Singlet–triplet bistability in a 1,3-phenylene-based bis(aminoxyl) diradical

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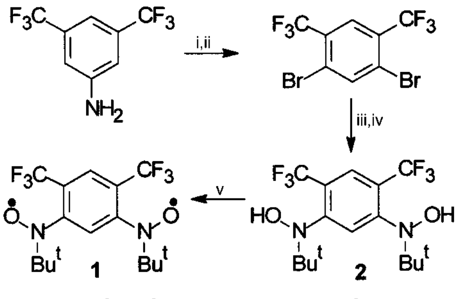
Rapid quenching of the title bis(aminoxyl) 1 in 2-methyltetrahydrofuran from ambient temperature to cryogenic temperatures (5 K or below) produces 1 in its singlet state, which slowly converts at low temperatures, with an S-shaped time-dependence, to the triplet ground state.

1,3-Phenylene-based diradicals are ubiquitous building blocks for both high-spin polyradicals and molecular magnets.[1,2] Although 1,3-phenylene is the most reliable mediator of ferromagnetic coupling in organics, it is well established that severe bond torsions in 1,3-phenylene-based diradicals may result in singlet ground states.[3–5] Therefore, different bond torsions associated with selected conformers may allow for the same diradical to be obtained in either a singlet or triplet ground state. Such a phenomenon was recently reported for a different class of organic diradicals, which have been obtained in either a singlet or triplet state, depending on the photon energy in the photochemical generation or the solvent.[6–8] However, the rate of such conformationally mediated conversion between the different spin states in diradicals was not observed.[8] Now we report the singlet and triplet ground state in a 1,3-phenylene-based diradical, 4,6-bis(trifluoromethyl)-*N*,*N*′-di-*tert*-butyl-1,3-phenylenebis(aminoxyl) **1**, with an observable rate of conversion between the low- and high-spin states.

Synthesis of **1** is outlined in Scheme 1. X-Ray crystallography, EPR, ^{1}H NMR, MS, IR and elemental analysis data confirm the structure and suggest a purity of $>95\%$.

X-Ray crystallography indicates that the aminoxyl moieties are twisted out of the plane of the 1,3-phenylene with torsional angles of −70 (C5–C6–N2–O2) and 49° (C3–C2–N1–O1); both oxygens point toward the trifluoromethyl groups.[9] The geometry and conformation of the trifluoromethyl groups suggests negligible radical–fluorine hyperconjugation (Fig. 1).[10]

The $\Delta m_s = 1$ region of the X-band EPR spectrum of **1** in frozen 2-MeTHF has six broad peaks consistent with a triplet state. The two inner most resonances show resolved hyperfine coupling with the two nitrogens; the center resonance, which would correspond to a monoradical impurity, is negligible. The spectral width of 0.0321 Tesla is constant in the 10–65 K range and it is of similar magnitude to that found for other 1,3-phenylene-connected bis(aminoxyl)s.[3,4,11] The $\Delta m_s = 2$ signal is also observed (Fig. 2). In the ^{1}H NMR spectrum of a 0.05 mol dm^{-3} solution of **1** in CDCl$_3$, two prominent peaks at −16 (broad) and 1.1 ppm (narrow) have a relative intensity of 36 : 1, they are assigned to the *tert*-butyl groups associated with the aminoxyl moiety and the diamagnetic impurity (presumably a hydroxyamine moiety), respectively.[12] Molecular ions in the EI MS for **1** and the dihydroxyamine **2** (Scheme 1) show a *m/z* difference corresponding to two hydrogen atoms.



Scheme 1 *Reagents and conditions*: i, Br$_2$, Fe, CH$_2$Cl$_2$; ii, NaNO$_2$, H$_2$SO$_4$, EtOH (45% for 2 steps); iii, Bu^{t}Li, Et$_2$O; iv, (Bu^{t}NO)$_2$; v, Ag$_2$O, CHCl$_3$ (20% for 3 steps).

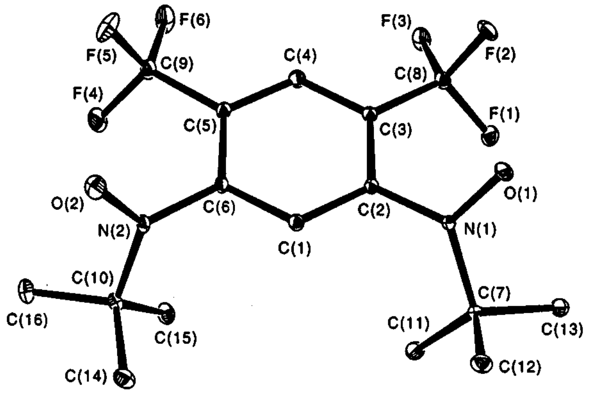


Fig. 1 Molecular structure of **1** in the solid state at 50 K; thermal ellipsoids at the 50% probability. The hydrogens are not shown.

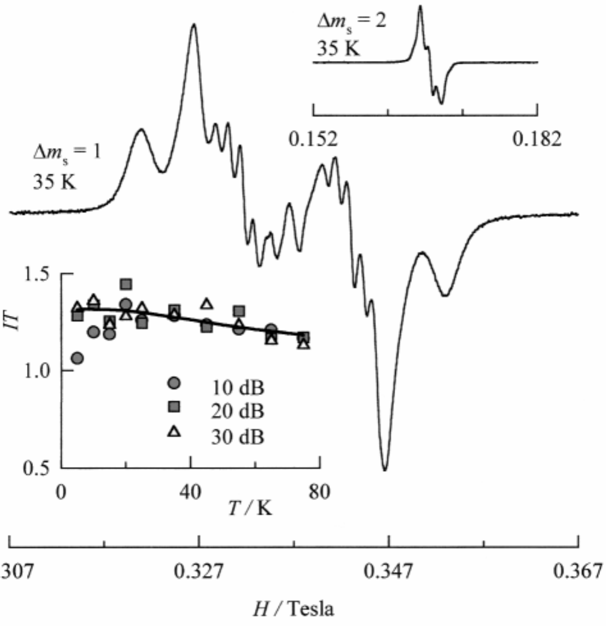


Fig. 2 The EPR spectrum of 0.001 mol dm^{-3} **1** in 2-MeTHF. Zero field splitting parameters for an $S = 1$ state are: $|D/hc| \approx 0.015$ cm^{-1} and $|E/hc| \approx 0.001$ cm^{-1}. Lower insert: plot of the product (IT) of the intensity (I) for the $\Delta m_s = 2$ resonance and the temperature (T) *vs.* T at three settings of microwave power (10, 20 and 30 dB); the 20 and 30 dB data are amplified by the consecutive factors of $3.2 \approx (10)^{1/2}$. The values of I are obtained by numerical double integration of the $\Delta m_s = 2$ region. The solid line corresponds to a numerical fit with the singlet–triplet energy gap corresponding to $2J/k = 80$ K (ref. 14) (J is a coupling constant from the Heisenberg Hamiltonian, $H = -2J\boldsymbol{S}_1{\cdot}\boldsymbol{S}_2$ with $|\boldsymbol{S}_1| = |\boldsymbol{S}_2| = 1/2$).

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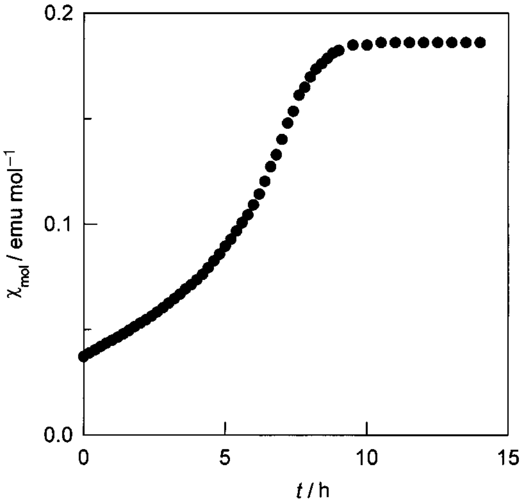

Fig. 3 Plot of molar magnetic susceptibility ($\chi_{\rm mol}$) *vs*. time, following rapid cooling of **1** (0.62 ± 0.07 mg) in 2-MeTHF (*ca*. 0.05 ml) from ambient temperature to 5 K. The applied magnetic field is 0.5 Tesla.

A sample of **1** in 2-MeTHF (10^{-2} mol dm^{-3}) was inserted, at a moderately rapid rate (5–10 min), into a SQUID magnetometer/susceptometer sample chamber kept at approximately 5 K. After establishing a stable temperature in the sample chamber (*ca*. 5 min), and an additional brief equilibration (2–5 min), the molar magnetic susceptibility ($\chi_{\rm mol}$) was measured at a constant applied magnetic field (H = 0.05–0.5 Tesla) as a function of time.[13] S-shaped plots were obtained, in which $\chi_{\rm mol}$ increases about five times (Fig. 3).[13] The onset of a sharp rise in $\chi_{\rm mol}$ is random and varies from several minutes to several hours. Gradual cooling of **1** in 2-MeTHF, *e.g.* temperature sweep from 290 to 5 K at 3, 5 or 10 K min^{-1}, gives the equilibrium value of $\chi_{\rm mol}$ at 5 K. Analogous S-shaped plots are obtained at 1.8 and 2 K. The observed phenomena are solvent dependent; the time-dependence of $\chi_{\rm mol}$ was not found for **1** in tetrahydrofuran (THF) or toluene (constant $\chi_{\rm mol}$ *vs*. time).

Diradical **1** in 2-MeTHF was kept at 1.8 or 5 K until $\chi_{\rm mol}$ (*vs*. time) reached a constant value, and then magnetization (M) was measured at T = 1.8 and 5 K as a function of H = 0–5 Tesla. The fit of the M *vs*. H/T data to the Brillouin functions gives $S = 1$, indicating a triplet ground state. Furthermore, the plateau value of $\chi_{\rm mol} = 0.19$ at 5 K (Fig. 3) is in good agreement with $\chi_{\rm mol} = 0.20$, as expected for a predominantly triplet ground state at 5 K. The plot of IT *vs*. T, where I is the intensity of the EPR signal in the $\Delta m_{\rm S} = 2$ region, slightly decreases at the higher end of the 10–75 K range (Fig. 2). Therefore, the triplet ground state is slightly depopulated at higher temperatures, suggesting a small energy gap between the triplet and the excited singlet state within the same conformer (weak ferromagnetic coupling) or conversion to another conformer with different ordering of states.

One of the most straightforward rationalizations for these results is by invoking two conformers (conformational isomers) for **1** with different torsions about the C(1,3-phenylene)–N bonds.[3] The low temperature conformer has a triplet ground state, probably with a rather small (Heisenberg $2J/k < 100$ K) singlet–triplet energy gap.[14] The high temperature conformer has a singlet ground state (at least, at low temperatures), with a non-negligible singlet–triplet energy gap. Upon rapid quenching from ambient temperature to 5 or 1.8 K, the high temperature conformer (or a large fraction of) is frozen in 2-MeTHF glass. Because the singlet–triplet thermal equilibration within the same conformer will remain very fast, the singlet ground state is predominantly populated in the 1.8–5 K range for the high temperature conformer. The observed S-shaped increase of $\chi_{\rm mol}$ *vs*. time in the 1.8–5 K range would involve a conformational change from the high temperature to the low temperature conformer. The resultant dramatic change between the population of the singlet *vs*. triplet states is responsible for a typically five-fold increase in $\chi_{\rm mol}$. The S-shape and random time span for the completion of the conformational change are associated with various glassy matrix effects, *e.g.* random distribution of non-equivalent sites in the matrix.[15] A somewhat vexing problem is the preference for the singlet ground state in the high temperature conformer. This would require overcoming the entropic advantage of the triplet state ($m_{\rm s}$ degeneracy) by other sources of entropy or enthalpy, *e.g.* relatively low energy vibrational modes in the singlets or different solvation in the liquid *vs*. glassy 2-MeTHF. Unfortunately, there are no structural data for the singlet state (or states) of **1**.

Although conformational isomers were invoked in studies of some organic di- and poly-radicals, the time-dependence of the magnetic susceptibility of **1** in 2-MeTHF is unprecedented and calls for prudent interpretation of magnetic data for organic molecules, especially in glassy matrices.[6] Ultimately, a rational design of spin-bistable diradicals (or polyradicals) may provide organic analogues of metal ion based spin crossover compounds.[16]

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9 *Crystal data* for **1**: $C_{16}H_{20}F_6N_2O_2$, M = 386.34, monoclinic, a = 5.849(2), b = 31.360(200), c = 9.436(6) Å, β = 93.8600(5)°, V = 1726.9(111) Å^3, T = 50(2) K, space group $P2_1/n$ (14), Z = 4, μ(AgKα) = 0.08 mm^{-1}. Structure solved by direct methods and refined by full-matrix least-squares on F^2. 5018 reflections observed [$F_{\rm o} > 4\sigma(F_{\rm o})$]. Final refinement statistics: $wR(F2)$ = 0.1168, $R(F)$ = 0.0502, GooF = 1.079. CCDC 182/1278. See http://www.rsc.org/suppdata/cc/1999/1249/ for crystallographic files in .cif format.

10 On the side of the relatively less twisted aminoxyl moiety in **1**, C8 (CF_3 group) and N1 (aminoxyl) are 0.16 and 0.15 Å, respectively, from the plane defined by the six carbons of the benzene ring (RMS 0.014 Å). All C–F bond lengths are 1.34 Å.

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12 The chemical shift of −17 ppm is found for protons of the Bu$^{\rm t}$ group in 2-methyl-*N*-*tert*-butylphenylaminoxyl: A. Calder, A. R. Forrester, J. W. Emsley, G. R. Luckhurst and R. A. Storey, *Mol. Phys.*, 1970, **18**, 481. Treatment of **1** in $CDCl_3$ in an NMR tube with phenylhydrazine gives quantitatively dihydroxyamine **2**, as expected.

13 A Quantum Design MPMS5S SQUID instrument was used with either standard or continuous temperature control. An approximate correction for diamagnetism ($\chi_{\rm dia}$) for each sample was obtained from extrapolation of χ *vs*. $1/T$ (χ = total magnetic susceptibility) plots using the data in the T = 160–280 K range in the cooling mode of the MPMS5S. Typical values $\chi_{\rm dia} \approx 4 \times 10^{-8}$ emu are an order of magnitude less than the total χ in the 5–1.8 K range.

14 The estimate of the Heisenberg coupling constant, J/k = 40 K (Fig. 2), can only be very approximate, as conformational effects may interfere with a simple two-state model.

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