peaks in the ESR spectra.

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Supplementary Material Available: ESR spectra for diradicals 1 and 2 after SQUID measurements (4 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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