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High-Spin Organic Molecules

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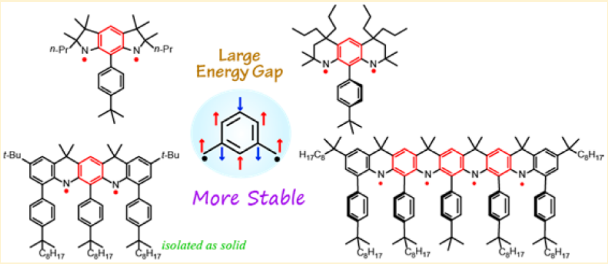
ABSTRACT: Organic molecules with high-spin ground states, besides being fundamentally interesting, possess numerous potential applications in diverse fields such organic magnetism, MRI contrast agents, and spintronics. Such molecules, once thought to exist only as highly reactive intermediates, can be rationally designed to have adequate stability for organic synthesis and characterization. This Synopsis provides an overview of the factors that lead to high-spin ground states as well as recent progress in the design and synthesis of high-spin organic molecules.



Organic molecules with high-spin ground states (total spin quantum number $S \geq 1$) are of fundamental interest to chemistry and physics, as they provide insight into how molecular structure affects the interaction of electrons and lead to macroscopic properties (e.g., magnetism).[1−9] The spin alignment in high-spin molecules defies the conventional spin pairing in chemical bonds of typical organic molecules, which nearly exclusively possess singlet ground states ($S = 0$) separated from the nearest excited triplet states ($S = 1$) by tens of kcal mol^{-1}. The challenge in the design and synthesis of high-spin organic molecules is to invert this large energy of spin pairing, thus providing a high-spin ground state that is at least a couple kcal mol^{-1} [$\gg$0.6 kcal mol^{-1} $\approx$ thermal energy (RT) at room temperature] below the nearest excited state.[10,11] Ideally, the high-spin molecule should be persistent at room temperature. When these conditions are satisfied, high-spin molecules possess enhanced paramagnetic properties at room temperature that scale with the $S(S + 1)$ factor. Molecules with strong paramagnetic properties should increase the sensitivity of organic paramagnetic relaxation reagents, including contrast agents in magnetic resonance imaging.[12−14] These high-spin molecules not only are important basic building blocks for organic magnets but also are of interest for the future development of spintronics.[15,16]

Molecular Design and Characterization. Organic monoradicals, which contain one unpaired electron, can be considered the most basic organic spin-bearing units ($S = {}^1/_2$). The primary goal in the molecular design of high-spin organic molecules is to conjugate multiple radical units, or spin centers (SC's), in such a way that the spins couple ferromagnetically, leading to a high-spin ($S \geq 1$) ground state. This ferromagnetic interaction should ideally be strong, leading to a large separation in energy between the high-spin ground state and low-spin excited states. In a diradical, the singlet triplet energy gap (ΔE_{ST}) is determined by the exchange coupling constant (J), which is given by a simplified Heisenberg−Hamiltonian for two electrons,[17,18] typically expressed as

$$\hat{H} = -2J\hat{S}_1\cdot\hat{S}_2 \qquad (1)$$

where the triplet is separated in energy from the singlet by an energy gap $-2J$ ($\Delta E_{ST} = 2J$).

In planar π-conjugated diradicals, ferromagnetic exchange coupling or antiferromagnetic exchange coupling between SCs depends on the π-connectivity and can be qualitatively predicted using simple Ovchinnikov parity models where each adjacent spin in the π-system is assumed to possess the opposite spin of its neighbor (Figure 1).[19]

The simplest examples may be illustrated using methyl radicals as SCs and ethylene as a coupling unit, in which the 1,1-connection and 1,2-connection lead to two distinct molecular structures, trimethylenemethane (TMM) and 1,3-butadiene. While non-Kekulé molecule TMM possesses a triplet ($S = 1$) ground state with $\Delta E_{ST} \approx 16$ kcal mol^{-1},[20] Kekulé molecule 1,3-butadiene possesses a singlet ($S = 0$) ground state with a very large energy gap ($\Delta E_{ST} \approx -74$ kcal mol^{-1}), as expected for a closed-shell molecule.[21] An extension of this example is further illustrated in Figure 1. As predicted by the parity models, non-Kekulé molecule tetramethylenethane (TME) possesses a singlet ground state with a very small $|\Delta E_{ST}|$, as shown by the measurement of $\Delta E_{ST} \approx -1$ K = -0.002 kcal mol^{-1} for 2,3-dimethylenecyclohexane-1,4-diyl (DMCHD).[22] In the case of phenylene as a coupling unit, *meta*-connectivity of the methyl radicals provides a non-Kekulé molecule *m*-xylylene, which possesses a triplet ground state with relatively large ΔE_{ST} (~10 kcal mol^{-1}).[23] In contrast, *para*/*ortho*-connectivities lead to singlet ground states, such as in Kekulé molecules *p*- and *o*-xylylene. 3,3′-Dimethylenebiphenyl (3,3′-DMBP) diradical, in which two methyl radicals are linked through a 3,3′-biphenyl unit, possesses a singlet ground state with a small $|\Delta E_{ST}|$, as demonstrated by the measurement of $\Delta E_{ST} \approx -0.1$ kcal mol^{-1} for diradical **1**.[24]

Coupling units that lead to ferromagnetic coupling between SCs (e.g., *m*-phenylene) are termed ferromagnetic coupling units (FCU's), and those that lead to antiferromagnetic

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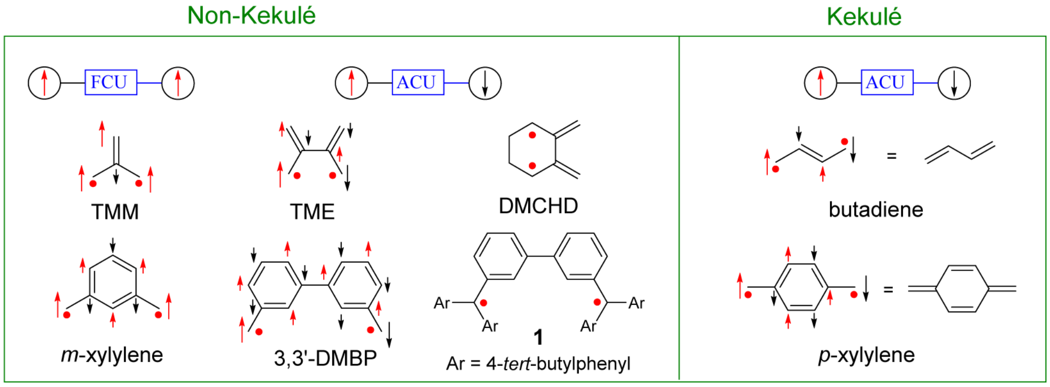


Figure 1. Ferromagnetic and antiferromagnetic coupling predicted using parity models.

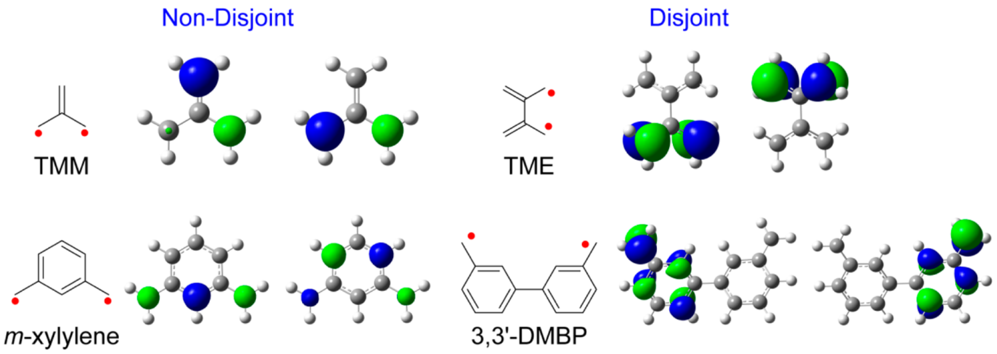


Figure 2. Singly occupied MOs (SOMOs) of triplet states for disjoint and non-disjoint non-Kekulé diradicals at the UB3LYP/6-311G(d,p) level.

coupling (e.g., *o*-phenylene, *p*-phenylene, 3,3′-biphenyl) are termed antiferromagnetic coupling units (ACU's).[6,25] Although these simple parity models are useful for qualitatively assessing the ground state, they do not address the strength of exchange coupling (ΔE_{ST}), especially in non-Kekulé molecules.

Electron-exchange interactions in organic molecules are governed by the Pauli exclusion principle, which leads to either ferromagnetic or antiferromagnetic coupling. Very strong antiferromagnetic coupling is nearly ubiquitous in organic chemistry and is easily understood in the case of Kekulé molecules with a significant HOMO−LUMO energy gap. Here, for two electrons to fill the HOMO, the spins must be antiparallel by the Pauli exclusion principle.

A different situation arises in non-Kekulé diradicals in which the frontier MOs are approximately equal in energy (degenerate MOs), leading to two singly occupied MOs (SOMOs). According to Borden and Davidson, the two SOMOs can be classified as either disjoint (not spatially coinciding at any atoms) or nondisjoint (spatially coinciding at some atoms), as illustrated for TME (and 3,3′-DMBP) and TMM (and *m*-xylylene) (Figure 2).[26]

For disjoint SOMOs, exchange coupling is very weak, leading to a small $|\Delta E_{ST}|$; it is assumed that, in this case, a singlet ground state arises due to small exchange coupling through σ-bonds.[26] For nondisjoint SOMOs, exchange coupling is strong and ferromagnetic. In other words, the two electrons will align their spins in order to introduce a node in the spatial part of the wave function and, thus, reduce their Coulombic repulsion within the area of spatial coincidence (an extension of the Pauli exclusion principle to multielectron wave functions).[6,25]

Electron paramagnetic resonance (EPR) spectroscopy and superconducting quantum interference device (SQUID) magnetometry are two common techniques utilized to characterize high-spin organic diradicals in frozen solutions (glassy matrices).[2,4] The use of glassy matrices is essential to minimize intermolecular interactions. EPR spectroscopy provides information concerning the unpaired electrons in the $S = 1$ state, such as zero-field splitting parameters (D and E) as well as hyperfine couplings to nuclei which possess significant electron-spin density.[6,27] SQUID magnetometry is used to measure sample magnetization (or closely related paramagnetic susceptibility, χ) as a function of temperature and external magnetic field. At low temperatures, the magnetization curve provides the ground-state spin multiplicity based upon thermal population of m_S-states.[6] In special cases in which ΔE_{ST} is similar in magnitude to RT (where T corresponds to the temperature range of the measurement), a decrease of χT at higher temperatures due to thermal population of the low-spin excited states can be used to assess ΔE_{ST}.[6] In those cases where ΔE_{ST} significantly exceeds RT, an experimental assessment of ΔE_{ST} becomes difficult, allowing only for determination of a lower limit for ΔE_{ST}. Variable-temperature EPR spectroscopy may analogously be used to assess $\Delta E_{ST} \approx RT$ via decrease of IT at higher temperatures, where I corresponds to the EPR intensity. The NMR-based paramagnetic shift method may also be utilized in a similar way.[6,28]

Various quantum-chemical calculations aim at accurate prediction of ΔE_{ST}. Density functional theory employing Noodleman's broken symmetry approach[29−31] (BS-DFT) has found widespread use due to its low computational cost; however, such methods tend to overestimate ΔE_{ST} of high-spin diradicals.[32] Post Hartree−Fock methods, such as difference dedicated configuration interaction (DDCI) and complete active space with second-order perturbation theory (CASPT2), offer increased accuracy with the disadvantage of increased computational cost.[33] In the CASPT2 method, all the single

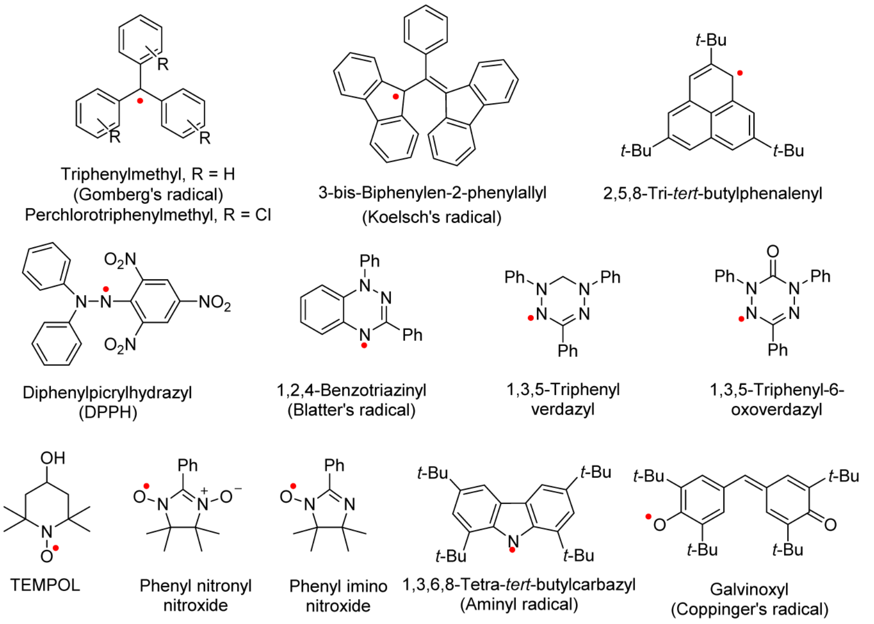


Figure 3. Examples of persistent organic radicals.

and double excitations are taken into account using second-order perturbation theory.[34,35] The DDCI approach, a complete active space single double configuration interaction (CAS-SDCI) method that discards the purely inactive double excitations, can be considered the most reliable method for estimating energy gaps in systems of synthetic interest at reasonable expense.[33,36,37]

Persistent Monoradicals as Spin Centers. Persistent organic radicals have been known for over a century and possess a very interesting history in organic chemistry.[38] Examples of a few notable monoradicals are shown in Figure 3.

Note that all of the radicals in Figure 3 are stabilized to some degree by delocalization and steric shielding of the unpaired electron. The carbon-based radicals are the ones of most historical importance, and the triphenylmethyl (Gomberg's radical) is considered the first persistent organic radical and a seminal discovery in organic chemistry.[39] The triphenylmethyl radical reacts with oxygen and is in equilibrium with its dimer in deoxygenated solutions. However, some chlorinated derivatives, such as perchlorotriphenylmethyl radical, are very stable, display no dimerization or oxygen reactivity in solution, and do not decompose in the solid state until heated to ~300 °C on air.[40] Koelsch's radical is also historically unique as it was the first carbon-based radical to display no reactivity toward oxygen; at the time, this was so unprecedented that the original manuscript was rejected and forgotten about for nearly 30 years.[41] Recently, water-soluble derivatives of Koelsch's radical have been developed for dynamic nuclear polarization (DNP) agents.[42] Phenalenyl-based radicals are fundamentally interesting and can be regarded as open-shell graphene fragments. The 2,5,8-tri-*tert*-butylphenalenyl radical, although more stable than the unsubstituted phenalenyl radical toward dimerization, forms a π-dimer in the crystalline state and is reactive toward oxygen.[43,44] Hydrazyl-based radicals, $[R_2NNR]^\bullet$, are typically very stable at ambient conditions. For example, DPPH has been commonly used as an EPR reference compound. Although DPPH possesses rather unique stability (stable in the solid state on air and can be heated to ~80 °C in solution before decomposing),[45] annulated hydrazyls such as Blatter's radical and verdazyl radicals possess even better stability due to enforced orbital overlap leading to enhanced resonance stabilization. For instance, Blatter's radical can be refluxed in chlorobenzene (bp 131 °C) without decomposition and can be heated in the solid phase to ~270 °C before decomposition begins.[46] Numerous derivatives of Blatter's radical have been recently prepared and their interesting magnetic properties studied.[47] Alkyl nitroxides, such as 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-oxyl or 4-hydroxy-TEMPO (TEMPOL), are well-known stable organic radicals and are heavily utilized in various applications such as EPR spin labels,[48] synthesis,[49] and as DNP agents for NMR spectroscopy.[50,51] Various nitroxides, nitronyl nitroxides, and imino nitroxides have been utilized as stable building blocks for organic magnetic materials[52,53] or model compounds to study exchange coupling and electron-spin relaxation.[54−57] Aminyl radicals are typically more reactive, and only two persistent cases are known, 1,3,6,8-tetra-*tert*-butylcarbazyl being one of them.[58,59] The galvinoxyl radical is also a well-known stable radical and is representative of the phenoxyl family of radicals.[60]

Although most of radicals in Figure 3 possess good kinetic stability, only some can be utilized as SCs in high-spin molecules. To be extendable into high-spin systems, the SC must be two- or three-coordinate and the unpaired electron of the SC must be significantly delocalized throughout a FCU π-system in order to interact significantly with other SCs. For instance, the unpaired electrons of hydrazyl-based radicals are delocalized almost exclusively to N atoms, and attempts to incorporate these into high-spin molecules have resulted in mostly biradicals (nearly degenerate singlet/triplet states) or singlet ground-state molecules.[61−64] The presence of odd-membered rings within π-conjugated system, such as in the carbazyl radical, typically results in singlet ground-state biradicals.[65]

High-Spin Molecules Incorporating Persistent Spin Centers. Nitroxide radicals are popular SCs in the design of high-spin organic molecules due to their inherent stability at ambient conditions and the established synthetic methodologies for incorporating them into various molecular designs.

We and others have prepared $S = 1$ ground-state diradicals **2**–**7** and $S = {}^{3}/_{2}$ ground-state triradical **8** (Figure 4).[66–70] In contrast to **2**, which decomposes in solution on a time scale of a couple hours,[66] **3**–**5** are relatively persistent at ambient conditions. Diradical **4** was observed to be stable in the crystalline state for several months, and pure samples of **4** are stable in solution at room temperature for at least 2 days.[70] Despite the additional steric shielding of the *ortho* position in the case of **5**, it surprisingly exhibits slow decomposition in solution.[70] Triradical **8** was observed to be stable in solution under air as well as in the crystalline state for weeks.[69]

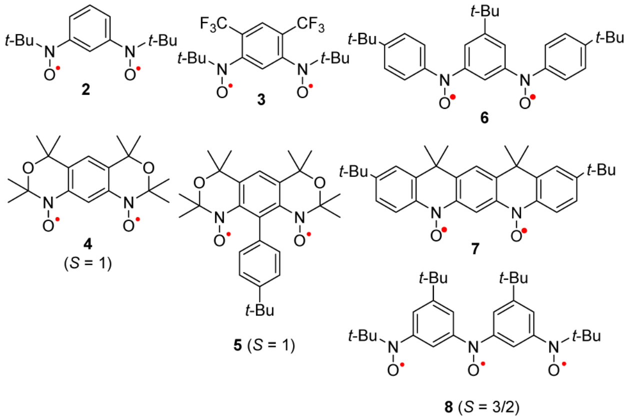


Figure 4. High-spin molecules incorporating nitroxide spin centers.

Because of the enforced coplanarity of nitroxide moieties with the FCU in **4**, its ΔE_{ST} is expected to be higher than that of **2**. ΔE_{ST} for both **2** and **4** is lower bounded by SQUID measurements ($\Delta E_{ST} \geq RT \approx 0.6$ kcal mol^{-1}.[69,70] Similarly, the ΔE_{ST} of **5** ($\approx$ 0.8–1.6 kcal mol^{-1} based upon SQUID measurements) is expected to be slightly less than **4** because the nitroxides are slightly less coplanar with FCU in order to accommodate the bulky *tert*-butyl phenyl substituent.[70] Indeed, BS-DFT estimates ΔE_{ST} of **2**, **4**, and **5** to be ~1.8 kcal mol^{-1}, 3.3 kcal mol^{-1}, and 2.2 kcal mol^{-1}, respectively. ($\Delta E_{ST} \approx 1.6$ kcal mol^{-1} was computed also by the DDCI method for diradical **2**.)[71] For triradical **8**, a low energy gap between the quartet and excited doublet states, $\Delta E_{DQ} \approx 0.5$ kcal mol^{-1}, was measured by magnetic susceptibility.[69]

Another set of interesting examples are diaryl nitroxide diradicals **6** and **7** (Figure 4).[72,73] Although **6** was not sufficiently stable for isolation and only low-temperature EPR spectra could be observed,[72] annelated diradical **7** could be isolated in low yields and was found to be stable in the solid state at ambient conditions; however, decomposition of **7** was observed in concentrated solutions.[73,74] The difference in stability between **6** and **7** is attributed to enhanced steric shielding of the *para*-positions of the central phenyl ring of **7** where significant spin density is expected from delocalization of both radicals. Because of the enforced coplanarity of nitroxide moieties with the benzene rings in the annelated structure, ΔE_{ST} of **7** is expected to be higher than that of **6**. BS-DFT estimates ΔE_{ST} of diradical **6** to be ~1.5–1.8 kcal mol^{-1}, while that of **7** is ~2.0 kcal mol^{-1} by BS-DFT and ~0.6 kcal mol^{-1} by Barone's DDCI calculations.[72,73,75] For **7**, $\Delta E_{ST} \geq 0.6$ kcal mol^{-1} was lower bounded by SQUID magnetic susceptibility measurements.[73]

Other recent efforts to incorporate nitroxides SCs in the design of high-spin organic molecules include diradicals **9** and **10** (Figure 5),[76] which may be considered analogous to TMM (illustrated for **9** in Figure 5). The ΔE_{ST}'s of these diradicals, 2.2 kcal mol^{-1} for **9** and 1.6 kcal mol^{-1} for **10** (obtained from magnetic susceptibility measurements), are similar in magnitude to nitroxide diradicals, such as **4** and **5**, which utilize the *m*-phenylene FCU. In **9**, the torsion angle between the SC and imino (C=N) FCU is ~40°, while the analogous torsion angle in **10** is substantially greater (~76°) due to steric repulsion between the *tert*-butyl group and the nitronyl nitroxide unit. The smaller torsion angle leads to an enhanced exchange interaction and a larger ΔE_{ST} for **9**. No decomposition of these diradicals is observed at ambient conditions, and they can even be sublimed at elevated temperatures (55–70 °C) without decomposition. Interestingly, although the TMM undergoes ring closure above 123 K through a thermally accessible singlet diradical state,[77] no ring closure of either **9** or **10** by formation of an O–O bond is observed even at elevated temperatures. This behavior is rationalized with DFT calculations, which suggest the five-membered –C–N–O–O–N– rings to be ~26–27 kcal mol^{-1} higher in energy than the diradicals, presumably due to enhanced repulsion of six electron lone pairs within the nearly planar rings.[76]

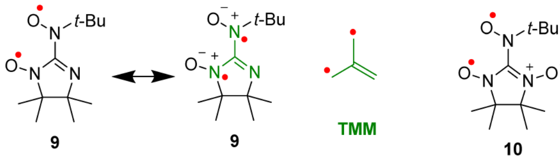


Figure 5. Nitroxide diradicals **9** and **10**, which may be considered analogous to TMM.

High-Spin Molecules with Very Large Energy Gaps. There have been numerous efforts to synthesize high-spin organic molecules with very large energy gaps between the high-spin ground state and the nearest excited state (at least an order of magnitude greater than $RT \approx 0.6$ kcal mol^{-1}). This is driven by the desire to have the high-spin ground state exclusively populated at room temperature in order to obtain high-spin materials that maintain their favorable magnetic properties for plausible room temperature applications. Figure 6 shows the occupancy of a triplet ground state in a diradical as a function of temperature for various energy gaps between the ground state and nearest excited state. For energy gaps

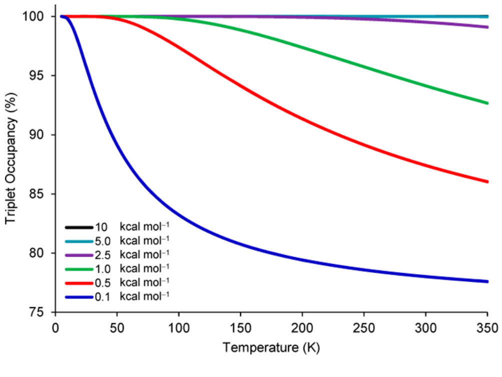


Figure 6. Occupancy of a triplet ground state using as a function of temperature for various values of ΔE_{ST}; occupancies are computed using a Boltzmann distribution with a 3-fold degeneracy for the triplet state and nondegeneracy for the singlet state (i.e., degeneracy $=2S + 1$).

exceeding ~5.0 kcal mol^{-1}, the ground state is nearly exclusively populated at temperatures as high as 350 K, hence the "order of magnitude greater than *RT* at room temeperature" benchmark for ΔE_{ST}.

Unfortunately, high-spin molecules with ΔE_{ST} of this magnitude tend to be much less kinetically stable than those with lower ΔE_{ST}. High-spin molecules with excellent persistence at room temperature (i.e., similar persistence to nitroxide diradicals) and a large singlet−triplet energy gap of at least 1 order of magnitude greater than the thermal energy at room temperature (~0.6 kcal mol^{-1}) remain elusive.

One factor that increases the magnitude of ΔE_{ST} is larger spin density within the FCU.[6,78,79] Consequently, one way to increase the ΔE_{ST} of a diradical is to utilize SCs that delocalize to the FCU to a greater extent. Comparing aminyl and nitroxide, aminyl is more effective than SC because spin density on the N atom is more readily delocalized into the FCU while that of nitroxide is dissipated away by the O atom. Thus, a smaller fraction of spin density is present in the FCU of nitroxide diradicals than in aminyl diradicals (Figure 7), leading to much lower ΔE_{ST} for nitroxide diradicals.

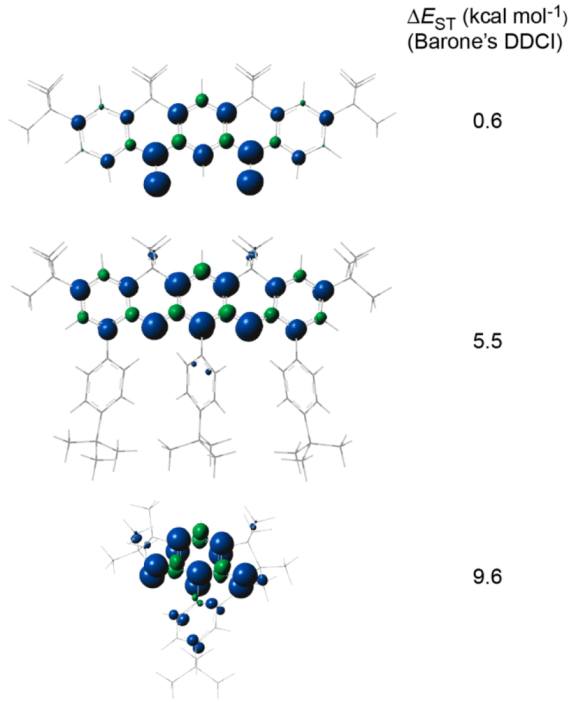
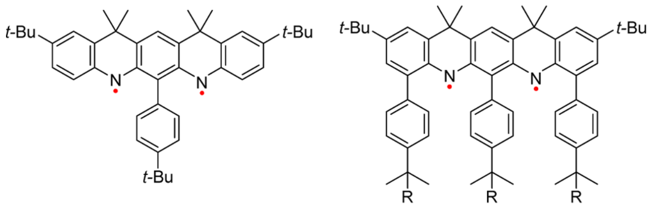


Figure 7. Spin density maps for the triplet ground states of nitroxide diradical **7** (top, UB3LYP/6-31G(d)), simplified structure **12a** of diaryl aminyl diradical **12** (middle, UB3LYP/6-31G(d)), and simplified structure **13a** of alkyl-aryl aminyl diradical **13** (bottom, UB3LYP/EPR-III//UB3LYP/6-311+G(d,p)). Positive (blue) and negative (green) spin densities are shown at the isodensity level of 0.006 electron/Bohr.[3] Singlet−triplet energy gaps are from Barone's DDCI calculations.

We recently illustrated this with the synthesis of aminyl diradicals **11** and **12** (Figure 8), which can be considered analogous to nitroxide diradical **7** (Figure 4).[79,80] A lower ΔE_{ST} is predicted for nitroxide diradicals relative to aminyl diradicals (i.e., ~0.6 kcal mol^{-1} for **7** vs ~7 kcal mol^{-1} for simplified structure **12a** by BS-DFT and ~5.5 kcal mol^{-1} by Barone's DDCI calculations).[75,80,81] Because of increased spin density at aromatic carbons in the planar diazapentacene backbone, kinetic stability of these aminyl diradicals decreases. Protection of those *ortho* carbons with aryl groups provides diradicals with improved stability. While **11** has a half-life of ~0.5 h at −70 °C in tetrahydrofuran (THF), **12** is the first example of an isolable aminyl diradical. Although **12** is stable in the solid state, its stability in solution at room temperature is lower than that of **7**. Diradical **12** has a half-life of 3 h in 2-methyltetrahydrofuran (2-MeTHF) solution and decays almost exclusively by hydrogen atom abstraction from solvent. Unlike nitroxide diradical **7**, we observed aminyl diradical **12** to exhibit unexpected π-dimer-like formation in solution ($K_a = 3 \times 10^2$ M^{-1} at 132 K) with very weak antiferromagnetic coupling between the two $S = 1$ monomers. The EPR signal attributed to thermal population of the $S = 2$ quintet state (with much stronger electron dipolar coupling than the $S = 1$ monomer), which was observed at higher concentrations.[80]

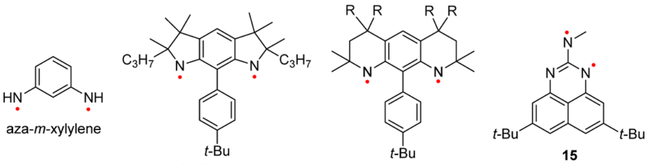


11

12 ($R = C_8H_{17}$)
Isolated at r.t.
$t_{1/2}$ ~ 3 hrs in 2-MeTHF
12a ($R = CH_3$)
ΔE_{ST} ~ 5.5 kcal mol^{-1}

Figure 8. Diaryl aminyl diradicals.

In diaryl aminyl diradicals, spin density is partially delocalized into the diazapentacene side units and dissipated away from the central *m*-phenylene FCU (Figure 7). It is expected that when spin density is delocalized nearly exclusively to the FCU, such as in alkylaryl aminyl diradical **13**, the ΔE_{ST} should increase further (Figure 9). Barone's DDCI computations predicted simplified structure **13a** of diradical **13** to possess ΔE_{ST} of 9.6 kcal mol^{-1} (vs 11 kcal mol^{-1} by BS-DFT), which is comparable to that of *m*-xylylene ($\Delta E_{ST} \approx 10$ kcal mol^{-1}).[81,82] We prepared **13** and determined its $\Delta E_{ST} > 0.4$ kcal mol^{-1} (SQUID magnetic susceptibility).[82] Whereas *m*-xylylene persists in solution for only hundreds of nanoseconds at room temperature,[83] **13** has a half-life of ~10 min at room temperature in 2-MeTHF solution.[82] The enhanced persistence of **13** is due to steric shielding of the SCs and reactive *ortho/para* positions of the FCU. Very recently, we synthesized aminyl diradical **14**, which is also predicted to possess a very high ΔE_{ST} based on the BS-DFT computed value of ~14 kcal mol^{-1} for simplified structure **14a**.[84] Using a novel, statistics-based approach to evaluating χT (product of magnetic susceptibility and temperature) by EPR spectroscopy, we are able to provide an



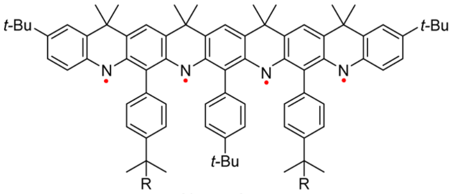
aza-*m*-xylylene

13 ($R = C_3H_7$)
13a ($R = CH_3$)

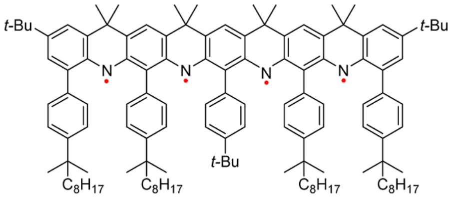
14 ($R = C_3H_7$)
14a ($R = CH_3$)

15

Figure 9. Aminyl diradicals analogous to *m*-xylylene (**13** and **14**) and TMM (**15**).



16 (R = C_8H_{17})
16a (R = CH_3)
(*S* = 2)



17
(*S* = 2)

Figure 10. High-spin (S = 2) tetraradicals.

experimental lower bound to the ΔE_{ST} of **14** in 2-MeTHF ($\Delta E_{ST} \geq 800$ K $\approx$ 1.6 kcal mol^{-1}), which is much higher than conventional determination of this lower limit possible using SQUID magnetometry in 2-MeTHF. We were also able to improve the lower bound of ΔE_{ST} for **13** in 2-MeTHF ($\Delta E_{ST} \geq$ 400 K $\approx$ 0.8 kcal mol^{-1}). Diradical **14** possesses a half-life of ~80−250 s at room temperature in 2-MeTHF solution.[84]

Other efforts to synthesize aminyl diradicals with large ΔE_{ST} have utilized FCU's other than *m*-phenylene.[85] Diradical **15**, which can be considered to utilize both TMM-like and 1,8-naphthyl FCU's, was recently synthesized. EPR triplet intensity vs reciprocal temperature for **15** was found to be linear at low temperatures (5−23 K), which, as a consequence of the Curie−Weiss Law, could indicate either $\Delta E_{ST} \gg RT$ or $\Delta E_{ST} \ll RT$. BS-DFT results, UB3LYP/6-31G* as well as (14/14)CASPT2/6-31G*, predict ΔE_{ST} of 8−10 kcal mol^{-1} and support the former conclusion. The diradical persisted at 77 K for several hours but decayed upon warming to 97 K.[85]

Extension to Higher Spin Multiplicities (*S* > 1). Molecules with $S = 1$ ground states present the simplest case of intramolecular ferromagnetic exchange coupling and can be considered a fundamental unit of high-spin materials. However, to achieve enhanced paramagnetic properties and functional magnetic materials, the transition from $S = 1$ to $S > 1$ ground states is a necessary one. Much of our early work focused on the design, synthesis, and characterization of high-spin polyarylmethyl polyradicals, which led to establishment of design principles necessary for achieving very high-spin ($S \gg 1$) polyradicals.[4,5,86−90] Although carbon-based radicals are prone to dimerization and are reactive toward oxygen, this work eventually culminated in the synthesis of the first very high-spin organic polymer (average $S \approx 5000$ with magnetic ordering at about 10 K), as well as organic molecules with the highest values of S such as $S = 13$.[7,90] The next challenge is to create stable polyradicals, leading to high-spin materials which are kinetically robust at room temperature and possess large energy gaps.[91]

We recently synthesized aminyl tetraradicals **16** and **17**, which are homologous extensions of aminyl diradicals **11** and **12** (Figure 10).[92,93] Tetraradicals **16** and **17** possess quintet (S = 2) ground states as established by SQUID magnetization and susceptibility measurements. The energy gap between the quintet and the nearest excited triplet state, $\Delta E_{TQ} \gtrsim 150$ K $\approx$ 0.3 kcal mol^{-1}, is determined by SQUID susceptibility measurements and, using the simplified structure **16a**, estimated by BS-DFT as ~5 kcal mol^{-1}. The large ΔE_{TQ} estimated by DFT predicts minimal occupation of excited lower-spin states at room temperature. Similar to diradical **12**, tetraradical **17** reacts with O_2 in solution at temperatures greater than 195 K. The half-life of tetraradical **17** at room temperature in 2-MeTHF solution is 1 h; this is significantly less than diradical **12** ($\tau_{1/2} \approx 3$ h). Analogous to **12**, tetraradicals **16** and **17** form π-dimer-like structures in concentrated solutions ($K_a = 60 \pm 15$ M^{-1} for **16** at 132 K), as evidenced by EPR spectroscopy. The intradimer exchange energy is antiferromagnetic and very weak ($J \approx -0.1$ K from SQUID measurements).[92]

Conclusion and Outlook. There is no doubt that sizable progress has been made in the arena of high-spin organic molecules. In fact, one could argue that the history of high-spin molecules closely parallels that of organic radicals themselves. Once considered to be exclusively highly reactive intermediates, high-spin molecules can now be designed and synthesized that do not decompose in the solid state under ambient conditions. Also, high-spin molecules have been synthesized that possess very large energy gaps (an order of magnitude greater than RT at room temperature) and possess half-lives on the order of minutes at room temperature. A fundamental understanding of the factors that lead to high-spin ground states in organic molecules has facilitated sophisticated molecular design, and it is now commonplace to qualitatively assess the ground-state multiplicity of a given molecule using parity methods as well as quantitatively assess the gap using ab initio quantum chemical computations. The structure−property relationship of organic diradicals is now well understood.

However, some of the most challenging problems in high-spin research still lie ahead. One challenge for molecular engineers/synthetic chemists is to create high-spin molecules that possess energy gaps an order of magnitude greater than RT at room temperature as well as kinetic stability that rivals the most stable organic monoradicals. A challenge for theoreticians is to simplify models for predicting ferromagnetic coupling strength in very large ($S \gg 1$) systems where ab initio methods clearly become intractable. One basic approach may rely on semiempirical methods to predict spin density within regions where ferromagnetic coupling occurs.

These challenges are certainly daunting, but the most daunting challenges often come with the most fruitful rewards. As the designs of high-spin molecules improve, they will positively impact other diverse fields such as spintronics; improvements could lead to the "holy grail" of high-spin research, a purely organic ferromagnet with Curie temperature greater than room temperature. Skeptics might question whether these goals can ever be attained. However, not long ago, skeptics also questioned the existence of stable organic radicals and stable high-spin molecules. If organic radical and high-spin research teaches one lesson, it is that enough time and innovation ultimately proves naysayers wrong.

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Notes

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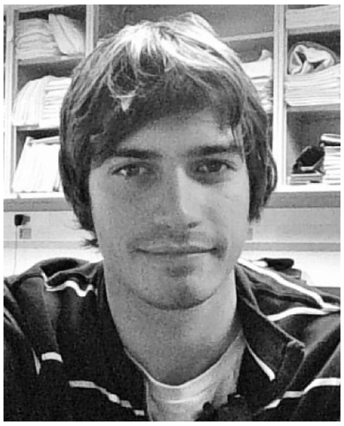

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