

# High-Spin Organic Diradical with Robust Stability

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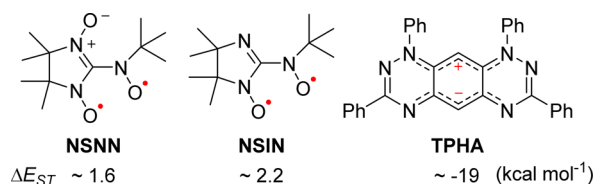
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**S** Supporting Information

**ABSTRACT:** Triplet ground-state organic molecules are interesting with respect to several emerging technologies but typically exhibit limited stability. We report two organic diradicals, one of which possesses a triplet ground state ( $2J/k_B = 234 \pm 36$  K) and robust stability at elevated temperatures. We are able to sublime this high-spin diradical under high vacuum at 140 °C with no significant decomposition.

Organic molecules with high-spin ground states possess inherently fascinating electronic structures. Their characteristic spin alignment contradicts the overwhelming tendency toward spin-pairing in molecular systems, exemplified by chemical bonding.<sup>1–3</sup> Such molecules are attractive candidates as building blocks for magnetic materials<sup>4–7</sup> and in the development of spintronics.<sup>8</sup> For instance, open-shell molecules have been predicted to possess interesting spin transport properties, and various organic spin filters utilizing organic diradicals have been proposed.<sup>9–13</sup>

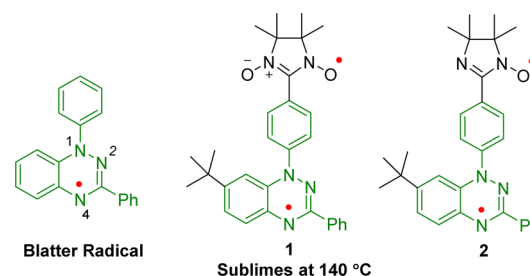
High-spin molecules that possess both strong ferromagnetic interactions between unpaired electrons and robust thermal stability could enable experimental verification of these novel properties predicted with theory. However, only a limited number of high-spin diradicals possess both stability permitting isolation and a singlet–triplet energy gap ( $\Delta E_{ST}$ ) on the order of  $RT$  (thermal energy at room temperature  $\sim 0.6$  kcal mol<sup>-1</sup>).<sup>14–22</sup> Furthermore, little is known about their stability at higher temperatures and in the vapor phase, a necessary consideration for growing organic films using chemical vapor deposition-based techniques.<sup>23,24</sup> Robust stability, spanning a wide temperature range, and in particular, permitting sublimation, would facilitate material processing and device fabrication. To the best of our knowledge, only two isolable high-spin diradicals, nitroxide-substituted nitronyl nitroxide (NSNN) and iminonitroxide (NSIN), undergo sublimation at 55–70 °C, facilitated by their low molecular weights.<sup>15</sup> The major drawback of these molecules is the lack of flexibility in the molecular design associated with their compact structures.



In the search for high-spin organic molecules with robust stability, we were drawn to the 1,2,4-benzotriazinyl (Blatter)

radical, a thermally robust monoradical.<sup>25</sup> Recently, we have shown that the unique stability of a Blatter monoradical derivative permits vapor-based fabrication of thin films that exhibit excellent air/vacuum stability and retention of the paramagnetic character in thin films for at least several months.<sup>24</sup> We note that the Blatter radical has not been utilized as a high-spin building block. While a few molecules that formally incorporate two Blatter radicals have been investigated, they possess singlet ( $S = 0$ ) ground states and can be classified as zwitterions (tetraphenylhexaazaanthracene = TPHA) or singlet diradicaloids.<sup>26,27</sup> Nevertheless, the 1,2,4-benzotriazinyl framework provides alternative sites for functionalization to facilitate design of novel high-spin systems.

We envisaged high-spin diradicals based on the Blatter radical substituted with nitronyl nitroxide (**1**) and imino nitroxide (**2**) (Figure 1). Diradicals **1** and **2** take advantage of spin density that



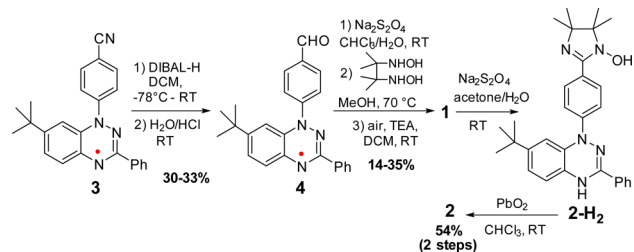
**Figure 1.** Diradicals **1** and **2** incorporating the Blatter radical.

delocalizes to the N1 phenyl of the 1,2,4-benzotriazinyl radical. This induces ferromagnetic interactions through the trimethylenemethane (TMM)-like ferromagnetic coupling of the nitronyl/imino nitroxides.<sup>13–15</sup> Indeed, broken-symmetry density functional theory (BS-UB3LYP/6-31G(d,p)) calculations<sup>28</sup> estimated  $\Delta E_{ST}$  as  $\sim 1.4$  kcal mol<sup>-1</sup> for **1** and  $\sim 0.6$  kcal mol<sup>-1</sup> for **2** (Supporting Information (SI)).<sup>29</sup> Encouraged by the results, we were intrigued to experimentally determine the  $\Delta E_{ST}$  and the thermal robustness of these diradicals.

Here we report the synthesis and study of high-spin diradicals **1** and **2** (Scheme 1). Diradical **1** is thermally robust, with stability up to  $\sim 175$  °C under inert atmosphere, and it sublimes under high vacuum at 140 °C with no significant decomposition. Diradical **2**, however, begins to decompose at  $\sim 75$  °C.

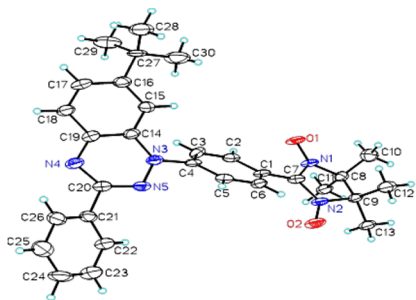
Our synthetic strategy takes advantage of the rather unusual stability of the Blatter radical, such that it can undergo many ordinary chemical transformations.<sup>30</sup> Cyano-substituted Blatter

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Scheme 1. Synthesis of **1** and **2**

radical **3** was synthesized using procedures similar to those available in the literature.<sup>31–34</sup> Treatment of **3** with DIBAL-H and subsequent hydrolysis of the imine group provides formyl-substituted Blatter radical **4**. Reduction of radical **4** followed by condensation with 2,3-bis(hydroxyamino)-2,3-dimethylbutane<sup>35</sup> and aerobic oxidation provides diradical **1**. The nitronyl nitroxide moiety of **1** can then be converted into the corresponding imino nitroxide moiety of **2** by utilizing a strong reductant (providing **2-H<sub>2</sub>**) followed by reoxidation with lead(IV) dioxide. The diradicals possess sufficient stability to be purified on silica with no additional precautions.

The single crystal geometry of diradical **1** is shown in Figure 2. Notably, the phenyl at the N1 position is twisted relative to both

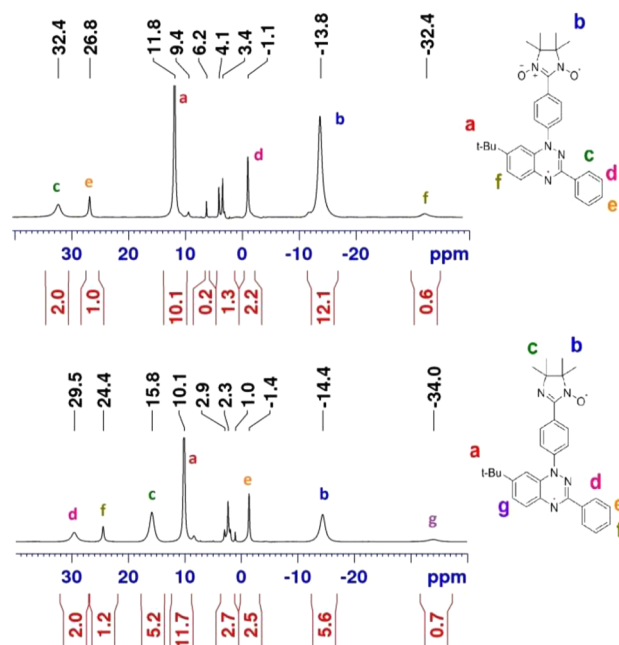


**Figure 2.** Single-crystal X-ray geometry of **1** with thermal ellipsoids shown at the 50% probability level. Additional details can be found in the SI, Figures S1–S4 and Tables S1 and S2, and CIF file.

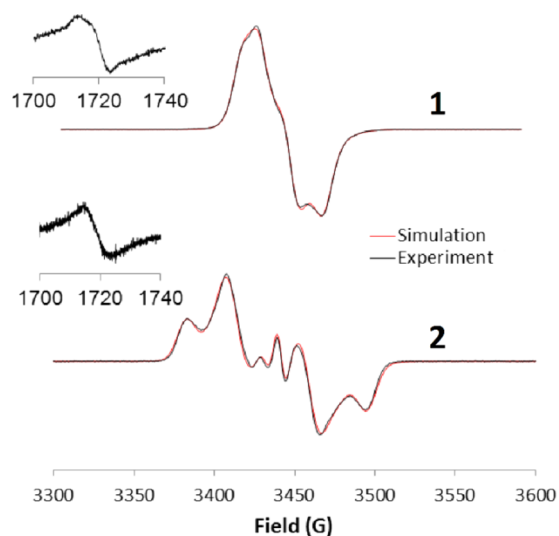
the 1,2,4-benzotriazinyl and nitronyl nitroxide moieties (dihedral angles of ~49° and 30°, respectively). Additional details as well as molecular packing along the different crystallographic axes can be found in the SI.

The structures of diradicals **1** and **2** are also supported by <sup>1</sup>H NMR spectra (Figure 3), in which **2-H<sub>2</sub>** (Scheme 1) serves as a diamagnetic reference. Peak assignments for diradicals **1** and **2** are aided by the plots of DFT-predicted hyperfine coupling constants (hfcc's) vs chemical shift difference ( $\Delta\delta$ , paramagnetic shift), which are fairly linear for both diradicals ( $R^2$  of 0.9915 and 0.9709 for **1** and **2**, respectively). The prediction of the *tert*-butyl proton hfcc's is complicated by multiple conformations, so this assignment is instead based on peak integration. The majority of remaining protons are predicted to possess hfcc's >0.5 G. Protons for which the <sup>1</sup>H hfcc's exceed ~0.5 G are difficult to observe by <sup>1</sup>H NMR at concentrations of ~1 M due to excessive peak broadening.<sup>18a,36,37</sup> For additional details, as well as hfcc/ $\Delta\delta$  plots, see the SI.

Electron paramagnetic resonance (EPR) spectra of 0.4–1.3 mM diradicals **1** and **2** in frozen glasses at low temperatures (Figure 4) can be well-simulated as triplet species. In the case of **2**, monoradical is included in the simulation to account for the less intense center peaks.



**Figure 3.** <sup>1</sup>H NMR (700 MHz) spectra of 1.6–1.7 M diradical **1** (top) and **2** (bottom) in CDCl<sub>3</sub>. Additional details can be found in the SI, Figures S17–S19 and Tables S9 and S10.



**Figure 4.** Low-temperature ( $T = 139$ – $147$  K) EPR (X-band,  $\nu = 9.65$  GHz) spectra of 1.3 mM diradical **1** and 0.4 mM diradical **2** in a frozen glass (toluene/CHCl<sub>3</sub>, 4:1). The  $\Delta m_s = 2$  transitions are shown as insets. Diradical **2** has smaller center peaks, which are simulated as monoradical impurities (spectral parameters estimated from monoradical **4**). Further details are reported in the SI, Figures S5–S7.

The monoradical spectral parameters for the simulation are estimated from monoradical **4** in frozen glass matrices (see SI for all simulation parameters). More importantly, weak  $\Delta m_s = 2$  transitions are detected for each diradical, as expected for diradicals with relatively low values of zero-field splitting (zfs) parameter  $|D/hc|$ . Notably, the zfs parameter  $|D/hc|$  in diradical **1** is much smaller than that in diradical **2** ( $|D/hc| = 2.32 \times 10^{-3}$  and  $5.58 \times 10^{-3} \text{ cm}^{-1}$  for **1** and **2**, respectively). This trend is predicted to a lesser extent with B3LYP/EPR-II calculations ( $D/hc = -5.47 \times 10^{-3}$  and  $-6.91 \times 10^{-3} \text{ cm}^{-1}$  for **1** and **2**, respectively).<sup>38</sup> These methods tend to overestimate components of the **D** tensor for *m*-xylylene-based diradicals.<sup>39–42</sup>

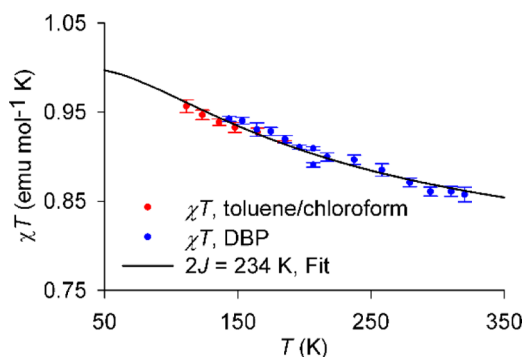
EPR spectra of both **1** and **2** show unresolved hyperfine coupling. Line broadening along the molecular *y*-axis (second largest axis of the **D** tensor) in both diradicals is assumed to be due to the unresolved hyperfine coupling to five nitrogens (in both diradicals, the line width along the *y* direction is 3–4 times the line width along the *x* or *z* directions). Together with  $D/hc < 0$  predicted for both diradicals, this suggests the overall spin density possesses a “prolate-like” shape in contrast to planar aminyl diradicals.<sup>39</sup>

To determine the triplet ground state and  $\Delta E_{ST}$  for **1**, we measure  $\chi T$ , the product of paramagnetic susceptibility ( $\chi$ ) and temperature (*T*), in the  $T = 111\text{--}320$  K range using quantitative EPR spectroscopy.

We measure values of  $\chi T$  for **1** in toluene/chloroform (4:1) or in dibutyl phthalate (DBP) using a spin-counting standard (eq 1).

$$\chi T = \left\{ \frac{[\text{std}]}{[\mathbf{1}]} \right\} \times \left\{ \frac{\text{Int}_{\mathbf{1}}}{\text{Int}_{\text{std}}} \right\} \left( \times 1/2 \right) \times S(S+1)_{\text{std}} \quad (1)$$

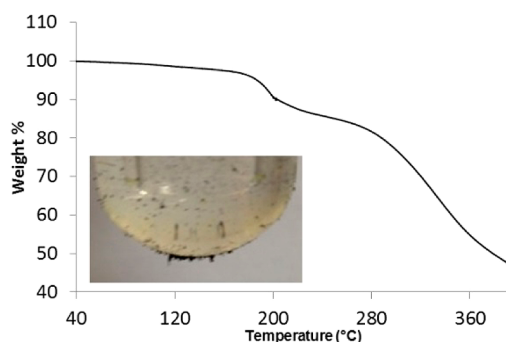
Each data point in Figure 5 corresponds to multiple independent measurements of  $\chi T$ , i.e., 4–8 independent



**Figure 5.** Quantitative EPR spectroscopy of diradical **1**: experimental values of  $\chi T$  (mean  $\pm$  SE), the product of paramagnetic susceptibility ( $\chi$ ) and *T* in the  $T = 111\text{--}320$  K range and numerical one-parameter fit with the variable parameter,  $2J/k_B = 234 \pm 36$  K (mean  $\pm$  SE), and with weight of  $1/\chi$ . Further details are reported in the SI, Tables S3–S5 and Figure S8.

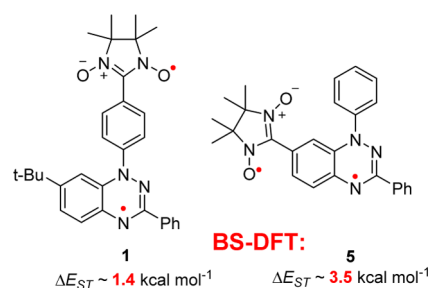
measurements of **1** and the same number of independent measurements of a nitroxide (TEMPO) standard. Generally, the data points at higher temperatures required more measurements to obtain a reasonable value of standard error (SE). To ensure that multiple measurements of  $\chi T$  are independent, diradical **1** and TEMPO (dissolved in the same solvent) were measured in an alternating sequence so that each sample was warmed (or cooled) to room temperature in between successive measurements.<sup>40,41</sup> Although the data obtained by this technique exhibits more scatter relative to SQUID magnetometry,<sup>19,39,43</sup> the EPR-based method is advantageous for stable diradicals. This method permits evaluation of  $\chi T$  in both rigid matrices and in fluid solution at higher temperatures (up to 320 K), while SQUID measurements are typically limited to rigid matrices.

The highly robust stability of diradical **1** facilitates sublimation under high vacuum ( $p \approx 6 \times 10^{-6}$  mbar) at temperatures as high as 140 °C with no significant decomposition. Our thermogravimetric analysis/differential scanning calorimetry results suggest that thermal decomposition of **1** begins at  $\sim 175$  °C (Figure 6). Indeed, annealing **1** at 200 °C under  $N_2$  for 15 min leads to complete decomposition of the nitronyl nitroxide radical, while the Blatter radical remains largely intact (as evidenced by EPR). On the other hand, diradical **2** begins to decompose at  $\sim 75$  °C (SI, Figures S12–S16).



**Figure 6.** Thermogravimetric analysis (TGA) of diradical **1** under  $N_2$ ; heating rate =  $5$  °C  $\text{min}^{-1}$ . Inset: Diradical **1** after sublimation at  $T = 140$  °C,  $p \approx 6 \times 10^{-6}$  mbar. We carried out additional experiments to confirm the purity of **1** following sublimation, as well as confirm that the TGA weight loss from 175 to 200 °C corresponds to decomposition of the nitronyl nitroxide moiety (see SI, Figures S12–S16).

Is it possible to augment  $\Delta E_{ST}$  and still maintain this extraordinary stability? Our more recent DFT calculations suggest that by altering the connectivity of the same radical units (for instance, in diradical **5**, Figure 7), it should be possible to increase



**Figure 7.** BS-DFT (UB3LYP/6-31G(d,p)) estimates of  $\Delta E_{ST}$  for diradical **1** and putative diradical **5**. For additional details, see the SI, Tables S7 and S8.

the magnitude of  $\Delta E_{ST}$  by a factor of 2–2.5.<sup>29</sup> Given that BS-DFT overestimates  $\Delta E_{ST}$  for **1**,<sup>29</sup> an actual  $\Delta E_{ST} = 1\text{--}2$  kcal  $\text{mol}^{-1}$  is likely for putative diradical **5**. Using a Boltzmann distribution,<sup>2</sup> such a singlet–triplet gap would lead to 95–99% occupancy of the triplet ground state at room temperature.

Thus, we anticipate it will be possible to obtain high-spin diradicals with very robust high-temperature stability and full or near-full occupation of the triplet ground state at ambient temperatures. Current efforts are underway in the syntheses of similar diradicals with increased  $\Delta E_{ST}$  (e.g., **5**), as well as the planned investigation of thin-film properties of **1** for future applications in spintronics.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.6b05080.

General procedures and materials, additional experimental details, and complete ref 28 (PDF)

X-ray crystallographic files for **1** (CIF)

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## Notes

The authors declare no competing financial interest.

## ACKNOWLEDGMENTS

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this discrepancy worsens when using the UM06-2X functional (instead of UB3LYP), with the corresponding values of  $\Delta E_{\text{ST}} \approx 2.1, 0.7$ , and  $3.7 \text{ kcal mol}^{-1}$  (Table S7): Mañeru, D. R.; Pal, A. K.; Moreira, I. P. R.; Datta, S. N.; Illas, F. *J. Chem. Theory Comput.* **2014**, *10*, 335–345.

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