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Triplet ($S = 1$) Ground State Aminyl Diradical

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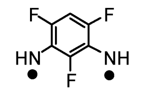
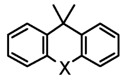
Aminyl radicals ($R_2N\bullet$) are important reactive intermediates.[1,2] Such radicals are generally short-lived; only recently metal- or heteroatom (O, S) stabilized aminyl radicals were isolated.[3,4] To date, there is only one report of an aminyl diradical (Platz diradical) in a triplet state, though the ground state for this matrix isolated diradical is not established.[5] This is in contrast to nitroxide radicals, a popular choice for applications in materials science and biology.[6]

We examine aminyl radicals as building blocks in the design of high-spin molecules and polymers for organic magnetic materials.[7] Our analysis of the EPR ^{1}H-hyperfine splittings (a_H) for 9,9-dimethyl-9,10-dihydroacridine aminyl radical (**DDAN**) indicate that the para a_H and ortho a_H are greater than those of the corresponding nitroxide radical (**DDANO**) by a factor of 2.[8,9] From this factor and the empirical relationship between the singlet−triplet energy gaps ($2J/k$) and a_H, $2J/k \approx |a_H|^2$,[10] we postulate that *m*-phenylene aminyl diradical **1** should possess triplet ($S = 1$) ground state with large singlet−triplet energy gap ($2J/k$), greater by a factor of 4 than that for the corresponding nitroxide diradical.[11] Thus, *m*-phenylene aminyl diradicals, especially if constrained to planarity, should possess triplet ground states with extraordinary strong ferromagnetic coupling.

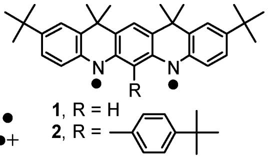
The next challenging problem is the design of the diradical with adequate stability, while maintaining ultrastrong ferromagnetic coupling. Because of the high degree of spin delocalization in *m*-phenylene aminyl diradicals, we predict that all ortho and para positions in the *m*-phenylene should be sterically shielded, but without perturbing the planarity of the cross-conjugated π-system.



Platz diradical



DDAN, X = N●
DDANO, X = N-O●
DDANH, X = NH ●+



1, R = H
2, R =

Herein we describe the synthesis and magnetic characterization of aminyl diradical **2** that is long-lived and possesses an $S = 1$ ground state with strong ferromagnetic coupling.

Bromination of diamine **3**[12] at its most activated position for electrophilic substitution gives **4**, which is subjected to Suzuki cross-coupling with 4-*tert*-butylphenyl boronic acid, to give **5** (Scheme 1). The structure of diamine **5** is confirmed by X-ray crystallography (Figure 1). The five collinearly annelated six-membered rings form an approximately planar cross-conjugated π-system;[13a] the 4-*tert*-butylphenyl group is nearly perpendicular to this π-system,[13b] providing steric shielding. Treatment of diamine **5** with *n*-BuLi produces a yellow suspension of dianion. The dianion is oxidized by iodine at about −105 °C to provide a red solution of aminyl diradical **2** (Scheme 1); the oxidation process is being monitored by EPR spectroscopy.

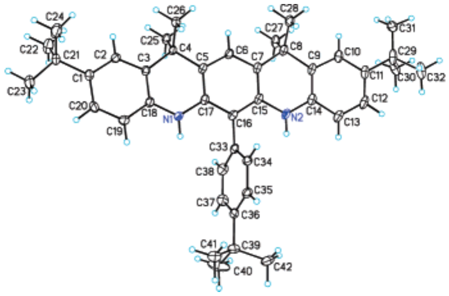


Figure 1. Molecular structure and conformation of diamine **5**. Carbon and nitrogen atoms are depicted with thermal ellipsoids set at the 50% probability level. Disorder for *tert*-butyl groups and solvent of crystallization (benzene) are omitted for clarity.

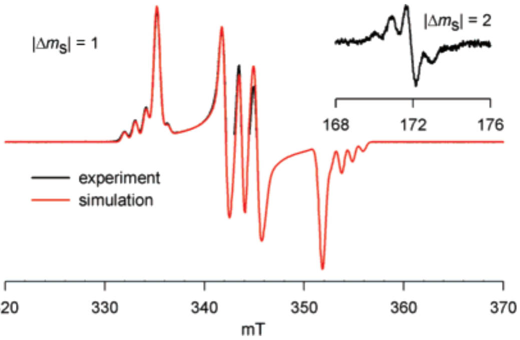
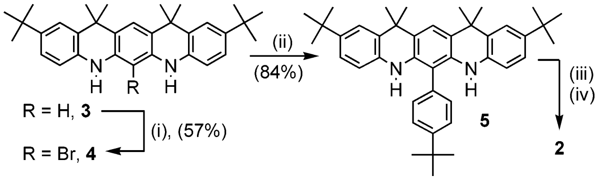


Figure 2. EPR (X-band, $\nu = 9.6376$ GHz) spectrum of **2** in 2-MeTHF at 132 K. The simulation parameters for the $S = 1$ state are $|D/hc| = 9.18 \times 10^{-3}$ cm^{-1}, $|E/hc| = 2.10 \times 10^{-3}$ cm^{-1}, $|A_{zz}/2hc| = 1.00 \times 10^{-3}$ cm^{-1}, $g_x = 2.0030$, $g_y = 2.0042$, $g_z = 2.0019$, Gaussian line ($L_x = 0.6$, $L_y = 0.65$, $L_z = 0.55$ mT). The center lines correspond to an $S = {}^1/_2$ byproduct, simulated with the identical *g*-values, and $|A_{zz}/hc| = 2.00 \times 10^{-3}$ cm^{-1}.

Scheme 1. Synthesis of Aminyl Diradical **2**[a]



[a] Conditions: (i) NBS in chloroform, $NaHCO_3$ (excess), Na_2SO_4 (excess), −40 °C for 1 h; (ii) 4-*tert*-butylphenylboronic acid (1.3 equiv), $Pd(PPh_3)_4$ (5 mol %), Na_2CO_3, benzene/EtOH/water, 2:1:2, 80 °C for 18 h; (iii) *n*-BuLi (2.4 equiv), THF/hexane, −20 °C for 1 h, (iv) I_2, THF, −105 °C (2-MeTHF, −105 or −112 °C).

EPR spectra of **2** in 2-MeTHF at 133 K show six symmetrically disposed side peaks, corresponding to the zero-field splitting parameters $|D/hc| = 9.15 \times 10^{-3}$ cm^{-1} and $|E/hc| = 2.10 \times 10^{-3}$ cm^{-1} in the $|\Delta m_s| = 1$ region and an intense transition in the $|\Delta m_s| = 2$ region (Figure 2). The two outermost peaks (*z*-turning points) appear as pentuplets, which may be simulated by the ^{14}N hyperfine coupling of two nitrogen nuclei with spacings of $|A_{zz}/2hc| = 1.00$

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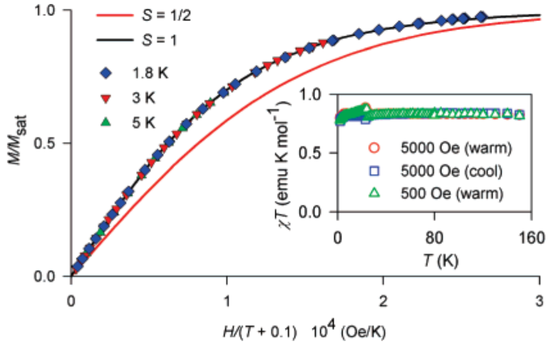

Figure 3. SQUID magnetometry of ∼15 mM **2** in THF. The main and inset plots show M/M_{sat} versus $H/(T - \theta)$ and χT versus T, with $\theta = -0.1$ K, $M_{sat} = 0.84\ \mu_B$, $S = 0.99$, and $\chi T = 0.84$ emu K mol^{-1}.

$\times 10^{-3}$ cm^{-1} ($|A_{zz}/2g\mu_B| \approx 1.1$ mT). As the largest principal value ^{14}N hyperfine tensor in nitrogen-based radicals coincides with the direction of the nitrogen 2p$_\pi$-orbital,[14] the ^{14}N-hyperfine splitting of the outermost lines implies that the 2p$_\pi$-orbital is approximately parallel to the *z*-axis, which is the direction of the largest principal value of the magnetic dipole tensor.[15] Therefore, the aminyl moieties and the *m*-phenylene in diradical **2** adopt approximately coplanar conformation.

Notably, in planar nitroxide diradicals, the largest principal value of the magnetic dipole tensor (*z*-axis) is in the direction connecting nitroxide moieties, that is, the direction perpendicular to the 2p$_\pi$-orbital.[16] The fact that the *z*-axis is parallel to the 2p$_\pi$-orbital in aminyl diradical **2**, precludes the possibility that **2** could be a nitroxide diradical. This conclusion is supported by the *g*-values. Anisotropic *g*-values for **2** (Figure 2) correspond to the isotropic $g = (g_x + g_y + g_z)/3 = 2.0030$, which is comparable to $g = 2.0031$ for **DDAN** and $g = 2.0027$ for **DDANH**, but it is significantly different from $g = 2.0051$ for the nitroxide radical **DDANO**.[8,9,17] Additional evidence for the aminyl diradical is based on the analysis of ^{1}H-hyperfine splittings. Doubletlike isotropic ^{1}H-splitting $|A/g\mu_B| = 1.006$ mT for the α-hydrogen of the NH moiety in **DDANH**[17] suggests that the corresponding $S = 1$ aminium diradical should have tripletlike anisotropic ^{1}H-splittings from two NH moieties with the spacings of $|A_{zz}/2g\mu_B| \approx 0.5$ mT, $|A_{yy}/2g\mu_B| \approx 0.75$ mT, and $|A_{xx}/2g\mu_B| \approx 0.25$ mT.[14] In particular, the spacing of $|A_{yy}/2g\mu_B| \approx 0.75$ mT is expected to be discernible, as it exceeds the observed line-width ($L_y = 0.65$ mT) in the spectrum of **2**.

Another set of samples of 10−30 mM **2** in tetrahydrofuran (THF) is prepared in homemade tubes that allow for strictly low-temperature handling, as well as for sequential examination of the same sample by both EPR spectroscopy and SQUID magnetometry (Figures S3−S8, Supporting Information).[18] The SQUID magnetometry unequivocally reveals the $S = 1$ paramagnetic behavior for both magnetization (M) versus magnetic field (H) and magnetic susceptibility (χ) versus temperature (T); only small intermolecular antiferromagnetic coupling, as measured by a mean-field parameter, $\theta \approx -0.1$ K, is observed (Figure 3).[19]

The numerical fits to the curvature of the M/M_{sat} versus $H/(T - \theta)$ plots at 1.8, 3, and 5 K (M_{sat}, magnetization at saturation) give the value of $S = 0.99$, which is independent of the spin concentration of the sample. When the measured value of $\chi T = 0.84$ emu K mol^{-1} is corrected by the spin concentration ($M_{sat} = 0.84\ \mu_B$, per aminyl radical site), $\chi T \approx 1.0$ emu K mol^{-1} is obtained, which is exactly the value expected for an $S = 1$ diradical. Furthermore, the χT versus T plot is flat up to 150 K, just below the softening temperature of solid THF. These results unequivocally establish a triplet ground state for diradical **2** and provide a lower limit for the singlet−triplet gap, $2J/k > 200$ K (∼0.4 kcal mol^{-1}).

The stability (persistence) of **2** in THF is monitored by SQUID magnetometry; after 30 min at 203 K, M_{sat} and χT decrease to about half of their original values, though the average S is still ∼0.9. After 2 h at room temperature, only an $S = {}^1/_2$ radical is detected. Furthermore, EPR studies show that a solution of **2** in 2-MeTHF is inert toward O_2 gas at 165 K (Supporting Information).

In summary, a triplet ground-state aminyl diradical with strong ferromagnetic coupling is efficiently prepared in solution, thus providing a promising pathway to high-spin aminyl polyradicals.

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Supporting Information Available: Complete ref 11b, experimental section, X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) (a) These predictions are supported by the UB3LYP/6-31G* calculations, providing extraordinary large value $2J/k = 4000$ K (8.0 kcal mol^{-1}) in aminyl diradical **1**, which is four times greater than the $2J/k$ calculated for the corresponding nitroxide diradical. (b) Frisch, M. J.; et. al. *Gaussian 03*, Gaussian, Inc.: Wallingford, CT, 2004.
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(13) (a) In diamine **5**, the mean deviation from a calculated least-square plane including all five co-linearly annelated six-membered rings (C1−C20, N1, N2) is 0.0763 Å. (b) The angle between the least-square plane, defined by C1−C20, N1, N2, and the least square plane of the benzene ring of the 4-*tert*-butylphenyl group (C33−C38) is 75.82(4)°.
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(19) Annealing the THF matrix at low temperatures (e.g., 170 K) does not significantly change values of S, M_{sat}, and χT but it increases values of θ, for example, $\theta \approx -0.2$ K; in EPR spectra at 140 K, the intensity of the center peak significantly increases several times relative to the side bands.

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