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JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
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Triplet Ground State Derivative of Aza-*m*-xylylene Diradical with Large Singlet–Triplet Energy Gap

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Ⓢ *Supporting Information*

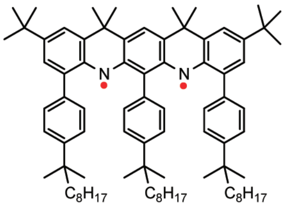
ABSTRACT: Organic molecules with a strong preference for triplet ground states, in which the triplet state is below the lowest singlet state by ≥10 kcal/mol, are typically short-lived and mostly detected as reactive intermediates. We now report a triplet ground state derivative of aza-*m*-xylylene diradical with a large singlet–triplet energy gap (ΔE_{ST}) of ~10 kcal/mol, which is comparable to ΔE_{ST} for the well-known reactive intermediate *m*-xylylene diradical. The aminyl diradical persists in solution at room temperature on the time scale of minutes.

m-Xylylene is a well-known high-spin diradical with a very strong spin–spin interaction, and its triplet ground state lies below the lowest singlet state by 9.6 ± 0.2 kcal/mol,[1–3] one of the largest known singlet–triplet energy gaps (ΔE_{ST}) for an organic molecule. Such molecules typically are short-lived, as in the case of *m*-xylylene, which is observable in solution at room temperature for hundreds of nanoseconds.[4]

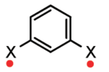
Derivatives of *m*-xylylene with improved stability have been prepared to provide numerous high-spin diradicals. Over the past decades, *m*-xylylene-based diradicals have been employed as building blocks in the designs of very high spin polyradicals and magnetically ordered organic polymers.[5,6] However, the strength of spin–spin interactions in these radicals is reduced by 1–3 orders of magnitude relative to the ΔE_{ST} value of 9.6 kcal/mol in *m*-xylylene[5] because of dissipation of spin density over the extended π-system and/or resonance stabilization that renders improved stability. Therefore, triplet ground state diradicals that possess both large ΔE_{ST} (≥10 kcal/mol) and stability at room temperature remain elusive. Such diradicals may be viewed as building blocks for high-spin polyradicals with strong spin–spin interactions at room temperature that could enable the development of robust magnetic polymers and organic spintronics.[5,7,8]

Nitrogen-centered (aminyl) radicals are typically short-lived,[9] and only two aminyl monoradicals are known to be stable under ambient conditions.[10] Recently, we reported the isolation of a triplet ground state aminyl diradical under an inert atmosphere.[11] The diaazapentacene-derived aminyl diradical was estimated by density functional theory (DFT) computations to possess $\Delta E_{ST} \approx 7$ kcal/mol,[11] which is significantly greater than 0.6 kcal/mol, the thermal energy at room temperature. This result encouraged us to explore stable aminyl diradicals with $\Delta E_{ST} \geq$ 10 kcal/mol.

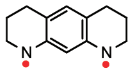
We examined model diradicals, including the octahydropyridoquinoline (OHPQ) diradical computed by Schreiner and coworkers.[12] In particular, we considered planar derivatives of aza-*m*-xylylene diradical in which the π delocalization is largely limited to *m*-phenylene in order to maximize the spin–spin interactions. The estimated values of ΔE_{ST} between the triplet ground states and the lowest open-shell singlet states (computed at the DFT level) for OHPQ diradical, diradical **1**, aza-*m*-xylylene, and *m*-xylylene are 13.5,[12] 11.0, 15.8, and 12.0 kcal/mol, respectively.[13,14] In addition, the EPR ^{1}H hyperfine splittings (a_H) for *N*-*tert*-butylanilino radical indicate that the para and ortho a_H values are slightly larger than those of benzyl radical (by a factor of 1.1–1.2).[15,16] On the basis of the empirical correlation $\Delta E_{ST} \sim |a_H|^2$,[17] the values of ΔE_{ST} in planar derivatives of aza-*m*-xylylene and *m*-xylylene should be comparable.



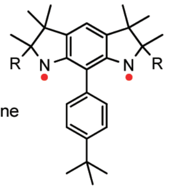
Diaazapentacene-derived aminyl diradical



X = CH_2, *m*-Xylylene
X = NH, Aza-*m*-xylylene



Octahydropyridoquinoline aminyl diradical



R = Me, **1**
R = *n*-Pr, **2**

Herein we describe the synthesis and magnetic characterization of a sterically shielded planar derivative of aza-*m*-xylylene, aminyl diradical **2**, which possesses a triplet ground state having a ΔE_{ST} comparable to that in *m*-xylylene but is persistent at room temperature in solution on the time scale of minutes.

The synthetic route to **2** started with Fisher indole synthesis to provide indolenine derivative **3** (Scheme 1).[18] Addition of an excess of allyl Grignard reagent yielded diamine **4** as a mixture of diastereomers. Analogous additions of methyl Grignard reagents did not produce the corresponding diamines,[19] and thus, the synthesis of diradical **1** was not feasible. In the next step, the allyl groups in **4** were catalytically reduced with H_2 to the corresponding *n*-propyl (*n*-Pr) groups in **5**. Diastereomers **5** were brominated at low temperature to yield **6**, which was subjected to Suzuki cross-coupling with 4-*tert*-butylphenyl boronic acid to give **7**. Treatment of diastereomers **7** with *n*-BuLi produced an orange solution of the dianion. Oxidation of the dianion with iodine at about −115 °C, which was monitored by EPR spectroscopy, provided a dark-red solution of aminyl diradical **2** in 2-methyltetrahydrofuran (2-MeTHF). The last step was

Received: January 24, 2011
Published: March 14, 2011

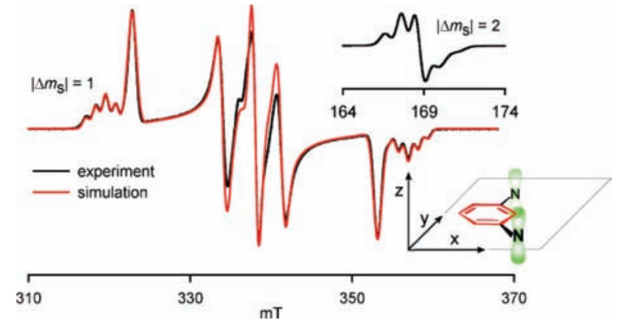
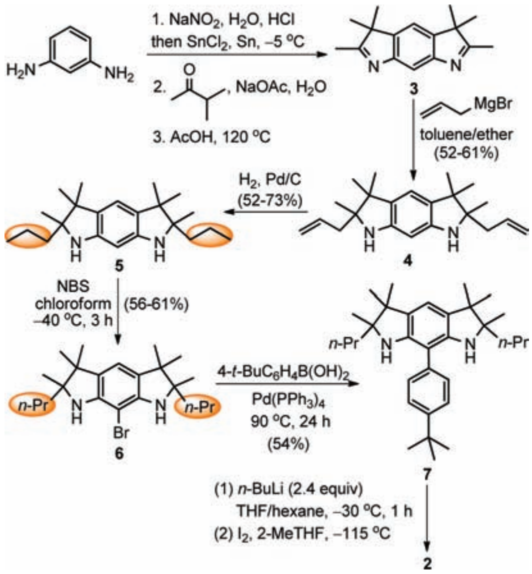


Figure 1. EPR spectrum (X-band, $\nu = 9.4780$ GHz) of **2** in 2-MeTHF at 133 K. Selected parameters for the $S = 1$ state are $|D/hc| = 1.749 \times 10^{-2}$ cm^{-1}, $|E/hc| = 3.60 \times 10^{-3}$ cm^{-1}, $|A_{zz}/2hc| = 1.134 \times 10^{-3}$ cm^{-1}, $g_x = 2.0046$, $g_y = 2.0030$, and $g_z = 2.0019$. Further details concerning the simulation of the EPR spectrum, including the center lines for an $S = {}^1/_2$ byproduct, may be found in Figure S2 in the SI.

Scheme 1. Synthesis of Aminyl Diradical 2



typically carried out on a 0.9−2 μmol scale in custom-made quartz tubes, enabling sequential examination of each sample of **2** in 2-MeTHF by EPR spectroscopy and SQUID magnetometry.

The EPR spectra of **2** in 2-MeTHF at 133 K showed six symmetrically disposed side peaks in the $|\Delta m_s| = 1$ region and an intense half-field transition ($|\Delta m_s| = 2$), as expected for a triplet state with significant D and E zero-field splitting parameters (Figure 1).

The two outermost peaks (z turning points) appear as pentuplets, which may be simulated by the ^{14}N hyperfine coupling (A_{zz}) of two nitrogen nuclei. A_{zz} is the largest principal value of the ^{14}N hyperfine tensor (the **A** tensor), so it coincides with the direction of the nitrogen 2p$_\pi$ orbital.[20] This implies that the 2p$_\pi$ orbital is approximately parallel to the z axis, which is the direction of the largest principal value of the D tensor, as observed in diaazapentacene-derived aminyl diradicals.[11,21] Therefore, the aminyl moieties and the m-phenylene in diradical **2** adopt an approximately coplanar conformation.

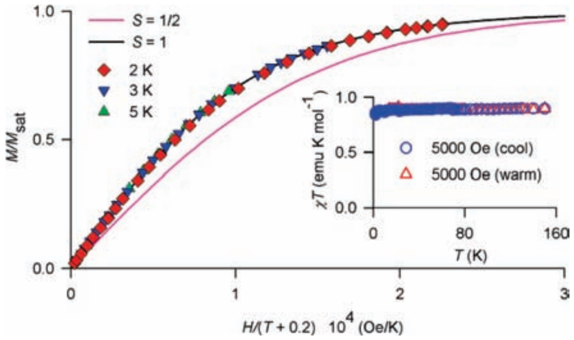
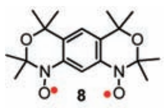
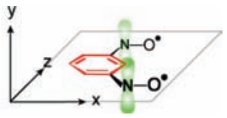


Figure 2. SQUID magnetometry data for ~20 mM **2** in 2-MeTHF. The main plot and inset show M/M_{sat} vs $H/(T - \theta)$ and χT vs T, respectively, with $\theta = -0.2$ K, $M_{\mathrm{sat}} = 0.89\ \mu_{\mathrm{B}}$, $S = 1.0$, and $\chi T = 0.89$ emu K mol^{-1}.

B3LYP/EPR-II computations of the **D** and **A** tensors in **1** confirmed the approximately parallel orientation of their largest principal values to the direction of the 2p$_\pi$ orbitals on the nitrogens.[22] Excellent agreement between the calculated $A_{zz}/2hc$ value of 1.131×10^{-3} cm^{-1} in **1** and the experimental pentuplet ^{14}N splitting, $|A_{zz}/2hc| = 1.134 \times 10^{-3}$ cm^{-1} in **2**, was obtained. Although the calculated D/hc value of 3.4×10^{-2} cm^{-1} for **1** overestimated the experimental $|D/hc|$ value of 1.749×10^{-2} cm^{-1},[22,23] the positive sign ($D > 0$) indicates an "oblate-like" shape for the overall spin density, as expected for spin density that is largely delocalized into the π system of m-phenylene.[24]

For comparison, the overall spin density of the analogous nitroxide diradical **8** with a planar nitroxide−m-phenylene−nitroxide moiety attains "prolate-like" shape because about half of the spin density is localized on the oxygens of the NO moieties.[25] The elongated shape of the spin density was supported by the calculated result $D/hc < 0$ in **8**.[22] The computed **D** and **A** tensors[22] and the EPR spectra[25,26] indicate that the second-largest principal value of the **D** tensor and the largest principal value of the **A** tensor are approximately parallel to the direction of the 2p$_\pi$ orbitals on the nitrogens (y axis).





These qualitatively different spin density distributions in planar aminyl and nitroxide diradicals may correlate with the much larger ΔE_{ST} values for triplet ground state aminyls.[11,21,25,27]

The triplet ground state for **2** in 2-MeTHF was unequivocally confirmed by SQUID magnetometry, as evidenced by the $S = 1$ paramagnetic behavior for both the magnetization (M) as a function of magnetic field (H) and the magnetic susceptibility (χ) as a function of temperature (T) (Figure 2). A small antiferromagnetic coupling, as measured by the mean-field parameter $\theta \approx -0.2$ K, is assigned to very weak intermolecular interactions in 20 mM solutions of **2**.

Specifically, the numerical fits to the curvature of the M/M_{sat} vs $H/(T - \theta)$ plots at 1.8, 3, and 5 K (where M_{sat} is the magnetization at saturation) gave the value $S = 1.0$, which was independent of the spin concentration of the sample. After the

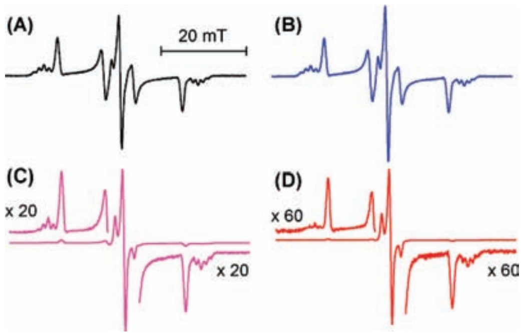


Figure 3. Persistence of aminyl diradical **2** in 2-MeTHF monitored by EPR spectroscopy at 134−136 K: (A) before annealing; (B) after 10 min at −27 °C; (C, D) after 10 and 20 min at room temperature.

measured χT value of 0.89 emu K mol^{-1} was corrected for the spin concentration (M_{sat} = 0.89 μ_{B} per aminyl radical site), the value $\chi T \approx 1.0$ emu K mol^{-1} was obtained, which is exactly the value expected for an $S = 1$ diradical. Furthermore, the χT vs T plot was flat up to 150 K, the highest temperature of the measurement, providing a lower limit of 200 K (~0.4 kcal/mol) for ΔE_{ST}.

We investigated the reactivity/stability of aza-*m*-xylylene diradical **2** in 2-MeTHF by EPR spectroscopy. In the presence of iodine at −115 °C, a decay of the EPR signals corresponding to the triplet diradical was observed. Brief warming to −78 °C led to the disappearance of the EPR signals for **2**. The diradical reactivity toward iodine at low temperature made generation of **2** challenging [Scheme 1; also see Table S4 in the Supporting Information (SI)]. In another experiment, brief exposure of **2** in 2-MeTHF to O_2 at −105 °C resulted in a sharp decrease of the EPR signal intensity and, in particular, complete disappearance of the triplet resonances for **2**.

In the absence of iodine and oxygen, changes in the EPR spectra of **2** in 2-MeTHF after brief annealing at −27 °C were negligible. However, at room temperature, the intensity of the EPR signals corresponding to the triplet diradical decreased on the time scale of minutes, and the EPR spectrum of **2** was still detectable after 20 min (Figure 3 and Figure S9 in the SI).

We also carried out similar experiments using SQUID magnetometry. Magnetic measurements after a sample of **2** in THF was annealed at −27 °C for 30 min showed data corresponding to the triplet diradical. After consecutive annealing sequences of 30 min at 0 °C, 30 min at 22 °C, and another 30 min at 22 °C, the data indicated a sharp decrease in the diradical signal, though a trace of the diradical was still detectable after total of 1 h at room temperature (Figure S11).

After extended annealing of **2** in 2-MeTHF or THF at room temperature, we isolated the starting diamine **7** as the main product (see the SI), thus suggesting a hydrogen abstraction mechanism similar to that observed for other triplet aminyl diradicals.[11,28]

In summary, a planar derivative of aza-*m*-xylylene diradical was prepared in solution, thus providing first example of an organic diradical that is persistent at room temperature in solution on the time scale of minutes and possesses a triplet ground state with a singlet−triplet energy gap of the order of 10 kcal/mol.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Complete ref 13 and experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENT

We thank the National Science Foundation for support of this work through Grants CHE-0718117 and CHE-1012578.

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(14) (a) Calculated values of ΔE_{ST} were corrected for spin contamination and are expected to overestimate the experimental ΔE_{ST} values; diradical **1**, aza-*m*-xylylene, and *m*-xylylene were treated at the UB3LYP/6-311+G(d,p) + ZPVE level and the OHPQ diradical at the UB3LYP/6-311G(d,p) + ZPVE level. (b) For the correction for spin contamination, see: Yamaguchi, K.; Jensen, F.; Dorigo, A.; Houk, K. N. *Chem. Phys. Lett.* **1988**, *149*, 537–542.(c) Delocalization of spin density into the 4-*tert*-butylphenyl pendant in **1** and its effect on the value of ΔE_{ST} were not significant (see Figure S15 and Table S3 in the SI).

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(23) (a) At a similar level of theory, the DFT-computed D value of ~0.03 cm^{-1} overestimated the experimental value of 0.011 cm^{-1} in *m*-xylylene. See: Sinnecker, S.; Neese, F. *J. Phys. Chem. A* **2006**, *110*, 12267–12275. (b) A D value of 0.013 cm^{-1} for *m*-xylylene was computed at the CASSCF(6,6)/cc-pVDZ level. See: Havlas, Z.; Michl, J. *J. Chem. Soc., Perkin Trans. 2* **1999**, 2299–2303.

(24) The values of D, E, and A_{zz} for **2** are significantly greater than those for the diaazapentacene-derived aminyl diradical: $|D/hc| = 9.18 \times 10^{-3}$ cm^{-1}, $|E/hc| = 2.10 \times 10^{-3}$ cm^{-1}, and $|A_{zz}/2hc| = 1.00 \times 10^{-3}$ cm^{-1}.

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(28) In the presence of oxygen, the nitroxide diradical corresponding to **2** would be expected because *N-tert*-butylanilino monoradicals react with oxygen to provide nitroxides (see ref 15). However, we isolated only diamagnetic products (see the SI).