Alkyl-substituted Schlenk hydrocarbon diradicals with triplet and singlet ground states in frozen solutions

Andrzej Rajca * and Suchada Rajca

Department of Chemistry, University of Nebraska, Lincoln, NE 68588-0304, USA

Ground states for alkyl-substituted Schlenk hydrocarbon diradicals 1–4 in frozen 2-MeTHF or THF are determined at low temperatures by EPR spectroscopy (4–80 K) or SQUID magnetometry (2–80 K). Diradicals 1, 2, and 3 are triplet ground states. Diradical 4 is the singlet ground state with the singlet–triplet gap, $\Delta E_{ST} \approx -0.2$ kcal mol^{-1}. Another minor diradical present in the samples of 4 possesses $\Delta E_{ST} \approx -0.02$ kcal mol^{-1}; most likely, this diradical corresponds to another conformational isomer of 4. Compound 4 is the first hydrocarbon diradical with antiferromagnetic coupling through 1,3-phenylene, a ubiquitous mediator of a ferromagnetic coupling.

Introduction

Determination and understanding of spin coupling in organic molecules with more than one unpaired electron is one of the key issues in the interdisciplinary topic of organic magnetism.[1] From the point of view of electronic structure, hydrocarbon diradicals are among the most straightforward systems.[2] For the diradical, the limiting possibilities for the ground state are triplet (spin, $S = 1$) and singlet (spin, $S = 0$), corresponding to ferromagnetic and antiferromagnetic coupling, respectively. The strength of the coupling may be measured by the singlet–triplet energy gap (ΔE_{ST}).

As far as magnetism and bonding is concerned, diradicals with strong ferromagnetic coupling are the most interesting.[1d] Such diradicals typically have a 1,3-phenylene unit to mediate spin coupling between 'unpaired' electrons. Both theory and experiment are in general agreement with topological origin of the ferromagnetic coupling through 1,3-phenylene.[3] Schlenk hydrocarbon, first prepared in 1915, is a prototype example.[4] An EPR spectrum for its triplet state, accompanied by a large amount of the doublet state ($S = 1/2$) impurity, was observed at ≈80 K. Assignment of the triplet state as the ground state was based on a linear Curie plot of the EPR signal intensity (I *vs.* $1/T$) at relatively high temperatures.[5] This result did not preclude the possibility of the triplet states being close in energy, with either triplet or single as the ground state ($\Delta E_{ST} \ll RT$).[6] Measurement of I at lower temperatures (*e.g.*, near 4 K) would narrow the uncertainty in both sign and magnitude of ΔE_{ST} but, ultimately, bulk magnetic studies on the pure diradical could provide an unequivocal assignment of the ground state. The purity of the diradical would greatly affect the magnetic studies, which are based on measurement of 'average spin' (or its counterpart) of the sample. More stable diradicals, closely related to Schlenk hydrocarbon, have been prepared: alkyl-substituted **1**–**5**,[7] perchlorinated **6**,[8] and phenylated **7** and **8**.[9] These diradicals have much improved purity compared with Schlenk hydrocarbon.

Diradicals **1**–**4** are especially important from the point of view of spin coupling. Of **1**–**8**, diradical **1** best models Schlenk hydrocarbon. Diradicals **1**–**4** are relevant to the homologous high-spin polyarylmethyl polyradicals.[1d] Magnetic studies of **2**–**4** in the solid state have been interpreted in terms of triplet ground states.[7a] The 'average spin' values (or effective magnetic moments) were lower than the theoretical values for pure diradicals with triplet ground states. This discrepancy was associated with various degrees of dimerization (including covalent bond formation) in the solid state.[7a] Recently, reactions of **2**–**4** with oxygen, forming corresponding peroxides, have been studied and it was found that **4** in the solid state showed drastically different reactivity than in THF.[10]

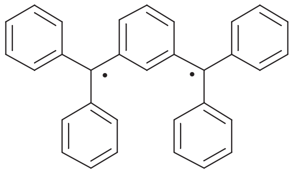
Several examples of diradicals, in which spin coupling through 1,3-phenylene leads to a singlet ground state, have been reported. They may be characterized as having spin-bearing sites with significant spin localization at heteroatoms and being predisposed to significant twist out of π-conjugation with the 1,3-phenylene moiety.[11] Other relevant examples are hydrocarbon tetraradicals, in which trimethylenemethane-based moieties (TMM) are coupled through 1,3-phenylene; quintet and triplet EPR spectra are detected at near 4 K when one and two TMMs, respectively, are sterically forced out of conjugation with 1,3-phenylene. These results were interpreted as the presence of ferromagnetic coupling and absence of detectable spin coupling through 1,3-phenylene, respectively.[12] Calculations on 1,3-benzoquinodimethane and 1,3-phenylenebis(nitroxide) suggest singlet ground states for dihedral angles of ≈90° between the benzene ring and the spin-bearing moieties.[13]

Diradicals **1**–**4** are relevant to Schlenk hydrocarbon and provide a suitable series for systematic study of the effect of steric hindrance on spin coupling through 1,3-phenylene. Here we report the determination of the ground states for diradicals **1**–**4** in frozen solutions, using EPR spectroscopy and SQUID magnetometry.

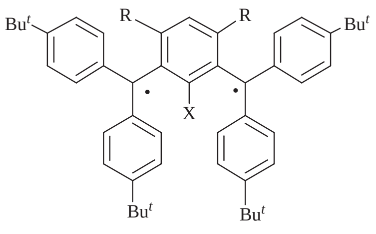
Results and discussion

The preparation of diradicals **1**–**4** has previously been reported.[7a,14] Frozen solutions of **1**–**4** were studied by SQUID magnetometry and EPR spectroscopy. For SQUID magnetometry, typical samples of ≈3×10^{-2} M diradicals in THF were prepared by I_2 oxidations of the corresponding carbodianions at low temperatures.[7a,15] A band of diradical in THF, ≈5 mm high, was flanked by bands of frozen pure THF, ≈50 mm high, in a flame-sealed 4 mm OD quartz EPR sample tube.[16] After the magnetic studies, selected samples were melted at low temperature, leading to a >10-fold dilution of diradicals with THF, and EPR spectra for the dilute samples were obtained at ≈80 K. Samples of the diradicals **2**–**4** in 2-MeTHF, with pure THF as background, were also prepared; their magnetic data showed larger error from residual diamagnetism compared with samples in THF.[16] For EPR spectroscopy, solutions of **1** in THF (≈3×10^{-2} M) were diluted several times with 2-MeTHF at low temperature; solutions of **2**, **3**, and **4** in 2-MeTHF were prepared from the corresponding solid diradicals.

Diradicals **1**–**4** in frozen 2-MeTHF–THF, 2-MeTHF, or THF gave intense EPR spectra at ~80 K. The $\Delta m_s = 1$ regions



Schlenk hydrocarbon



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2 R = Me, X = H
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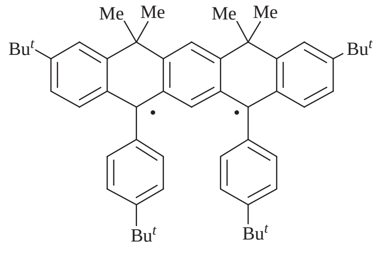

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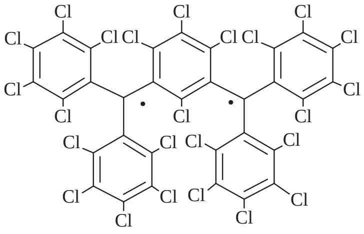

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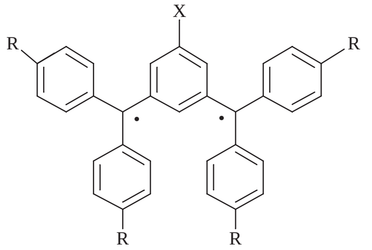

7 R = Ph, X = H
8 R = Ph, X = Ph

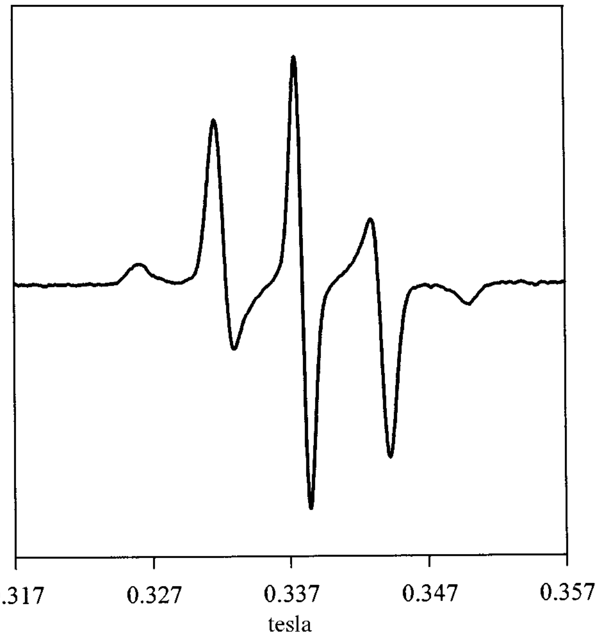

Fig. 1 X-Band EPR spectrum in the $\Delta m_s = 1$ region for diradical **4** in THF at ≈80 K, following SQUID magnetometry

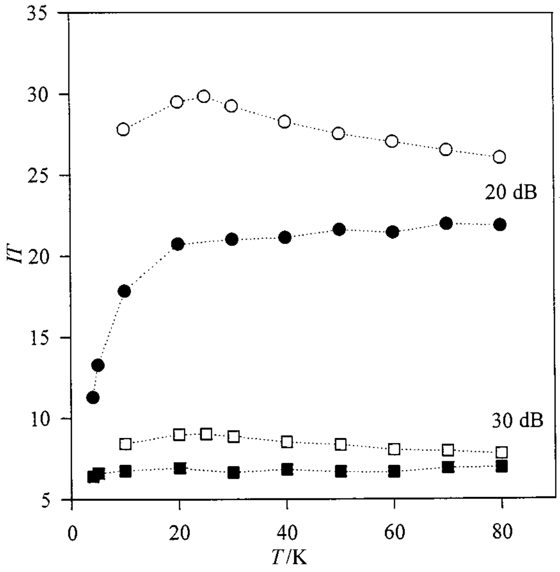

Fig. 2 EPR spectroscopy for diradicals **2** and **3** in 2-MeTHF. The EPR intensities (I) for the $\Delta m_s = 2$ signal are plotted as the product (IT) of I and T *vs.* T at two different microwave power attenuation settings (20 dB and 30 dB); filled and empty symbols are used for **2** and **3**, respectively. The decrease in values of IT at low T is due to partial microwave saturation.

of the spectra were consistent with the triplet states ($S = 1$); the center peaks are assigned to monoradical ($S = 1/2$) impurities (Fig. 1). Values for $|D/hc|$, zero field splitting (zfs) parameters,[17] increased from $\approx 6 \times 10^{-3}$ to $\approx 11 \times 10^{-3}$ cm^{-1} in the series **1**–**4**, as reported previously.[7a] The $|D/hc|$ zfs parameter is $\approx 8 \times 10^{-4}$ cm^{-1} for **1** and it is negligible within spectral resolution for **2**–**4**.[7a,18] Relative differences in values of $|D/hc|$ in THF *vs.* 2-MeTHF do not exceed ≈5%. Detection of weak transitions in the $\Delta m_s = 2$ region further confirms significant population of the triplet state ($S = 1$) for all diradicals at ≈80 K.

The ground states for diradicals **1**–**4** were determined by variable temperature EPR spectroscopy and/or SQUID magnetometry.

Diradicals 1, 2, and 3

Diradicals **2** and **3** in 2-MeTHF were studied by variable temperature EPR spectroscopy. The EPR spectra in both $\Delta m_s = 1$ and $\Delta m_s = 2$ regions for **2** and **3** were very intense at ≈4 K. 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 Fig. 2.[19a] The IT *vs.* T plot is constant for **2** but a small, reproducible, drop-off at the higher temperatures (about 10% at 80 K) was detected for **3**. Therefore, in the studied temperature range, changes in population of the triplet states are undetectable in **2** and they are very small in **3**. This suggests that either the triplets are the ground states with $\Delta E_{ST} > RT$ or the triplet and singlet states are nearly degenerate $\Delta E_{ST} < RT$ ($T = 10$–80 K).[20] Unequivocal assignment of the ground state may be obtained from magnetization studies.

Magnetization (M) was measured for diradicals **1**, **2**, and **3** in THF and 2-MeTHF as a function of magnetic field ($H = 0$–5.5 T) and temperature ($T = 2$–80 K). M *vs.* H data at low temperature $T = 2$, 5, 10 K, were corrected for intermolecular anti-

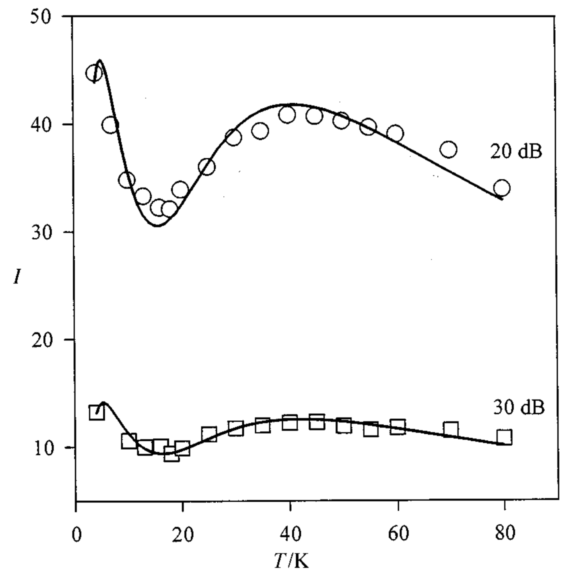

Fig. 3 Plot of the EPR intensity (I) for the $\Delta m_s = 2$ signal *vs.* T in the $T = 4$–80 K range for diradical **4** in 2-MeTHF. Experimental points are shown at two microwave attenuation settings (20 dB and 30 dB). The solid lines correspond to fits, using eqn. (2) of the Experimental section. The fitting parameters (parameter dependence) for the 20 dB data are: normalization factor for the first diradical, 2.6×10^4 (0.732), normalization factor for the second diradical, 3.8×10^2 (0.810) and the corresponding spin coupling constants, $J_1/k = -38.8$ K (0.827), $J_2/k = -4.0$ K (0.721). Analogous values for the 30 dB data are: 7.9×10^3 (0.751), 1.2×10^2 (0.804), $J_1/k = -40.3$ K (0.851), $J_2/k = -4.2$ K (0.672).

ferromagnetic interactions with a mean-field parameter, $\theta < 0$. For all three diradicals, the expected $S \approx 1$ and very small $|\theta| < 0.1$ K were obtained from the M *vs.* $H/(T - \theta)$ fits to Brillouin functions with two variable parameters: S and magnetization at saturation, M_{sat}.[1d,21] The M *vs.* T data ($T = 2$–30 K, $H = 0.5$ or 1.0 T), which are plotted as MT *vs.* T, were adequately reproduced with S, M_{sat}, and θ from the M *vs.* $H/(T - \theta)$ fits at $T = 2$ K.[22a] For diradical **3** in THF, the MT *vs.* T plot is also flat in the $T = 30$–80 K range, within experimental error caused by low signal-to-noise and incomplete offset of diamagnetism.[18,22b] Therefore, diradicals **1**–**3** in THF are triplet ground states with a significant ΔE_{ST}.

Diradical 4

Upon lowering of the temperature from ≈80 K to ≈4 K, the EPR spectra in both $\Delta m_s = 1$ and $\Delta m_s = 2$ regions for diradical **4** in 2-MeTHF became very weak, suggesting that the observed triplet state is thermally populated and the singlet state is the ground state. Also, the spectral width of the $\Delta m_s = 1$ region ($2|D/hc|$) decreased by about 5% in this temperature range. The plot of the intensity (I) for the $\Delta m_s = 2$ signal *versus* the temperature ($T = 4$–80 K) shows a maximum at $T_{\text{max}} \approx 40$ K and an unusual minimum at $T_{\text{min}} \approx 20$ K (Fig. 3). Qualitatively, a maximum in the I *vs.* T plot for the $\Delta m_s = 2$ signal suggests a singlet ground state diradical with $\Delta E_{\text{ST}} \approx RT_{\text{max}}$. The increase in I at low temperature ($T < T_{\text{min}}$) may be associated with the presence of another singlet or triplet ground state diradical. A numerical fit of these data as I *vs.* T to a model based upon the two-site Heisenberg Hamiltonian, $H = -2J\mathbf{S}_1\cdot\mathbf{S}_2$, assuming a mixture of two diradicals with coupling constants J_1 and J_2, gives $J_1/k = -40 \pm 5$ K and $J_2/k = -3 \pm 2$ K; the molar ratio of the diradicals is tentatively estimated as ≈7 : 1, respectively, assuming identical $|D/hc|$ for both diradicals [Fig. 3, eqn. (1) in the Experimental section].[19b,21,23,24]

Both decrease in $|D/hc|$ and some microwave saturation at the lowest temperatures of the 4–80 K range affect the intensity of the $\Delta m_s = 2$ signal and, consequently, contribute to the errors determination of the values of J_1 and J_2. Moreover, the molar ratio of the diradicals, which is derived from their normalization factors for the intensities of the $\Delta m_s = 2$ signals, will strongly depend on the relative values of $|D/hc|$.[19b] Magnetization studies not only verified the values of J_1 and J_2 but also revealed the molar ratio of the diradicals as well.

For **4** in frozen THF, magnetization (M) was measured as a function of magnetic field ($H = 0$–5.5 Tesla) and temperature ($T = 2$–80 K) (Fig. 4). The M *vs.* T data ($T = 2$–80 K) were fit to the model is analogous to that for the EPR data, except for an additional term, which is used to account for 'monoradical impurities' ($S = 1/2$) [eqn. (3) in the Experimental section]. Numerical fitting was carried out on the selected sample, in which diamagnetism of **4** in THF is completely offset (to within experimental error) by the surrounding background of pure THF. This procedure avoids overparametrization of the numerical fit. The five-parameter fit (J_1/k, J_2/k, number of moles of the first diradical, number of moles of the second diradical, number of moles of monoradical) gave $J_1/k = -40 \pm 5$ K and $J_2/k = -7 \pm 2$ K, in qualitative agreement with the EPR data. The molar ratio of the diradicals and the monoradical impurity is 8 : 1 : 2, respectively (Fig. 4). The molar ratio of the two diradicals, 8 : 1, is comparable to the ratio of their normalization factors for the I *vs.* T data for the $\Delta m_s = 2$ region of the EPR spectrum; this suggests that the values of $|D/hc|$ are similar for both diradicals.[19b]

The M *vs.* H data at $T = 2$ K and $H = 0$–5.5 Tesla should contain contributions from both the diradical with $J_2/k = -7$ K and the $S = 1/2$ monoradical; at $T = 2$ K, contribution to magnetization from the diradical with $J_1/k = -40$ K is negligible. The M *vs.* H/T plot adheres to the $S = 1/2$ Brillouin curve at low H and significantly exceeds it at high H, as qualitatively expected for a mixture of an $S = 1/2$ monoradical and a singlet ground state diradical with a small ΔE_{ST}. An adequate numerical three-parameter fit (diradical plus monoradical) is precluded by overparametrization. When the contribution to the M *vs.* H data from the diradical is subtracted, using $J_2/k = -7$ K and number of moles of the second diradical from the M *vs.* T fit, the M *vs.* H/T plot follows the $S = 1/2$ Brillouin curve. The two-parameter M *vs.* H/T fit (S and magnetization at saturation, M_{sat}) to a Brillouin function gives $S = 0.50$; M_{sat} is 95% of the calculated value from the number of moles of the monoradical in the MT *vs.* T fit (Fig. 4).[21]

In summary, the EPR and magnetization data for **4** in 2-MeTHF and THF revealed two singlet ground states diradicals with similar values of $|D/hc|$. The major and minor diradicals possess stronger and weaker antiferromagnetic coupling with $J_1/k \approx -40$ K ($\Delta E_{\text{ST}} \approx -0.2$ kcal mol^{-1}) and $J_2/k \approx -5$ K ($\Delta E_{\text{ST}} \approx -0.02$ kcal mol^{-1}), respectively. Most likely, the two diradicals correspond to conformational isomers of **4**.

Spin coupling through the 1,3-phenylene unit

Diradicals **1**–**3** possess triplet ground states in frozen THF and 2-MeTHF; however, diradical **4** has a singlet ground state. Consequently, spin coupling through the 1,3-phenylene moiety is ferromagnetic ($J > 0$) for **1**–**3** and antiferromagnetic ($J < 0$) for **4**.

It was conjectured that spin coupling through a 1,3-phenylene unit in diradicals may be related to spin densities (*e.g.*, measured by electron–nuclear couplings) in the corresponding monoradicals, which formally contain the coupling unit.[1d] The value of J was postulated to be proportional to the square of the spin density in the ferromagnetic coupling unit; *i.e.*, it should depend on spin delocalization in the π-conjugated system. Using tris(2,6-dimethoxyphenyl)methyl and perchlorotriphenylmethyl as sterically hindered reference monoradicals, values of J in diradicals **2**–**4** and **6** were estimated to be $J/k \approx 500$ K and 300 K, respectively. However, the present experimental results show that $J/k < 0$ K for **4** in solution. In tris(2,6-dimethoxyphenyl)methyl, spin density may only delocalize into sterically hindered 2,6-dimethoxyphenyls. In **4** (and related diradicals), spin density may delocalize more readily into the 4-

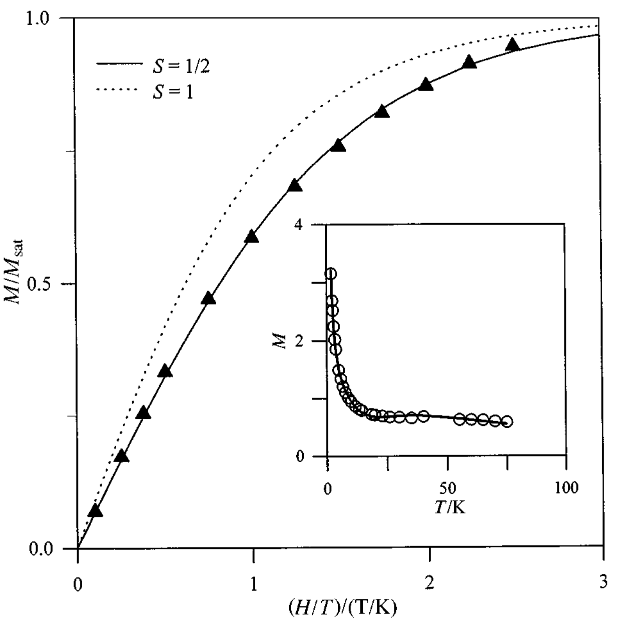

Fig. 4 SQUID magnetometry for diradical **4** in THF. Main plot: M/M_{sat} *vs.* H/T, $H = 0$–5.5 T. Experimental points at $T = 2$ K are shown after subtraction of magnetization of the conformer with the less negative coupling constant (see insert plot). Solid and intercepted lines correspond to Brillouin functions. The fitting parameters are $S = 0.499$ and $10^3 M_{sat} = 1.83$ emu; the parameter dependence is 0.78. Insert plot: M *vs.* T at $H = 0.5$ T. The empty circles are the experimental points. The solid line is the numerical fit using eqn. (4) (Experimental section). The fitting parameters and their parameter dependences are $J_1/k = -41.4$ K (0.82), $n_1 = 1.19 \times 10^{-6}$ mol (0.70), $J_2/k = -7.4$ (0.85), $n_2 = 1.49 \times 10^{-7}$ mol (0.85), $n_3 = 2.44 \times 10^{-7}$ mol (0.54).

tert-butylphenyls than the relatively hindered 2,4,6-trimethyl-1,3-phenylene, leading to a smaller than expected spin density in the spin coupling unit and decreased J-value. In order to estimate the J-value for diradical **4** (and **2**–**3**), an adequate reference monoradical [*e.g.*, 2,4,6-trimethylphenylbis(4-*tert*-butylphenyl)methyl] would have to be prepared and studied. For small J-values, other interactions may become comparable in energy and determine the spin coupling, including antiferromagnetic coupling.[1*d*,13] All diradicals reported to date with antiferromagnetic coupling through 1,3-phenylene, such as sterically hindered 1,3-phenylene-base dinitroxides and more recent analogous diradicals with heterocyclic spin-bearing groups, fall into this category.[11,25]

Among **1**–**4**, diradical **3** possesses the second largest out-of-plane twisting of the spin-bearing groups; in 2-MeTHF at ≈80 K, its $|D/hc|$ is approximately 10% less than that of **4**. Diradical **3** has the triplet ground state, however, EPR data for **3** in 2-MeTHF may tentatively be interpreted in terms of a slight thermal depopulation of the triplet ground state at $T > 30$ K. This suggests that in **3**, ferromagnetic coupling through 1,3-phenylene might be weaker compared with **1** and **2**. Diradicals analogous to **3**, such as diradical anion **9** and diradical dianion **10** (Fig. 5), have flat IT *vs.* T plots of the EPR $\Delta m_s = 2$ signal in 2-MeTHF–THF in the 10–80 K range.[26] This suggests stronger ferromagnetic coupling for **9** and **10** in 2-MeTHF–THF, compared with **3** in 2-MeTHF. Values of $|D/hc|$ for **9** and **10** are slightly smaller (by 3–5%) compared with that of **3**.[26] Another comparison can be made to tetraradical **11**, which possesses a quintet ground state ($S = 2$) (Fig. 5). EPR spectra for **11** in 2-MeTHF–THF suggest a mixture of at least two ($S = 2$) isomers; both linear Curie plots and flat IT *vs.* T plots were obtained for the $\Delta m_2 = 2$ signal in the 10–80 K, range, suggesting the absence of detectable depopulation of the quintet ground states.[15] In this context, it is interesting to look into the topology of spin coupling in diradical **3** and tetraradical **11**. The most straightforward model considers only pairwise nearest-neighbor ferromagnetic coupling constants through 1,3-phenylenes, which are designated J_{di} and J_{tetra} in **3** and **11**, respectively. Energy eigenvalues from the Heisenberg Hamiltonian indicate that energy gaps between the ground and the lowest excited states are $2J_{di}$ and $1J_{tetra}$ in **3** and **11**, respectively (Fig. 5).[27] In conjunction with the results from EPR spectroscopy, this suggests that ferromagnetic coupling through 1,3-phenylene is much stronger in **11** compared with that in **3** ($J_{tetra} > J_{di}$). This result can be rationalized by similar steric hindrance arguments as discussed above. In **11**, the central triarylmethyl has all three aryls, which are ferromagnetic coupling units, sterically hindered; *i.e.*, the spin density has to delocalize into ferromagnetic coupling units or remain at the 'methyl' carbon. Therefore, each of the three ferromagnetic coupling units in **11** is expected to possess more spin density than the spin coupling unit in **3**. We refer to such apparent increase in J in more sterically hindered system as 'steric compression of spin density'.

Increased steric hindrance around the 1,3-phenylene unit in the **1**–**4** series may lead to diminished π-overlap between spin-bearing bis(4-*tert*-butylphenyl)methyls and the alkyl-substituted 1,3-phenylene. Higher values of $|D/hc|$ provide support for the out-of-plane twisting of the spin-bearing groups in the **1**–**4** series.[7*a*] Because two conformational isomers, associated with propeller isomerism,[28] are expected for each of diradical in the **1**–**4** series, one would expect superposition of two triplet EPR spectra with different $|D/hc|$ values for each diradical. [Two triarylmethyl propellers may have same or opposite helicities.] Apparently, either the values of $|D/hc|$ (dipolar coupling) for the two isomers are very similar, or the ratio of the isomers under the experimental conditions is large. However, both EPR and magnetization data for the 2,4,6-trimethyl-1,3-phenylene-based diradical **4** are best interpreted in terms of two conformational isomers with similar values of $|D/hc|$. Values of $|J/k|$ for the two isomers of **4** are rather small and differ by an order of magnitude, facilitating detection of the two isomers. In contrast with values of J/k, the relative differences in values of $|D/hc|$ for the two isomers do not exceed 5%. (Incidentally, $|D/hc|$ in **4** is approximately twice that in **1**.) Therefore, small differences in conformation, as measured by values of $|D/hc|$, translate into significant differences in weak spin coupling in isomers of **4**.

Conclusion

Diradicals **1**, **2**, and **3** in frozen THF and 2-MeTHF have triplet ground states with significant singlet–triplet energy gaps. 2,4,6-Trimethyl-1,3-phenylene-based diradical **4** in frozen THF and 2-MeTHF has a singlet ground state with a small singlet–triplet energy gap. Spin coupling through the 1,3-phenylene unit is ferromagnetic in diradicals **1**–**3** and antiferromagnetic in diradical **4**.

In polyarylmethyl di- and poly-radicals, steric hindrance may influence relative delocalization of spin density to the 1,3-phenylene units *vs.* the other benzene rings. Increased steric hindrance may either diminish the ferromagnetic coupling and lead to the low-spin ground state (*e.g.*, diradicals **4** *vs.* **1**–**3**), or increase ferromagnetic coupling (*e.g.*, tetraradical **11** *vs.* diradical **3**).

Experimental

Materials and special procedures

Tetrahydrofuran (THF) and 2-methyltetrahydrofuran (2-MeTHF) for use on a vacuum line were distilled from sodium–benzophenone under a nitrogen atmosphere.

Diradicals **1**–**4** have to be handled in the inert atmosphere; rigorous exclusion of oxygen is important.[7*a*] Diradical **1** is persistent only in solution at low temperature.[14] Diradicals **2**, **3**, and **4** are obtained as solids; they can be stored in a glovebox refrigerator (−30 °C) for extended periods and handled at ambient temperature.[7*a*]

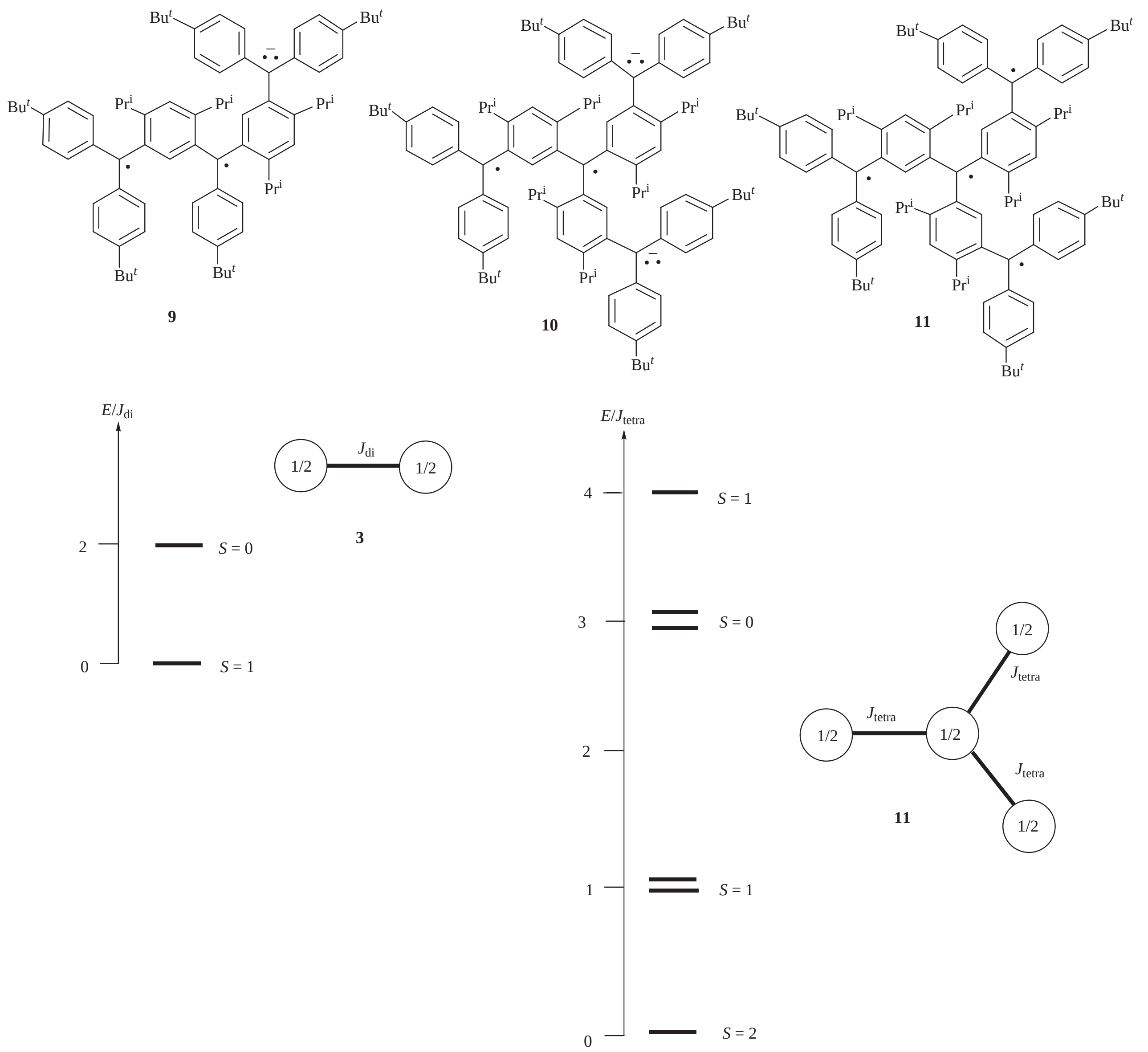

Fig. 5 Structures for diradical anion **9**, and diradical dianion **10**, and tetraradical **11**. Energy eigenvalues from the Heisenberg Hamiltonian for diradical **3** and tetraradical **11** are shown for $J_{\mathbf{dirad}} > 0$ and $J_{\mathbf{tetrarad}} > 0$, which are ferromagnetic couplings through 4,6-diisopropyl-1,3-phenylene units in **3** and **11**, respectively.

EPR Spectroscopy

Preparation of triarylmethyl-based di- and poly-radicals for EPR spectroscopy has been described.[15] EPR spectra were acquired with a Brucker 200D instrument, equipped with an Oxford Instruments ESR900 liquid helium cryostat or liquid nitrogen insert Dewar, as described elsewhere.[15] The intensities used for the I *vs.* T and IT *vs.* T plots were checked for microwave saturation by using two or three power settings different by at least 10 dB throughout the studied temperature range; temperatures were stepped up and down in each experiment. The modulation amplitude was kept at or below a fifth of the estimated peak-to-peak width for all spectra. Numerical values of I were taken as peak-to-peak heights; double integration (Gramms386 software package) of the selected sets of data gave identical results (to within other experimental errors).

SQUID magnetometry

The samples for magnetometry were prepared as described previously.[16] Quantum Design (San Diego, CA) MPMS5 was used.

Numerical curve fitting

The SigmaPlot for Windows software package was used for most numerical curve fitting and graph plotting. The reliability of a fit was measured by the parameter dependence, which is defined as: dependence = 1 − [(variance of the parameter, other parameter constant)/(variance of the parameter, other parameters changing)]. Values close to 1 indicate an overparametrized fit.

As far as diradicals **1**–**3** are concerned, the previously described fitting procedures to Brillouin functions were used.[22]

For fitting EPR and SQUID data for diradical **4**, all equations were based upon the Heisenberg Hamiltonian, $H = -2J\mathbf{S}_1{\cdot}\mathbf{S}_2$, where, $S_1 = S_2 = 1/2$ and $\Delta E_{ST} = 2J$.[21] The equations for magnetization (M) per mole as a function of temperature (T) and magnetic field (H) were of the following form:[24]

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

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). The following equations are used in the fitting:

$i = 1$, *i.e.*,

'one diradical', two variable parameters (J_1, n_1) (1)

$i = 1, 2$, *i.e.*,

$$\text{‘two diradicals’, four variable parameters } (J_1, n_1, J_2, n_2) \quad (2)$$

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

$$i = 1, 2, 3, \text{ and } J_3 = 0, \textit{ i.e.}, \text{ ‘two diradicals plus monoradical’, five variable parameters } (n_1, J_1, n_2, J_2, n_3) \quad (4)$$

The *M vs. T* data were fit with eqn. (4). For the *M vs. H* data, the contribution from the diradical with weak coupling, which is calculated using eqn. (1), was subtracted and the remainder fit to a Brillouin function. For samples in which diamagnetism is not adequately offset by the surrounding pure THF in the sample tube, an additional fixed parameter (M_{dia}) to account for residual diamagnetism was used to correct all data before fitting.

Eqn. (2) was used for fitting of X-band EPR intensities (I) in the $\Delta m_s = 2$ region; *i.e.*, M is replaced with I, H is set to 0.16 T, $2Ng\mu_B$ and number of moles are lumped into a ‘normalization factor’ to account for arbitrary units of I.

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