

From Stable Radicals to Thermally Robust High-Spin Diradicals and Triradicals.

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Abstract

Stable radicals and thermally robust high-spin di- and triradicals have emerged as important organic materials due to their promising applications in diverse fields. New fundamental properties, such as SOMO/HOMO inversion of orbital energies, are explored for the design of new stable radicals, including highly luminescent ones with good photostability. A relation with the singlet triplet energy gap in the corresponding diradicals is proposed. Thermally robust high-spin di- and triradicals, with energy gaps that are comparable to or greater than a thermal energy at room temperature, are more challenging to synthesize but more rewarding. We summarize a number of high-spin di- and triradicals, based on nitronyl nitroxides that provide a relation between the experimental pairwise exchange coupling constant J/k in the high-spin species vs. experimental hyperfine coupling constants in the corresponding monoradicals. This relation allows us to identify outliers, which may correspond to radicals where J/k is not measured with sufficient accuracy. Double helical high-spin diradicals, in which spin density is delocalized over the chiral π -system, have been barely explored, with the sole example of such high-spin diradical possessing alternant π -system with Kekulé resonance form. Finally, we discuss a high-spin diradical with electrical conductivity and derivatives of triangulene diradicals.

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1. Introduction

Persistent organic radicals have been known for well over a century.¹⁻⁵ While they contributed to the rich history of organic chemistry,⁶ more recently they emerged as important class of organic materials and biomaterials that are under intense investigations for a wide range of applications. Applications will of course be facilitated with emergence of not only stable radicals but also, thermally robust, with highly tunable structures. Not surprisingly, they are the subject of many recent reviews, for example, refs 7 – 16.

When we refer to a radical or polyradical as stable, we will start with the classic guideline given by Ingold:¹⁷ “The word stable should only be used to describe a radical so persistent and so unreactive to air, moisture, etc., under ambient conditions that the pure radical can be handled and stored in the lab with no more precautions than would be used for the majority of commercially available organic chemicals.” We propose to augment this definition by adding designations of “thermally robust” and “thermally ultra-robust” concerning solid radicals under inert atmosphere; the “thermally ultra-robust” radicals are those with the thermogravimetric analysis (TGA) onset of decomposition temperature (T_d) above 250 °C, and the “thermally robust” radicals are those with T_d above 150 °C, where T_d corresponds to the mass loss of 1%. TGA-based definitions of thermal robustness are especially relevant to applications of open-shell molecules as organic materials that frequently require preparation of stable thin films via evaporation (sublimation).

Ingold’s definition of persistent radical is less practical;¹⁷ in this review, we will refer to persistent radical as such that can be handled without significant decomposition under either inert atmosphere or on air in fluid solution at specified temperature, ideally at room temperature or above.

As mentioned above some radicals are used as biomaterials – especially in biomedicine and biophysics. Because *in vivo* or in live cells most radicals typically undergo rapid one-electron reduction by antioxidants or enzymes, persistence of the radical in this situation will be decided by rates of these

reductive processes.

We will start with an overview of selected stable or persistent monoradicals, focused on new properties and applications in biomedicine, biophysics, and organic materials (Section 2). New fundamental properties such as SOMO/HOMO inversion (SHI) of orbital energies are being uncovered and explored for the design of new stable radicals, including highly luminescent ones with good photostability. For a subset of twelve SOMO/HOMO inverted monoradicals, a relation with the singlet triplet energy gap (ΔE_{ST}) in the corresponding diradicals is proposed as discussed in Section 3.

Section 4 will focus on high-spin di- and triradicals. High-spin di- and triradicals, with nearly planar π -systems, thermal robustness, and low-spin high-spin energy gaps that are comparable to or greater than the thermal energy at room temperature, are more challenging to synthesize but they may be more rewarding. Such di- and triradicals possess relatively large populations of the high-spin states at room temperature and their properties related to paramagnetism scale with the factor of $S(S + 1)$, where the total spin quantum number S corresponds to the high-spin ground state. This implies scaling with approximately n^2 , where n is the number of “unpaired” electrons, for many properties including relaxivity of MRI contrast agents, dynamic nuclear polarization (DNP), assuming that other controlling factors can be optimized too. Such di- and triradicals form interesting thin films that may be prepared via evaporation, thus facilitating their potential applications in electronics and spintronics. One example of such high-spin diradicals, so far, is a good electrical conductor – contrary to expectations. For about a dozen of high-spin di- and triradicals, based on nitronyl nitroxides, a relation between the experimental pairwise exchange coupling constant J/k (equal to the half of the singlet triplet energy gap in a diradical) in the high-spin species vs. experimental hyperfine coupling constants in the corresponding monoradicals is established. Such a relation allows us to identify outliers, which may correspond to radicals where J/k is not measured with sufficient accuracy, e.g., because of the large magnitude. Double helical (or helical) high-spin di- and polyradicals, in which spin density is

delocalized over the chiral π -system, have been barely explored, with only one example of such high-spin diradical, which also possesses alternant π -system with Kekulé resonance form. Finally, we discuss recent progress in studies of derivatives of triangulene and aza-triangulene diradicals with large ΔE_{ST} .

2. Persistent and Stable Monoradicals as Spin Centers

Examples of notable C-, N-, O-, N,O-, and N,S-centered neutral monoradicals are described in the next three sub-sections and in Figures 1 – 5.

2.1. Carbon-centered monoradicals

We note that all radicals in Figure 1 are stabilized to some degree by delocalization and steric shielding of unpaired electron, i.e., atoms with large spin densities. The carbon-based radicals are the ones of most historical importance, and the triphenylmethyl (Gomberg's radical) is considered the first room temperature persistent organic radical; it is a seminal discovery in organic chemistry (Figure 1).^{1,2,6} The triphenylmethyl radical reacts with oxygen and under inert atmosphere, it is in equilibrium (association constant, $K_{\text{assoc}} \approx 3 \times 10^3 \text{ M}^{-1}$ at 293 K)¹⁸ with its C-C bonded dimer (σ -dimer) in solution. The correct structure for the σ -dimer, which was originally proposed by Jacobsen in 1905,¹⁹ was established by NMR spectroscopy in 1978.^{20,21} Substitution at the *para*-positions, leads to monomeric triarylmethyls, e.g., 4,4',4''-tris(*tert*-butylphenyl)methyl.²² Sterically hindered derivatives of triphenylmethyl were engineered into very high-spin polyradicals,²³⁻³¹ including the first organic polymer with magnetic ordering,³² which were found to be persistent at low temperatures in solution, while the most sterically shielded diradicals could be either isolated or handled at room temperature under inert atmosphere.³³⁻³⁵

Chlorinated derivatives of triphenylmethyl, such as perchlorotriphenylmethyl (**PTM**)³⁶⁻³⁹ or tris(2,4,6-trichlorophenyl)methyl (**TTM**),^{40,41} are thermally ultra-robust. They show neither dimerization nor reactivity toward oxygen in both solution or solid state, and do not decompose in the

solid state until heated to ~ 300 °C. This extraordinary stability is associated with the steric shielding of *ortho*-chlorines.⁴² **PTM** was used for the design of high-spin diradical and triradical.⁴³⁻⁴⁵ Both **PTM** and **TTM**, functionalized with electron donating π -systems, led to the discovery of efficient doublet state light emitters, including high efficiency organic light emitting diodes (OLEDs). Because photostability of such radicals may be associated with SOMO/HOMO energy level inversion, they are discussed in more detail in Section 3.

Another class of highly persistent triarylmethyls is illustrated by the structure of Finland trityl (**FT**) radical and its more hydrophilic version **Ox-063**.⁴⁶⁻⁴⁸ Analogous to **PTM** or **TTM**, here the persistence is attained by severe out-of-plane twisting of the *ortho*-substituted aryl rings. Both radicals are monomeric and persistent at ambient conditions, and especially **Ox-063** and **Ox-063-d₂₄** are well soluble in water, biocompatible and lacking of interactions with blood albumin.⁴⁹ Because of negligible hyperfine couplings and the *g*-values that are close to that of the free electron, derivatives of both **FT** and **Ox** radicals feature relatively narrow electron paramagnetic resonance (EPR) lines and possess relatively long electron spin relaxation times (T_m and T_1).⁵⁰ Their derivatives found applications as dynamic nuclear polarization (DNP) agents in NMR,⁵¹⁻⁵⁴ and as oxygen and pH sensors in biomedicine,⁵⁵ as spin labels in biophysics, e.g., derivatives of **FT** or **Ox-063-d₂₄** for EPR distance measurements,⁵⁶⁻⁶² especially at up to 150 K in cell^{60,61} and at room temperature in vitro.⁵⁶⁻⁵⁸ ¹³C-labeled (at center C) **Ox-063-d₂₄** and its derivatives possess enhanced anisotropy of the hyperfine coupling providing relatively wide EPR spectrum that is also sensitive to molecular tumbling;⁶³ this allows for applications such as viscosity sensors in biomedicine⁴⁹ and spin labels for distance measurements using widely available double electron-electron resonance (DEER) spectroscopy.⁶²

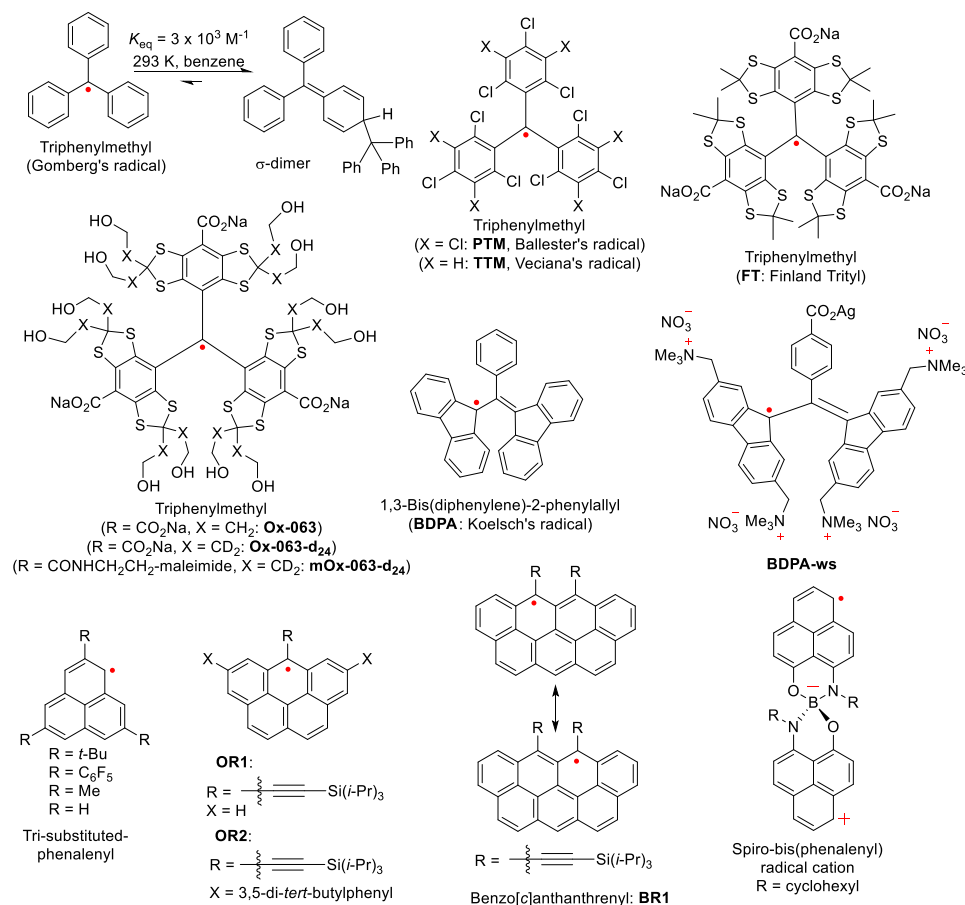


Figure 1. Examples of persistent and stable C-centered organic radicals.

Koelsch's radical, 1,3-bisdiphenylene-2-phenylallyl (**BDPA**), is also historically unique as it was the first carbon-based radical to display no significant reactivity toward oxygen; at the time, this was so unprecedented that the original Koelsch's manuscript was rejected in 1930's and forgotten for nearly 30 years.⁶⁴ Recent studies showed that **BDPA** and its derivatives, including TEMPO-based biradicals, are not as stable as previously thought, e.g., 5 mM **BDPA** decomposes in DMSO at room temperature with the initial half-life of the order of 1 day, most likely via σ -dimer formation.⁶⁵ For the solid **BDPA**, no decomposition was detected after 2 weeks under vacuum; however, under air, a half-life of the order of 10 days was found.⁶⁵ Nevertheless, such persistence is sufficient for the use of **BDPA**, including its water soluble^{66,67} and partially deuterated derivatives,⁶⁸ as DNP agents in NMR.^{69,70} Recently, more persistent water soluble derivative of **BDPA**, such as **BDPA-ws** (Figure 1) was synthesized⁷¹ and studied as DNP agent.⁷²

Phenalenyl-based radicals are fundamentally interesting and may be viewed as open-shell

graphene fragments.^{9,73} While parent phenalenyl radical (R = H, Figure 1) exists predominantly as diamagnetic σ -dimer,⁹ 2,5,8-tri-*tert*-butylphenalenyl radical forms a centrosymmetric π -dimer in the crystalline state with $\Delta E_{ST} = -4$ kcal mol⁻¹ and is reactive toward oxygen.⁷⁴ Based on studies by Kochi group, in dichloromethane solution, $K_{\text{assoc}} = 0.2$ M⁻¹ at 298 K for the π -dimer was determined by both EPR and UV-vis-NIR spectroscopy but a much larger $K_{\text{assoc}} = 70 - 90$ M⁻¹ at 298 K was found for π -pimer (radical plus cation); however, enthalpy of association $\Delta H_{\text{assoc}} = -9$ kcal mol⁻¹ for the π -dimer was larger than $\Delta H_{\text{assoc}} = -7$ kcal mol⁻¹ for the π -pimer, with a more negative ΔS_{assoc} for the π -dimer.^{75,76} In contrast, R = Me derivative formed two distinct σ -dimers and one π -dimer (all diamagnetic).⁷⁷ Kubo and co-workers determined that tri-substituted-phenalenyl with R = perfluorophenyl (C₆F₅) can form either σ -dimer or one-dimensional π -stack in the crystalline state.^{78,79} Although, based on the X-ray structure at 10 K, π -stacks are relatively spin-insulated with a perfectly equidistant phenalenyl moieties with a somewhat elongated plane-to-plane distance of 3.503 Å, the magnetic susceptibility data could not be reasonably fit to a uniform 1-dimensional $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain.⁷⁹ DFT computations predict greater thermodynamic stability for σ - vs. π -dimers, even for derivatives of phenalenyls, for which only π -dimers were isolated;⁸⁰ this phenomenon may be ascribed to kinetic control of dimerization or solvent effects (*vide*: dicyanomethyl radicals), or inherent deficiency of DFT as outlined in ref 75.

Sterically shielded dibenzo-fused derivatives of phenalenyl **OR1** and **OR2** (Figure 1) were reported to form π -dimers, with $K_{\text{assoc}} = 6 - 21$ M⁻¹ (at 298 K) and $\Delta E_{ST} \approx (-2) - (-3)$ kcal mol⁻¹ in toluene.⁸¹ The reported K_{assoc} (and underlying thermodynamic parameters, e.g., ΔH_{assoc}) were widely different, based on UV-vis-NIR vs. EPR spectra,⁸¹ in contrast to those for π -dimer of 2,5,8-tri-*tert*-butylphenalenyl radical reported by Kochi.^{75,76} Most likely these authors⁸¹ failed to do properly quantitative EPR spectroscopy (Section 4.2.1). These radicals may be viewed as air stable, with half-live in air saturated solutions of 7 – 34 days, and presumably, less associated than σ -dimer forming

Gomberg triarylmethyl. Crystalline **OR1** was an insulator with room temperature conductivity, $\sigma_{RT} < 10^{-10} \text{ S cm}^{-1}$, and the average intermolecular distance of 3.29 Å was found within π -dimer.⁸¹

Even more benzo-fused derivative of phenalenyl, i.e., benzo[c]anthanthrenyl radical derivative, **BR1** (Figure 1),⁸² crystallized as a slipped 1D chain with equidistant average π - π contacts of 3.565 Å along the stacking direction. However, fit of magnetic susceptibility data to 1-dimensional $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain was overparametrized and thus unreliable. Also, room temperature conductivity, $\sigma_{RT} \approx 2.5 \times 10^{-9} \text{ S cm}^{-1}$, indicated that the material was practically an insulator.⁸²

Haddon and coworkers reported spiro-bis(phenalenyl) derivatives, which correspond to spiroconjugated radical cations ($R = \text{alkyl}$) and are mostly isolable as stable monomeric crystalline solids.⁸³⁻⁸⁶ Because of formal negative charge on boron, these compounds may be viewed as “neutral” (actually zwitterionic) radicals. While the $R = n\text{-hexyl}$ derivative was reported as the first phenalenyl-based neutral radical molecular conductor, the room temperature conductivity, $\sigma_{RT} = 0.05 \text{ S cm}^{-1}$, was low and activation energy to the charge transfer, $E_a = 0.13 \text{ eV}$, was large.⁸³ Better optimized, in terms of crystal packing, the $R = \text{cyclohexyl}$ derivative possessed a good electrical conductivity $\sigma_{RT} = 0.3 \text{ S cm}^{-1}$ and low charge transfer $E_a = 0.05 \text{ eV}$.⁸⁴ Interestingly, $R = \text{benzyl}$ derivative forms a uniform one-dimensional $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain ($J/k = -75 \text{ K}$), with closest C---C contacts of 3.47 and 3.58 Å along the stacking direction; the material had $\sigma_{RT} = 1.4 \times 10^{-3} \text{ S cm}^{-1}$ with a relatively large $E_a = 0.2 \text{ eV}$.⁸⁵ In contrast, a benzannulated spiro-bis(phenalenyl) derivative with $R = \text{benzyl}$ showed complex temperature dependent interconversion between σ -dimer and stacked π -chain radical in the crystals.⁸⁶

Dicyanoarylmethyl radicals were initially studied as reactive intermediates. In 1966, Hartzler⁸⁷ reported that 1,2-diaryl-1,1,2,2-tetracycanoethane ($R = \text{H}$) in chloroform-*d* underwent rearrangement to the aromatized σ -dimer of dicyanoarylmethyl radical ($R = \text{H}$) (Figure 2), after overnight at ambient temperature. Although Hartzler could not detect EPR spectrum for the radical, including its $R = \text{NO}_2$

derivative,⁸⁷ de Jongh could obtain a resolved EPR spectrum for the $R = \text{CH}_3$ radical and to determine, by NMR line broadening, the rate constant, $k_{\text{diss}} = 20 \text{ s}^{-1}$ at 373 K, as well as the activation parameters ($\Delta H_{\text{act}} = 26 \text{ kcal mol}^{-1}$ and $\Delta S_{\text{act}} = +13 \text{ cal mol}^{-1} \text{ K}^{-1}$) for the dissociation of 1,2-diaryl-1,1,2,2-tetracycanoethane ($R = \text{CH}_3$) into the radicals in the 353 – 393 K range (Figure 2).⁸⁸

More recently multiple groups, including especially those of Winter and Seki, recognized potential of air and thermally stable dicyanoarylmethyl radicals co-existing with their σ -dimers and/or π -dimers (Figure 2).^{89-100,102}

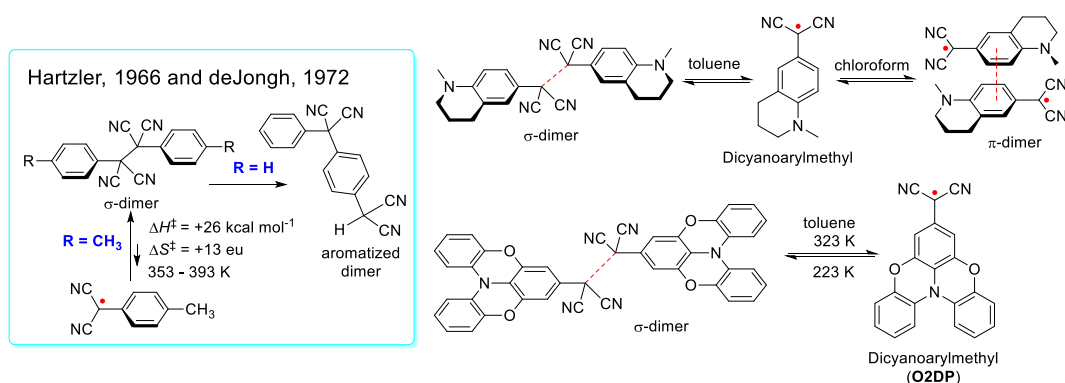


Figure 2. Examples of dicyanoarylmethyl radicals.

In 2016, Seki synthesized self-assembling biradicals, in which either triphenylamine or carbazole was substituted with dicyano radicals, based on dicyanoarylmethyls. The self-assembly created cyclic oligomers which showed thermochromic and mechanochromic properties due to generation of radicals by C–C bond cleavage (σ -dimers).⁸⁹ Winter measured association constants for formation of σ -dimers of *para*-mono-substituted dicyanophenylmethyl radicals, $K_{\text{assoc}} = 10^5 - 10^8 \text{ M}^{-1}$ and found that they decrease for electron donating substituents, giving linear Hammett plots.⁹¹ In 2017, Seki demonstrated the first example of dicycanoarylmethyl radical (with the julolidine skeleton) forming π -dimer (in toluene solution).⁹² Winter have shown that for some radicals greater solvent polarity, which is associated with increased electron spin delocalization,⁹³ leads to preferential π -dimer formation (Figure 2).⁹⁴ While several factors were considered to determine the mode of dimerization (σ - or π -dimer),^{95,96} curiously the magnitude of ΔE_{ST} in the π -dimers was neither considered nor measured.

Seki studied another radical, **O2DP** (Figure 2), which possesses modified julolidine skeleton, and it forms σ -dimer at low temperature in toluene. Notably, the **O2DP** radical possesses a strong NIR absorption at $\lambda_{\text{max}} = 1059 \text{ nm}$, with a wide optical window in the visible region and a relatively small dimerization enthalpy, $\Delta H_{\text{assoc}} \approx -10 \text{ kcal mol}^{-1}$.⁹⁷ Winter suggested that antiaromaticity relief within planarized electron donating group of dicyanoarylmethyl radicals (e.g., analogous to **O2DP**, Figure 2) may stabilize their zwitterionic resonance form, thus leading to overall improvement in radical stability.⁹⁸ In addition, Osuka and coworkers demonstrated monomeric (even at low temperatures) stable dicyanoarylmethyl radical in solution by appending dicyanomethyl radical to B^{III}-subporphyrin.⁹⁹ Finally, based on discovery of Malishewski that oxidation power of tetracyanoquinodimethane (TCNQ) can be increased dramatically by coordination of cyano groups by a strong Lewis acid such as B(C₆F₅)₃,¹⁰¹ the analogous coordination approach led to increased dissociation of σ -dimer of dicyanoarylmethyl radical, perhaps due to better stabilization of the radical by capto-dative effect.¹⁰²

2.2. Nitrogen-centered monoradicals

Aminyl radicals have long history as reactive intermediates,^{103,104} including in organic synthesis^{105,106} and biochemistry.¹⁰⁷ Only 1,3,6,8-tetra-*tert*-butylcarbazyl, **TTBC** (Figure 3), and perchlorodiphenylaminyl are historically known to be persistent at ambient conditions.^{108,109} More recently, alkyl-aryl and diaryl aminyl radicals were employed as building blocks for high-spin di-, tri-, and tetraradicals with low- and high-spin energy gaps of up to about 10 kcal mol^{-1} and with half-lives of up to 6 h at room temperature in a fluid 2-methyltetrahydrofuran solutions;¹¹⁰⁻¹¹⁵ also, highly resonance stabilized and sterically shielded high-spin aminyl triradical was reported by Shimizu and Osuka.¹¹⁶ Derivatives of carbazole radical cations were also incorporated into polymers, for which triplet ground states were detected.¹¹⁷

PEGylated derivatives of **TTBC** were reported.^{118,119} At 295 K in acetone, **PEGC** (Figure 3) has

a half-life, $\tau_{1/2} = 48$ s, compared to $\tau_{1/2} = 2.3$ h for its octa-deuterated isotopomer, which corresponds to an extraordinary large kinetic isotopic effect, $k_H/k_D \approx 150$ at room temperature. While large values of k_H/k_D and unusual activation parameters are consistent with quantum mechanical tunneling, the Arrhenius and Eyring plots are linear over a wide temperature range of 116 K.¹¹⁸ Notably, constitutional isomer of **PEGC**, in which positions of *tert*-alkyl substituents are inverted, is much more persistent with $\tau_{1/2} = 49$ h in acetone at 295 K.¹¹⁹

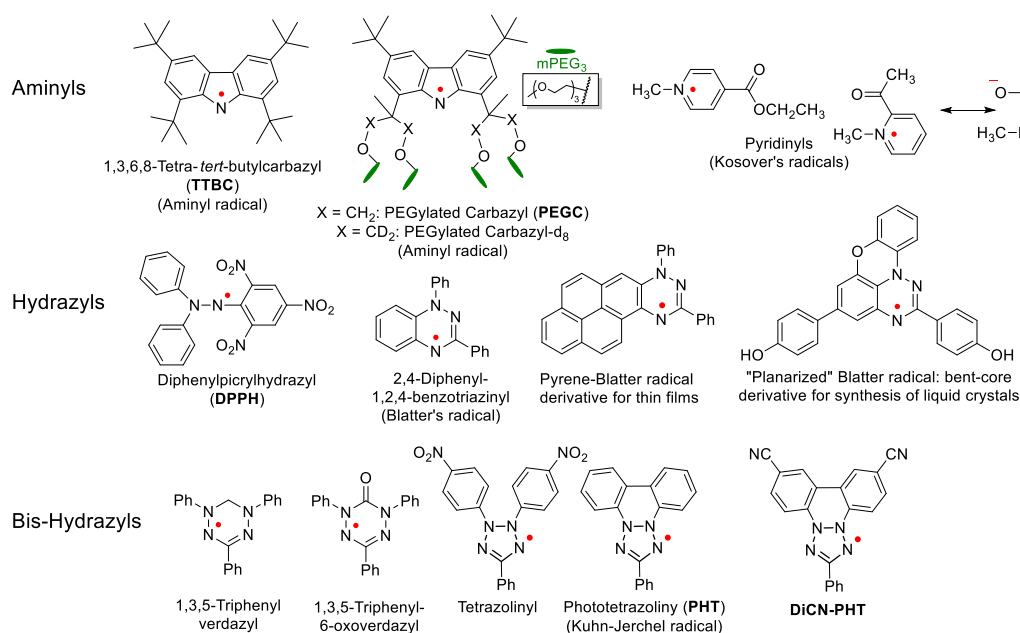


Figure 3. Examples of persistent and stable N-centered radicals.

Pyridinyl radicals were discovered by Kosower and co-workers in 1960's.¹²⁰⁻¹²² Their unusual persistence at room temperature (under inert atmosphere) is associated with a favorable zwitterionic resonance form (Figure 3). Both pyridinyls in Figure 3 are about 95% monomeric at room temperature and in equilibria with their σ -dimers; they can be purified by distillation under vacuum.¹²² In addition, 2,4,6-triphenyl-substituted pyridinyl radical was demonstrated to be monomeric;¹²³ Kubo, Matsumoto, and co-workers used 2,6-diphenyl pyridinyl as building block for high-spin diradical, persistent at room temperature.¹²⁴

Hydrazyl-based radicals, $[R_2NNR]^\bullet$ ($R = \text{aryl}$) are typically persistent at ambient conditions. For example, **DPPH** is commonly used as an EPR reference; it possesses a good stability, as it is

monomeric and stable in the solid state on air, and can be heated to ~ 80 °C in solution before decomposing.^{125,126} DPPH is practically an insulator with single crystal conductivity, $\sigma_{\text{RT}} \approx 10^{-10}$ S cm^{-1} at room temperature ($E_a = 1.5$ eV).^{127,128} We note that thin films of DPPH, prepared by sublimation under vacuum ($p = 10^{-6}$ Torr), are very air-sensitive.¹²⁷

Annulated hydrazyls such as Blatter's radical¹²⁹ possess even better stability due to enforced orbital overlap leading to enhanced resonance stabilization. For instance, a derivative of 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.¹³⁰ Numerous derivatives of Blatter's radical have been recently prepared and their interesting properties studied;¹³¹⁻¹⁴⁶ this includes DNP agents for NMR spectroscopy,¹³⁶ the magnetically ordered thin film of Pyrene-Blatter on SiO_2/Si substrate that is stable at ambient conditions,¹³⁷⁻¹⁴⁰ self-assembled films of Blatter radical on Au,¹⁴¹ paramagnetic liquid crystals of "planarized" Blatter,^{142,143} batteries,¹⁴⁴ and potential molecular qubits.^{145,146}

Derivatives of Blatter radical are important building blocks for thermally robust and ultra-robust high-spin di- and triradicals (Sections 4.3 and 4.5).¹⁴⁷⁻¹⁵⁰

Bishydrazyl radicals,¹⁵¹ such as verdazyl and 6-oxoverdazyl, are also extraordinarily stable because their spin density can delocalize over two hydrazyl moieties. Carbazole substituted derivative of verdazyl was found to be luminescent with quantum yield of fluorescence at room temperature of about 8%.¹⁵² Derivatives of 1,3,5-triphenyl-6-oxoverdazyls were used as building blocks for thermally robust high-spin di- and triradicals; however, their low-spin high-spin energy gaps were rather low (Section 4.3).^{153,154}

Another family of bishydrazyl radicals,¹⁵¹ such as tetrazoliny¹⁵⁵ and Kuhn-Jerchel radical (phototetrazoliny¹⁵⁶, **PHT**), have a long history¹⁵⁶⁻¹⁵⁸ but their thermal robustness and other properties were explored only recently.¹⁵⁹⁻¹⁶¹ For example, dicyano-substituted derivative of phototetrazoliny¹⁵⁹ (**DiCN-PHT**) is found to be stable under inert atmosphere up to 260+ °C (polycrystalline) and, in

benzene solution at room temperature, its estimated half-life is a few months.¹⁶¹ In polycrystalline **DiCN-PHT**, uniform one-dimensional $S = \frac{1}{2}$ antiferromagnetic Heisenberg chains ($J/k = -22$ K) are formed.¹⁶¹ Upon controlled evaporation on SiO₂/Si substrate under ultra-high vacuum,¹³⁹ **DiCN-PHT** forms nanoneedle assemblies.¹⁶¹ The stability of this planar radical is unusual because of relatively large spin densities at the *ortho*- (and *para*-) positions with respect to the nitrogens of the tetrazoliny moiety, as indicated by hyperfine coupling constant, $A(^1\text{H}) = 5.8$ MHz, which is greater by a factor of 3 than that in 1,3,5-triphenyl-6-oxoverdazyl radical (Section 4.3).¹⁶¹

2.3. Nitrogen,oxygen-, oxygen-, and nitrogen,sulfur-centered monoradicals

Piperidine nitroxides, such as 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) or 4-hydroxy-TEMPO (TEMPOL), are well-known stable organic radicals, which were pioneered by Rosantzev (Figure 4).^{162,163} Various TEMPO derivatives are heavily utilized in various applications, such as oxidation catalysts in organic synthesis,¹⁶⁴ polymerization mediators,¹⁶⁴ and DNP agents for NMR spectroscopy.^{166,167} TEMPOL (and its derivatives) was explored for multiple biomedical applications, based on its ability to modify oxidative stress and report (or alter) the redox status of tissues; e.g., as reporters of redox status in cancer or as protectors against ionizing radiation,^{168,169} TEMPO (and TEMPOL) derivatives, when incorporated into polymers or molecular gelators, are important components of organic batteries – pioneered by Nakahara et al.¹⁷⁰ and developed by Nishide and co-workers.¹⁷¹⁻¹⁷⁴

Although crystalline TEMPOL is an insulator with conductivity, $\sigma_{\text{RT}} \approx 10^{-11}$ S cm⁻¹ at room temperature, in the molten state (neat liquid), its conductivity increases to $\sigma \approx 5 \times 10^{-4}$ S cm⁻¹ at 380 K; it is not clear whether this increase is an intrinsic radical property or it occurs because of “doping” of the liquid with the products of partial decomposition of the radical at higher temperatures.¹⁷⁵ We note that films of DPPH, which include some of the decomposition products, show significantly higher

conductivities, compared to single crystals.¹²⁷ A better defined system, such as **PTEO** – polymeric TEMPOL derivative (Figure 4), studied by Boudouris group, possesses $\sigma_{RT} \approx 0.3 \text{ S cm}^{-1}$ at room temperature – an achievement considering the nitroxides are not conjugated.¹⁷⁶

Nitroxide radicals, including piperidine nitroxides, have important applications in biophysics as spin labels,¹⁷⁷ especially for EPR distance measurements in biomolecules.¹⁷⁸⁻¹⁸⁰ The distance measurements, especially few-nm long, require spin labels with long electron spin coherence times T_m of the order of a few μs ,¹⁸⁰ preferably at temperatures above 80 K. In typical *gem*-dimethyl nitroxides, onset of rotation of methyl groups on EPR time scale at $T > 80 \text{ K}$, lowers T_m significantly.¹⁸¹⁻¹⁸³ To solve this problem, a number of “methyl-less” spin labels were prepared;¹⁸⁴⁻¹⁸⁸ for example, **Spiro-IA** enabled EPR distance measurements in immobilized proteins at room temperature¹⁸⁷ and diazaadamantane derivative **IA-DZD** was used to demonstrate supramolecular approach to EPR distance measurement in proteins up to 150 K (Figure 4).¹⁸⁸

Among pyrroline nitroxides, **MTSL** stands out as the most common spin label used for labeling of proteins (Figure 4).^{178,179,189} Bis-spirocyclic pyrroline nitroxides, **Spiro-Ox** and **-THF**, possess promising electron spin relaxation properties as indicated by the $T_m = 0.71$ and $0.50 \mu\text{s}$ (vs. $0.34 \mu\text{s}$ for MTSL) measured at room temperature in 9:1 trehalose/sucrose matrix.¹⁹⁰ Other pyrroline nitroxides, such as **gem-DiCarboxy**, in which the methyl groups bear a tiny fraction of spin density, show more modest values of T_m at room temperature.^{190,191} In vitrified glycerol- d_8 /H₂O/D₂O (“DNP-juice”), a mixture of **gem-DiCarboxy** with triarylmethyl **Ox-063** (Figure 1) led to the discovery of a truncated cross-effect (tCE) in DNP NMR.¹⁹² This unusual DNP effect, is very likely associated with aggregation of **gem-DiCarboxy** in DNP juice and/or association with **Ox-063**. Aggregation (and/or association) leads to very low electron spin T_1 (and T_m) observed for 15 mM **gem-DiCarboxy** in DNP juice, which is more than 2 orders of magnitude lower, compared to **Ox-063** in DNP juice or to 0.1 mM **gem-DiCarboxy** in trehalose/sucrose at similar temperature.^{191,192} Because of their electron withdrawing

groups, **gem-DiCarboxy** and a related derivative are readily reduced, including rapid reduction by ascorbate;¹⁹³ this is in contrast to tetraethyl pyrroline (**TEP**) nitroxides, which are among the most difficult to reduce nitroxide radicals.^{193,194} Consequently, a derivative of **TEP**, such as **sTEO-TEP**, provided rapid and specific spin-labeling of tetrazine-amino-acid-containing proteins both *in vitro* and in live cells. Resistance of **TEP** to reduction enabled EPR distance measurements on native (sub-micromolar) concentrations of labeled proteins in live eukaryotic cells.¹⁹⁵

Numerous compact profluorescent probes were designed and studied, based on covalent linking of tetramethyl isoindoline nitroxides (**TMII**) with various chromophores (Figure 4).¹⁹⁶ The stability of nitroxide and the presence of benzene ring has facilitated functionalization radicals via Pd-catalyzed and click reactions.^{197,198} In 2000, Rassat group showed that tetraethyl isoindoline nitroxides (**TEII**) possess greatly increased resistance to reduction of radical, compared to **TMII** – the first case for the unusual effect of the *gem*-diethyl substitution.¹⁹⁹ **TEII** linked to fluorescein was an excellent agent for imaging of oxidative stress in live cells by two-photon fluorescence microscopy.²⁰⁰ Recent studies indicated lower stability of **TEII** derivative in the presence of rat liver microsomes, compared to that for tetraethyl-derivatives of pyrrolidine (**Carboxy-TEP**) and analogous pyrroline nitroxides.²⁰¹

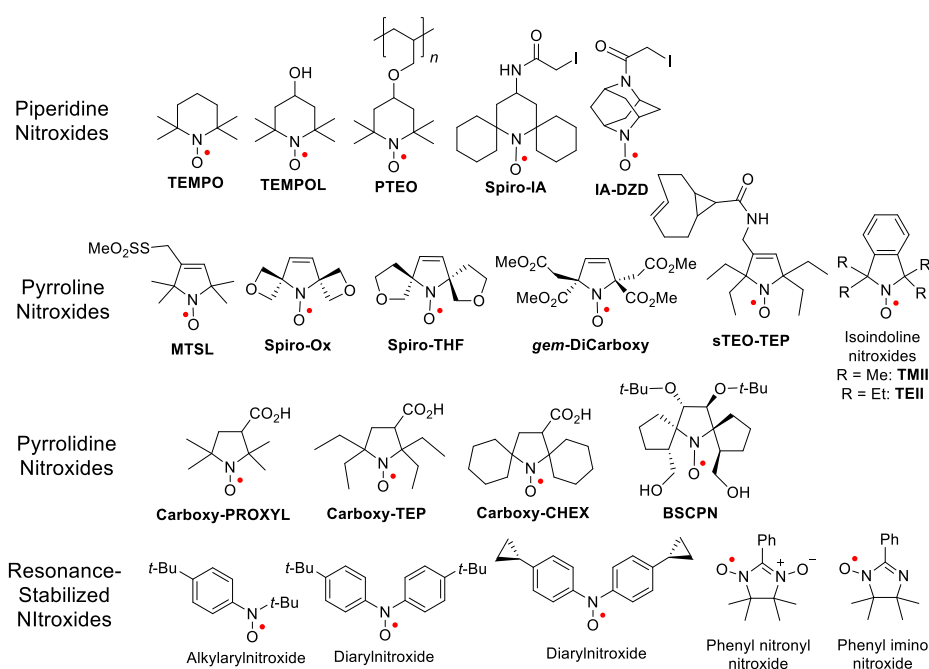


Figure 4. Examples of nitroxide radicals.

Pyrrolidine nitroxides, such as **Carboxy-PROXYL** and in particular tetraethyl-derivatives, are among the most difficult to reduce organic radicals.²⁰²⁻²⁰⁵ For example, **Carboxy-TEP** (Figure 4) is slightly more resistant to reduction than C-centered radical such as Finland trityl (**FT** in Figure 1).²⁰⁵ Derivatives of **Carboxy-CHEX** incorporated into various polymers provided organic radical contrast agents (ORCA) for MRI, with superior resistance to reduction and outstanding ¹H water relaxivities.²⁰⁶⁻²¹⁰ Although **BSCPN** has somewhat inferior resistance to reduction, compared to **Carboxy-TEP**, it provides an interesting example of a chiral, non-racemic nitroxide with bis-spirocyclic structure.²¹¹

Alkylaryl- and diarylnitroxides, together with phenyl nitronyl nitroxides and phenyl imino nitroxides (Figure 4),^{212,213} were used as building blocks to design various high-spin di- and triradicals (Section 4.3). As di- and polyradicals, they have been also employed as model compounds to study exchange coupling and electron-spin relaxation.²¹⁴⁻²¹⁹

Interestingly, half-lives of 2 months and 1 month in benzene at room temperature for bis-cyclopropyl- and bis-*tert*-butyl-substituted diarylnitroxide were determined, respectively. Greater persistence of cyclopropyl derivative may be associated with delocalization of spin density onto the cyclopropane moiety; that spin density is likely small enough not to trigger the potential radical clock reaction.^{220,221}

Galvinoxyl radical (Figure 5) is also a well-known stable radical that is inert to oxygen, and is representative of the phenoxyl family of radicals.²²² Galvinoxyl radicals attached as pendants to a polystyrene backbone served as the n-type redox material in memory devices²²³ and as cathode in all-organic batteries.²²⁴

Dioxyphenalene and trioxytriangulene (Figure 5) represent more recent additions to the phenoxyl family of radicals. Dioxyphenalenes, R = H and *t*-Bu, were stable in the absence of air at room temperature as solids and in toluene solution.²²⁵ X-ray structures of π -dimers of dioxyphenalenes, R = *t*-Bu, *p*-BrC₆H₄, and *p*-IC₆H₄, show intradimer plane-to-plane distances of 3.49 – 3.55, 3.38 – 3.51,

and 3.36 – 3.43 Å, respectively. These distances are considerably longer than 3.20 – 3.32 Å in π -dimer of 2,5,8-tri-*tert*-butylphenalenyl (Figure 1); consequently, $\Delta E_{ST} = -0.77$ kcal mol⁻¹ for R = *p*-BrC₆H₄ corresponds to considerably weaker antiferromagnetic interaction than $\Delta E_{ST} = -4$ kcal mol⁻¹ found in 2,5,8-tri-*tert*-butylphenalenyl (Section 2.1).²²⁶

Precursors to 4,8,12-trioxytriangulene radical (**TOT**) (Figure 5), may be traced to the corresponding phenol (R = H) in the classic work by Clar²²⁷ and to the pioneering work by Bushby in 1990's on the corresponding monoanion and triplet ground state diradical trianion (R = *t*-Bu).^{228,229} In 2011, Takui group reported first derivatives of **TOT** (R = *t*-Bu and Br) radical and demonstrated their promising applications as electrode active materials in organic batteries;²³⁰ this promise was based on outstanding stability of **TOT** derivatives (see: below) and their ability to undergo reversible 4-electron reductions (to tetraanions), providing materials with good electrical conductivity (see: below).²³⁰

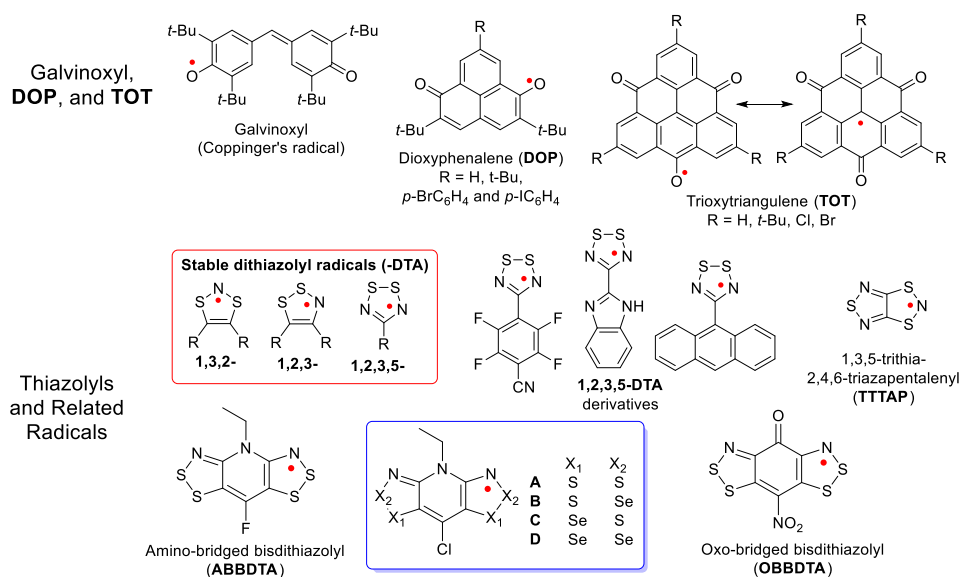


Figure 5. Examples of phenoxy, thiazyl, and related radicals.

Single crystal of **TOT** (R = Br) measured along the stacking direction had $\sigma_{RT} = 1.8 \times 10^{-3}$ S cm⁻¹ with $E_a = 0.31$ eV; this good electrical conductivity, coincided with the presence of equidistant **TOT** moieties (3.43 Å) within the slipped π -stack. The highest conductivity, $\sigma_{RT} = 125$ S cm⁻¹ with $E_a = 12$ meV, was obtained in the combination of **TOT** (R = Cl) radical and monoanion with Li⁺ as counterion. The crystal of this compound contained 1-D π -stacks with the equidistant stacking distance

of 3.29 Å.²³¹

In addition to various substituted **TOTs**,^{232,233} **TOT** (R = H),²³⁴ as well as dicyanomethylene-substituted triangulene derivative (R = *t*-Bu),²³⁵ were prepared. For **TOT** (R = H), the onset of thermal decomposition (TGA), defined as 1% mass loss, is perhaps at about 100–150 °C, compared to >300 °C for **TOT** (R = *t*-Bu); similar findings were obtained by UV-vis spectral follow-up in solution saturated with air with half-lives of the radicals being ca. 18 and 56 days, respectively.²³⁴ Moderately thick films (100 – 1000 nm) of **TOT** (R = H) were prepared by evaporation under vacuum, however, no evidence for intact radicals in the films was provided.²³⁶ At high evaporation rates (ca. 1 nm/s), an edge-on-oriented films, in which the 1-dimensional π -stacks of **TOT** are parallel to the SiO₂/Si or ITO glass substrates. The films showed anisotropic conductivities, $\sigma_{RT} = 0.025$ and 2×10^{-5} S cm⁻¹ parallel and perpendicular to the glass substrate. Notably, single crystal sample of **TOT** (R = H) gave an excellent $\sigma_{RT} = 0.32$ S cm⁻¹ with $E_a = 90$ meV.²³⁶ Films grown on graphite substrates provided a face-on orientation independent of deposition rate.²³⁶ Such films were found to yield slightly more durable cathode materials in lithium batteries, compared to edge-on films on ITO glass.^{237,238} More recently, electrochemical growth of conducting films of **TOT** was explored.²³⁹ **TOT** (R = *t*-Bu) was also used as a building block for triplet ground state diradical.²⁴⁰

Stable dithiazolyl (**DTA**) radicals occur in three major classes,^{241,242} as outlined in Figure 5. In particular, 1,2,3,5-**DTA** (or dithiadiazolyl) derivatives, which generally show strong propensity for dimerization,^{241,242} provided both organic radical with the highest ordering temperature and interesting cases of magnetic bistability;²⁴³⁻²⁴⁶ that is, 4-cyanotetrafluorophenyl derivative is a weak ferromagnet (canted antiferromagnet) with ordering temperature of 36 K.^{243,244,247,248,249} At high pressure, this material reaches ordering temperature of 70 K but with the trade-off of decreased spontaneous magnetization (decreased canting).²⁴⁴

Another interesting stable **DTA**-radical is **TTTAP** (Figure 4), originally reported by

Wolmershäuser and Johann in 1989.²⁵⁰ Ten years later, magnetic properties of this radical were studied by Awaga who discovered a first-order magnetic phase transition with an unusually wide thermal hysteresis loop in the 230–305 K range.²⁵¹ The same compound was thoroughly studied by Rawson and Palacio groups giving hysteresis loop in the 234 – 317 K range.²⁵² As it is typical for this type of transitions, the high- and low-temperature phases are paramagnetic and diamagnetic, respectively; paramagnetic phase is modelled by 1D $S = \frac{1}{2}$ Heisenberg chain with antiferromagnetic $J/k = -320$ K, with relatively strong interchain couplings, and diamagnetic phase corresponds to formation of dimers with strong intermolecular antiferromagnetic coupling ($\Delta E_{ST} < -4$ kcal mol⁻¹).^{252,253}

Interestingly, one of the crystalline polymorphs of amino-bridged bis(1,2,3-DTA), **ABBDTA** (Figure 5), forms essentially diamagnetic σ -dimer, containing hypervalent S-S bond, up to 380 K. Above this temperature there is a sharp increase in χT leading to paramagnetic phase with S-S bonds broken. Upon cooling, the σ -dimers are reformed at 375 K, thus providing a narrow thermal hysteresis loop but at high temperature.²⁵⁴

The selenium-based radicals (**B** – **D**, Figure 5) also displayed strong exchange interactions, which gave rise to ferromagnetically ordered phases with relatively high ordering temperatures (up to 17 K for **D**) and coercive fields (up to 1400 Oe for **D**).^{255,256} Although for **A** – **D**, $\sigma_{RT} < 0.001$ S cm⁻¹, σ_{RT} shows an increase by 2 orders of magnitude together with E_a decrease with increasing selenium content from $E_a = 0.43$ eV in **A** to 0.19 eV in **D**.²⁵⁵

Finally, oxo-bridged bis(1,2,3-DTA), **OBBDTA** (Figure 4), may be viewed as a recent culmination of research on neutral DTA-radical-based single component conductors, with σ_{RT} near 0.04 S cm⁻¹ and $E_a = 0.05$ eV.²⁵⁷ This radical also exhibits Pauli-like temperature independent paramagnetic behavior, with $\chi_{TIP} = 6 \times 10^{-4}$ emu mol⁻¹. At the pressure of 6 – 8 GPa, $\sigma_{RT} \approx 10$ S cm⁻¹ and $E_a < 0$.²⁵⁷ For comparison, both σ_{RT} and σ_{383K} for **ABBDTA** are only $\sim 10^{-4}$ S cm⁻¹ (at pressure of 0.5 GPa).²⁵⁴

3. Radicals and Radical Ions with SOMO-HOMO Inversion (SHI)

3.1. General overview.

There are now quite a few organic radicals with an electronic energy structure, defined as SOMO-HOMO level inversion, which then formally violates the Aufbau principle,²⁵⁸ that is, the energy level of singly occupied molecular orbital (SOMO) is below the level of the highest occupied molecular orbital (HOMO). The topic of SOMO-HOMO inversion (SHI) was the subject of three recent reviews.²⁵⁹⁻²⁶¹

In our review, we define SHI by the difference in energy of electrons in HOMO (average of α -MO and β -MO) vs. SOMO (α -MO); i.e., $\text{SHI} > 0$ implies that the energy of SOMO is below the energy of HOMO on the per electron basis (Eq. 1). Alternatively, $\text{SHI} < 0$ implies that the energy of SOMO is above that of the HOMO on the per electron basis, i.e., orbital electron energies follow the usual Aufbau principle.

Our definition encompasses, the more restrictive, commonly used criterion for SHI in terms of α -MO's, that is, $\text{SHI} > 0$ means that the energy of α -SOMO is below α -HOMO (Eq. 2).

$$\text{SHI} = [(\alpha\text{-HOMO} + \beta\text{-HOMO})/2] - \alpha\text{-SOMO} \quad (1)$$

$$\alpha\text{SHI} = \alpha\text{-HOMO} - \alpha\text{-SOMO} \quad (2)$$

The initial hint for possibility of $\text{SHI} > 0$ came from unrestricted INDO computation on galvinoxyl radical (Figure 5, Section 2.3), which showed the energy of α -SOMO in between α -HOMO and β -HOMO, with apparent $\text{SHI} < 0$.²⁶² The first organic radical with $\text{SHI} > 0$ was reported for **TEMPO-TTF** in 1993 by Sugimoto et al. (Figure 6).²⁶³ Significance of $\text{SHI} > 0$ was first recognized by Sugawara and coworkers in a series of '1990 – '2000 publications,²⁶⁴⁻²⁶⁸ describing an effort to develop

purely organic ferromagnetic metals, which was beautifully summarized in their '2011 review article.²⁶⁹ Their radicals largely consist of nitronyl nitroxide connected via C2 to an electron-rich π -systems (Figure 6); upon 1-electron oxidation of the π -system $S = 1$ ground state diradical cation is typically obtained, as discussed in Section 4.3. The $\text{SHI} > 0$ in such radicals may be rationalized²⁷⁰ by higher electronegativity of oxygens and nitrogens, associated with nitronyl nitroxide, at which SOMO orbital is primarily localized; HOMO is primarily localized on the π -system.

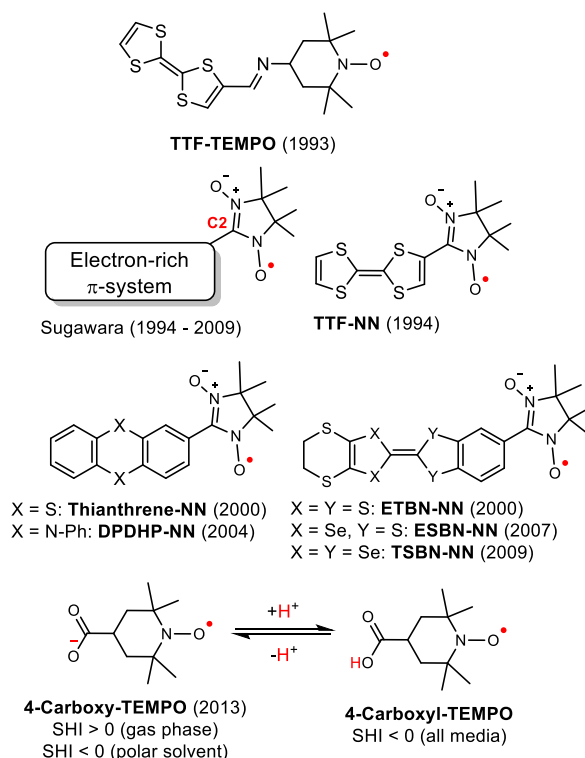


Figure 6. Examples of Sugimoto (1993), Sugawara (1994 – 2009), and Coote (2013) radicals with $\text{SHI} > 0$.

The '2013 landmark publication by Coote and co-workers demonstrated both computationally and experimentally that distonic radicals (spin and charge localized on separate atoms), such as **4-Carboxy-TEMPO** (Figure 6), are stabilized by $\text{SHI} > 0$ in the gas phase, as shown by smaller NO-H bond dissociation energies associated with the $\text{SHI} > 0$ radical.²⁷¹ However, later they showed that the effect is diminishing in polar solvents, and especially in water, where $\text{SHI} < 0$ is obtained.²⁷² Luccarini et al. confirmed experimentally the absence of extra stabilization in polar solvents for the radicals such as **4-Carboxy-TEMPO**.²⁷³

While organic radicals in general serve as efficient fluorescence quenchers,^{196,274} certain radicals with donor acceptor structures (D–A•), where A• is an electron withdrawing radical unit, may be luminescent.¹⁵² In such radicals, the ground state and excited state are both doublet ($S = 1/2$) states, facilitating spin-allowed radiative transitions, which is especially important for organic light emitting diodes (OLEDs).²⁷⁵ Discovery of photoluminescence in tris(2,4,6-trichlorophenyl)methyl (TTM) radical substituted with electron-rich π -systems based on carbazoles dates to 2006/2007, though the reported quantum yields of fluorescence were rather low, $\Phi_f < 0.6\%$.²⁷⁶ Analogous perchlorotriarylmethyl (PTM) radicals, with $\text{SHI} > 0$, showed outstanding photostability, e.g., **PTM-3NCz** (Figure 7).²⁷⁷⁻²⁸⁰ A few other PTM and TTM radicals π -conjugated with electron-rich carbazole-based non-alternant π -systems were found to possess very high values of Φ_f (Figure 7).^{275,277,281-284} Moreover, such radicals provide building blocks for near infra-red OLEDs.^{277,280,282,284} Such radical-based red-colored OLEDs could be refined to give a very good maximum external quantum efficiency (EQE_{max}) of up to 27% (Figure 7).^{280,284}

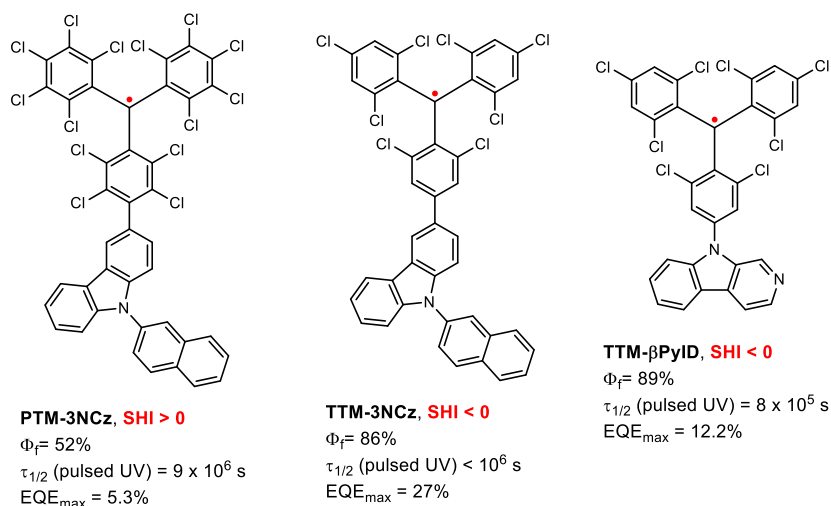


Figure 7. Examples of luminescent chlorinated triarylmethyl radicals.

3.2. Radicals and radical ions embedded in helical π -systems.

[n]Helicenes and corresponding double helical structures are fascinating compounds with some of the strongest molecular chiroptical properties.²⁸⁵⁻²⁸⁷ Paramagnetism, associated with an $S = 1/2$ radical

conjugated within helical or double helical π -system, may render unique properties due to the combination of chirality and delocalized electronic spin that could facilitate discovery of new organic magneto-optic materials and devices.²⁸⁸⁻²⁹⁴ There are relatively few open-shell helical molecules with such a distinctive combination of properties, and they are mostly represented by radicals or radical ions of short helical structures. In Figure 8, we show recent examples helical radicals, for which the sign of SHI was not reported.²⁹⁵⁻²⁹⁸

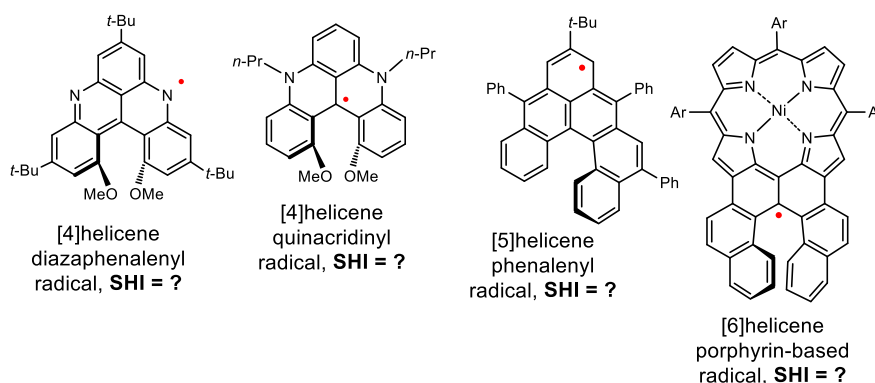


Figure 8. Examples of helical $S = \frac{1}{2}$ radicals.

Notably, monolayer of diamagnetic [4]helicene quinacridinyl cation (derived from the radical in Figure 8) on highly oriented pyrolytic graphite (HOPG) provides efficient spin filtering with ca. 50% spin polarization at room temperature, as measured with magnetic conductive probe atomic force microscopy; also, the same cation gives an unusual temperature independent (1.6 – 300 K), antisymmetric magnetoresistance, $MR = 2\%$, with the enantiomer-dependent sign.²⁹⁰ Considering that achiral organic $S = \frac{1}{2}$ radicals were computed to provide significant spin polarizations, depending on the radical type and substitution,²⁹⁴ chiral helical and double helical radicals have a significant potential in development of organic spin filters.

Since $SHI > 0$ becomes commonly associated with improved stability of the radical, it is important to compare different radicals vs. their SHI status (Figure 9). For example, among hetero[7]helicene radical cations^{299,300} and aminyl radical,³⁰⁰ $SHI > 0$ may be associated with longer $\tau_{1/2}$ in solution at room temperature, e.g., for relatively sterically unencumbered aminyl radical **AT7HA** $\tau_{1/2} = 8$ h in

dichloromethane/acetonitrile (DCM/MeCN) at room temperature was determined in 2016 (Figure 9).³⁰⁰ Conjoined double helical radical cation **CD5H** shows $\text{SHI} > 0$ according to Eq. 1 (Figure 9), though as reported in 2019 its αSHI is less than 0 (“near degenerate $\alpha\text{-SOMO}$ and $\alpha\text{-HOMO}$ ”).³⁰¹ The persistence of the radical cation, which could be isolated and handled on air with near perfect spin concentration, was not studied rigorously. However, the corresponding $S = 1$ ground state diradical dication, which is most likely more reactive than the radical cation, possessed $\tau_{1/2} = 16$ d in air-saturated dibutyl-phthalate in the presence of excess of oxidant ($[\text{NO}][\text{SbF}_6]$).³⁰¹

In 2020, Favereau and coworkers were able to isolate, resolve, and characterize two radical cations with $\text{SHI} > 0$: axially chiral **DCb** and helical **DCb7H**.³⁰² The greater persistence of **DCb**, compared to **DCB7H**, may possibly be associated with the stronger SHI (Figure 9).²⁵⁹

Racemic radical cations of thiophene double helix, with high spin concentrations, were studied in solution in 2021.³⁰³ Interestingly, spin density was delocalized just over the carbon atoms (g -values of 2.0012 and 2.0017) in the single α,β -cyclooctatetrathiophene ($\alpha,\beta\text{-COTh}$) moiety, highlighted in yellow color for **TDH-TMS₈** and **TDH-TMS₁₂** (Figure 9). Consequently, reduction potentials for both radical cations were similar (ca. +1.33 V vs SCE). It should be noted that while D_2 -symmetric radical cation **TDH-TMS₈** consists of a single central $\alpha,\beta\text{-COTh}$ moiety, which is flanked by the two $\beta,\beta\text{-COTh}$ moieties, C_2 -symmetric radical cation **TDH-TMS₁₂** consists of three $\alpha,\beta\text{-COTh}$ moieties, flanking the two $\beta,\beta\text{-COTh}$ moieties. Notably, **TDH-TMS₈** with $\text{SHI} < 0$ was considerably more persistent ($\tau_{1/2} > 12$ h in degassed DCM at rt), compared to **TDH-TMS₁₂** ($\tau_{1/2} \approx 5$ min in degassed DCM at rt). This is an unusual case where SHI does not control the persistence of radicals. The greater persistence of **TDH-TMS₈** was associated with steric shielding of all carbons bearing significant spin density within $\alpha,\beta\text{-COTh}$ moiety by the two adjacent $\beta,\beta\text{-COTh}$ moieties (and TMS groups).³⁰³

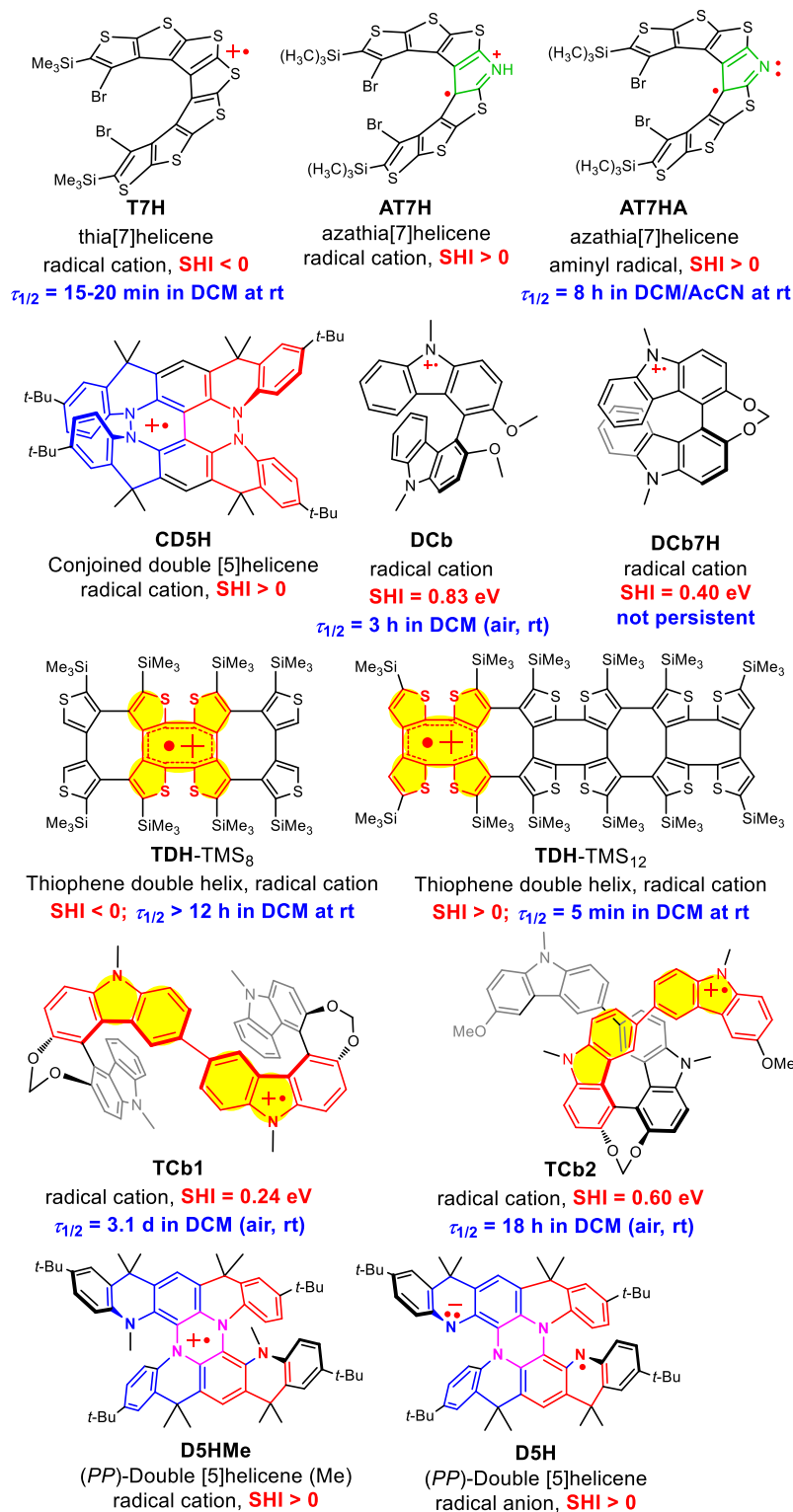


Figure 9. Examples of helical and double helical $S = \frac{1}{2}$ radicals for which SHI (eq. 1) was determined.

In 2022, Favereau and coworkers were able to synthesize, resolve, and study tetra-carbazole radical cations (and the corresponding diradical dications) **TCb1** and **TCb2**, both with $\text{SHI} > 0$, derived from previously prepared **DCb7H** (Figure 9).³⁰⁴ In these radical cations, spin density is localized primarily on the 6,6'-dicarbazole (6,6'-DiCb) moiety as highlighted in yellow for **TCb1**. In analogy

to the thiophene double helices discussed above, **TCb1** consists of a single central 6,6'-DiCb moiety, flanked by two carbazoles, **TCb2** consists of two terminal 6,6'-DiCb moieties. Based on the discussion in the preceding paragraph, it is not surprising that **TCb2** is less persistent (vs. **TCb1**), in spite of having stronger $\text{SHI} > 0$ and being “protected” by the methoxy groups. We note that enantiomerically enriched tetra-carbazole radical cations provided surprisingly weak chiroptical properties, e.g., $\Delta\epsilon$ of the order of $5 \text{ L mol}^{-1} \text{ cm}^{-1}$.³⁰⁴

We conclude this section with a note concerning the ground states of the single electron oxidized species corresponding to compounds in Figure 9, to be discussed in a more general fashion in the following Section 3.3. While the radical cation derived from relatively persistent aminyl radical **AT7HA** was predicted computationally to possess $S = 1$ ground state (Section 3.3),³⁰⁰ we were not able to confirm it experimentally. Diradical dication of **CD5H** in dibutyl-phthalate possesses $S = 1$ ground state with experimentally determined $\Delta E_{\text{ST}} \approx 0.3 \text{ kcal mol}^{-1}$ (Section 4.4).³⁰¹ Favereau’s diradical dications and those derived from thiophene double helices are either singlet ground states or possess near degenerate singlet and triplet states.^{303,304} Diradical dication of **D5HMe** and aminyl diradical of **D5H** are predicted by DFT computations to be triplet ground states (Section 3.3).

3.3. Is there a relation between the SOMO-HOMO electron energy difference (SHI) in monoradicals (ions) and singlet triplet energy gap (ΔE_{ST}) in diradicals (ions)?

Sugawara in his ‘2011 review noted that when some of the nitronyl nitroxide radicals with $\text{SHI} > 0$ are oxidized to the corresponding radical cations, triplet ground state species are obtained,²⁶⁹ with some exceptions.^{264,266} Here we seek a more quantitative relationship between SHI in $S = \frac{1}{2}$ monoradicals, defined by Eq. 1, and ΔE_{ST} in the corresponding diradicals. Since SHI is derived from DFT computations, we explore a relationship between DFT-determined ΔE_{ST} and SHI in the gas phase. In Figure 10, we summarize the structures of $S = \frac{1}{2}$ monoradicals with their SHI values, which provide

an excellent linear regression with ΔE_{ST} in the corresponding diradicals (Figure 11). Structures of the three outliers, not included in the regression, are shown in Figure 12.

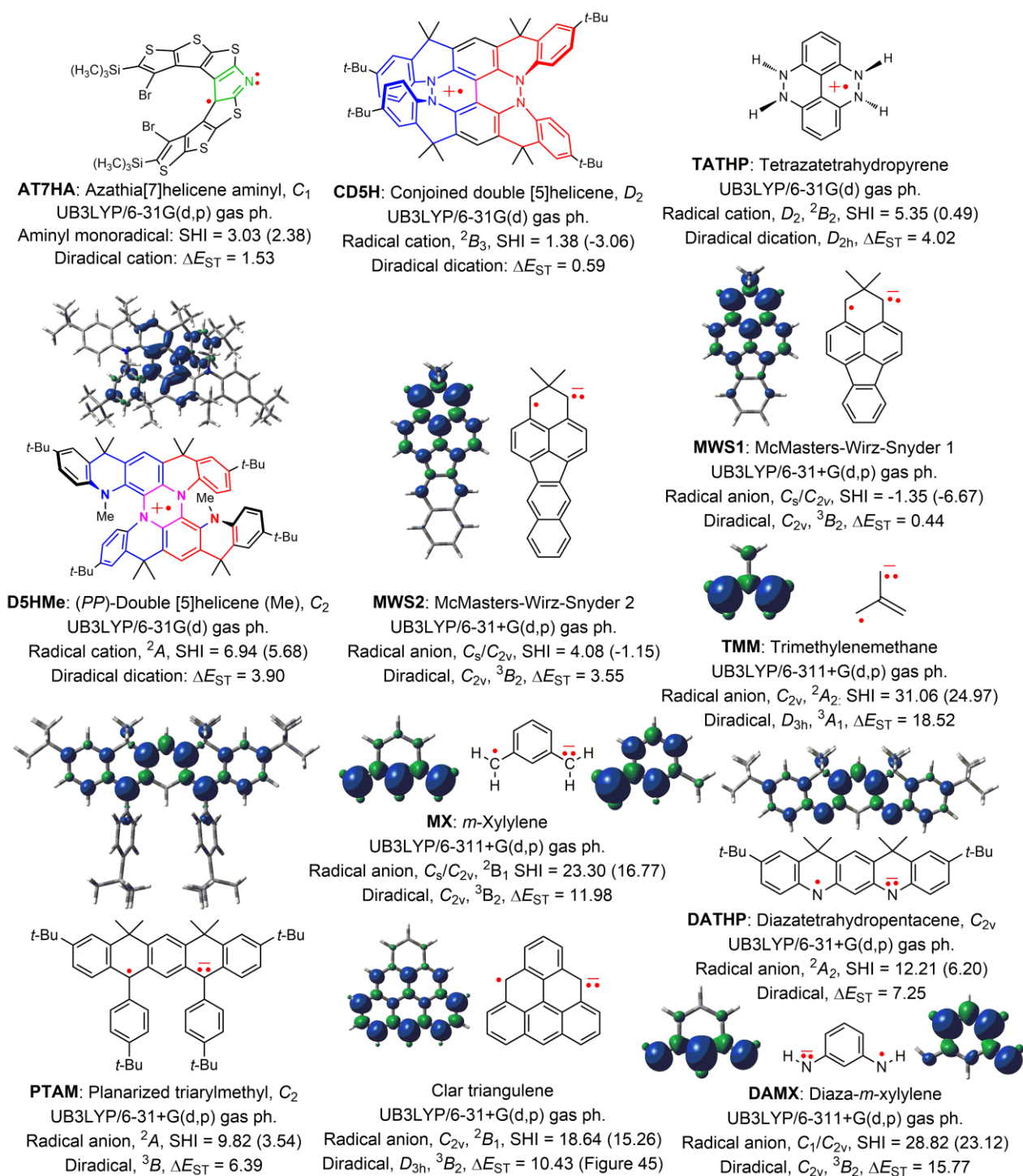


Figure 10. Structures and spin density maps (isodensity level of 0.002 electron/Bohr) used for linear regression of singlet-triplet energy gaps, ΔE_{ST} (kcal mol⁻¹) vs. SHI (kcal mol⁻¹); see: the following Figure 11. ΔE_{ST} values are for diradicals and SHI values are for one-electron reduced species; e.g., radical anions for neutral diradicals. Except for double helical **D5HMe**, all diradicals were studied before; also, spin density maps for **AT7H**, **CD5H**, and **TATHP** may be found in refs 300 and 301. SHI values are from eq. 1 and the values in parentheses are in terms of α -MO's (eq. 2). Values of ΔE_{ST} were typically computed at the UB3LYP/6-31G(d,p)+ZPVE (or UB3LYP/6-311+G(d,p)+ZPVE) level of theory (gas phase) and were corrected for spin contamination; geometries for both triplet and BS singlet (checked for stability) were optimized.

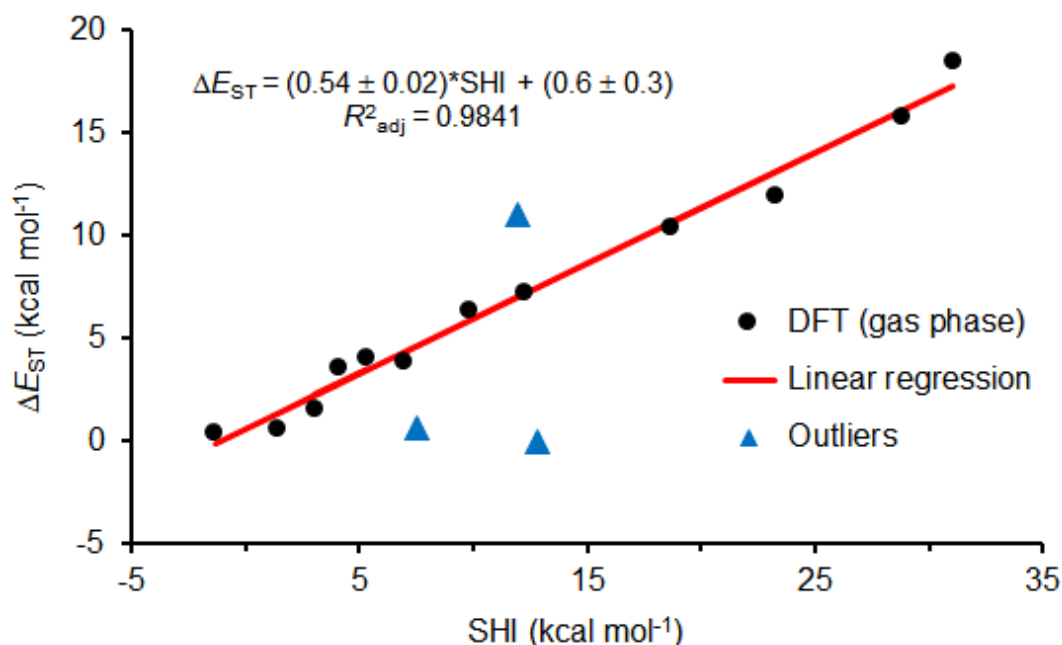


Figure 11. Linear regression between DFT-computed ΔE_{ST} and SHI (Eq. 1) for twelve C- and N-centered diradicals. The value of $P = 1.55 \times 10^{-10}$ for slope indicates that the value of 0.54 is reliably determined, however, $P = 0.099 > 0.05$ for intercept indicates that the value of 0.6 is not statistically significant. All ΔE_{ST} and SHI values are computed in the gas phase (see: preceding Figure 10), typically, at the UB3LYP/6-31G(d,p)+ZPVE and UB3LYP/6-31+G(d,p)+ZPVE levels of theory, respectively. Outliers are not included in the linear regression (see: following Figure 12).

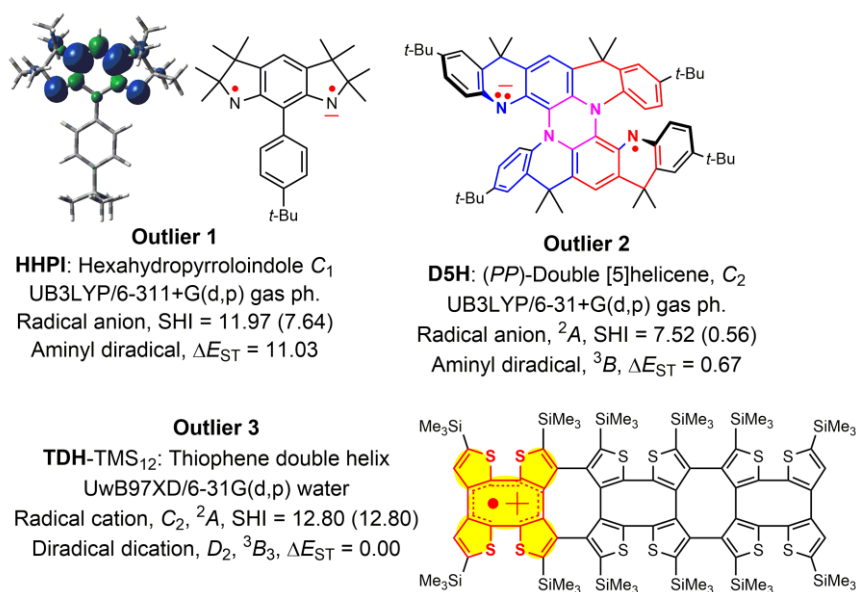


Figure 12. Structures for outliers in the linear regression of singlet-triplet energy gaps, ΔE_{ST} (kcal mol⁻¹) vs. SHI (kcal mol⁻¹); see: the preceding Figure 11. ΔE_{ST} values are for diradicals, and SHI values are one-electron reduced species, e.g., radical anions derived from neutral diradicals. Aminyl diradical (corresponding to Outlier 1)^{112,114} and radical cation (Outlier 3)³⁰³ were studied both experimentally and computationally. Radical anion **D5HMe** and corresponding aminyl diradical were not previously studied. SHI values in parentheses are in terms of α -MO's. Values of ΔE_{ST} were typically computed at the UB3LYP/6-31G(d,p)+ZPVE (or UB3LYP/6-311+G(d,p)+ZPVE) level of theory (gas phase) and were corrected for spin contamination.

Notably, the correlation between the twelve values of ΔE_{ST} (Figures 10 and 11) and corresponding

values of α SHI (as defined by Eq. 2) is significantly worse, as indicated by the values of statistically adjusted coefficients of determination, i.e., $R_{\text{adj}}^2 = 0.935$ vs 0.984 (Figure 11).

One of the weaknesses of the present approach is the use of the UB3LYP functional in the gas phase, which provides symmetric structures for radical anions, especially for *m*-phenylene-based structures. Already in 1991, it was established experimentally that in tetrahydrofuran or 2-methyltetrahydrofuran (THF or 2-MeTHF) in the non-planarized *m*-phenylene-based triarylmethyl radical anions (for a “planarized” version, i.e., **PTAM**, see: Figure 10), spin density is localized on one of the triarylmethyl moieties on the EPR spectroscopic time scale. This distortion was rationalized in terms of second order Jahn-Teller effect.³⁰⁵ Consequently, for radical anion of *m*-xylylene, **MX** (Figure 10), we find that while using UB3LYP C_{2v} -symmetric structure is obtained, but when employing UwB97XD functional in THF PCM solvent model, C_s -symmetric structure, with spin density confined to one phenylmethyl moiety, is found to be the global minimum. Analogous results were found for **TDH-TMS**₁₂ (and related radical cations)³⁰³ and radical anions **DAMX** (Figure 10), as well as **PTAM**.

Next, we investigated nitronyl nitroxide based radical anions derived from $S = 1$ ground state diradicals, spanning a wide range of DFT-computed ΔE_{ST} from 1.4 to 9.8 kcal mol⁻¹ (Figure 13). The first three radical anions in Figure 13 are derived from thoroughly studied experimentally $S = 1$ ground state diradicals (Section 4.3). The other three radical anions or diradicals are not explored experimentally yet. We were somewhat surprised by the bad linear regression between ΔE_{ST} and SHI (Figure 14), despite structural similarity between all six diradicals. In particular, P -values of $\gg 0.05$ for slope and intercept, 0.60 and 0.38, indicate that they are not statistically significant.

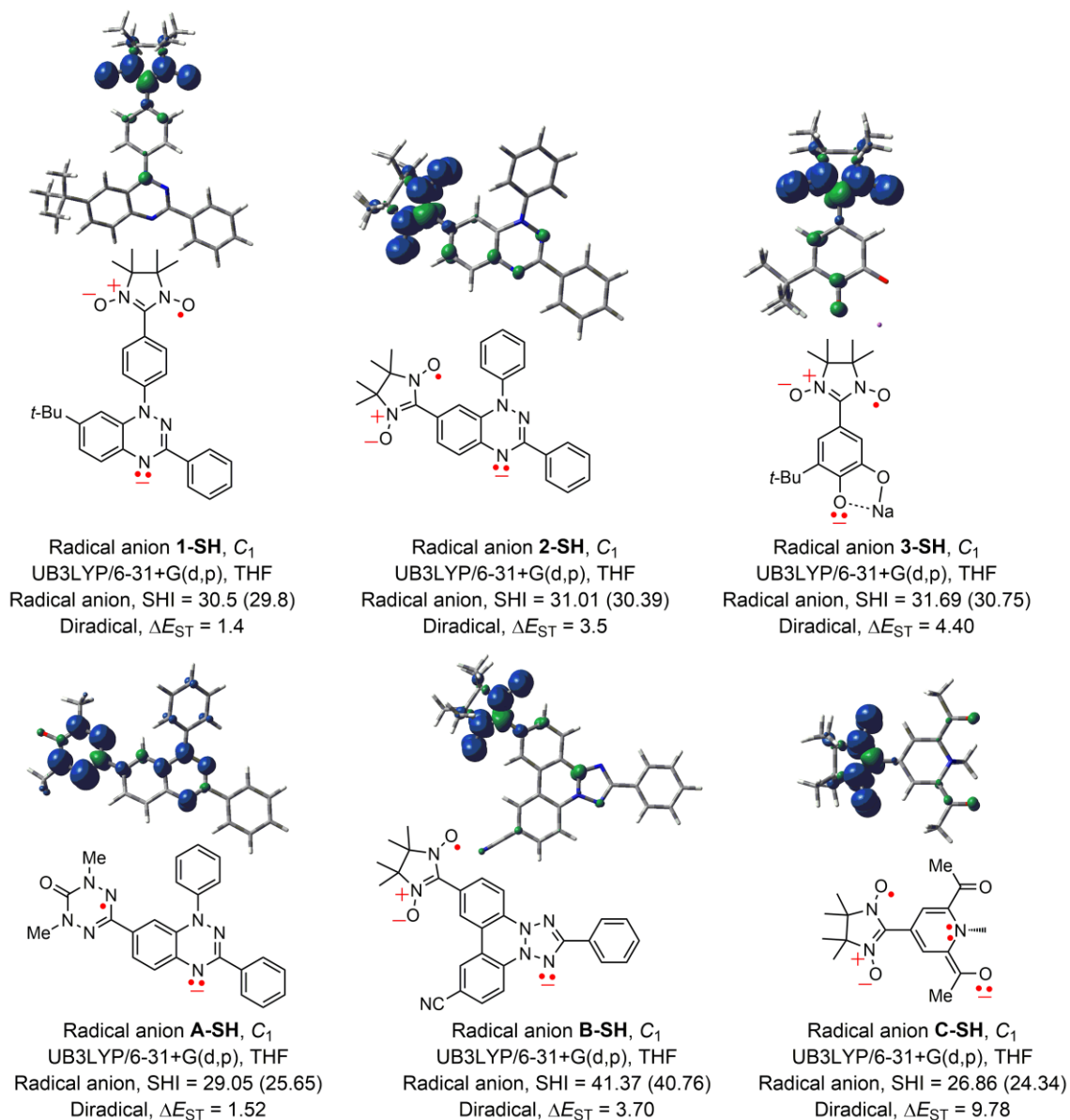


Figure 13. Structures and spin density maps (isodensity level of 0.002 electron/Bohr) of radical anions with strong SHI (kcal mol^{-1}), which fail to provide linear regression with corresponding diradicals singlet-triplet energy gaps, ΔE_{ST} (kcal mol^{-1}); see: following Figure 14. Radical anions **1-SH** – **3-SH** are derived from previously synthesized diradicals; radical anions **A-SH** – **C-SH** and corresponding diradicals were not previously studied. SHI in parenthesis is in terms of α -MO's. Values of ΔE_{ST} were typically computed at the UB3LYP/6-31G(d,p)+ZPVE (gas phase) level of theory and were corrected for spin contamination.

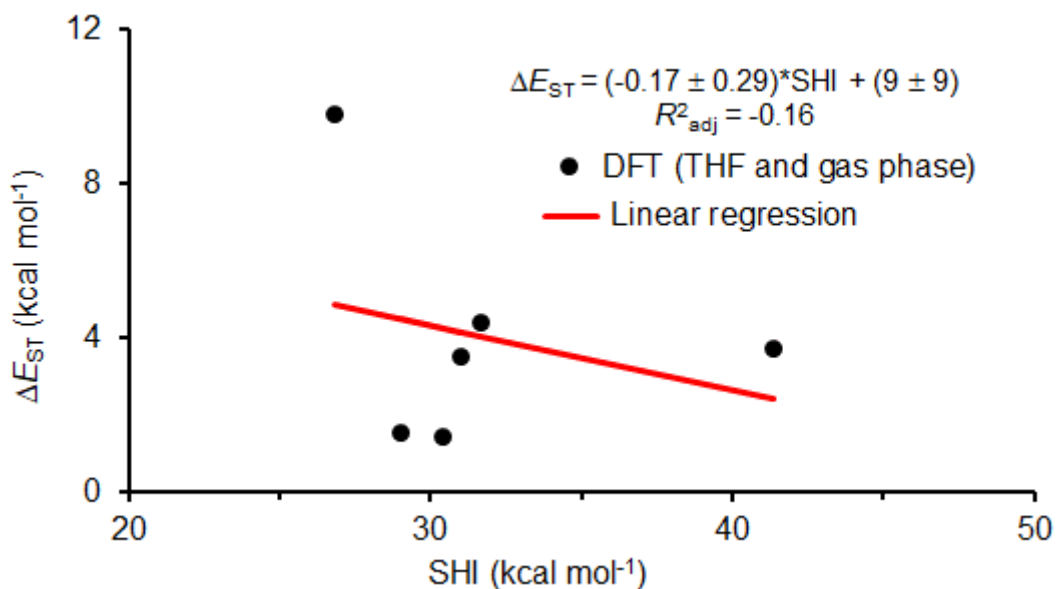


Figure 14. Failed linear regression between DFT-computed ΔE_{ST} (gas phase) and SHI (THF) for nitronyl nitroxide (and oxo-verdazyl) based high-spin diradicals and corresponding radical anions; see: preceding Figure 13.

We associate this failed linear regression (Figure 14) to dominance of electronegativity as the major factor controlling the value of SHI in nitronyl nitroxide based radical anions. Also, some of the structures show significant distortions from planarity.

4. High-Spin Di- and Tri-Radicals.

4.1. Design rules for high-spin di- and polyradicals.

Stable high spin organic radicals ($S \geq 1$) are attractive targets for organic materials for potential applications such as organic magnets,^{32,306,307} spintronics,^{7,308} spin filters,³⁰⁸⁻³¹⁰ and memory devices.^{311,312} Compared to many existing stable $S = 1/2$ monoradicals, only relatively few of stable and even fewer thermally robust high-spin organic radicals were reported. Developing new high-spin molecules is challenging, and this part of the review will focus on recent work from ours and other groups.

Organic monoradicals, containing one unpaired electron, can be considered as the fundamental spin-bearing units or centers ($S = 1/2$). In a di- or triradical, in which multiple radical $S = 1/2$ centers are

conjugated, exchange coupling between $S = \frac{1}{2}$ spin centers may lead to either high- or low-spin ground state. The main objective in the molecular design of high-spin di- and triradicals is to obtain ferromagnetic coupling between $S = \frac{1}{2}$ centers, 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.

Design of high-spin di- and triradicals for practical applications requires that the following two minimal conditions are satisfied.^{313,14}

- (1) The high-spin ground state should be at least a couple of kcal mol⁻¹ ($\gg RT = 0.6$ kcal mol⁻¹ $\approx$ thermal energy at room temperature) below the lowest excited state,
- (2) The radicals should be stable, or at least persistent, at room temperature to be easily handled without special precautions.

In a diradical, exchange coupling between two $S = \frac{1}{2}$ spin centers $\mathbf{S}_1$ and $\mathbf{S}_2$ could be described by the effective Heisenberg Hamiltonian:^{314,315}

$$\mathbf{H} = -2J\mathbf{S}_1 \bullet \mathbf{S}_2 \quad (3)$$

where the factor of “-2” is traditionally used in chemistry literature. Parameter J is the exchange coupling constants, usually given in Kelvins (K) as J/k (k is the Boltzmann constant), or alternatively, singlet triplet energy gap, $2J = \Delta E_{ST}$, usually reported in kcal mol⁻¹. Negative J value requires the lowest energy state to have antiparallel spins, leading to antiferromagnetic interaction, i.e., the case of low-spin ground state. Positive J value means the lowest energy states have parallel spins and ferromagnetic interaction occurs, i.e., the case of high-spin ground state. The energy gap between singlet and triplet states (ΔE_{ST}) therefore is given by $2J$. In other words, the ground state type, high-spin or low-spin, and the corresponding energy gap are decided by the sign and magnitude of J value.^{313,14}

In planar π -conjugated diradicals, corresponding to alternant π -systems, ferromagnetic vs.

antiferromagnetic exchange coupling between $S = 1/2$ spin centers is governed by the π -connectivity and can be qualitatively predicted using Ovchinnikov parity models.³¹⁶ It is also assumed that the through-bond exchange interactions between $S = 1/2$ spin centers are dominant in π -conjugated radicals.^{313,14} In the models, each adjacent spin in the π -system is assumed to possess the opposite spin of its nearest neighbor. The difference between the spin-up count vs the spin-down count decides the ground state, e.g., if difference equals to two, then the $S = 1$ triplet ground state is predicted (Figure 15).³¹⁶

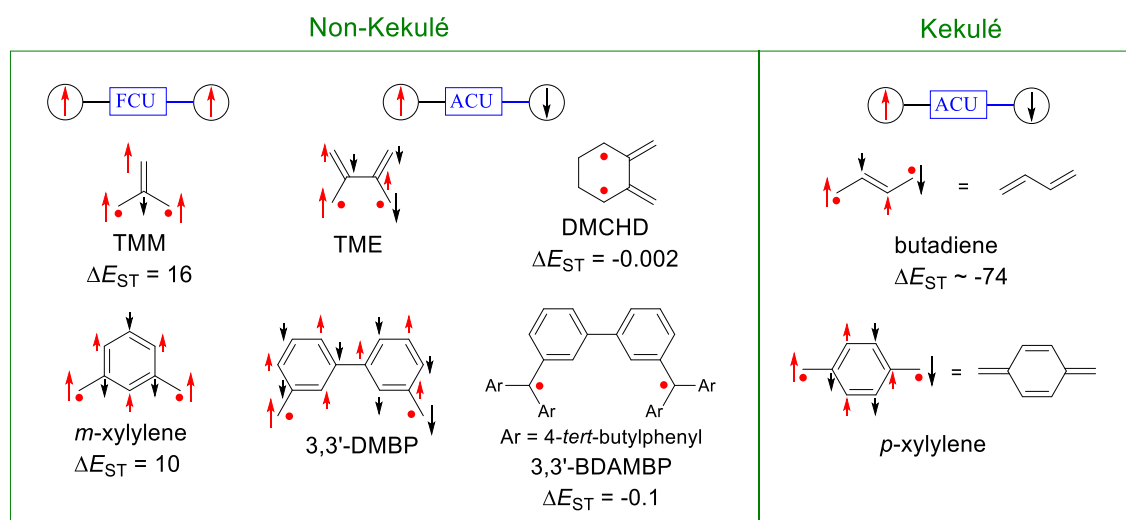


Figure 15. Ferromagnetic and antiferromagnetic exchange coupling predicted using Ovchinnikov parity models. Values of ΔE_{ST} are in kcal mol⁻¹. Reproduced from ref 314. Copyright 2015 American Chemical Society.

Using methyl radicals as $S = 1/2$ spin centers and ethylene as a coupling unit, we can see that the 1,1-connection at ethylene leads to non- Kekulé TMM, a triplet ground state molecule and 1,2-connection provides Kekulé butadiene, a closed shell molecule with a singlet ground state. While TMM and butadiene possess large ΔE_{ST} ,³¹⁷⁻³¹⁹ another non- Kekulé molecule such as TME, obtained by 1,1-connection of two ethylenes with two methyl radicals, is a singlet ground state with a very small ΔE_{ST} .^{320,321} Analogous results are obtained for *m*-xylylene, *p*- and *o*-xylylene and 3,3'-dimethylenediphenyl (3,3'-DMBP) (Figure 15).^{322,323}

Coupling units that lead to ferromagnetic coupling between $S = 1/2$ spin centers (e.g., 1,1-ethylene,

m-phenylene) are termed ferromagnetic coupling units (FCU's), and those that lead to antiferromagnetic coupling (e.g., 3,3'-biphenyl) are termed antiferromagnetic coupling units (ACU's) (Figure 15).^{313,324}

Although it was believed for a long time that the presence of Kekulé resonance form implied a singlet ground state, the exceptions to this rule will be discussed in Section 4.4.

Ovchinnikov parity models are simple and convincing tools for predicting the ground state of π -conjugated diradicals. However, the strength of exchange interaction is unclear from the parity models. What causes the huge difference in $|\Delta E_{ST}|$ between TMM and TME? To understand this problem, the singly occupied molecular orbitals (SOMOs) are considered in the diradicals. Borden and Davidson classified the SOMOs can be non-disjoint (spatially coinciding at some atoms) and disjoint (not spatially coinciding at any atoms).³²⁵ Exchange interaction is weak for disjoint SOMOs such as in TME, while exchange interaction is strong and ferromagnetic for non-disjoint SOMOs in TMM (Figure 16).^{318,319,321} In TMM, when two unpaired electrons align parallel, a node is introduced in the spatial part of the wave function and, as a result, the Coulombic repulsion is reduced effectively in the spatially coinciding area.³²⁵ Analogous conclusions are reached for *m*-xylylene and 3,3'-DNBP (Figure 16).

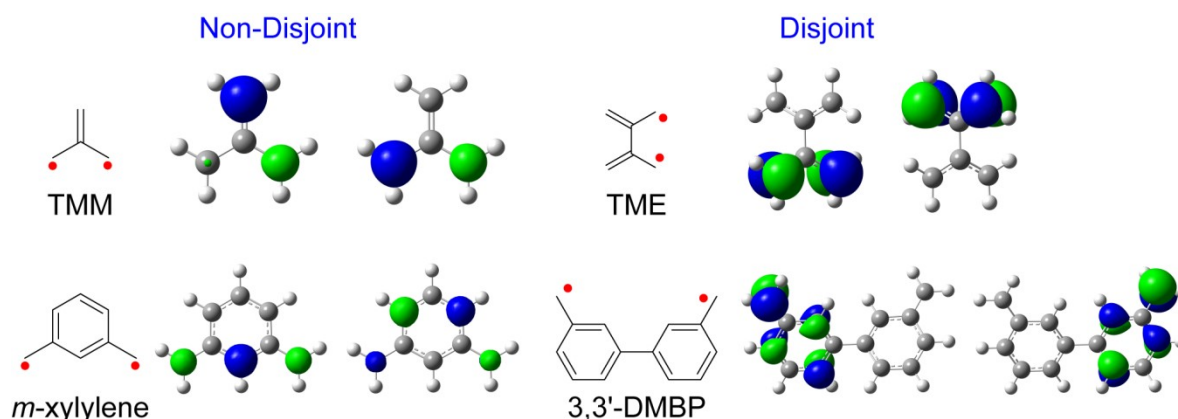


Figure 16. Singly occupied MO's (SOMO's) of triplet states for disjoint and non-disjoint non-Kekulé diradicals at the UB3LYP/6-311G(d,p) level. Reproduced from ref 314. Copyright 2015 American Chemical Society.

4.2. Magnetic characterization of diradicals and triradicals.

Electron paramagnetic resonance (EPR) spectroscopy and superconducting quantum interference device (SQUID) magnetometry are two dominant tools for studying magnetic properties of high-spin radicals. There is also a role for NMR spectroscopy. Most important objectives are determination of ground state and of energy gaps between low- and high-spin states, $\Delta E_{\text{LS-HS}}$.

4.2.1. EPR spectroscopy.

Continuous wave (CW) EPR spectroscopy is widely utilized to measure the high-spin state spectra of radicals ($S \geq 1$), for which g -tensor and zero-field splitting (ZFS) parameters D and E , and in favorable cases, large components of nuclear hyperfine coupling tensors A , are obtained. Because the ZFS parameters are inherently anisotropic, the samples are measured in frozen glassy matrices, with typical radical concentration of <1 mM, to minimize the intermolecular interactions. Specifically in organic radicals, composed of light elements, ZFS parameters largely originate in purely anisotropic magnetic dipole – dipole interactions, thus D -value in diradicals provides approximate measure inter-spin distance.^{326,327}

For $S \geq 1$ states with significant (D/ν) -values, where ν is microwave frequency, characteristic half-field, formally forbidden transitions ($|\Delta m_S| = 2$) may be detected; in the absence of resolvable nuclear hyperfine couplings, $|\Delta m_S| = 2$ transition corresponds to a single peak for $S = 1$ state, while more complex pattern is observed for $S \geq 3/2$ states.^{24,328,329} In favorable cases, $|\Delta m_S| = 3$ transition (third-field) may be detected for triradicals at low temperature using commonly available X-band instruments ($\nu = 9$ GHz).^{24,328,329}

Detection of EPR spectra for high-spin state only shows that the high-spin state is significantly populated at the temperature of measurement, and *it does not establish the ground state*. This is especially true for diradicals because the low-spin state ($S = 0$) is typically EPR silent. The same

statements are valid for more sophisticated pulse EPR nutation spectra, where the frequencies characteristic for $S = 1/2, 1, 3/2 \dots$ states may be observed. Note that that even if only nutation frequencies corresponding to $S > 1$ state are observed, this does not mean that this state is the ground state, because the low-spin $S \geq 1/2$ states may possess unfavorable electron spin relaxation times to be efficiently observed in the nutation experiment.

The traditional way to obtain a better insight to the nature of the ground state was to study the double integrated intensity (I) of EPR spectrum vs. temperature (T). When a curved plot of IT vs. T or I vs. $1/T$ is obtained then the ground state may be unequivocally established, when the precautions against microwave saturation are taken (see: below). That is, if the plots are curved upwards at lower T , which implies increased population of high-spin state, and this, in turn, implies high-spin ground state.³¹³ Downward curvatures at lower T imply low-spin ground state.³¹³ Energy gaps between the low- and high-spin state, $\Delta E_{\text{LS-HS}}$, may be obtained by numerical fitting to equations obtained by solutions of Heisenberg Hamiltonian (eq. 4),

$$\mathbf{H} = -2\sum J_{kj}\mathbf{S}_k \bullet \mathbf{S}_j \quad (4)$$

where the nearest neighbor spins are typically considered, J_{kj} is the pairwise exchange coupling constant, and the summation is done over all nearest neighbors for k, j from 1 to n (n = total number of $S = 1/2$ sites).^{313,330} For a diradical, singlet triplet energy gap, $\Delta E_{\text{ST}} = 2J_{kj}$; more complex, connectivity dependent formulas are found for doublet quartet energy gap ΔE_{DQ} in triradicals.³³⁰

However, the most common occurrence is a flat plot of IT vs. T or linear plot of I vs. $1/T$, which indicates the temperature independent ratio of the high- to low-spin states; consequently, *this implies either high-spin ground state (case 1) or near degenerate high- and low-spin states (case 2)*. Specifically, in the second case, the energy gap between the low- and high-spin state, $|\Delta E_{\text{LS-HS}}| < 0.5RT_{\text{lowest}}$, where T_{lowest} is the lowest temperature at which the I is measured; in the first case of the high-spin ground state, this means approximately $\Delta E_{\text{LS-HS}} > 2RT_{\text{highest}}$, where T_{highest} is the highest

temperature of the I -measurement. For example, if $T_{\text{lowest}} = 5$ K and $T_{\text{highest}} = 150$ K, then the following limiting values may be obtained: $|\Delta E_{\text{LS-HS}}| < 0.005$ kcal mol⁻¹ or $\Delta E_{\text{LS-HS}} > 0.6$ kcal mol⁻¹ for the second and first case, respectively. It is important to avoid microwave saturation, especially at low temperatures, by either obtaining rigorous microwave saturation plots (I vs. $P^{1/2}$) at near T_{lowest} , where P is microwave power in the range of at least two orders of magnitude, or by acquiring the I vs T data at significantly different microwave powers.^{323,329,331} Typically, I of $|\Delta m_S| = 2$ transition is studied, because this partially forbidden transition is much more difficult to saturate³³² and it may be well separated from the impurity peaks. In addition, when claiming purity of $S = 1$ diradical, one has to make sure that the spectrum is obtained under the conditions, in which the $S = \frac{1}{2}$ monoradical is not partially saturated.

More recently, our group introduced quantitative variable temperature EPR spectroscopy for studies of di- and triradicals.^{147,149,150,301,333} Instead of IT vs. T plots, χT vs. T are plotted, where χ is paramagnetic susceptibility of the sample, determined with $S = \frac{1}{2}$ reference. The χT vs. T plots are advantageous when trying to extract more than one J -value¹⁵⁰ because, if the radical is pure and its weight is known accurately,¹⁵⁰ then there are no additional parameters, beyond the J -values, to fit, thus avoiding over parametrization – a common problem when fitting EPR intensity or magnetic data. Notably, in selected not-too-polar solvents and matrices, such as dibutyl phthalate, toluene/chloroform, etc., reliable values of χT can be obtained at near and above room temperature in a fluid solvent.^{147,150,301} It is important that the $S = \frac{1}{2}$ reference (e.g., TEMPONE) is dissolved in the identical solvent as the sample and its spectra are obtained with comparable parameters. Now there is no ambiguity concerning the ground state because, if only high-spin ground state is predominantly populated, then, assuming $g \approx 2$, $\chi T = S(S+1)/2$ emu K mol⁻¹, e.g., $\chi T = 1.00$ emu K mol⁻¹ for $S = 1$ ground state diradical. In contrast, when low- and high-spin states are near degenerate, which essentially means a mixture of $S = \frac{1}{2}$ radicals, for polyradical with n $S = \frac{1}{2}$ sites, $\chi T = n \cdot 0.5(0.5+1)/2$

emu K mol⁻¹, e.g., $\chi T = 0.75$ emu K mol⁻¹ for a diradical with near degenerate singlet and triplet states.

For some di-, tri-, and tetraradicals, the χT vs. T plots are not feasible up to near room temperature because of limited stability and/or preparation conditions for radical, requiring use of relatively polar ethereal solvents such as 2-MeTHF. In those cases, χT -values are measured at low temperatures ($T < 130$ K), near or below the glass transition of the solvent.^{114,115} In special cases, such as $S = 3/2$ aminyl triradicals **AT1** and **AT2** (Figure 17), where the EPR spectra for $S = 3/2$ ground state and $S = 1/2^*$ excited state (as well as for other admixed species) are significantly different, then the doublet-quartet energy gap $\Delta E_{DQ} \approx 1$ kcal mol⁻¹ may be obtained from direct spectral simulation by finding the ratio of $S = 1/2^*$ to $S = 3/2$ state.¹¹⁵ The obtained values of ΔE_{DQ} are in excellent agreement with those obtained from the SQUID data (see: below) but they require spectral simulations of multiple samples.

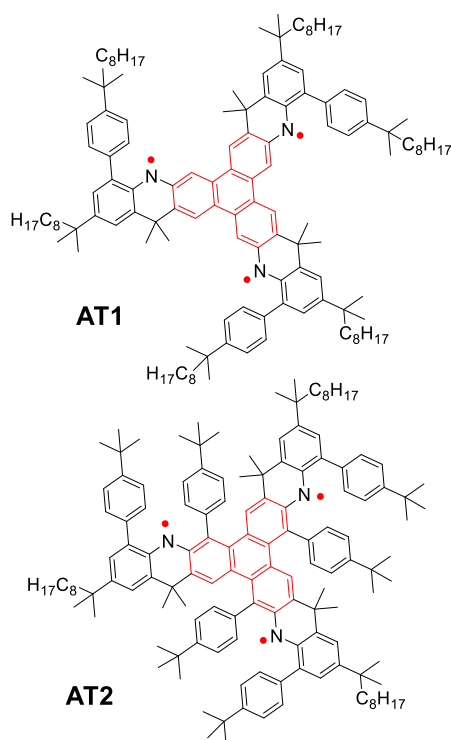


Figure 17. Aminyl triradicals with $S = 3/2$ ground states.

EPR spectroscopy is also a useful tool to investigate the persistence of radicals. When well-resolved spectra are available, monitoring of I vs. time is equivalent to obtaining concentration vs. time curve. When overlapped spectra are present, this approach provides depressed rate constants for the original high-spin radical, leading to overestimated half-lives, e.g., for $S = 3/2$ triradicals **AT1** and

AT2 (Figure 17). To obtain correct concentration (or molar fraction) vs. time curves, the spectra of decayed mixture of radicals must be simulated and corrected for the presence of diamagnetic species by the measurement of χT at each time point.¹¹⁵ This allows to unravel complex consecutive kinetics, such as for **AT1** and **AT2**.¹¹⁵

4.2.2. SQUID magnetometry.

Determination of the ground state value of total spin S and the energy gap $\Delta E_{\text{LS-HS}}$ by SQUID magnetometry is based on thermal population of either m_S -substates or low- vs. high-spin electronic (spin) states.

Magnetic measurements are traditionally carried out on polycrystalline solids. Because most organic radicals exhibit weak-to-moderate intermolecular antiferromagnetic interactions, this prevents implementation of the most powerful Brillouin function-based method for determination of the ground state for high-spin radical. This method is fundamentally based on detection of thermal population of m_S -substates in the presence of external magnetic field. To weaken the intermolecular interactions, SQUID measurements may be performed on dilute, 5 – 20 mM, samples in matrices. While various high- T_g polymer matrices were used for this purpose, our group have developed and perfected over the years solution/matrix sample containers that allow sample preparation at low temperature and minimize diamagnetic background.^{31,111,115} Using 5 – 20 mM radical samples, magnetization (M) is measured vs. external magnetic field (H) at low temperatures (usually 1.8, 2, 3, and 5 K). The saturated magnetization M_{sat} and the total spin S are obtained by fitting the plots of normalized magnetization M/M_{sat} vs. $H/(T - \theta)$ to the Brillouin function, where θ corresponds to the mean-field correction for residual intermolecular interactions (typically, $\theta < 0.1$ K). Because the *values of S* are based upon the curvature of the M/M_{sat} vs. $H/(T - \theta)$ plots, they are *independent of sample concentration*. The values of M_{sat} (in μ_B = Bohr magnetons) are concentration dependent and they provide spin concentration,

i.e., fraction of unpaired electron per radical site, e.g., $M_{\text{sat}} = 1.0 \mu_{\text{B}}$ implies perfect, 100% spin concentration per radical site.^{110-113,115,148}

For pure polycrystalline radicals, measurement of M vs. T at fixed values of H (e.g., 3, 0.5, and 0.05 Tesla) in both warming and cooling modes allows for routinely obtaining reliable χT vs. T plots in the wide temperature range (1.8–400 K). With the oven option for SQUID instrument, an extended temperature range of up to 800 K is available (Figure 18).³³⁴

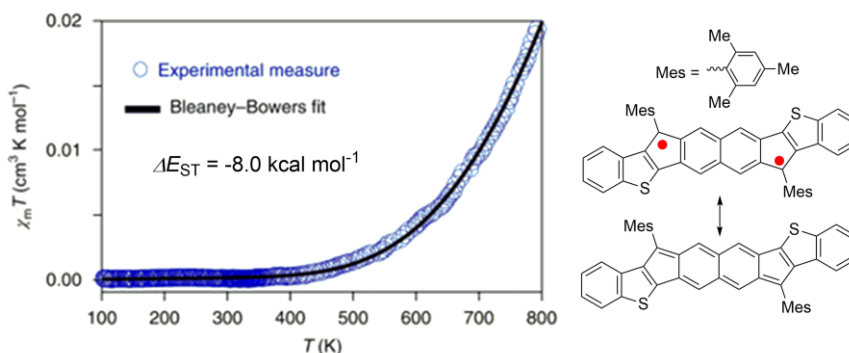


Figure 18. Example of SQUID magnetometry in the temperature range of 100 – 800 K, with fit to χT vs. T data giving $\Delta E_{\text{ST}} \approx -8.0 \text{ kcal mol}^{-1}$.³³⁴ Reproduced with permission from ref 334. Copyright 2018 Springer Nature.

To obtain reliable values of χ , especially at high T (near or above the room temperature) two critical conditions must be met.

- (1) The sample must be perfectly free of magnetic impurities (e.g., rust or other magnetic metal contaminants); i.e., as a minimum, χT vs. T plots must be coinciding at widely different values of H ,
- (2) A reliable correction for diamagnetism should be performed; as Pascal constant-based correction usually overestimates amount of diamagnetism, and thus leads to overestimated values of ΔE_{ST} – a common problem in the literature. A better approach is to do point-by-point correction with the diamagnetic precursor to the radical.

For a dilute radical in solution/matrix, obtaining a reliable χT vs. T plot is much more challenging. First, the positive $M_{\text{rad}} > 0$ with $M_{\text{rad}} \sim 1/T$ from radical will be superposed on a large negative $M_{\text{matrix}} < 0$ that is constant (i.e., independent of temperature); therefore, it is expected that for the measured $M = M_{\text{rad}} + M_{\text{matrix}}$, diamagnetic $M < 0$ values at high T and paramagnetic $M > 0$ at low T will be obtained.

Consequently, at some intermediate temperature range where $M \approx 0$, the value of M could not be measured reliably. Second, correction for diamagnetism is much more demanding; for solution samples, complete point-by-point correction is practical for radicals with limited persistence,³¹ and for polymer matrix samples, point-by-point correction can be carried out in order to at least offset the diamagnetism of the matrix and the sample holder.^{148,150} Third, while for thermally robust di- and triradicals in polystyrene matrix ($T_g = 373$ K), in custom-made quartz tubes, practical temperature range of 1.8 – 370 K is available.^{148,149} For radicals in organic solvents (e.g., THF and 2-MeTHF), a more limited range of 1.8 – 150 K is typical.^{110-113,115} (For a relatively concentrated, 20 mM tetraradical in 2-MeTHF, the χT vs. T data in the 1.8 – 200 K in the cooling mode could be obtained.)²¹⁴

Once a reliable χT vs. T plot is obtained, and assuming that no strong intermolecular exchange interactions are present, the ground state may be determined as outlined in the EPR spectroscopy Section 4.2.1. Because the SQUID data are typically obtained with less scatter, compared to χT -values in quantitative EPR spectra, the more reliable values of $\Delta E_{\text{LS-HS}}$ may be extracted from fits to the χT vs. T (or χ vs. T) data; in the case, of a flat χT vs. T plot, significantly more robust limiting values for $\Delta E_{\text{LS-HS}}$ (or $|\Delta E_{\text{LS-HS}}|$) are available from SQUID measurements.

As shown in the Figure 19 (below), determination of ground state and ΔE_{ST} for a diradical faces the following challenges:

- (1) for very low values of $\Delta E_{\text{ST}} \sim \pm 2$ K the sample must consist of magnetically isolated diradicals, that is, laborious SQUID studies on progressively more dilute samples are needed and
- (2) for very high values $\Delta E_{\text{ST}} > 1000$ K, correction for diamagnetism has to be perfect and the sample should be perfectly pure, especially without traces of magnetic impurities; for example, when the highest temperature of measurement is typical 300 K, the relative difference in χT is only of the order of 1.1%, when comparing diradicals with $\Delta E_{\text{ST}} = 1000$ K and $\Delta E_{\text{ST}} = 2000$ K; when comparing $\Delta E_{\text{ST}} = 2000$ K and $\Delta E_{\text{ST}} = 4000$ K, the difference becomes a negligible 0.04%.

The plots in Figure 19, also illustrate why diradicals with $\Delta E_{ST} \gg 0.6 \text{ kcal mol}^{-1}$ are important. That is for a diradical with $\Delta E_{ST} > 2.0 \text{ kcal mol}^{-1}$, occupancy of the triplet state is greater than $\sim 99\%$ at room temperature. It should be noted that, for a diradical, value of χT (in emu K mol^{-1} and $g = 2$) is equal to a molar fraction of triplet state.

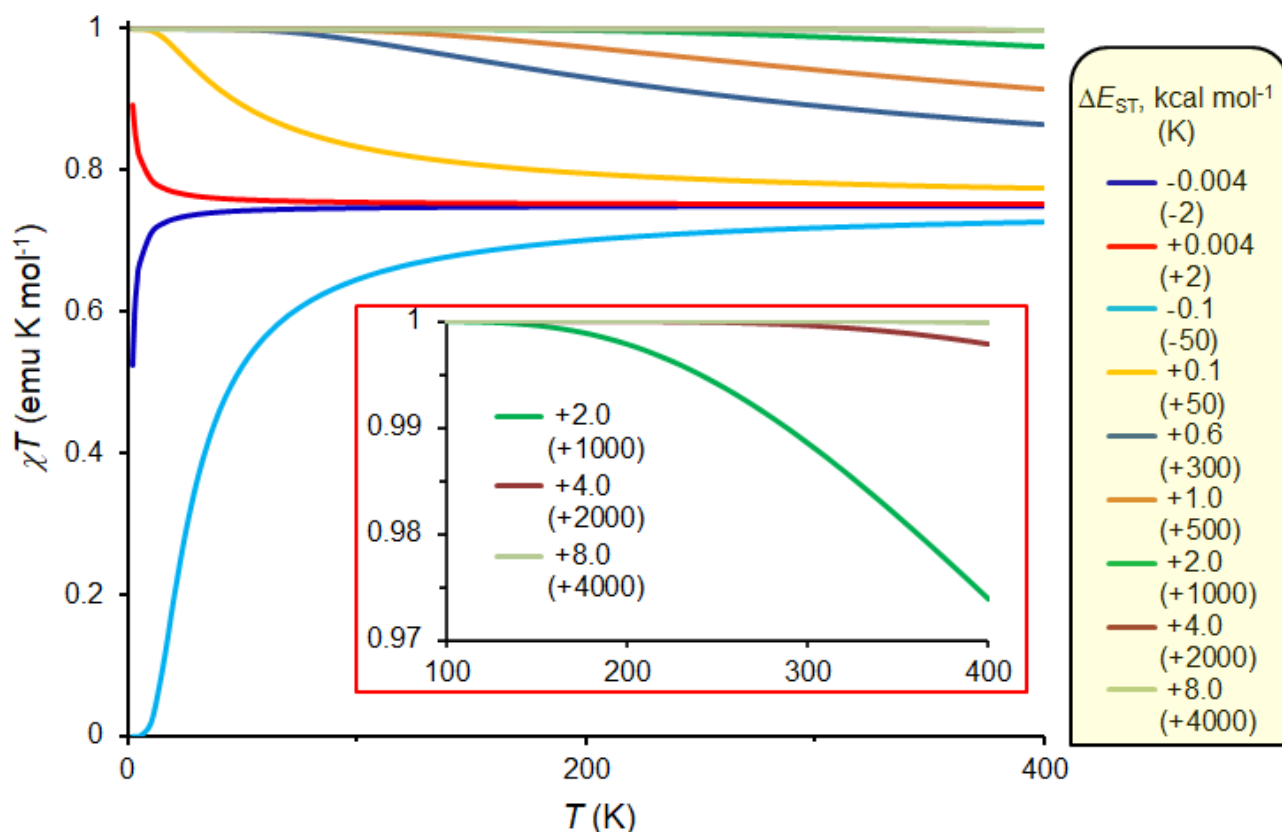


Figure 19. Plots of χT vs. T , with $T = 2 - 400 \text{ K}$, for diradicals with various values of ΔE_{ST} . Note that value of χT (as plotted in emu K mol^{-1} and $g = 2$) is equal to a molar fraction of triplet state; alternatively, $\chi T \cdot 100\%$ is equivalent to a percent occupancy of triplet state. Inset plot: expanded plot for diradicals with $\Delta E_{ST} = 2.0 - 8.0 \text{ kcal mol}^{-1}$ ($1000 - 4000 \text{ K}$) illustrating challenge of determination large values of $\Delta E_{ST} > 2.0 \text{ kcal mol}^{-1}$.

We also note the feasibility of determining relatively small ΔE_{LS-HS} (and especially negative) based on fitting the plots of normalized magnetization M/M_{sat} vs. H/T at low temperatures, e.g., $\Delta E_{ST} \sim -1 \text{ K}$, $H = 0 - 5 \text{ Tesla}$, $T = 1.8 - 3 \text{ K}$. In this approach, the thermal population of m_S -substates is perturbed by the presence of nearby low-spin state.^{214,321,323}

Although rarely used, the variable temperature NMR-based paramagnetic shift method may be used to assess $\Delta E_{ST} \approx RT$,^{313,335} analogously to the IT vs T data, where I corresponds to the EPR

intensity, in variable temperature EPR spectroscopy. In addition, ^1H NMR Evans method^{336,337} is occasionally used to determine values of χT , especially at room temperature – this is a useful tool to confirm purity of radicals.^{214,217}

4.3. High-spin di- and triradicals based on nitronyl nitroxide (NN)

According to Ovchinnikov parity models, trimethylenenemethane (TMM) is a high-spin diradical possessing a triplet ground state with $\Delta E_{\text{ST}} \approx 16 \text{ kcal mol}^{-1}$ (Figure 15).^{318,319} TMM is a great prototype for designing high-spin radicals.^{35,124} Moreover, nitronyl nitroxide can be regarded as a potential TMM-type radical if the C2 position, possessing negative spin density, is connected to other radical center with positive spin density at the atom X, forming C2-X bond; consequently, a diradical with high-spin ground state is obtained (Figure 20). Alternatively, when the spin density at atom X is negative (e.g., a node in the SOMO at atom X), then the singlet ground state diradical, with connectivity analogous to TME (Figure 15), is obtained (Figure 20).

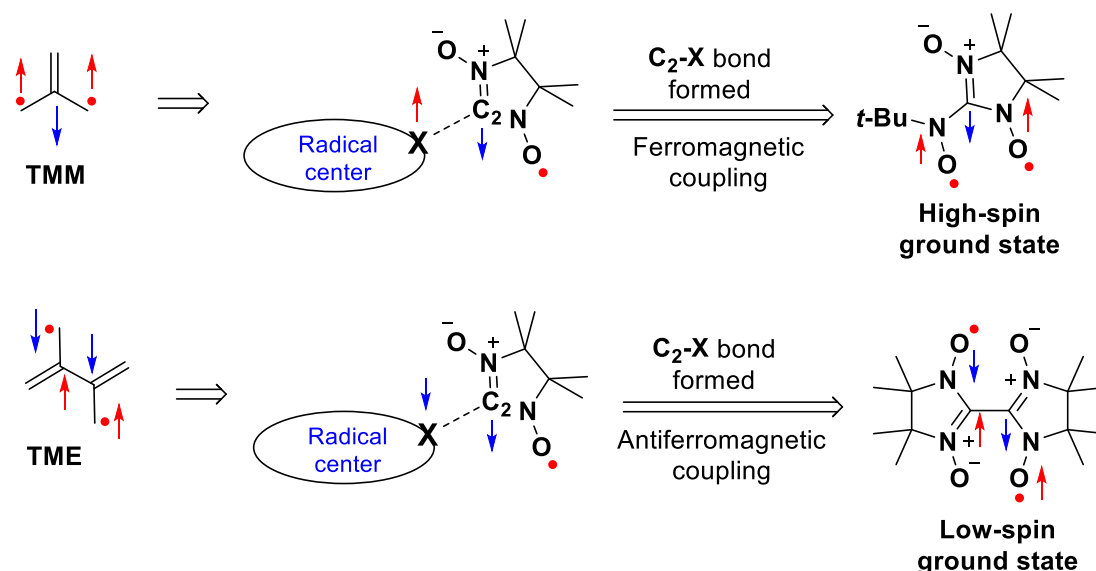


Figure 20. The structures of trimethylenenemethane (TMM) and tetramethyleneneethane (TME), and C2-substituted nitronyl nitroxides.

In general, radical stability could be improved when radical center is well shielded by bulky groups, or its spin density delocalized via resonance. Among many types of radicals, nitroxides play pivotal

role in radical families. Most of nitroxides are stabilized by tertiary alkyl groups at α -carbon position to prevent dimerization or hydrogen abstraction. In addition, spin delocalization over two nitrogen and two oxygen atoms provides good thermodynamic and chemical stability. In summary, the nitronyl nitroxides possess excellent stability, enabling wide range of applications.^{253,338}

4.3.1. Synthetic routes to high-spin nitronyl nitroxide-based radicals

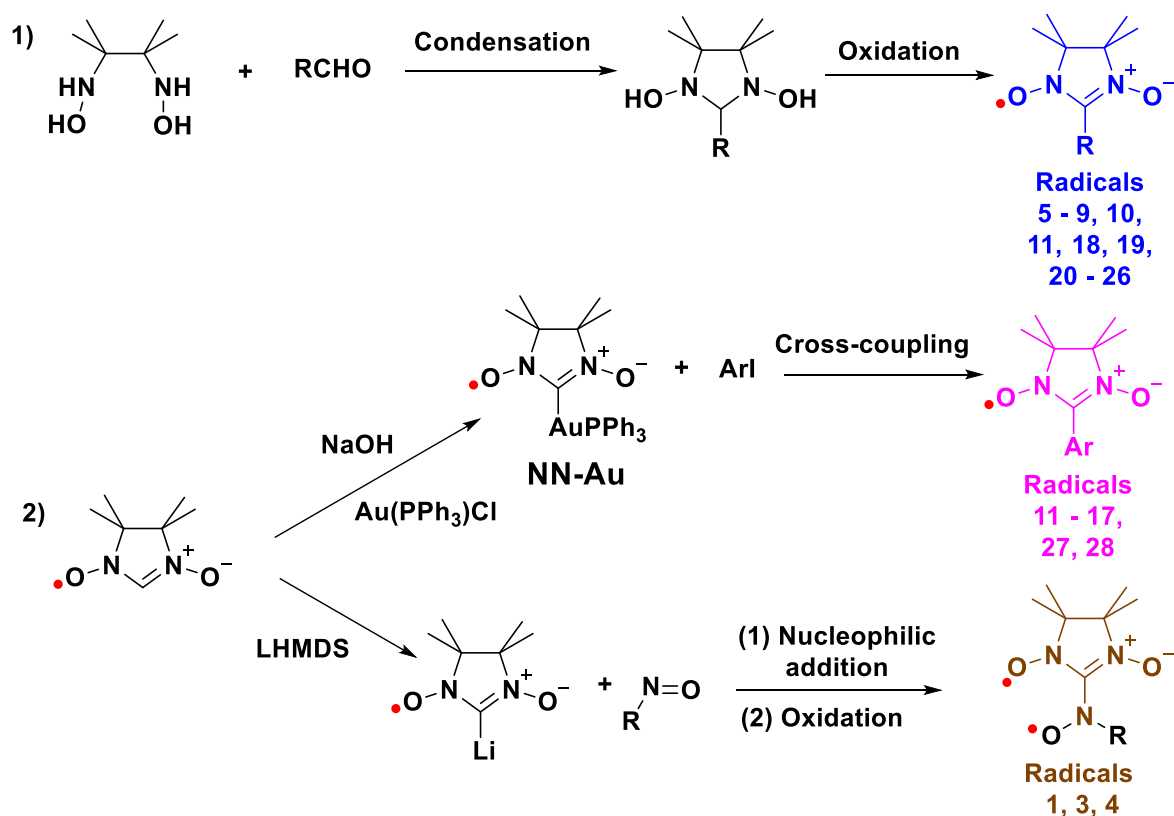
In 1968, Osiecki and Ullman first reported a new stable nitroxide radical called nitronyl nitroxide,²¹² which was prepared by condensation of aldehydes with 2,3-bis(hydroxyamino)-2,3-dimethylbutane followed by oxidation reaction with NaIO₄ (Scheme 1).³³⁹ It is worth noticing that for nitronyl nitroxide with R = H (Scheme 1), the pK_a of the C2-H (C2 is the carbon atom between two nitrogen atoms) is 21.9,³⁴⁰ allowing many further modifications after deprotonation, including reactions with electrophilic reagents.^{341,342} Since seminal derivative R = Au-PPh₃ (NN-Au) reported by Okada group,^{343,344} a series of organometallic derivatives R = M-L have been prepared and investigated,³⁴²⁻³⁴⁷ such as, R = Li from Tretyakov group³⁴² and R = ZnCl from Suzuki group.³⁴⁶ Those NN derivatives dramatically promote the discovery of high-spin radicals through direct coupling compared to the condensation reactions.

The NN-based high-spin di- or tri-radicals are generally prepared through condensation or coupling method. In the condensation reaction, the nitronyl nitroxide is synthesized through reaction of aldehydes (R-CHO) and 2,3-bis(hydroxyamino)-2,3-dimethylbutane and followed by oxidation reaction.²¹² If the R group in aldehydes is either a stable radical or it can be converted to radical fragment, the final NN-based high-spin di- and triradicals are possible (*vide infra*).^{147,148,348} However, this approach requires multistep reactions to construct final high-spin molecules, and the yield sometimes is far from satisfying.

An alternative approach is based on the low pK_a of C2-H, which was mentioned in the preceding

paragraph. This allows for C2-functionalization of nitronyl nitroxide by deprotonation with NaOH or LHMDS, and then reacting with electrophilic reagents, such as nitrones,³⁴⁹ or cross-coupling with aryl iodide.³⁴⁴⁻³⁴⁶ One of the recent advances involve the use of electron rich sterically encumbered phosphines as ligands in NN-Au or in Pd-catalysts, which enables cross-couplings with aryl bromides or electron-rich open-shell aryl iodides.^{149,350} This direct coupling method also can install skeletons of high-spin NN radicals, providing a powerful and flexible way to synthesize and increase the diversity of high-spin NN radicals. Based on these two approaches, high-spin radicals have been synthesized (Scheme 1).

Scheme 1. Synthetic approaches to nitronyl nitroxide-based high-spin radicals.



4.3.2. High-spin nitronyl nitroxide-based neutral di- and triradicals

The simplest stable TMM-analogues are based on the connection of the NN (or imino nitroxide) moiety with alkyl or aryl nitroxide fragments (Figure 20); the short through-bond pathway between two spin centers leads to strong ferromagnetic exchange interactions in diradicals **1** – **4** (Figure

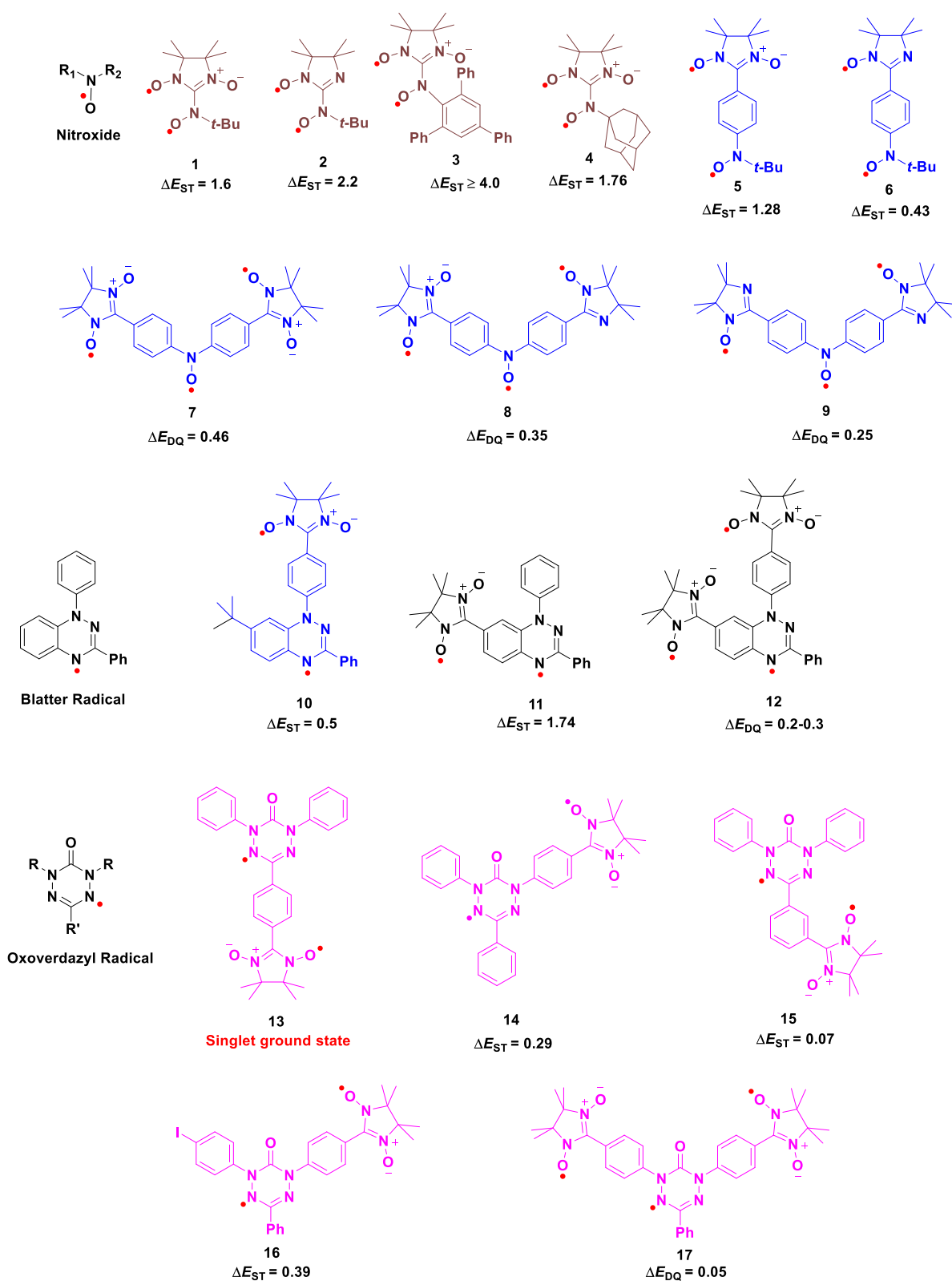


Figure 21. Structures of stable, neutral high-spin di- and tri-radicals based on the nitronyl nitroxide. ΔE_{ST} and ΔE_{DQ} (doublet quartet energy gap) are in kcal mol⁻¹.

In 2010, Okada and co-workers prepared nitronyl nitroxide **1** and imino nitroxide **2**.³⁴⁹ Diradical **1** was assembled by nucleophilic addition of the 2-lithio(nitronyl nitroxide) with *tert*-butyl nitronyl

followed by oxidation with lead (VI) dioxide. Deoxygenation of nitronyl nitroxide **1** by nitrous acid provided imino nitroxide **2**. Using analogous nucleophilic addition strategy, the same group synthesized diradical **3** in 2022,³⁵¹ and very recently, Tretyakov group synthesized diradical **4**.³⁵²

These diradicals are stable under ambient conditions and possess strong ferromagnetic interactions: reported values of ΔE_{ST} are 1.56, 2.2, >4.0, and 1.76 kcal mol⁻¹ for **1**, **2**, **3**, and **4** respectively. Furthermore, **1** and **2** can be sublimed at 55 – 70 °C without decomposition under reduced pressure. The dihedral angles between the nitronyl nitroxide and C, N, O unit of the *tert*-butylnitroxide group in **1** and **2** are 73° and 40°, which may explain the larger ΔE_{ST} in **2** since an enhanced intramolecular exchange interaction with less torsional angle. Analogous dihedral angles in **3** and **4** are 18 and 64°. We note that diradicals **1** and **2** are analogous to diradicals **5** and **6**, and the stronger intramolecular exchange interactions stem from the shorter exchange coupling pathway between two spin centers.

The EPR spectra of **1** and **2** in glassy diethylphthalate matrix exhibit $|\Delta m_S| = 1$ and partially forbidden $|\Delta m_S| = 2$ transitions, characteristic for triplet state of a diradical (Figure 22). Stronger $|\Delta m_S| = 2$ transition of **2** agrees with larger spectral width (higher $|D|$ value) of the $|\Delta m_S| = 1$ transitions. Diradical **1** and **2** possess strong intramolecular interactions and weak intermolecular interactions based on SQUID results. When decreasing temperature from 300 to 150 K, the χT vs T plots of diradical **1** increase from 0.983 emu K mol⁻¹ to 1.000 emu K mol⁻¹. Compared to diradical **1**, the χT vs T plots of radical **2** is slightly increased from 0.990 emu K mol⁻¹ to 0.995 emu K mol⁻¹ for broader temperature range of 300 to 100 K. When lowering temperature from 150 to ~2 K, χT values of diradical **1** and **2** decrease dramatically due to the intermolecular antiferromagnetic interaction. The plots of χT vs T are fitted to the modified Bleaney-Brower equation (eq. 5) for diradical ($H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$).

$$\chi T = \frac{2N_A\mu_B^2g^2T}{k_B(T - \theta)[3 + \exp\left(-\frac{2J}{k_BT}\right)]} \quad (5)$$

Where N_A is the Avogadro constant, μ_B is Bohr magneton and k_B is Boltzmann constant. Mean-field

parameter θ (in K) is used to characterize the strength of intermolecular interaction.⁷ When the θ is positive value, it suggests ferromagnetic interaction between molecules. Otherwise, negative θ value means antiferromagnetic interaction between molecules. Diradical **1** and **2** have moderate antiferromagnetic interactions with θ value of -1.5 and -2.7 K, respectively. The key parameters for magnetic characterization of diradicals **1** – **4** are listed in Table 4.3.2.

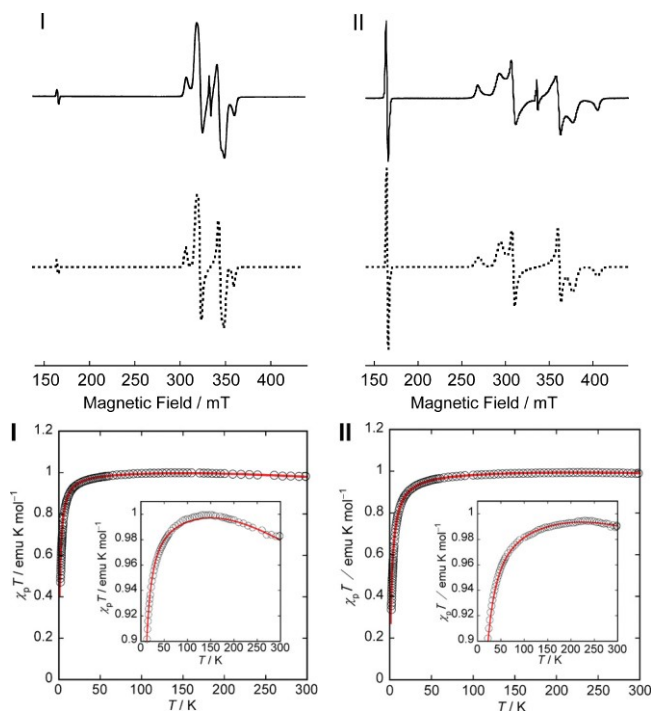


Figure 22. Top: EPR spectrum of **1** (I) and of **2** (II) measured in frozen diethylphthalate matrix at 200 K with $\nu = 9.416402$ GHz (for **1**) and $\nu = 9.425181$ GHz (for **2**). Bottom: Variable temperature χT vs T for **1** (I) and **2** (II). The red solid lines are the simulation lines based on a modified Bleaney-Bowers model. Reproduced from ref. 349. Copyright 2010 American Chemical Society

Table 4.3.2. Magnetic properties of diradicals **1**, **2**, **3**, and **4**.

Radical		D (MHz)	E (MHz)	J/k (K)
1	EPR/SQUID	758	48	390
2	EPR/SQUID	1916	150	550
3	EPR/SQUID	561	38	>1000
4	EPR/SQUID	845	60	440

In 1995, Iwamura and Inoue synthesized a stable high-spin diradical **5**, 2-[*p*-(*N*-*tert*-butyl)-*N*-

oxyamino)phenyl]-4,4,5,5-tetramethyl-4,5-dihydroimidazol-3-oxide-1-oxyl and analogous imino-nitroxide diradical **6** (Figure 21).³⁴⁸ The diradical **5** was prepared by condensation method and isolated as violet needles. X-ray crystal structure of **5** shows the three moieties, nitronyl nitroxide, *para*-phenylene ring and C, N, O unit of the *tert*-butylnitroxide group, are twisted (the dihedrals are 27° and 22°, respectively). The moderate dihedrals facilitate the delocalization of spin densities, producing large intramolecular exchange interaction. Polycrystalline diradical **5** and **6** form chain structure with the contacts between the NO groups as the intermolecular antiferromagnetic interactions. Subsequently, ΔE_{ST} is determined to 1.28 kcal mol⁻¹ for diradical **5** and 0.43 kcal mol⁻¹ for imino-nitroxide diradical **6** by spin-1/2 Heisenberg ferromagnetic-antiferromagnetic alternating chain model (HFAA chain model).³⁵³

Subsequently, Iwamura group synthesized triradical **7**,³⁵⁴ using condensation method, as they utilized in preparation of diradical **5**. By deoxygenation of **7**, imino-nitroxide (IN) triradicals **8** and **9** were obtained.³⁵⁴ These triradicals are stable and isolated as powders. X-ray crystal structure of **8** shows the NN moiety has resonance contribution of quinonoid form, while IN moiety does not contribute to such resonance form. Specifically, two short C-C bond distances are 1.370 Å and four long C-C bond distances are 1.401 – 1.431 Å in *para*-phenylene ring linked to the NN moiety, leading to the change from a regular hexagon structure towards a bond-alternating quinonoid structure. However, the C-C bond distances in *para*-phenylene linked to the IN moiety are more uniform (1.380 – 1.411 Å) and the ring maintains the regular hexagon structure. The quinonoid form enhances the exchange interaction between center nitroxide and nitronyl nitroxide (Figure 23); therefore, the exchange coupling J_1/k and J_2/k in **8** are expected to be different.³⁵⁴ This phenomenon was not obvious in diradical **5**: the crystal structure analysis shows the bond distances in *para*-phenylene ring is changed by 0.01 – 0.02 Å (two short C-C bond distances: 1.365 and 1.373 Å, four long C-C bond distances: 1.387 – 1.393 Å).³⁴⁸ The quinonoid form enhances the exchange interaction between nitroxide and

nitronyl nitroxide; therefore, the exchange coupling J_1/k in **5** vs. **8** are expected to be somewhat different (Figure 24).

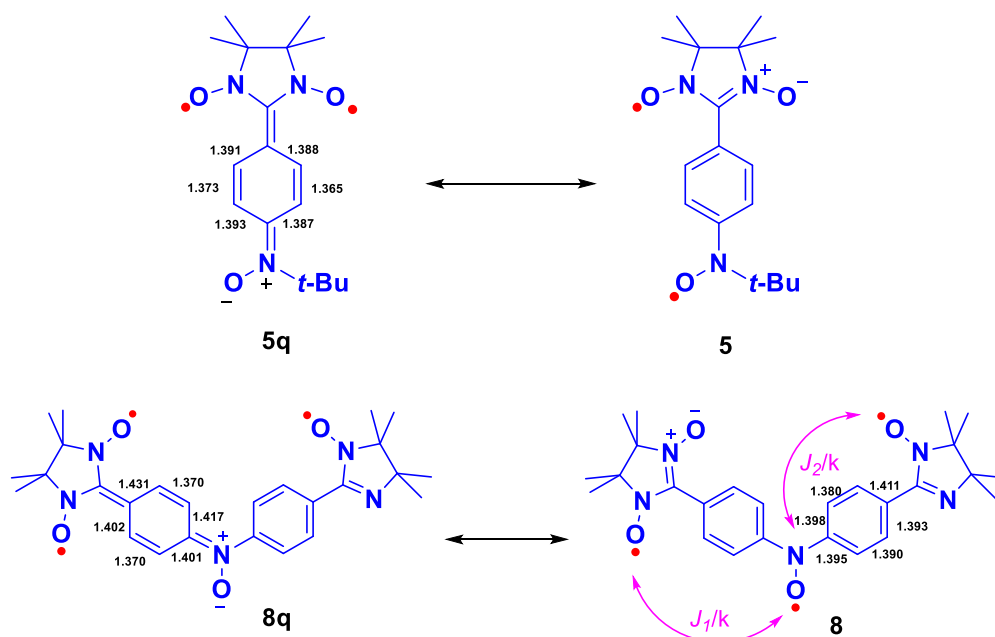
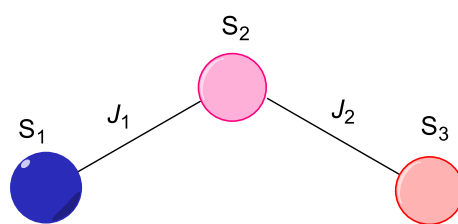


Figure 23. The resonance structures of **5** and **8**, and selected bond distances (Å).

EPR spectra of triradicals **7** – **9** in glassy 2-methyltetrahydrofuran at 7 – 12 K show an intense center peak for all triradicals. All the χT vs T plots of triradicals show the magnetic susceptibilities increase from 300 K to roughly 60 K then decrease dramatically to 2 K. The former increase is due to the greater population of molecules in the quartet ground state when temperature is decreasing. The latter decrease comes from the intermolecular antiferromagnetic interaction at lower temperature. The intramolecular coupling constants are determined by the asymmetric linear triradical model (eq. 6).

$$H = -2(J_1 \mathbf{S}_1 \cdot \mathbf{S}_2 + J_2 \mathbf{S}_2 \cdot \mathbf{S}_3) \quad (6)$$

Where J_1 (J_2) is the exchange coupling constant between $\mathbf{S}_1$ and $\mathbf{S}_2$ ($\mathbf{S}_2$ and $\mathbf{S}_3$); eq. 6 corresponds to specific case for a more general eq. 4. Intramolecular coupling constant J_{13} between two terminal radicals is ignored because it is much smaller than J_1 and J_2 . Here J_{13} is assumed to be 2 orders of magnitude smaller than J_1 and J_2 , according to study the properties of one-dimensional nonclassical polymers (NCP).³⁵⁵ In triradicals **7** – **9**, coupling constants are in a good agreement with the intramolecular coupling constants of diradicals **5** and **6** (Figure 24).



$$\Delta E_{\text{DQ}} = J_1 + J_2 - [J_1^2 + J_2^2 - (J_1 J_2)]^2$$

$$\Delta E_{\text{DQ}2} = J_1 + J_2 + [J_1^2 + J_2^2 - (J_1 J_2)]^2$$

Radical		J_1/k (K)	J_2/k (K)
5	SQUID	319	-
6	SQUID	108	-
7	SQUID	231	231
8	SQUID	349	130
9	SQUID	127	127

Figure 24. Model for exchange coupling in triradicals **7 – 9** (linear triradical model, it is asymmetric when $J_1 \neq J_2$) and doublet-quartet energy gap ΔE_{DQ} for the lowest $S = 1/2$ excited state, $\Delta E_{\text{DQ}2}$ for the second lowest $S = 1/2$ excited state.³⁵⁴ The table summarizes exchange coupling constants J/k of diradicals **5**, **6** and triradicals **7 – 9**.

Annulated hydrazyls such as 1,2,4-benzotriazinyl radical (Blatter radical) and oxoverdazyl radical possess excellent stability. Their stability originates from excellent spin delocalization optimized by π -orbital overlap between the atoms in the 6-membered ring structure, making them great radical fragments for constructing stable high-spin radicals.³ In addition, Okada and co-workers recently discovered the Pd(0)-catalyzed cross-coupling reaction between gold(I)-nitronyl nitroxide(NN-Au) complex and aryl iodides,³⁴⁴ inducing the development of cross-coupling reaction between gold(I)-nitronyl nitroxide complex and derivatives of Blatter radical and oxoverdazyl radical.^{149,153,154}

In 2016 – 2021, our group had designed and synthesized high-spin diradicals **10**,¹⁴⁷ **11**,^{148,149} and triradical **12**¹⁴⁹ based on NN and Blatter radical (Figure 21). These NN-Blatter diradicals and triradical possess robust thermal stability and good magnetic properties, which have been applied to form thin films via evaporation under controlled conditions.^{148,149} Diradicals **10** and **11** are originally synthesized by the condensation of corresponding formyl-benzotriazinyl (formyl-Blatter) radical and 2,3-bis(hydroxyamino)-2,3-dimethylbutane followed by oxidation reaction, with isolated yields of 4 – 12 % and 18 – 29 % in the multistep syntheses. The overall yield of a similar procedure for triradical **12** is rather low, $\leq 1\%$.

In contrast to the disappointing yield under condensation conditions, direct cross-coupling reaction of di-iodo-Blatter radical with **NN-Au** (Scheme 1), using the highly reactive Pd(0)-catalyst, Pd[(*t*-Bu)₃P]₂, gives significantly higher 19 – 42 % yield, in a shorter, more convergent synthesis. Similarly, diradical **11** is generated in 30 – 44 % yield when mono-iodo-Blatter radical is cross-coupled with **NN-Au**.¹⁴⁹

We discuss X-ray crystal structures of **10**, **11**, and **12** (Figure 25) to better understand the structure-property relationships regarding magnetic properties.

In diradical **10**, two dihedral angles between the NN moiety and Blatter radical π -system are $\sim 30^\circ$ and 49° , respectively. Two nonequivalent molecules, A and B, are observed in diradical **11**. In molecule A, the NN moiety is nearly coplanar with the Blatter radical π -system with the corresponding torsional angle in the $(-13) - (-15)^\circ$ range, while in molecule B, there is considerably greater out-of-plane twisting with the corresponding torsions of $28 - 30^\circ$. In the crystal, molecules A and B pack in an alternating fashion into one-dimensional chains along crystallographic *a*-axis with close intermolecular N $\cdots$ N and O $\cdots$ N contacts.

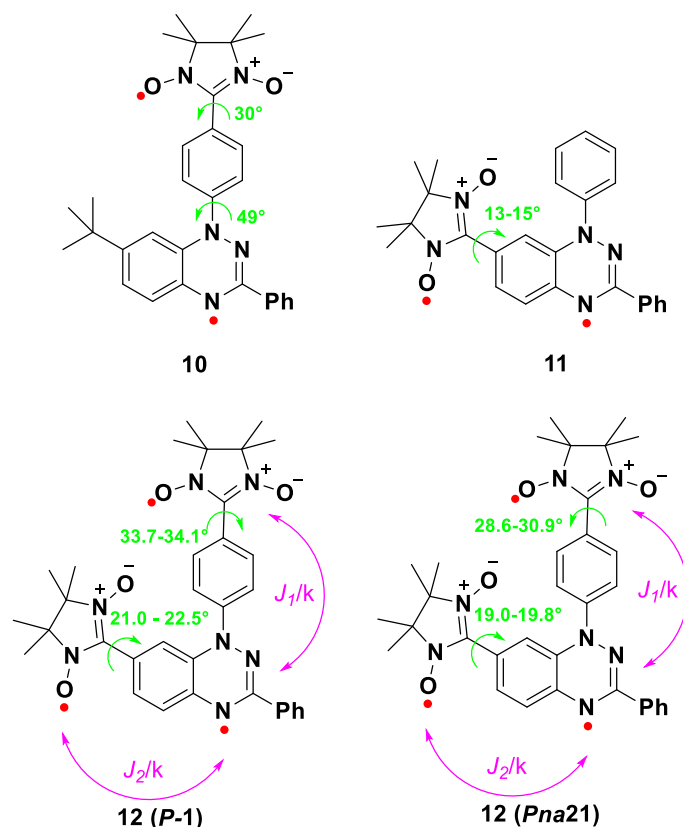


Figure 25. Structures of diradicals **10**, **11** (molecule A), and triradical **12** with selected torsional angles. For **12**, two pseudo polymorphs are shown.

For triradical **12**, two single crystal X-ray structures were obtained: triclinic (centrosymmetric *P*-1) and orthorhombic (*Pna*21). The orthorhombic structure contains one molecule of chloroform, which is a solvent polymorph. The two pseudo polymorphs have significantly different crystal packing. The triclinic structure consists of C_i -symmetric dimers of triradical molecules, while the orthorhombic structure contains one-dimensional π -stacks of triradical molecules. For triclinic structure, both NN moieties are nearly coplanar with the Blatter radical π -system with torsional angles of 21.0 – 22.5° and 33.7 – 34.1°. Similar torsional angles between NN moieties and Blatter radical π -system are found in the orthorhombic structure, i.e., 19.0 – 19.8° and 28.6 – 30.9°. We note that the exchange coupling pathways between NN moiety and Blatter radical π -system are different. Therefore, the exchange couplings constants, J_1/k and J_2/k , are expected to be significantly different in **12** (Figure 25).

Furthermore, quantitative EPR spectroscopy and SQUID magnetometry of radicals in various glassy matrices and/or polycrystalline powders give $\Delta E_{ST} = 0.5 \text{ kcal mol}^{-1}$ for **10**, $\Delta E_{ST} \geq 1.7$ for **11** and $\Delta E_{DQ} \approx 0.2 - 0.3 \text{ kcal mol}^{-1}$, $\Delta E_{DQ2} \approx 1.2 - 1.8 \text{ kcal mol}^{-1}$ for triradical **12**. Triplet ground states are

established unequivocally by magnetization data. Low-temperature EPR spectra of diradical **10** and **11** show triplet state ($S = 1$) and diradical **10** has a much smaller ZFS parameter $|D|$, compared to that for **11**. For polycrystalline **10** and **11**, strong intermolecular antiferromagnetic interactions are observed in SQUID magnetometry. The plots of χT vs. T are fitted to the modified Bleaney-Brower equation for diradical requiring relatively large absolute value of negative mean-field parameters, $\theta \approx -6$ K and -14 K, respectively. Notably, fitting both χT vs. T and χ vs. T data at low temperatures of polycrystalline **11** satisfies 1-D antiferromagnetic $S = 1$ chain model, with relatively large intrachain $J'/k = -14$ K, which is consistent with its crystal packing.

Low-temperature EPR spectra of triradical **12** show a quartet state ($S = 3/2$) in 2-MeTHF or toluene/chloroform (3:1) glassy matrices. Only a weak $|\Delta m_s| = 2$ transition can be detected and no $|\Delta m_s| = 3$ transition is observed. The spectral width for $S = 3/2$ triradical **12** in toluene/chloroform glass is $4D \approx 320$ MHz, which is intermediate between $2D \approx 140$ MHz for $S = 1$ diradical **10** and $2D \approx 480$ MHz for **11**. This reflects the intermediate strength of magnetic dipole-dipole interactions in **12** that dominate the EPR spectra in glassy matrices. Energy gaps $\Delta E_{DQ} \approx 0.2$ kcal mol⁻¹ and $\Delta E_{DQ2} \approx 1.2$ kcal mol⁻¹ are obtained by variable temperature quantitative EPR spectroscopy on triradical **12** in toluene/chloroform glass/solution. When the triradical **12** is prepared in polystyrene glass and measured by SQUID magnetometry, the quartet ground state is unequivocally confirmed by magnetization data, as well as $\Delta E_{DQ} \approx 0.30$ kcal mol⁻¹ and $\Delta E_{DQ2} \approx 1.83$ kcal mol⁻¹ are obtained from χT vs T plots. We speculate that different values for doublet quartet energy gaps might be associated with slightly different conformations (dihedral angles) for **12** in different glassy matrices/solutions. Both EPR and SQUID data of triradical **12** are fitted to the asymmetric linear triradical model (Figure 24).

Both diradicals and triradical are very stable and they can be purified by silica gel column chromatography under ambient conditions. It is worth noticing that diradicals **10**, **11** and triradical **12**

may be viewed as thermally robust; they show onsets of decomposition in thermal gravimetry analysis (TGA) at 175 °C, 160 °C and 160 °C, respectively. Diradical **10** can be sublimed without decomposition at 140 °C under vacuum ($p \approx 6 \times 10^{-6}$ mbar). Such excellent thermal stable di- and tri-radicals paved avenue for further pure organic high-spin materials designs and applications. The diradical **11** and triradical **12** were evaporated under ultra-high vacuum (UHV) conditions to form thin films (ca. 1 nm nominal thickness) on SiO₂/Si (111) wafers by using organic molecular beam deposition (OMBD) at room temperature. The films were investigated by X-ray photoelectron spectroscopy (XPS), which can report on the chemical environment of C 1s core and N 1s core. Specifically, the C 1s core level line and the N 1s core level line of diradical **11** and triradical **12** are similar since they are both from NN moieties and Blatter radical π -system and have similar chemical environment. Specifically, the spectra show 3 types of carbon and 4 types of nitrogen with different ratios, e.g., the high bonding energy peak (~ 402 eV) in N 1s core level spectrum of triradical **12** is more intense than that of diradical **11** owing to the contribution of two NN moieties. While the films are stable under UHV, they show signs of decomposition in XPS after few hours at ambient conditions.^{148,149} Notably, drop-cast films of **12**, with thickness of the order of hundreds nm, show much slower decay at ambient conditions, with XPS spectra showing saturation (plateau) behavior after a few days.¹⁴⁹

Recently, a series of high-spin radicals **14** – **17** have been designed and synthesized in good yields via the cross-coupling reaction of iodo-oxoverdazyl radicals and NN-Au by Tretyakov and co-workers.^{153,154} The design is similar relying on connection of two stable radicals to provide TMM topology, which generates a spin exchange coupling through the connecting C-C bond. However, the degree of spin delocalization onto the phenyl groups in oxoverdazyl radical is smaller than that in Blatter radical, leading to lower spin density at the carbon, which is bonded to carbon C2 of the NN moiety. Consequently, significantly weaker exchange couplings between oxoverdazyl radical and

nitronyl nitroxide are found. Thus, these diradicals and triradicals possess rather small ΔE_{ST} and ΔE_{DQ} .^{153,154}

All these radicals are very stable, and they can be purified by silica gel column chromatography under ambient condition as well. In addition, diradicals **13**, **14** and **15** show an apparent onset of decomposition in TGA at 217 °C, 192 °C and 183 °C, respectively. No TGA data of diradical **16** and triradical **17** was reported.¹⁵⁴

In these radicals, different torsional angles (9 – 36° in **13** – **15**, 28.3 – 51.3° in **16** and **17**) are found between the NN moieties and respective phenyl rings, and between the phenyl rings and oxoverdazyl moieties (13 – 47° in **13** – **15**, 6.9 – 53.2° in **16** and **17**).

Singlet ground state for diradical **13** is confirmed by SQUID magnetometry and characterization of **13** will not be discussed here. Low-temperature EPR spectra of diradical **14** and **15** are recorded. Simulation of low-temperature EPR spectra of diradical **14** and **15** show axial symmetry ($E = 0$). Larger $|D|$ for diradical **15** is consistent with stronger $|\Delta m_s| = 2$ transition. The simulation of room temperature EPR spectra of **14** and **15** corresponds to 6 nitrogen hyperfine interaction (2 from NN moiety and 4 from verdazyl moiety). For diradical **16** and triradical **17**, only room temperature EPR spectra are reported. Simulations of EPR spectra for **16** and **17** indicate that the hyperfine couplings originate from 6 and 8 nitrogens (^{14}N), respectively.

Polycrystalline samples of diradicals **14** – **16** and triradical **17** are investigated by SQUID magnetometry. The χT vs T data for diradical **14** and **15** show the value of χT is close to 0.75 K·emu·mol⁻¹ at 300 K, which is close to the theoretical value of two magnetically independent $S = \frac{1}{2}$ spins. Relatively small singlet-triplet energy gaps, $\Delta E_{ST} \approx 0.29$ kcal mol⁻¹ for **14**, $\Delta E_{ST} \approx 0.07$ kcal mol⁻¹ for **15** are reported. High-spin diradical **16** and triradical **17** have moderate low-spin high-spin energy gaps, $\Delta E_{ST} \approx 0.39$ kcal mol⁻¹ for **16**, and $\Delta E_{DQ} \approx 0.05$ kcal mol⁻¹, and $\Delta E_{DQ2} \approx 0.43$ kcal mol⁻¹ for **17**, obtained by fitting to the modified Bleaney-Bowers equation of diradical and the asymmetric linear

triradical model (Figure 24), respectively.

4.3.3. High-spin nitronyl nitroxide-based diradical anions

The radical metal complexes are significant in the design of single-molecule magnet (SMM) because the paramagnetic spin centers can be bridges between metal centers and enhance the spin exchange interaction between metal centers and radicals.³⁵⁶ Among these radicals, both semiquinone radical anion and nitronyl nitroxide radical are widely used as paramagnetic ligands in SMMs.³⁵⁶

In 2000 and 2003, Shultz and co-workers reported semiquinone-nitronyl nitroxide diradical anion Zn complexes **18** and **19** (Figure 26).^{357,358} The complexes **18** and **19** were prepared by the condensation method (Scheme 1), starting with catechol-aldehyde synthetic intermediate, and then reacted with metal complexes and oxidized on air.³⁵⁷ Magnetic susceptibilities of polycrystalline complexes **18** and **19** are measured by SQUID magnetometry. Notably, strong intramolecular ferromagnetic coupling constant J in **18** is estimated as the lower limit >0.89 kcal mol⁻¹ (>310 cm⁻¹) by the absence of curvature in the plot of χT vs T of polycrystalline sample.³⁵⁷ Intramolecular coupling constant J in **19** is determined to 0.28 kcal mol⁻¹ (100 cm⁻¹) by fitting to the Bleaney-Brower equation without intermolecular interaction.³⁵⁸

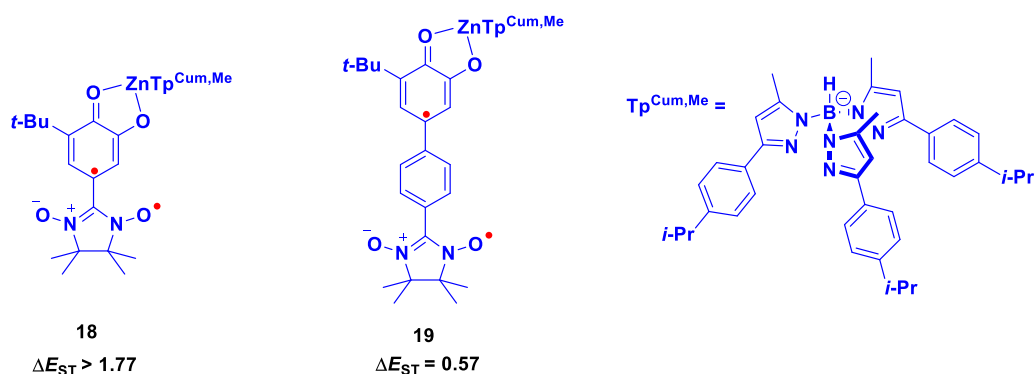


Figure 26. Structures of Shultz semiquinone – nitronyl nitroxide high-spin diradicals (diradical anions). Values of ΔE_{ST} are in kcal mol⁻¹.

4.3.4. High-spin nitronyl nitroxide-based di- and triradical cations.

Stable organic radical cations provide another attractive feature in the design of high-spin di- and triradicals. The important prerequisite for the design of stable radical-substituted radical cation systems is that the 1st oxidation potential (E_1°) for the radical is significantly more positive, compared to the 1st oxidation potential of the neutral precursor to the radical cation. Because heteroatom substituted extended π -systems have typically E_1° of the order of +0.5 V (vs. SCE), nitronyl nitroxide with $E_1^\circ \approx +0.9$ V³¹¹ for nitronyl nitroxide or even oxoverdazyl $E_1^\circ \approx +0.6$ V (vs. SCE)³⁵⁹ are good choices. We note that Blatter radical ($E_1^\circ = +0.10$ V)³⁶⁰ and phototetrazolynyl radical **DiCN-PHT** ($E_1^\circ = -0.14$ V) (Figure 3)¹⁶¹ are too easy to oxidize, and thus they are not suitable.

In 2000, thianthrene linked nitronyl nitroxide radicals **20**, **21**, and **22** were synthesized by Sugawara and co-workers (Figure 27).²⁶⁵ High-spin states in diradical cation and triradical cations are detected by pulsed EPR nutation spectroscopy at low temperatures. However, the energy gaps, ΔE_{ST} and ΔE_{DQ} were not measured.²⁶⁵ We note that the 1st oxidation potential for thianthrene, $E_1^\circ = +1.26$ V (vs. SCE),³⁶⁰ though comparable to $E_1^\circ \approx +0.9$ V for nitronyl nitroxide, implies that a significant fraction of nitronyl nitroxide radical will get oxidized to diamagnetic cation, giving complex mixtures of radicals.

More recently, Okada and his co-workers have rationally designed and synthesized high-spin stable NN-linked electron donors di- and triradical cations, based on diphenyldihydrophenazine (DPP⁺⁺-NN, **23 – 25**),^{361,362} trioxytriphenylamine (TOT⁺⁺-NN, **26** and DOT⁺⁺-NN, **27**),^{363,364} and phenothiazine (PTZ⁺⁺-NN, **28**).³⁶⁵ These high-spin di- and triradical cations **23**, **25 – 28** have good stability and large intramolecular exchange couplings between electron-donor moiety and nitronyl nitroxide (Figure 27).

In 2004, Okada and co-workers synthesized high-spin diradical cation **23** based on diphenyldihydrophenazine (DPP⁺⁺-NN).³⁶¹ The diradical cation salt can be isolated as perchlorate (ClO₄⁻) salt and is stable at ambient conditions. X-ray crystallography of **23** shows formation of a

dimer (Figure 28). Intramolecular interaction in polycrystalline **23** is determined from χT vs. T data using SQUID magnetometry. Lower limit for singlet triplet energy gap, $\Delta E_{ST} \geq 2.8$ kcal mol⁻¹, is obtained by fitting dimer model ($H = -2J_1(\mathbf{S}_{NN1} \cdot \mathbf{S}_{DPhz1} + \mathbf{S}_{NN2} \cdot \mathbf{S}_{DPhz2}) - J_2 \mathbf{S}_{DPhz1} \cdot \mathbf{S}_{DPhz2}$).³⁶¹ This result is apparently only reproducible at $T > 100$ K. However, we doubt the reliability of the finding of such large $\Delta E_{ST} \geq 2.8$ kcal mol⁻¹ (or pairwise $J/k \geq 800$ K) in **23** (*vide infra*). In addition, when tetrabromoferrate (FeBr₄⁻) is used as a counter anion for diradical cation **23**, a three-dimensional, long-range ferrimagnet is observed with ordering at $T_c = 6.7$ K, based upon measurements of dc and ac magnetic susceptibilities and heat capacity.³⁶⁶

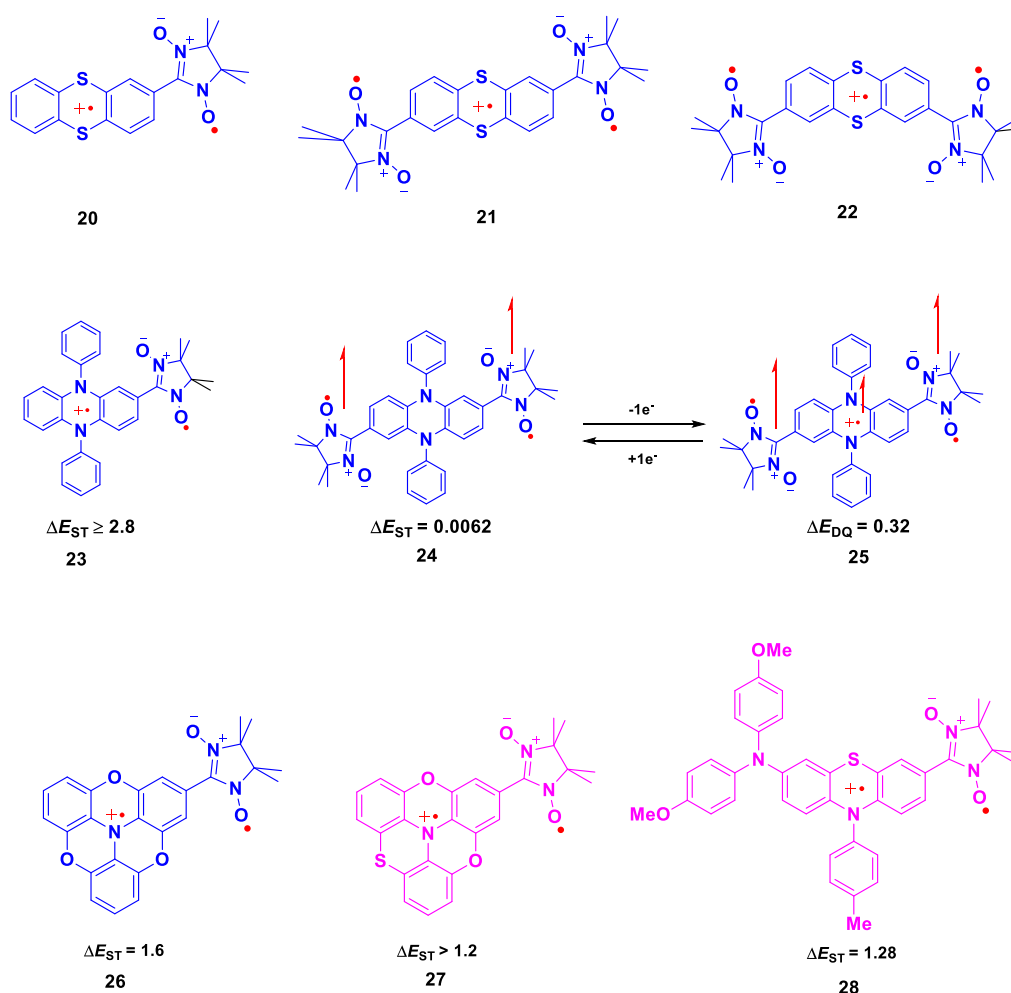


Figure 27. Structures of stable high-spin diradicals and triradical cations based on nitronyl nitroxide. Values of ΔE_{ST} and ΔE_{DQ} are in kcal mol⁻¹.

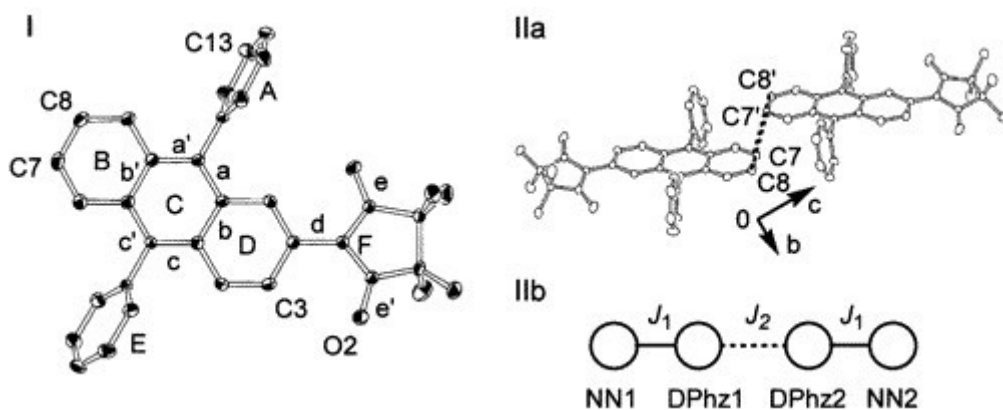


Figure 28. Molecular structure (I), a dimer structure in the crystal packing (IIa), and a schematic diagram of magnetic interaction (IIb) for diradical cation **23**. (I) Drawn at 50% ellipsoids level; hydrogen atoms, the counter anion, and the solvent are eliminated for clarity. Reproduced from ref. 361. Copyright 2004 American Chemical Society

In 2020, Okada group reported another high-spin diradical/triradical system based on NN-DPP-NN **24**, which can be switched by redox-induced modulation.³⁶² Triradical cation NN-DPP^{•+}-NN **25** is generated by one-electron oxidation of diradical **24**. Both neutral diradical and triradical cation are stable and can be isolated as solids. For diradical **24**, very weak intramolecular exchange coupling between two nitronyl nitroxide is observed due to the long through-bond, cross-conjugated pathway between two spin centers. In contrast, NN-DPP^{•+}-NN **25** has stronger intramolecular exchange interaction because of the shorter exchange coupling pathways and smaller dihedral angles between the dihydrophenazine plane and the NN moieties. EPR spectrum of diradical **24** at room temperature shows a well-resolved nine-line spectrum, which corresponds to four equivalent ¹⁴N nuclei (Figure 29a). EPR spectrum of triradical cation **25** at 200 K show a strong center single peak and two small side peaks. Forbidden $|\Delta m_S| = 2$ transitions are observed and their intensities are increased when the temperature is decreasing, which suggests the quartet ground state of **25**. Intramolecular interactions of polycrystalline **24** and **25** are determined by χT vs T from SQUID magnetometry. High-spin diradical **24** and triradical cation **25** have small singlet-triplet energy gap, $\Delta E_{ST} = 0.0062$ kcal mol⁻¹ for **24**, and moderate doublet quartet energy gap, $\Delta E_{DQ} = 0.32$ kcal mol⁻¹ ($J/k = 160$ K) for **25** by fitting to the modified Bleaney–Brower equation of diradical and symmetric linear triradical model (Figure 24), respectively.

We note that for $\Delta E_{\text{DQ}} \approx 0.3 \text{ kcal mol}^{-1}$, there will be a significant population of the lowest $S = \frac{1}{2}^*$ excited state at 200 K; presumably, large part of the difference between the experimental and simulated intensity for the center peak of **25** might be assigned to the $S = \frac{1}{2}^*$ state, in addition to incidental $S = \frac{1}{2}$ impurities (Figure 29b). This suggests that the pairwise $J/k = 160$ is correct, at least concerning order of magnitude; this would imply that pairwise $J/k \geq 800 \text{ K}$ (and $\Delta E_{\text{ST}} \geq 2.8 \text{ kcal mol}^{-1}$) in diradical cation **23** are badly overestimated (see: further discussion in Section 4.3.5). We add that the pairwise J/k values in the classic Iwamura's nitroxide di- and symmetric triradicals are similar: 319 K (**5**) vs. 231 K (**7**) and 108 K (**6**) vs 127 K (**9**) as illustrated in Figure 24.

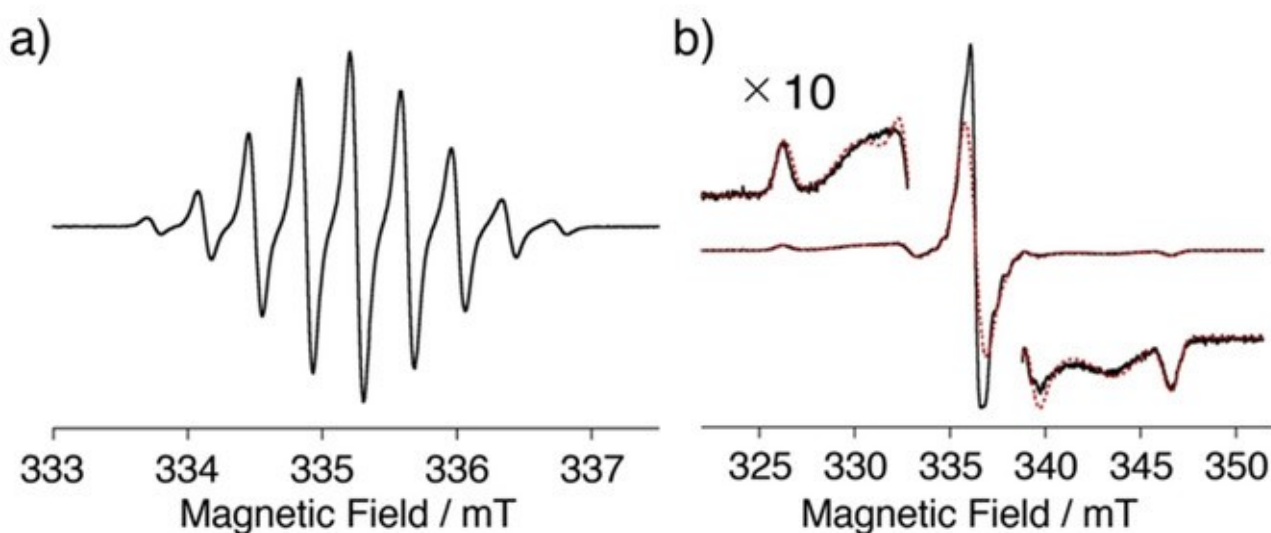


Figure 29. EPR spectra of a) **24** in toluene at 293 K (9.41575 GHz, $g_{\text{iso}}=2.0067$) and b) **25**. For b), black solid and red broken lines showed the observed spectrum of the allowed transition in a glassy diethyl phthalate matrix at 200 K (9.438855 GHz) and simulated spectrum of the quartet species by using $g_{xx}=2.0080$, $g_{yy}=2.0040$, $g_{zz}=2.0030$, $g_{\text{av}}=2.0055$, $|D/hc| = 0.00473 \text{ cm}^{-1}$, and $|E/hc| = 0.00057 \text{ cm}^{-1}$, respectively. Reproduced with permission from ref. 362. Copyright 2020 Wiley.

Subsequently, Okada and coworkers reported the diradical cations **26** (NN-TOT⁺) and **27** (NN-DOTT⁺) (Figure 27).^{363,364} NN-TOT was synthesized by condensation of TOT-formyl derivative with 2,3-bis(hydroxyamino)-2,3-dimethylbutane and followed by oxidation reaction. NN-DOTT was assembled by Pd(0) cross-coupling reaction of iodo-DOTT and NN-Au. X-ray structures show moderate dihedral angles between radical cation plane and NN moiety (28° for **26** and 33° for **27**, respectively), which is helpful in generating large spin exchange intramolecular interaction.

The χT vs T of polycrystalline **26**-GaCl₄⁻ and **27**-SbF₆⁻ are investigated by SQUID magnetometry. The χT value of **26**-GaCl₄⁻ is 0.964 emu K mol⁻¹ at 300 K and increases to 0.992 emu K mol⁻¹ at 200 K. This value is so close to 1.000 (pure $S = 1$ spin with $g = 2.000$), which implies there is a strong intramolecular exchange coupling, $J/k > 300$ K, between the NN moiety and TOT⁺ radical cation. Simulation of the χ vs T data in the $T = 3 - 300$ K range, using modified “ $S = 1$ ” Fisher chain model provided intramolecular ferromagnetic exchange coupling $J/k = 400$ K and intra-chain (inter molecular) antiferromagnetic exchange coupling $J'/k = -1.85$ K; this corresponds to $\Delta E_{ST} = 1.6$ kcal mol⁻¹ ($2J/k = 800$ K).³⁶³

For **27**-SbF₆⁻, χT value is 0.884 emu K mol⁻¹ at 300 K and slightly decreases to ~ 0.8 emu K mol⁻¹ at 100 K. The intramolecular exchange coupling between the NN moiety and DOTT⁺ radical cation is assumed to be larger than thermal energy, $J/k > 300$ K (*vide infra*), and $S = 1$ (NN-DOTT⁺) spin is applied to χ vs T data when simulating the intermolecular antiferromagnetic interactions, using modified Fisher $S = 1$ chain model. A weak intra-chain interaction, $J'/k = -7.4$ K, and a comparable inter-chain interaction, $zJ''/k = 2.5$ K are found. While the fit of χT vs T data with the modified Fisher chain model is satisfactory at low temperatures, near the room temperature, the fit is not as good. Most likely, the interaction between NN moiety and DOTT⁺ is not strong enough to regard as a $S = 1$ spin near the room temperature. We note that the value of $\chi T = 0.884$ emu K mol⁻¹ at 300 K is close to 0.89 emu K mol⁻¹ for a diradical with singlet triplet gap, $2J/k = 300$ K (Section 4b2, Figure 19).

In addition, diradical cation **27** shows a magnetic phase transition from the antiferromagnetic state to the weak ferromagnetic state at $T_N = 2.65$ K based on susceptibility and heat capacity measurements. For the FeBr₄ salts of **27** magnetic phase transition into a weak ferromagnet at 7 K is suggested.

Recently, Okada also reported a diradical cation **28** (DAA-PTZ-NN⁺) (Figure 27), which was synthesized by Pd(0) cross-coupling reaction of iodophenothiazine DAA-PTZ-I with NN-Au (Scheme 1) followed by oxidation reaction of the PTZ moiety to corresponding radical cation. Here, both GaBr₄⁻

($S = 0$) and FeBr_4^- ($S = 5/2$) are used as counter anions.³⁶⁵ The EPR spectrum is relatively narrow with $|D| = 60$ MHz and a weak $|\Delta m_S| = 2$ transition is found for **28**-GaBr₄ in butyronitrile glass at 100 K. The χT vs T plot for polycrystalline **28**-GaBr₄⁻ is obtained using SQUID magnetometry. Specifically, the χT value of **28**-GaBr₄⁻ is 0.96 emu K mol⁻¹ at 300 K and the value is approaching 0.99 emu K mol⁻¹ at 100 K, then the χT value decreases rapidly when temperature is lowered to about 0.5 emu K mol⁻¹ at 2 K. This indicates a strong intramolecular and weak intermolecular exchange coupling in polycrystalline **28**-GaBr₄⁻. Value of $\Delta E_{\text{ST}} = 1.28$ kcal mol⁻¹ ($J/k = 320$ K) for **28**-GaBr₄⁻ is determined. It should be mentioned that diradical cation of NN-PTZ without diarylamine substituent could not be isolated – presumably due to its lack of sufficient persistence.³⁴⁶

4.3.5. The relation between the hyperfine coupling constant in monoradicals and pairwise exchange coupling constant J/k in NN-based diradicals and triradicals.

Large spatial “coincidence” of spin density at the two adjacent radical fragments, one with α and one with β spin at the connecting atoms, are necessary for strong ferromagnetic exchange interaction in the resultant TMM-like, NN-based high-spin di- or triradical (Figure 20). Spin density delocalization into the ferromagnetic coupling unit (FCU) can then affect the pairwise exchange coupling constant J/k in the high-spin di- or triradical, with the greater spin density within the FCU, corresponds to the greater J/k .³¹³ The magnitude of spin density within the FCUs of these high-spin di- and triradicals, and thus the magnitude of pairwise J/k will be governed by two factors: spin density at the atom X within the C2-X bond and average torsion angle θ (Figure 30). Since spin density at atom X is directly related to absolute value of hyperfine coupling constant, $|A(^1\text{H})|$, for ¹H within the X-H bond in the corresponding monoradical, we should be able to correlate J/k with $|A(^1\text{H})|$ and θ (Figure 30).

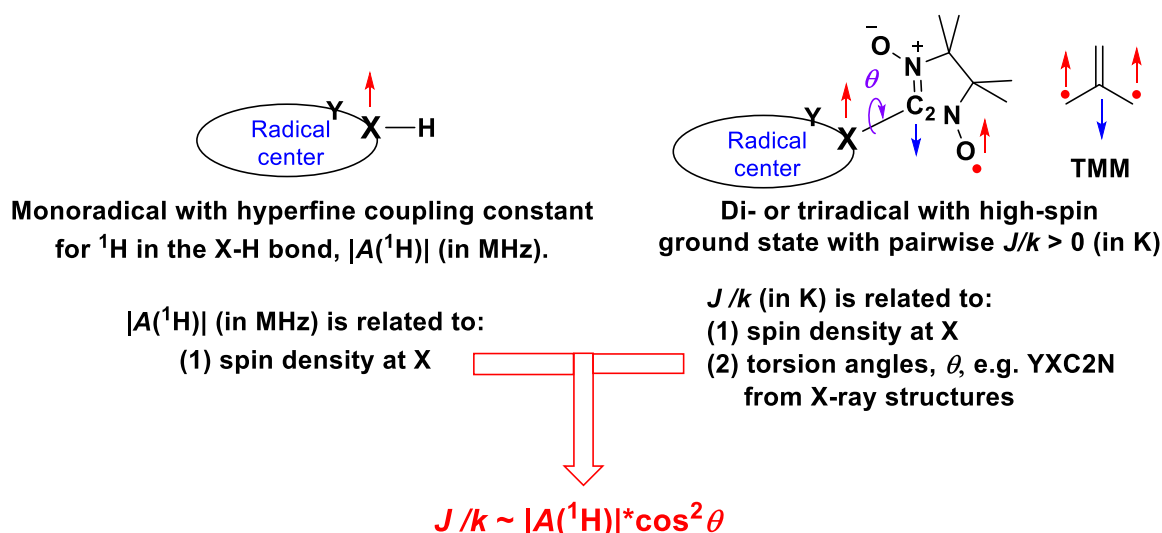


Figure 30. Conceptual relationship between pairwise J/k in NN-based high spin di- and triradicals, and $|A(^1\text{H})|$ in monoradicals.

McConnell's relationship³⁶⁷ estimates of the spin density at sp^2 -hybridized carbon atom in organic radicals as:

$$A(^1\text{H}) = Q_{\text{CH}} \cdot \rho_{\text{C}} \quad (7)$$

where $A(^1\text{H})$ (in MHz) is hyperfine coupling constant for ^1H within the C-H bond and ρ_{C} is the spin density at carbon. Value of the "constant" Q_{CH} generally depends on the type of monoradical, as its value decreases with negative and increases with positive charge.^{368,369} Typical values of Q_{CH} (in MHz or Gauss) fall into the following ranges:³⁶⁸

- (1) radical anions, $-56 - (-76)$ MHz or $-20 - (-27)$ Gauss
- (2) neutral radicals, $-64 - (-84)$ MHz or $-23 - (-30)$ Gauss
- (3) radical cations, $-73 - (-90)$ MHz or $-26 - (-32)$ Gauss

A relationship analogous to that in eq. 7 can be applied to sp^2 -hybridized nitrogens:^{368,370}

$$A(^1\text{H})_{\text{N}} = Q_{\text{NH}} \cdot \rho_{\text{N}} \quad (8)$$

where $A(^1\text{H})_{\text{N}}$ is hyperfine coupling constant for ^1H within the N-H bond and ρ_{N} is the spin density at nitrogen. We will use unambiguously determined value $Q_{\text{NH}} = A(^1\text{H})_{\text{N}} = -72.5$ MHz ($A_{\text{NH}} = -25.9$ Gauss) in NH_3 radical cation.³⁷¹ Because in isoelectronic methyl radical, $Q_{\text{CH}} = A(^1\text{H}) = -64.5$ MHz ($A_{\text{CH}} = -23.0$ Gauss),³⁶⁹ we will use a factor of $Q_{\text{CH}}/Q_{\text{NH}}$ to convert experimentally determined values

of $A(^1\text{H})_{\text{N}}$ (or A_{NH}) to “adjusted $|A(^1\text{H})|$ ” (or “adjusted A_{CH} ”).

Values of experimental $|A_{\text{CH}}|$ (or “adjusted $|A_{\text{CH}}|$ ”) in Gauss for the following monoradicals are converted to $|A(^1\text{H})|$ in MHz, using experimental g -values, as summarized in Figure 31 and Table 4.3.5: methyl nitroxide (its “adjusted $|A(^1\text{H})|$ ” is used for *tert*-butyl nitroxide),^{372,373} phenyl nitroxide,^{374,375} *tert*-butylphenyl nitroxide,³⁷⁶ diphenyl nitroxide,³⁷⁷ Blatter radical,³⁷⁸ oxoverdazyl radical,³⁷⁹ 3,5-di-*tert*-butyl-semiquinone,³⁸⁰ 3-*tert*-butyl-5-phenylsemiquinone,³⁵⁸ dihydro-phenazine radical cation,³⁸¹ trioxytriphenylamine radical cation,³⁸² and phenothiazine radical cation.³⁸³

Linear regression of J/k vs. $|A(^1\text{H})|$ is reasonable,^{313,358} only when diradical cation **23** and diradicals **1**, **3**, and **4** are excluded as outliers (Figure 32). The reasons for exclusion of **23** were discussed in the preceding paragraphs – **23** is a clear-cut outlier. Diradicals **1** and **4** must be excluded because of large torsion angles θ and **3** is excluded because of large error in its large value of J/k reported as the lower limit. For other 16 values of J/k , good correlation with $|A(^1\text{H})|$ is obtained, with statistically adjusted $R^2 = 0.8777$, because in the corresponding di- and triradicals the torsion angles θ are low to moderate (Table 4.3.5). In addition, this may suggest that differences in McConnell constants (Q_{CH} , Eq. 8) between neutral radicals and radical ions are either not significant in our set of monoradicals (Figure 31) or these differences are built-in to J/k . In the second case, this would mean that, with identical spin densities at atom X, values J/k are in the following order: radical cations > neutral radicals > radical anions.

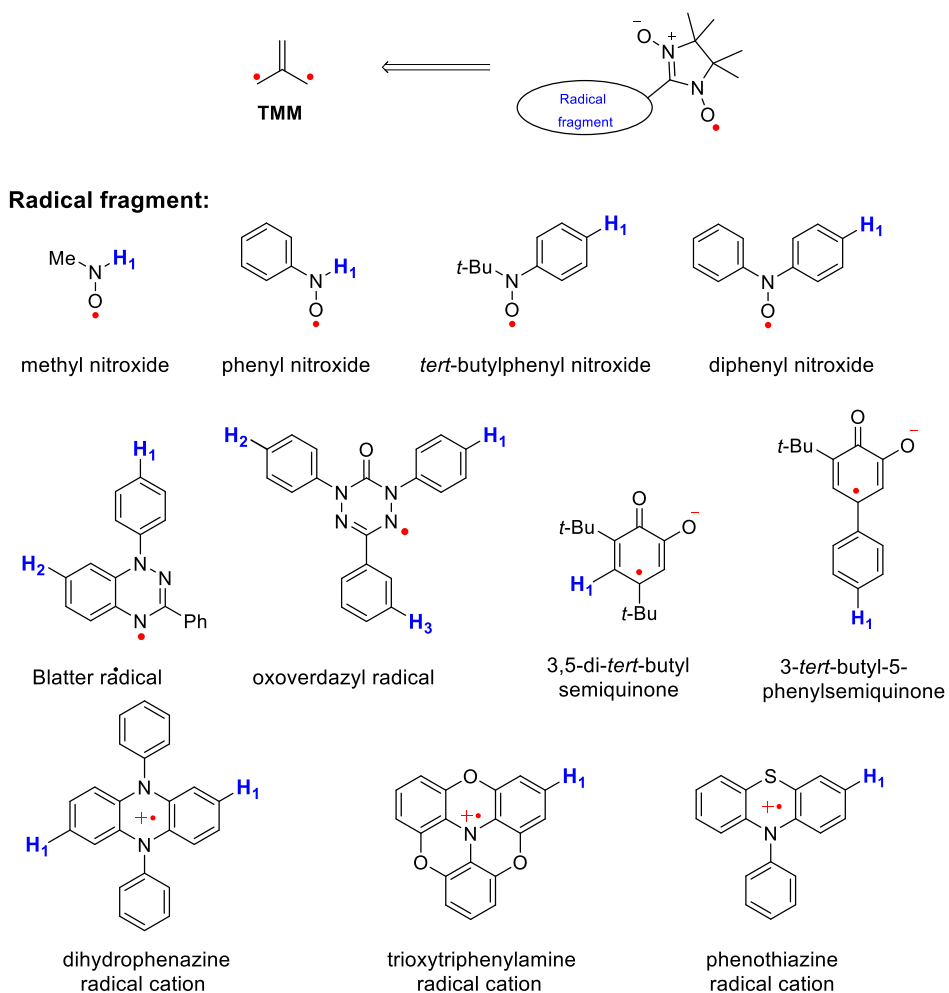


Figure 31. Structures of monoradical centers – fragments of NN-based di- and triradicals. Hydrogen atoms (protons), for which values of A_{CH} and $|A(^1\text{H})|$ are listed in Table 2, are highlighted in blue color. For 3,5-di-*tert*-butyl semiquinone, it is assumed that the spin densities at C4 and C5 are very similar.³⁸⁰

Table 4.3.5. Experimental J/k for selected high-spin di- and triradicals (Figures 21, 26, and 27) and hyperfine coupling constants ($|A(^1\text{H})|$) for the corresponding monoradicals (Figure 31).

Di- or triradical	Corresponding monoradical	^a g	$ A_{\text{CH}} $ (Gauss)	^b $ A(^1\text{H}) $ (MHz)	^c θ_{avg} (°)	$ A(^1\text{H}) *\cos^2\theta$ (MHz)	^d J/k (K)	Monoradical reference
1	alkyl nitroxide	2.0055	^e 12.3	34.49	72.7	3.05	390	372/373
3	phenyl nitroxide	2.0055	^e 11.3	35.75	17.6	28.85	>1000	374/375
4	alkyl nitroxide	2.0055	^e 12.3	34.49	64.1	6.58	440	372/373
5	<i>tert</i> -butylphenyl nitroxide	2.0060	1.9	5.33	27.4	4.62	319	376
7	diphenyl nitroxide	2.0056	1.83	5.14	^f 26.5	4.11	231	377
8	diphenyl nitroxide	2.0056	1.83	5.14	25.5	4.18	349	377
10	Blatter radical	^g 2.0033	0.61	1.71	28.6	1.32	121.5	36
11	Blatter radical	^g 2.0033	1.84	5.16	ⁱ 21.5	4.46	438	37
12	Blatter radical	^g 2.0033	0.61	1.71	31.8	1.23	94	38
			1.84	5.16	20.6	4.52	352	38
14	oxoverdazyl radical	2.0037	0.65	1.82	35.7	1.20	72	39
15	oxoverdazyl radical	2.0037	0.18	0.50	21.5	0.44	17.8	39
17	oxoverdazyl radical	2.0037	0.65	1.83	51.2	0.72	17	40
			0.65	1.83	28.1	1.42	105	40
18	3,5-di- <i>tert</i> -butyl-semiquinone	^h 2.0047	3.33	9.33	1.0	9.33	446	380
19	3- <i>tert</i> -butyl-5-phenylsemiquinone	^h 2.0047	0.61	1.71	ⁱ 10.5	1.65	144	358
23	dihydrophenazine radical cation	2.0029	1.75	4.90	20.4	4.31	700	381
25	dihydrophenazine radical cation	2.0029	1.75	4.91	10.1	4.75	160	381
26	trioxytriphenylamine radical cation	2.0031	2.60	7.28	29.8	5.48	400	382
28	phenothiazine radical cation	2.0052	2.15	6.03	13.1	5.72	320	383

^a g is the isotropic g -value of monoradicals. ^b $\Delta\nu = \Delta B(g\mu_B/h)$, conversion from Gauss to MHz, where h is the Plank's constant, g is the isotropic g and μ_B is the Bohr magneton. ^cThe θ is the average of torsional angles between NN moieties and corresponding monoradical-fragments in di- and triradicals; all data are from the crystallographic files. ^dThe J/k is from SQUID, while the values of J/k for **10** and **12** are the averages from SQUID and quantitative EPR spectroscopy. ^e The “adjusted $|A_{\text{CH}}|$ ” of alkyl nitroxides is derived from that of methyl nitroxide, $|A_{\text{NH}}| = 13.8$ G, and for 1,3,5-triphenylphenyl nitroxide from that of phenyl nitroxide, $|A_{\text{NH}}| = 12.75$ G; these values are converted to the corresponding “adjusted $|A_{\text{CH}}|$ ” by correcting for the different values of McConnell's Q constants for nitrogen vs carbon; e.g., for alkyl nitroxides “adjusted $|A_{\text{CH}}|$ ” = $13.8/(-25.9)*(-23.0)$ G = 12.3 G. ^fThe single crystal structure of **7** is not obtained, thus for this triradical θ is assumed to be the average θ for **5** and **8**. ^gThe g -value is from SI of ref 384. ^hThe g -value is from ref 385. ⁱThe structures of diradical **11** and diradical anion **19** contain two different molecules, their θ is the average value of two molecules. When it is assumed that in DCM-free polycrystalline material of **11**, used for SQUID magnetometry, only molecules A are present, with $|\theta_{\text{avg}}| \approx 14^\circ$, then $|A(^1\text{H})|*\cos^2\theta = 4.86$.

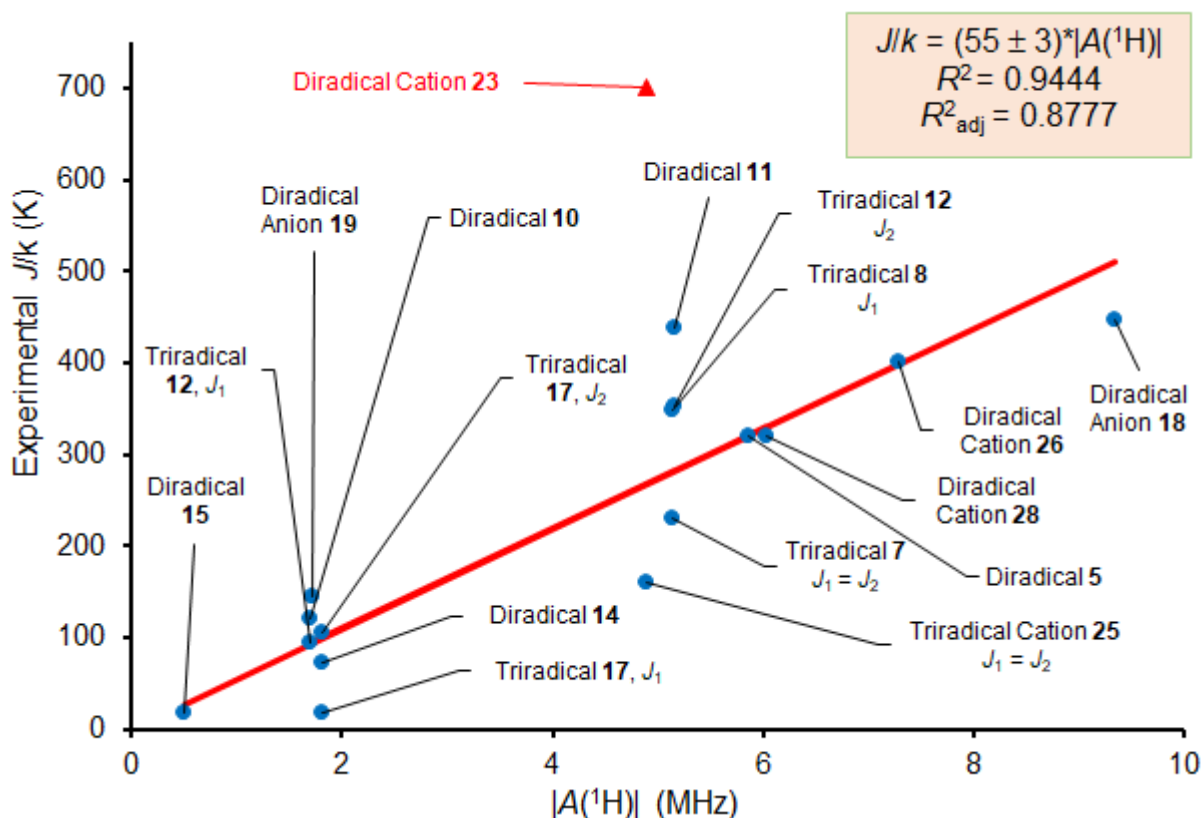


Figure 32. Plot of experimental J/k vs. $|A(^1H)|$ and linear regression. Outliers, such as diradical cation **23**, diradical **1**, diradical **3**, and diradical **4** are not included in the linear regression; diradical cation **23** is shown in red color and diradicals **1**, **3**, and **4** are out of range of the plot and are not shown. Based on linear regression, predicted values of J/k for **23** and **3** are 268 and 1700 K, respectively.

In 2003, in ground-breaking contributions, Shultz and coworkers^{386,387} established the Karplus-Conroy-type³⁸⁸ relation between pairwise exchange coupling constant J (cm^{-1}) and torsional angles θ between radical center (fragments) and ferromagnetic coupling unit, such as 1,2-connected ethene (Figure 33, Eq 9):

$$J = A \cos^2(\theta) - B \quad (9)$$

where A is the constant for ferromagnetic term and B is the constant for antiferromagnetic term.

Two series of TMM-based diradicals, bis(semiquinone) and bis(nitroxide), are studied (Figure 33). For bis(semiquinone) diradicals, $A = 213$ and $B = 44 \text{ cm}^{-1}$ and for bis(nitroxide) diradicals, $A = 44$ and $B = 17 \text{ cm}^{-1}$ are determined. Smaller values of A and B for bis(nitroxides) reflect smaller spin densities at the connecting atom of monoradical nitroxide fragment. Thus, when the torsional angle is smaller than $\sim 50^\circ$ for bis(semiquinone) diradicals and less than $\sim 60^\circ$ for bis(nitroxide) diradicals, they possess

ferromagnetic intramolecular exchange interactions. Otherwise, they possess antiferromagnetic intramolecular exchange interactions. It should be noted that in these diradicals, the larger θ leads to increased antiferromagnetic through-space exchange coupling between the monoradicals, thus leading to relatively large values of B .

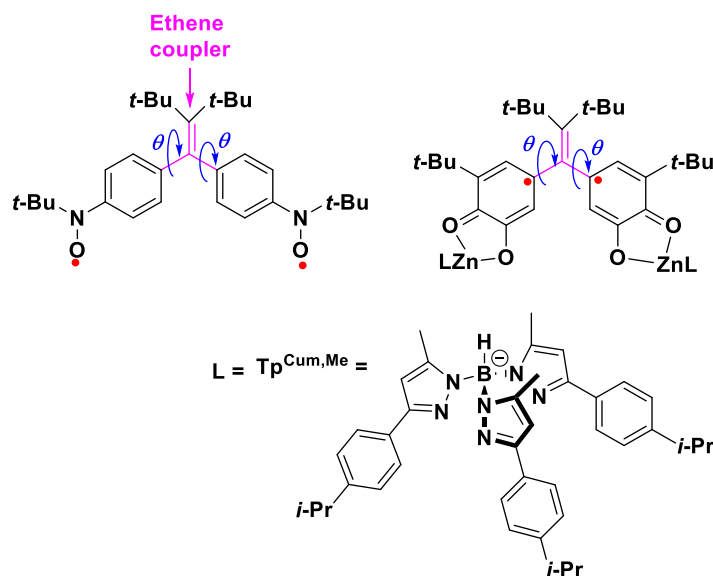


Figure 33. Selected TMM-type bis(nitroxide) and bis(semiquinone) diradicals. The ethene coupler and torsional angle θ are shown.

In addition to Shultz's relation (eq. 9), we should consider Heller-McConnell relation^{389,390} for hyperfine coupling constant for β protons (eq. 10):

$$A(^1\text{H})_{\beta} = Q_{\text{CH}^{\beta}} \rho_{\text{C}} \cos^2(\theta) \quad (10)$$

where $A(^1\text{H})_{\beta}$ (in MHz) is the hyperfine coupling constant for β proton (H_{β}), ρ_{C} is the spin density at α carbon (C_{α}), $Q_{\text{CH}^{\beta}}$ is the constant (in MHz). Dihedral (torsion) angle θ is defined by the $\text{H}_{\beta}\text{-C}_{\beta}\text{-C}_{\alpha}$ plane and the axis of $2p_{\pi}$ orbital with unpaired electron at C_{α} (Figure 34).

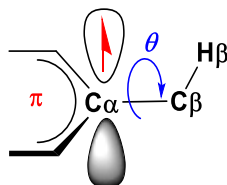


Figure 34. Hyperfine coupling to β protons.

Based on the above discussion, the torsional angle between NN moiety and bonding radical fragment in the NN-based high-spin radicals may need to be considered in the intramolecular exchange

interaction. We note that in Shultz's relations, $A < B$, and, for each pairwise J/k , two average torsion (or dihedral) angles θ are involved. However, in our system only a single average torsion angle between NN moiety and the bonded radical fragment is involved (Figure 30), and thus much larger θ ($\sim 90^\circ$) might be required for crossover to antiferromagnetic J/k . In view of the above discussion and Heller-McConnell relation, we propose the relation between the following experimental variables: pairwise J/k in NN-based high-spin di- and triradicals (neutral and ions) and torsion corrected $|A(^1\text{H})|$ in related monoradicals:

$$J/k = A * |A(^1\text{H})| * \cos^2(\theta) \quad (11)$$

where A is the constant (slope in a linear regression). After exclusion of diradicals **1**, **3**, and **23** from linear regression, statistically adjusted $R^2 = 0.8721$ for the set of 17 values of J/k is obtained, indicating a reliable correlation. Based on the regression (Figure 35), we predict for **1**, **3**, and **23**, "correct" values of $J/k = 190, 1800$, and 268 K, compared to experimental values $390, >1000$, and >800 K, respectively.^{349,351,361} The experimental value of ΔE_{ST} for **1** was likely overestimated while for **23**, as discussed in the prior sections, it was incorrect. For diradical **3**, we confirm very large value of $\Delta E_{\text{ST}} \approx 7.2$ kcal mol⁻¹, which would be challenging to be determined by the experiment, based on the detection of thermal population of the lowest singlet excited state (Figure 19).

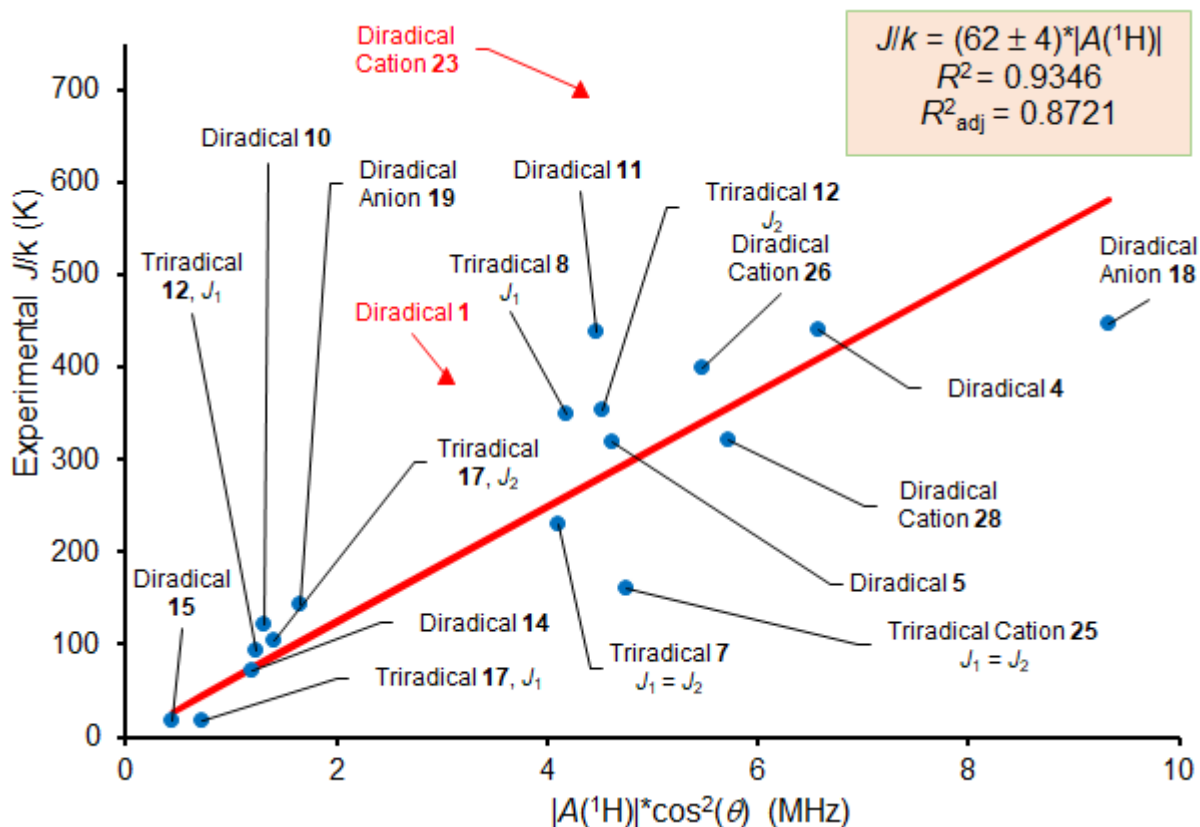


Figure 35. Plot of experimental J/k vs. $|A(^1H)| \cdot \cos^2(\theta)$ and linear regression. Outliers, such as diradical cation **23**, diradical **1**, and diradical **3** (not shown) are not included in the linear regression; data points for **23** and **1** are shown in red color. Based on the linear regression, predicted values of J/k for **23**, **1**, and **3** are 268, 190, and 1800 K, respectively.

In addition, the average torsional angles ε of the phenyl groups (connected to N or C) in Blatter and oxoverdazyl radical are considered (Figure 36). Because the change of ε angles can affect the overlap of $2p_\pi$ -orbitals and then alter the spin delocalization. For instance, the average ε in Blatter radical is 54.2° .³⁹¹ These angles decrease to 45.4° in **10**,¹⁴⁷ 41.1° in **11**,¹⁴⁸ and 45.1° or 49.8° in **12** (**12** has two pseudo polymorphs).¹⁴⁹ The smaller ε angle can increase the effective $|A(^1H)|$ in the Blatter radical moiety. Thus, the effective $|A(^1H)|$ in diradical **10** is larger than that of parent Blatter, thus **10** lies above the regression line (Figure 35).

Two ε angles in 1,3,5-triphenyl-6-oxoverdazyl radical are 38.2° .³⁷⁹ However, the ε angles in **17** are different, 25.3° and 46.6° .¹⁵⁴ As a result, two different ε angles in triradical **17** enhance the difference between J_1/k and J_2/k , due to two different θ angles (Table 4.3.5).

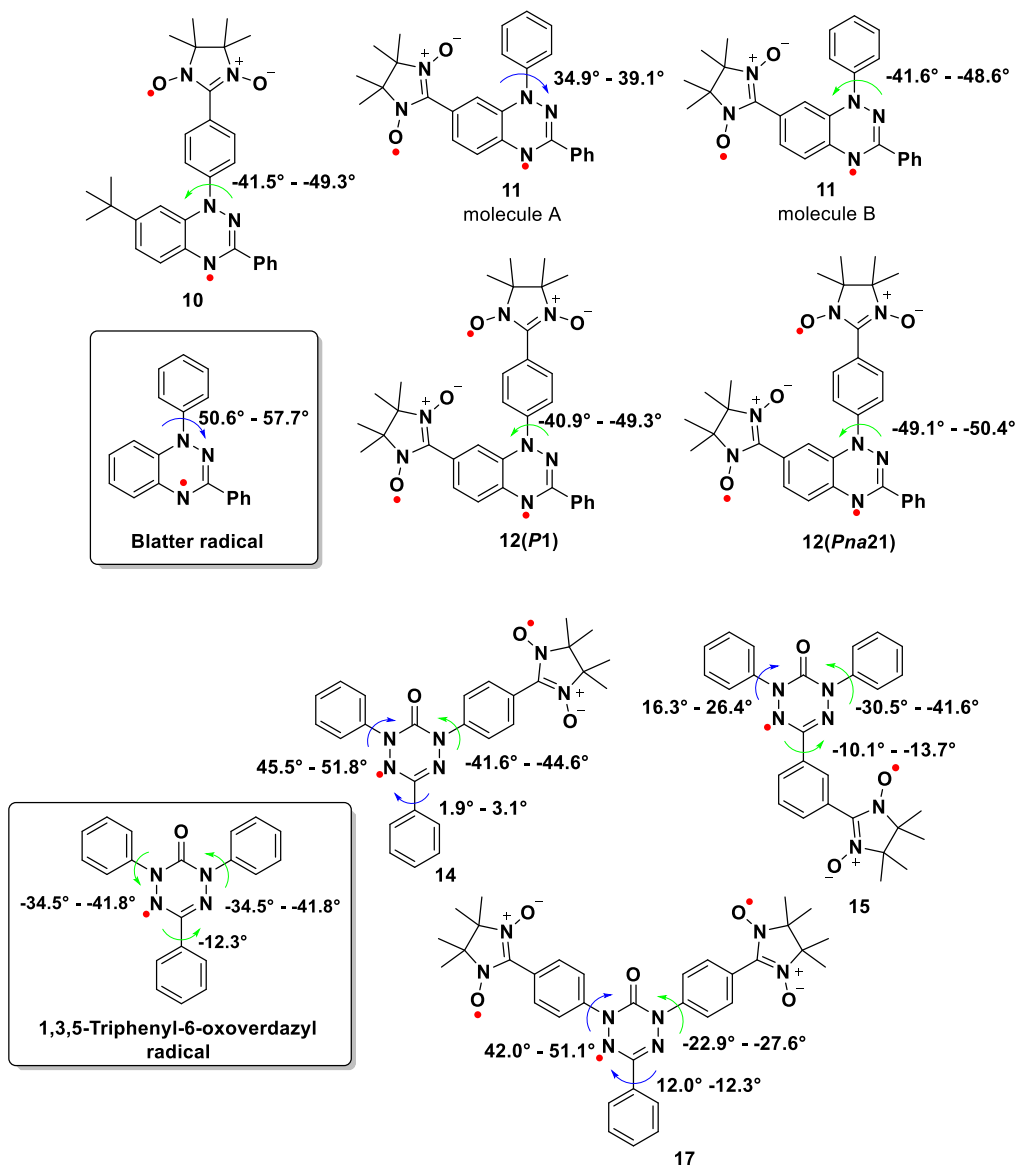


Figure 36. Structures of Blatter radical, oxoverdazyl radical, corresponding di- and tri-radicals and definition of torsional angles ϵ . All the angles are from the X-ray crystal structures. ^{147-149, 153, 154, 391}

4.4. High-spin diradicals with Kekulé resonance forms – rule breakers?

In this section, we discuss exceptional high-spin diradicals, which possess Kekulé resonance forms. There is a significant classic work done, both experimental and computational, on antiaromatic diradicals, such as pentadienyl cation³⁹²⁻³⁹⁵ and benzene dication.³⁹⁶⁻⁻³⁹⁸ In 2021, definitive work on triplet ground state of benzene dianion have appeared.³⁹⁹ We will focus our discussion on recent examples where the significant effort was done to determine the ground state, starting with odd alternant π -systems and ending with even-alternant chiral π -systems.

1,8-Perinaphthyldiyl is a well-known non-Kekulé, C_{2v} -symmetric molecule⁴⁰⁰ with planar, alternant π -system (Figure 37), possessing connectivity corresponding to triplet ground state (Figures 15 and 16). Recent computations by Borden et al at the (12/12)CASPT2/aug-cc-PVDZ+ZPVE level predict triplet ground state with $\Delta E_{ST} = 4.4 \text{ kcal mol}^{-1}$.⁴⁰¹ (We should note that at the same level of theory, analogous 1,8-naphthoquinodimethane is predicted to be singlet ground state with $\Delta E_{ST} = -2.1 \text{ kcal mol}^{-1}$.⁴⁰¹) Wirz et al studied R = H and R = Me derivatives of 1,8-perinaphthyldiyl and also concluded that both molecules are triplet ground state. This conclusion was largely based on the absence of temperature dependence in UV-vis absorption, excitation, and fluorescence spectra, and their agreement with the computed spectra for triplet state; experimental absorption spectra showed absence of NIR bands, which were computed for the spectra of singlet state. Unfortunately, EPR I vs. $1/T$ plots showed some downward curvature at low temperatures (e.g., for R = Me, $\Delta E_{ST} \approx -0.006 \text{ kcal mol}^{-1}$), which were tentatively associated with either inadequate temperature control or microwave saturation (Section 4b1).^{402,403} In summary, we conclude that 1,8-perinaphthyldiyls are triplet ground states with substantial ΔE_{ST} .

In 1997, McMasters, Wirz, and Snyder reported on two 1,8-perinaphthyldiyl derivatives, with nonalternant π -systems, that also possess Kekulé resonance forms, i.e., 2,2-dimethyl-2*H*-benzo[*cd*]fluoranthene (**29**) and 2,2-dimethyl-2*H*-dibenzo[*cd,k*]fluoranthene (**30**) (Figure 37).^{404,405} These molecules compensate the formal loss of a double bond in the diradical non-Kekulé resonance form with the aromatic resonance energy of fluoranthene and benzo[*k*]fluoranthene, respectively. Ground states for both diradicals are established based on the UV-vis-NIR absorption spectra; that is, for **29**, well-resolved NIR bands extending to ca. 1300 nm are found, while for **30**, the spectrum extends to just 665 nm, where a very sharp band is observed. These distinct spectral features for singlet vs. triplet states are reproduced by the Pariser–Pople–Parr (PPP) semiempirical type of computations.⁴⁰⁵

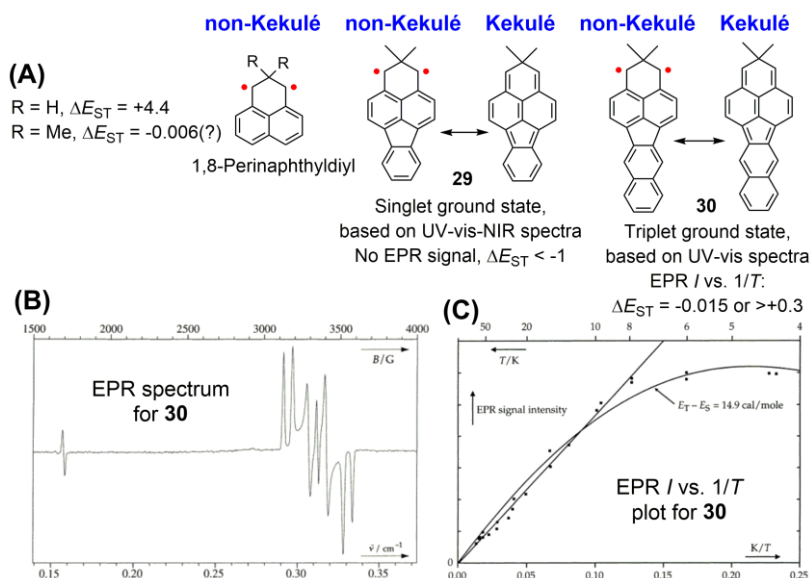


Figure 37. (A) McMaster, Wirz, and Snyder diradicals **29** and **30**. Values of ΔE_{ST} are in kcal mol⁻¹. (B) and (C) EPR spectroscopy of diradical **30**. Parts (B) and (C) of the figure are reproduced from ref. 405. Copyright 2001 American Chemical Society

Singlet ground state for **29** is also supported by the absence of EPR signal for triplet state at temperatures up to 170 K, thus providing a rough upper limit estimate, $\Delta E_{ST} < -1$ kcal mol⁻¹. In contrast to **29**, a strong EPR spectrum corresponding to paramagnetically pure triplet state of **30** is detected in 2-MeTHF at 90 K; that is, the center peak at 3340 Gauss was assigned to double quantum transition in the triplet state (Figure 37). While plot of I vs $1/T$ is approximately linear in the 50 – 8 K (and 75 – 8 K) temperature range, when data points at 6 and 4 K are included, a curved plot, corresponding to $\Delta E_{ST} < -0.015$ kcal mol⁻¹, is obtained. Analogously to the authors' studies of 1,8-perinaphthyldiyl (see above),^{402,403} the downward curvature of the I vs. $1/T$ plot is tentatively associated with inadequate temperature control or microwave saturation (Section 4b1).⁴⁰⁵ In summary, we conclude that diradical **30** is the triplet ground state with estimated lower limit of $\Delta E_{ST} > +0.3$ kcal mol⁻¹.

In 2022, Yasuda, Konishi, Kishi, and coworkers have succeeded in preparation of the 7th (final) nonalternant isomer of pyrene **31** (Figure 38A).⁴⁰⁶ Diradicals **31a** and **31b** are sensitive to air, with $\tau_{1/2} = 19$ and 73 h. Both diradicals possess singlet ground state, and not surprisingly **31b** possesses larger $|\Delta E_{ST}|$, suggesting better stabilization of zwitterionic singlet state by the electron withdrawing

group (Dcp). However, the magnitude of this effect ($3 - 4 \text{ kcal mol}^{-1}$) is rather surprising (Figure 38A).

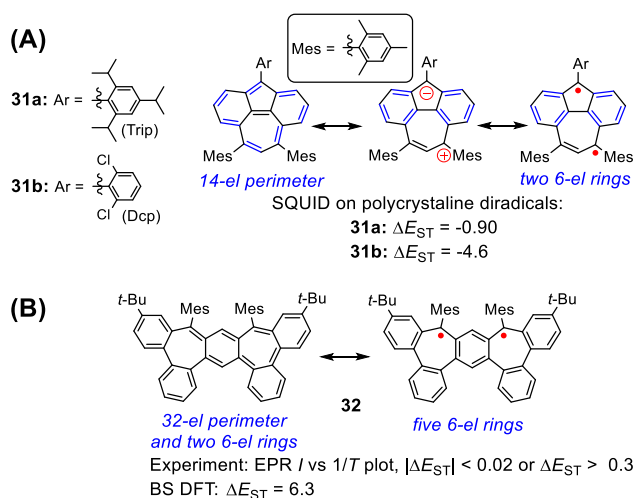


Figure 38. (A) Final nonalternant isomer of pyrene (azulene-based): singlet ground state with substituent dependent ΔE_{ST} . (B) Nonalternant diradical **32**: most likely, triplet ground state with large ΔE_{ST} . Values of ΔE_{ST} are in kcal mol^{-1} .

In 2022, Shintani, Sato, Shimizu and coworkers were successful in synthesis, isolation, and crystallographic characterization of air-sensitive ($\tau_{1/2} \ll 15 \text{ min}$ on air) diradical **32**.⁴⁰⁷ The diradical resonance form is clearly much better stabilized, compared to the Kekulé resonance form, which also comprises of antiaromatic 32 π -electron perimeter (Figure 38B). This is unlike in diradical **31**, where the Kekulé form has an aromatic 14 π -electron perimeter and zwitterionic form (with two benzenoid rings) is a significant contributor (Figure 38A). Consequently broken-symmetry DFT computations predict triplet ground state with large $\Delta E_{ST} = 6.3 \text{ kcal mol}^{-1}$, which is comparable to $\Delta E_{ST} = 6.4 \text{ kcal mol}^{-1}$ computed at the similar level of theory (UB3LYP/6-31G(d)+ZPVE) for the planarized triarylmethyl diradical (see: the corresponding radical anion **PTAM** in Figure 10). This is reasonable because the DFT-computed spin density distributions in the triplet states of **32** and diradical **PTAM** are similar (Figure 39). Because the EPR spectrum of **32** shows a significant contamination ($\geq 50\%$) with unknown $S = 1/2$ impurities (Figure 39ab,f), the authors are able to obtain only I vs. $1/T$ plot for $|\Delta m_s| = 2$ transition.⁴⁰⁷ (Authors fail to display full scale spectrum showing the center peak for $S = 1/2$ impurities and to demonstrate whether the spectrum was obtained under the conditions, in which $S =$

$\frac{1}{2}$ species are not partially saturated; this makes our estimate of amount of $S = \frac{1}{2}$ impurities very approximate.) An approximate linearity of this plot in the 4.7 – 68 K temperature range suggests either near-degenerate singlet and triplet states with $|\Delta E_{ST}| < 0.02$ kcal mol⁻¹ or triplet ground state with $\Delta E_{ST} > 0.3$ kcal mol⁻¹. We note that in the work done more than 30 years ago,³⁴ air-sensitive diradical **PTAM** could be isolated as a reasonably pure polycrystalline solid, with a clean triplet EPR spectrum in glassy 2-MeTHF and SQUID data on the polycrystalline sample provided clear-cut evidence of the triplet ground state. We conclude that diradical **32** is most likely triplet ground state.

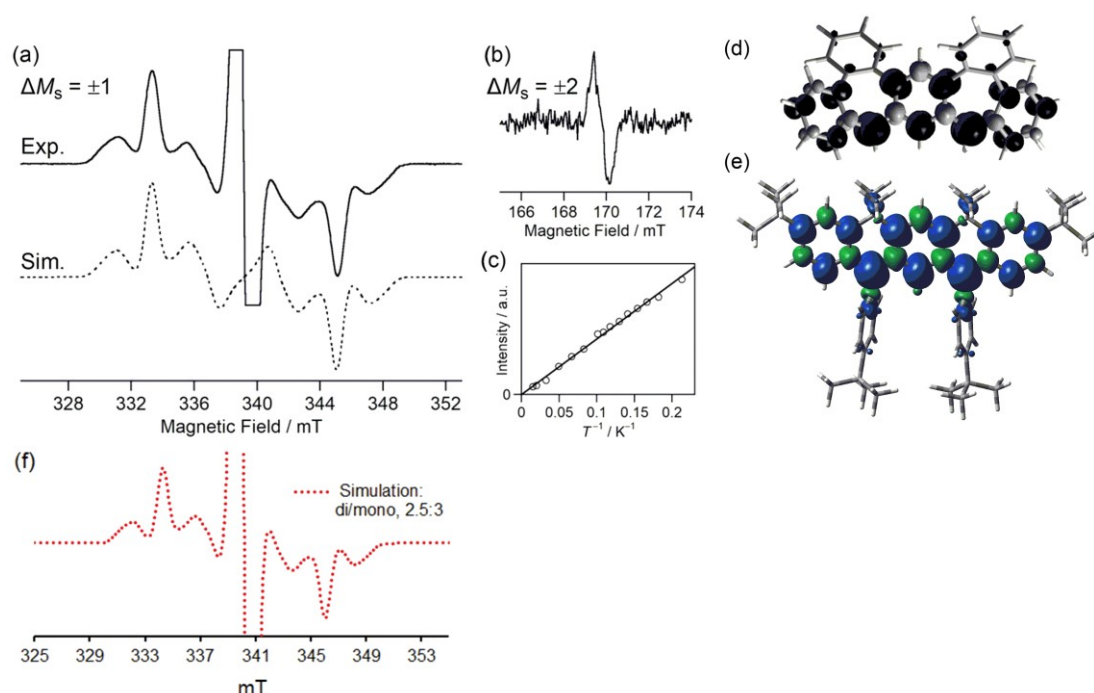


Figure 39. EPR spectra of diradical **32** in toluene at 69 K (solid line: experiment, dashed line: simulation), (a) $|\Delta m_s| = 1$ and (b) $|\Delta m_s| = 2$. (c) Plot of the temperature dependence of the triplet signal intensity I versus $1/T$ from 68 to 4.7 K. (d) and (e) Spin density maps for triplet states of diradicals: simplified **32** ((d)) and **PTAM** ((e), isodensity level of 0.002 electron/Bohr); darker and blue colors correspond to positive spin densities. (f) Simulation of the spectrum in (a) with monoradical-to- $S = 1$ diradicals molar ratio of 3:2.5; for both monoradical and two conformers of diradical (1.5:1), the parameters listed in ref 407 (Fig. S9, SI) are employed. Parts (a) – (d) of the figure are reproduced with permission from ref. 407. Copyright 2022 Wiley.

In 2019, our group reported an air-stable diradical dication **33** of chiral D_2 -symmetric conjoined bis[5]diazahelicene with a high-spin ($S = 1$) ground state and $\Delta E_{ST} \approx 0.3$ kcal mol⁻¹ (Figure 40).³⁰¹ (For a structure of analogous $S = \frac{1}{2}$ radical cation, see Figure 10.) This diradical dication possesses closed-shell (Kekulé) resonance forms with Hückel antiaromatic 16 π -electron perimeters, as shown for a simplified structures of **33a** in Figure 40.

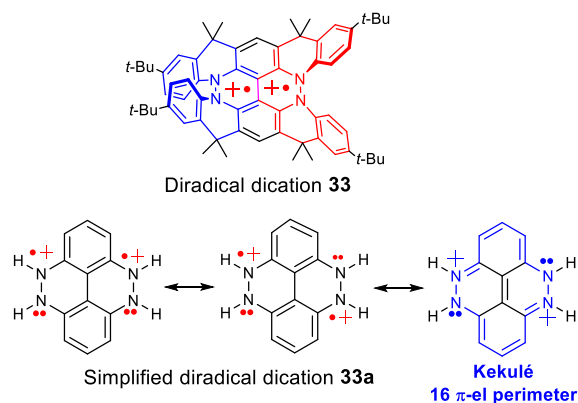


Figure 40. Structure drawing of diradical dication **33** and the representative resonance forms for simplified structure **33a**. Reproduced from ref. 301. Copyright 2019 American Chemical Society.

We note that the non-Kekulé resonance forms of **33a** possess Hückel antiaromatic 16 π -electron perimeters, but these are well offset by two benzenoid rings, thus leading to relative stabilization of open-shell forms.

The diradical dication is monomeric in dibutyl phthalate (DBP) solution/matrix and its EPR spectra are paramagnetically pure (Figure 41). Quantitative EPR spectroscopy is used to determine the ground state and ΔE_{ST} by the by measurements of χT in the $T = 105\text{--}330$ K range (Figure 41). The following standard procedure is employed: “Values of χT are obtained by spin counting using a standard such as TEMPONE in DBP (in triplicate, $n = 3$) and then are fit to the Bleaney–Bowers equation (e.g., eq. 5 with $\theta = 0$) to provide a singlet–triplet energy gap $2J/k = 145 \pm 4$ K (mean $\pm$ SE), i.e., $\Delta E_{ST} \approx 0.3 \text{ kcal mol}^{-1}$.”³⁰¹

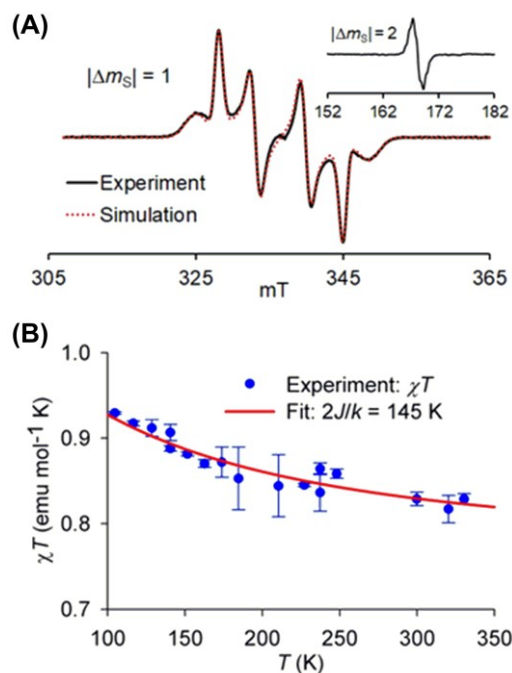


Figure 41. EPR spectroscopy of 0.82 mM diradical dication **33** in DBP: (A) spectra at 117 K; (B) plot of χT vs. T , obtained by quantitative EPR spectroscopy. Reproduced from ref. 301. Copyright 2019 American Chemical Society.

In a different experiment, quantitative EPR spectroscopy with 14 time points in the 0–48 h range and with accurate measurements ($n = 3$) of χT at 117 K, provides $\tau_{1/2} > 2$ weeks at ambient conditions (on air) in the presence of excess oxidant ($\text{NO}^+\text{SbF}_6^-$).

Partially enantiomerically enriched samples of **33** show good chiroptical properties with $\Delta\epsilon_{\text{max}} \approx 30 \text{ L mol}^{-1} \text{ cm}^{-1}$ and anisotropy factor $|g| = |\Delta\epsilon|/\epsilon \approx 0.005$,³⁰¹ this value will be re-measured, as recently, we are able to isolate enantiomerically and paramagnetically pure **33**, and to obtain its X-ray structure. The reported value of $|g|$ for **33** is comparable to $|g| = 0.004$ for the Osuka's air-stable porphyrin-based $S = 1/2$ radical (Figure 8)²⁹⁸ and to those of [6]helicene ($|g| = 0.007$)⁴⁰⁸ and neutral carbon–sulfur [7]helicene ($|g| = 0.004$)⁴⁰⁹ but smaller than the $|g| = 0.039$ for neutral carbon–sulfur double helix.⁴¹⁰

In summary, the first triplet ground state diradical (dication), in which the spin density is delocalized over double helical (or helical) π -system. Notably, *triplet ground state was found despite the presence of Kekule resonance form with alternant π -system*. Although its chiroptical properties

appear promising, the $\Delta E_{\text{ST}} \approx 0.3 \text{ kcal mol}^{-1}$ is still a bit too low and counterions are likely to affect the properties in the single crystals and thin films. We were able to identify two new triplet ground state diradicals, with double helical π -systems, one neutral and another dicationic but with higher ΔE_{ST} (Figures 10 and 12).

4.5. High-spin Blatter-based diradical as electrical conductor – rule breaker?

This Section is focused on high-spin diradical **34** (Figure 42), which also possesses good electrical conductivity, $\sigma_{\text{RT}} = 0.044 \pm 0.012 \text{ S cm}^{-1}$ (mean $\pm$ SE), at room temperature.¹⁵⁰ These measurements were carried out on 15 randomly selected single crystals, with the best single crystal device possessing $\sigma_{\text{RT}} = 0.13 \text{ S cm}^{-1}$.¹⁵⁰ The discovery of good electrical conductivity in **34** is unusual because its cross-conjugated π -system does not promote electron delocalization^{305,313,329} or conductance.⁴¹¹⁻⁴¹³ For example as mentioned in Section 3, in triarylmethyl-based radical anion, which formally derived by 1-electron reduction of high-spin ground state *m*-phenylene diradical, has the spin density localized on one of the two triarylmethyl moieties, based on EPR spectra (also, see: spin density maps for radical anion **MX** in Figure 10);^{305,313} similar localization of spin density is observed in high-spin diradical anions and diradical dianions formally derived from the corresponding high-spin tri- and tetraradicals.³²⁹ Significantly lower single molecule conductance observed for cross-conjugated π -systems^{412,413} may be associated with quantum interference.⁴¹¹

We will start with an overview of electrical conductivity in stable organic radicals, which were discussed throughout Section 2. Typical neutral π -radicals are insulators with $\sigma_{\text{RT}} < 10^{-10} \text{ S cm}^{-1}$, e.g., DPPH (Figure 3),^{127,128} galvinoxyl (Figure 5),¹²⁸ and TEMPOL (Figure 4).¹⁷⁵ Even recently prepared radicals forming π -dimers or equidistant π -stacks such as **OR1**,⁸¹ **BR1**,⁸² and Kubo's phenalenyl⁷⁹ with R = perfluorophenyl (Figure 1) possess very low conductivity $\sigma_{\text{RT}} < 3 \times 10^{-9} \text{ S cm}^{-1}$. We note that equidistant π -stacks for **BR1** and Kubo's phenalenyl has plane-to-plane distances of 3.565 and

3.503 Å, respectively. In comparison Haddon's zwitterionic spiro-bis(phenalenyl) (R = benzyl) (Figure 1), forming a uniform one-dimensional $S = \frac{1}{2}$ antiferromagnetic Heisenberg chain ($J/k = -75$ K) and possessing closest C---C contacts of 3.47 and 3.58 Å along the stacking direction, has $\sigma_{\text{RT}} = 1.4 \times 10^{-3} \text{ S cm}^{-1}$ with $E_a = 200 \text{ meV}$.⁸⁵ Similarly, single crystal **TOT** (R = Br) (Figure 5), which forms slipped π -stack with equidistant TOT moieties (3.43 Å), has $\sigma_{\text{RT}} = 1.8 \times 10^{-3} \text{ S cm}^{-1}$ with $E_a = 0.310 \text{ meV}$.²³¹ Single crystal **TOT** (R = H) (Figure 5) possesses is reported to possess even higher $\sigma_{\text{RT}} = 0.32 \text{ S cm}^{-1}$ with $E_a = 90 \text{ meV}$.²³⁶ This conductivity is similar to that in Boudouris' thin films of **PTEO** (Figure 4)¹⁷⁶ with $\sigma_{\text{RT}} \approx 0.3 \text{ S cm}^{-1}$ and Haddon's zwitterionic spiro-bis(phenalenyl) (R = *n*-hexyl) (Figure 1) with $\sigma_{\text{RT}} \approx 0.3 \text{ S cm}^{-1}$ and $E_a = 50 \text{ meV}$.⁸⁴ Oakley's best optimized neutral radical, oxo-bridged bisthiazolyl, **OBBDTA** (Figure 5), attains $\sigma_{\text{RT}} \approx 0.04 \text{ S cm}^{-1}$ with $E_a = 50 \text{ meV}$;²⁵⁷ at high pressure, this radical exhibits metal-like behavior with $\sigma_{\text{RT}} \approx 0.04 \text{ S cm}^{-1}$ and $E_a < 0$.²⁵⁷

Examination of the spin density in Blatter radical reveals large positive and negative spin densities at C7 and C3. Therefore, application of parity rules (Figure 15) indicates to us that a connection between the C7 and C3 positions would provide a di-Blatter high-spin diradical (Figure 42).

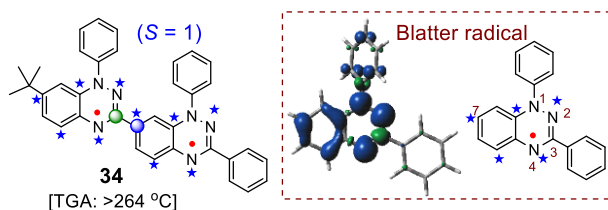


Figure 42. Structure drawing of diradical **34** and the design leading to high-spin ground state. An asterisk corresponds to spin-up in Figure 15; spin up at N2 spans both N1 and N2. TGA onset of decomposition $\approx 1\%$ mass loss. Blatter radical and its spin density map at the UB3LYP/6-31G(d,p) level of theory; positive (blue) and negative (green) spin densities are shown at the isodensity level of 0.002 electron/Bohr. Reproduced from ref. 150. Copyright 2022 American Chemical Society.

Diradical **34** may be viewed as thermally ultra-robust, based on the high onset temperature (1% mass loss) in TGA (Figure 42). In the crystal, two fused-ring Blatter radical moieties are nearly

coplanar, thus providing the conformation of **34** in the crystal that is near optimum for attaining both strong ferromagnetic coupling and electrical conductivity (Figure 43). The latter is promoted by the formation of 1D π -stacks along the

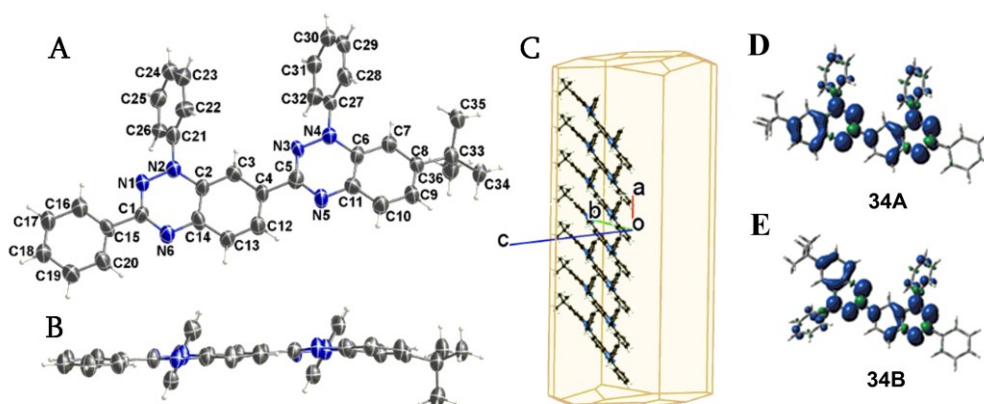


Figure 43. Single-crystal X-ray structure of diradical **34** at 100 K, with carbon and nitrogen atoms depicted using thermal ellipsoids set at the 50% probability level (A, B); the Bravais, Friedel, Donnay, and Harker (BFDH) crystal morphology of **34** (C), confirmed by the experimental face index; needle and stacking direction are along the *a*-axis. (D, E) Spin density maps for triplet states of two conformations **34A** and **34B** (at the UB3LYP/6-31G(d,p)+ZPVE level). Reproduced from ref. 150. Copyright 2022 American Chemical Society.

crystallographic *a*-axis, which coincides with the longest dimension of the single-crystal needle (Figure 43C), with an average plane-to-plane distance of 3.482 Å (planes defined by the N1–N6 and C1–C20 atoms). Because of multiple intermolecular C $\cdots$ C and N $\cdots$ C contacts within the sum of van der Waals radii plus 0.1 Å distances, in addition to a short C10 $\cdots$ C12 = 3.381 Å contact (within the 1D π -stack), involving predominantly atoms with significant (and same sign) spin densities, strong intermolecular antiferromagnetic interactions are anticipated in crystalline diradical **34**.

DFT computations at the UB3LYP/6-31G(d,p)+ZPVE level reveal that conformer **34A**, corresponding to that found in crystalline **34** (Figure 43), is a global minimum with $\Delta E_{ST} \approx 1.37$ kcal mol $^{-1}$, compared $\Delta E_{ST} \approx 0.34$ kcal mol $^{-1}$ for **34B**. Because the $\Delta E_{ST} > 0$ is overestimated at this level of theory, conformer **34B** may be a singlet ground state ($\Delta E_{ST} < 0$). Indeed, the χT vs. *T* data, obtained by quantitative EPR spectroscopy for the diradical in toluene/chloroform soft glass/fluid in the *T* = 110–331 K range, are best fit to a model of two conformations, one with $\Delta E_{ST} > 0$ (ca. +0.4

kcal mol⁻¹) and the other, a minor one, with $\Delta E_{ST} < 0$.¹⁵⁰ Major conformation may be trapped in a rigid polystyrene glass as confirmed by quantitative EPR spectroscopy, giving $2J/k = 275 \pm 36$ K, i.e., $\Delta E_{ST} \approx +0.5$ kcal mol⁻¹. The M/M_{sat} vs H/T data at $T = 1.8, 3$, and 5 K for **34** in polystyrene matrix approximately coincide with the $S = 1$ Brillouin curve, thus providing unequivocal evidence for the triplet ground state. Thus, we may conclude that **34A** found in the crystal is the triplet ground state with ΔE_{ST} of the order of 0.5 kcal mol⁻¹.¹⁵⁰

We are surprised to obtain unusual linear plots of conductivity, σ vs. T (Figure 44A, inset plot). Such plots may be interpreted in terms of temperature dependent effective E_a , which is ca. 12 meV and 0.03 meV in the high and low temperature ranges, respectively. To illustrate the smallness of E_a , it is perhaps better to express it as E_a/k ; in the high and low temperature ranges we have $E_a/k = 140$ and 0.06 K, respectively.¹⁵⁰ Therefore, $E_a/k \ll T$, especially in the low temperature range, where carrier–phonon interactions are lowered, implies band-like transport.¹⁷⁶

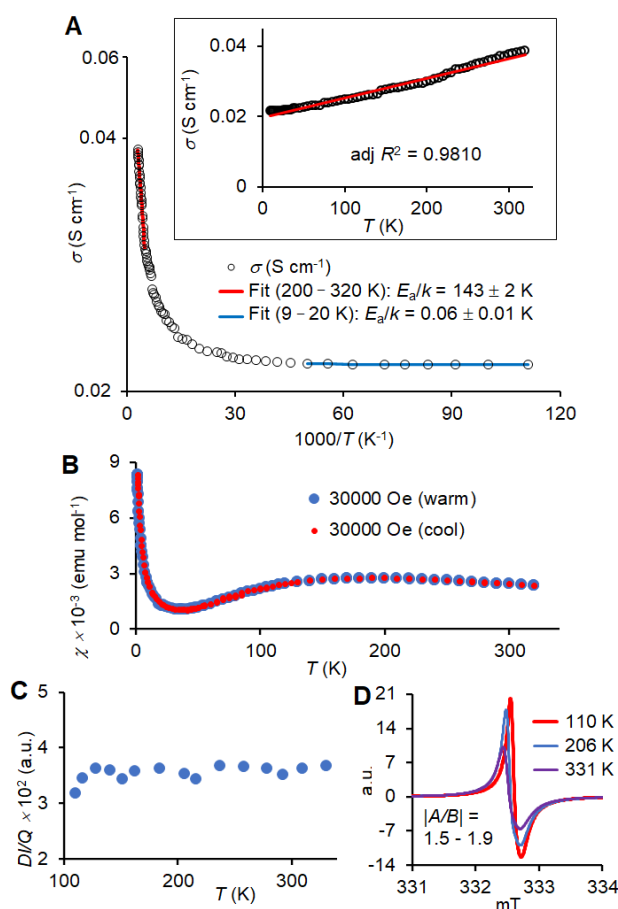


Figure 44. Solid state characterization of diradical **34**. **A**, main plot: single crystal conductivity, σ , of diradical **34** (plotted on a logarithmic scale) as a function of the reciprocal temperature ($1000/T$), with the fits

in the high- and low-temperature ranges, showing effective activation energies (E_a/k). Inset plot: single crystal σ vs. T , showing near-linear relationship. **B**, SQUID magnetometry of polycrystalline **34**: magnetic susceptibility, χ vs. T for $T = 1.8 - 320$ K. **C** and **D**, EPR spectroscopy of polycrystalline **34** with particle size of <75 μm : $DI/Q \sim \chi$ vs. T and representative EPR spectra, showing Dysonian line-shape, where DI is a double integrated intensity and Q is a microwave cavity quality factor. Reproduced from ref. 150. Copyright 2022 American Chemical Society.

Magnetic studies on polycrystalline **34** confirm this “near-metal-like” behavior.¹⁵⁰ The plot of static of χ vs. T is nearly temperature-independent in the range from 20 to 320 K, and the value of $\chi \approx 2-3 \times 10^{-3}$ emu mol⁻¹ is consistent with Pauli paramagnetism (Figure 44B). This value of χ is greater than $\chi \approx 5-6 \times 10^{-4}$ emu mol⁻¹ observed in spiro-bis(phenalenyl) ($R = n$ -hexyl) (Figure 1) and oxo-bridged bisthiazolyl, **OBBDTA** (Figure 5) monoradicals.^{84,257} Also, we note that the residual paramagnetism from some crystals in the polycrystalline sample appears as a shallow broad maximum at about 200 K due to one-dimensional $S = 1$ antiferromagnetic chains with a large $J/k \sim -150$ K.

The EPR spectroscopy on polycrystalline **34**, with particle sizes <75 μm , confirms the temperature-independent χ in the $T = 110-331$ K range (Figure 44C). In addition, a Dysonian line shape ($A/B > 1$) (Figure 44D) confirms good electrical conductivity of polycrystalline **34**.

Notably, this diradical can be evaporated under UHV to obtain thin films (nominal thickness of ca. 1 nm) on silicon substrates, which remain unchanged after exposure to air for at least 18 h – a testament to its thermal ultra-robustness.^{150,414}

4.6 High-spin triangulene diradicals.

As we discussed in Section 2.3, trioxytriangulenes have a long history dating to the classic contributions by Clar (**35**)²²⁷ and to the pioneering report by Bushby in 1993 of the triplet ground state diradical trianion **36** (Figure 45).²²⁸ Also, in 1925, Weiß and Korczyn synthesized derivatives of **35** and recognized them as “trimethylene-triarylmethanes”.⁴¹⁵

Clar’s attempts to obtain diradical **35** (Figure 45) by de-hydrogenation of various multihydro-

triangulenes, using Pd-catalyst, apparently resulted in polymers/oligomers, which could not be characterized at that time.²²⁷ In 2019, Richardson and coworkers developed a simplified synthesis of various dihydro-triangulenes and related compounds.⁴¹⁶ Oxidation of one of the dihydro-triangulenes with *p*-chloranil resulted in a solid product, which according to laser desorption ionization mass spectrometry (LDI-MS) analysis showed peaks up to $m/z = 1400$ – likely corresponding to oligomers of **35**.⁴¹⁶ It should be noted that Mou and Kertesz predicted by DFT the dimerization energy of -23 kcal mol⁻¹ for singly σ -bonded dimer of **35**,⁴¹⁷ thus, suggesting that oligomerization of **35** will be quite exothermic.

In 2017, Gross and coworkers prepared **35** on surface and characterized it by scanning tunneling and atomic force microscopy.⁴¹⁸ Surface synthesis of aza-triangulene diradical cation **40** (Figure 46) was reported in 2022.⁴¹⁹ Assignment of triplet state for **35** and **40** is based on weaker intensity of Kondo resonance, compared to $S = \frac{1}{2}$ radical, however, no clear-cut evidence about ΔE_{ST} is available.^{419,420}

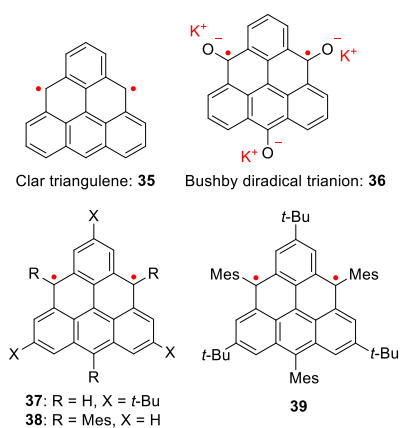


Figure 45. Triangulene diradicals. Abbreviation: Mes = 2,4,6-Me₃C₆H₂.

Bushby and coworkers²²⁸ were able to prepare three-fold symmetric $S = 1$ diradical **36** ($|D| = 192$ MHz and $|E| = 0$), with a modest admixture of the corresponding $S = \frac{1}{2}$ radical dianion. Although $|\Delta m_S| = 2$ is observed at 13 K, it is rather weak and not suitable for obtaining I vs $1/T$ plot. In the EPR spectrum, height of the center peak, assigned to $S = \frac{1}{2}$ radical, is only twice, compared to the $S = 1$

side peaks – a remarkable feat because the diradical was prepared by the challenging 2-electron reduction of the corresponding diamagnetic anion ($E^{1-/2-} = -2.07$ V and $E^{2-/3-} = -2.37$ V vs AgNO₃/Ag), using Na/K in dimethylformamide (DMF). Relatively low content of $S = 1/2$ impurity allows to obtain accurately fraction of $S = 1$ state intensity (I) by spectral simulation. Linear plot of I vs $1/T$ in the 13 – 37 K range is consistent with either near-degenerate singlet and triplet states with $|\Delta E_{ST}| < 0.01$ kcal mol⁻¹ or triplet ground state with $\Delta E_{ST} > 0.15$ kcal mol⁻¹. Based on what we know about triangulene system, this result suggests triplet ground state for **36**.

The authors²²⁸ report that a solution of **36** in DMF does not lose its EPR intensity, when stored for up to 5 months at room temperature, however, upon exposure to air, **36** is rapidly oxidized to the precursor diamagnetic anion.

In 2001, Nakatsuji and coworkers,⁴²¹ when attempting to prepare triangulene **37** (Figure 45), were able to obtain an EPR spectrum in toluene at 123 K, which they assigned to an $S = 1/2$ impurity (huge center peak of unknown height) and $S = 1$ state of **37**. The $S = 1$ spectrum consisted of four symmetrically disposed side peaks, corresponding to $D = 219$ MHz and $E = 0$. Half-field transition, $|\Delta m_S| = 2$, was referred to as “extremely weak”,⁴²¹ and therefore, not suitable to obtain I vs $1/T$ plot. Nevertheless, the authors show linear I vs $1/T$ plot in the 3.7 – 16 K temperature range, where I is claimed to be triplet intensity.⁴²¹ Assuming that I is associated with $S = 1$ state, then this linear plot would imply either near-degenerate singlet and triplet states with $|\Delta E_{ST}| < 0.004$ kcal mol⁻¹ or triplet ground state with $\Delta E_{ST} > 0.06$ kcal mol⁻¹. However, if I is obtained from the $|\Delta m_S| = 1$ spectrum, dominated by the $S = 1/2$ impurity, it is likely to be heavily weighted by the $S = 1/2$ intensity, which will always lead to the linear plot, when measured properly. In summary, the triplet ground state for **37** is not firmly established by the described experiments.

In 2022, Juriček and coworkers, have reported synthesis of triangulene **38**,⁴²² using similar methodology to that for **37**. Corresponding triangulene $S = 1/2$ radical was isolated and characterized

by X-ray crystallography. Although diradical **37** is claimed to be persistent at room temperature for up to 3 weeks, there is no magnetic characterization by SQUID magnetometry or by quantitative EPR spectroscopy; authors' EPR spectroscopic measurements does not even establish the triplet ground state.

Nakatsuji's '2001 communication, describing trinagulene **37**, concluded with the following sentence: "Further stabilization of triangulene by additional substitutions is under way to isolate genuine non-Kekule' PNBs in the crystalline state."⁴²¹ Some 20 years later, in 2021, Shimizu and coworkers have finally realized that vision, by reporting synthesis, isolation, and characterization of **39**.⁴²³ Triangulene diradical is prepared by the reduction of the precursor diol with SnCl₂ in the presence of trifluoroacetic acid anhydride – most likely, via two one-electron reductions of the corresponding carbocations. Diradical **39** is isolated and characterized by the first X-ray structure for a triangulene diradical. Triplet ground state is established by SQUID magnetometry, giving a flat χT vs. T plot in the 20 – 300 K temperature range, with the value of $\chi T > 0.75$ emu K mol⁻¹. This value is assigned to 82% $S = 1$ diradical and 18% $S = \frac{1}{2}$ radical; the same $S = 1/S = \frac{1}{2}$ ratio gives a reasonable fit to the M vs H/T Brillouin curve at 1.9 K.⁴²³ These data provide unequivocal confirmation of triplet ground state for triangulene diradical and suggest $\Delta E_{ST} \gg 1.2$ kcal mol⁻¹. Further evidence for triplet ground state is obtained from heat capacity measurements under magnetic fields.⁴²³ Notably, the CW EPR spectra in rigid matrices showed surprisingly small value of "apparent $|D|$ " and, consequently, extremely weak $|\Delta m_S| = 2$ transition (*vide infra*).

In 2022, Wu and coworkers⁴²⁴ attempted preparation of aza-triangulene diradical cation **41**. It is not clear whether the diradical cation was actually synthesized because its EPR spectrum at room temperature does not match the simulated spectrum (see: red arrows in Figure 46B),⁴²⁴ as noticed by the authors in ref 424. In addition, because DFT-computed spin density distributions in triangulenes and aza-triangulenes are similar, the reported $\Delta E_{ST} \approx 0.8$ kcal mol⁻¹ is way too small (Figure 46C).

While there may be many reasons for this result, it is plausible that this is an artefact due to Q-value of the cavity increasing at low temperatures. We should mention that for triangulene **35**, $\Delta E_{ST} \approx 10$ kcal mol⁻¹ is computed at the UB3LYP/6-31G(d)+ZPVE level of theory, with both triplet and broken-symmetry (BS) singlet geometries optimized (Figure 10), and Shimizu reports experimental value of $\Delta E_{ST} \gg 1.2$ kcal mol⁻¹ for triangulene **39**.⁴²³ In addition for aza-triangulene **42**, $\Delta E_{ST} > 2$ kcal mol⁻¹ is measured by SQUID magnetometry (*vide infra*). We note that the X-ray structure of **41** is refined with a large number of constraints, leading to a relatively small reflections/(parameters + restraints) ratio; also there is a large residual electron density of ca. 1.5 electrons, possibly associated with SbCl₆⁻ counterion.

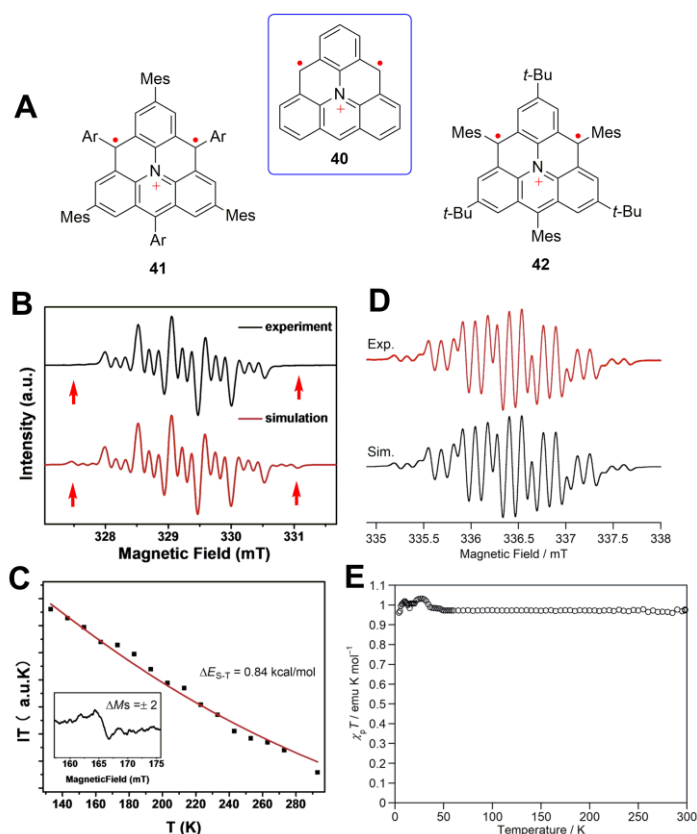


Figure 46. A: Aza-triangulene diradical cations **40**, **41**, and **42**. Abbreviations: Mes = 2,4,6-Me₃C₆H₂ and Ar = 2,4,6-Cl₃C₆H₂. **B** and **C**: EPR spectroscopy of **41**. **D** and **E**: EPR spectroscopy and SQUID magnetometry of **42**. Parts B, C, D, and E were reproduced from refs 424 and 425. Copyright 2022 and 2023 Wiley.

In 2023, Shintani and coworkers⁴²⁵ synthesized and isolated aza-triangulene diradical cation **42**. Its EPR spectrum at room temperature perfectly matches the simulated spectrum (Figure 46D). Magnetic studies of polycrystalline **42** by SQUID magnetometry provide a flat χT vs. T plot in the 50 – 300 K temperature range, corresponding to near perfect $\chi T \approx 0.95 - 0.98$ emu K mol⁻¹. These data provide unequivocal confirmation of triplet ground state for aza-triangulene diradical and, based on authors' analysis of correction for diamagnetism, suggest $\Delta E_{ST} > 2$ kcal mol⁻¹.⁴²⁵ X-ray structure of **42** is refined with adequate reflections/parameters ratio and small residual electron-and-hole densities.

Notably, aza-triangulene **42**, with nearly exclusively thermally populated triplet state at room temperature, shows a significant fluorescence at room temperature with quantum yield of about 1%.⁴²⁵

Somewhat surprisingly, CW EPR spectra in triangulenes **38**, **39**, **41**, and **42** in rigid matrices give only relatively narrow center peaks without any discernible side peaks and very weak $|\Delta m_S| = 2$ transitions. Even for **42** dispersed in diamagnetic matrix, consisting of precursor diol of triangulene **39**, a similar EPR spectrum, but with a relatively broader center peak, is obtained, which can be simulated with “apparent $|D| \approx 37$ MHz”. The question arises what is the possible origin of very low values of “apparent $|D|$ ” found in triangulenes **38**, **39**, **41**, and **42**?

It was noted by the authors in ref 425, that three-fold symmetric conformations ($E = 0$) of triradicals **AT1** and **AT2** (Figure 17) also have rather low values of $|D| = 36 - 37$ MHz,¹¹⁵ however, the inter-spin distances in the triradicals are significantly longer than in **42** and other triangulenes. For analogous $S = 1$ diradicals **AD-a-b** (Figure 47A), with similar inter-spin distances to **AT1** and **AT2**, experimental $|D| = 61 - 71$ MHz¹¹⁵ are comparable to $|D| = 75$ MHz, reported for the analogous 3,4'-biphenyl-based triarylmethyl diradical.³²³

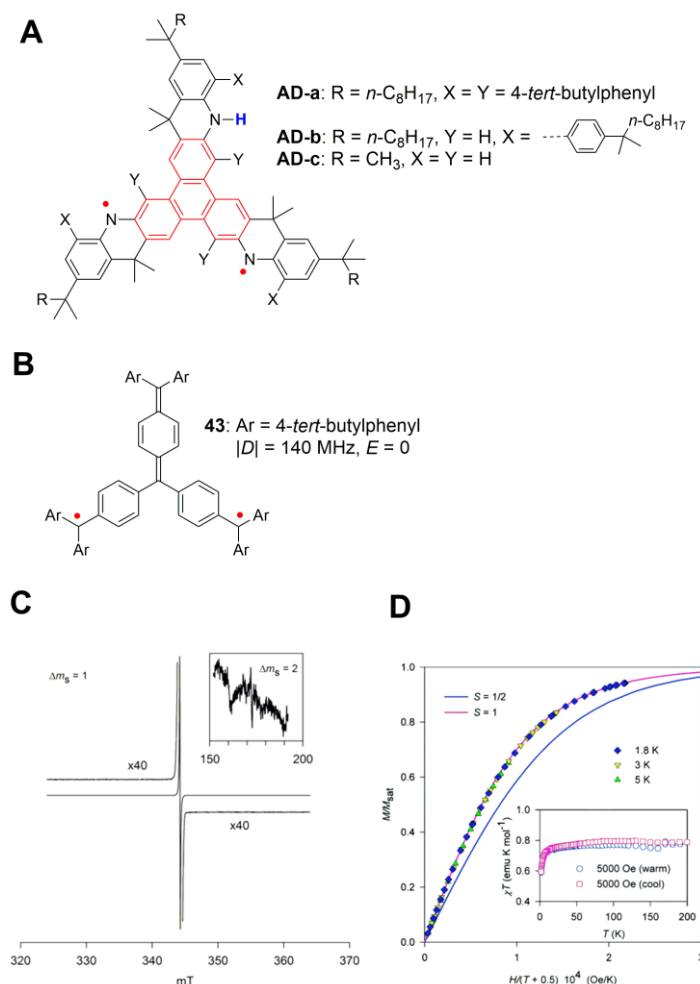


Figure 47. A and B: Structures of diradicals **AD-a-c** and **43** – diradicals relevant to the apparent small value of $|D|$ in triangulene diradicals. **C and D:** EPR spectra at 140 K and SQUID magnetometry for the identical sample of 20 mM diradical **43** in THF- d_8 , following annealing at room temperature for 1 h. After annealing at room temperature for additional 2 days, practically identical data are obtained, indicating that **43** is long-term persistent. Parts C and D are reproduced from ref 35. Copyright 2005 American Chemical Society.

We then turn to ORCA-computations of zero-field splitting (parameters D and E),⁴²⁶ that are carried out at the B3LYP/EPR-II (UNO) level of theory, using dipolar spin-spin approximation (DSS) and neglecting spin-orbit contributions.⁴²⁷ For triangulene **35**, we compute $E = 0$ and $D = +492 \text{ MHz}$. We note that for analogous diradicals, with the same D -tensor orientations ($D > 0$), values of D are overestimated by a factor of about 2 at the same level of theory.^{112,114} For diradicals

AD-a-c (Figure 47A) with $D < 0$, this overestimate is by a factor of about $2.5 - 3$.¹¹⁵ This would suggest that the experimental $|D|$ for triangulenes **38**, **39**, **41**, and **42** should be in the 200 – 250 MHz range, which is in good agreement with Nakatsuji's $|D| = 219$ MHz for **37**.⁴²⁰ Notably, Bushby obtained a smaller $|D| = 192$ MHz²²⁸ because in **36** effective inter-spin distances may be somewhat longer due to a small fraction of spin density residing at the oxygens.

We postulate that the very low values of “apparent $|D|$ ” found in triangulenes **38**, **39**, **41**, and **42** are due to exchange narrowing in aggregated samples that are relatively concentrated in poorly matched solvents/matrices. As early as 2005, we demonstrated this phenomenon in long-term persistent $S = 1$ ground state diradical **43** (Figure 47B).³⁵ In a dilute frozen solution of ca. 2 mM **43** in 2-MeTHF/THF at 100 K, EPR spectrum consists of a sharp center line (peak-to-peak line width of 0.09 mT) with relative peak height of 100 and four symmetrically distributed well-resolved side-peaks with relative peak height of one, corresponding to the triplet state with $E = 0$ and $|D| \approx 140$ MHz. The center peak does mostly correspond to an exchange narrowed diradical **43** because of the following findings.

In more concentrated frozen solutions of ca. 20 mM **43** in THF- d_8 , EPR spectrum at 140 K consists of narrow center peak with a line width of 0.08 mT, and $|\Delta m_S| = 2$ transition is practically not detectable (Figure 47C). SQUID magnetometry on the identical sample is clearly showing almost pure $S = 1$ ground state diradical, based on magnetization data; the value of $\chi T < 1.00$ emu K mol⁻¹ is found because of difficulty in attaining quantitative mass transfers during the low-temperature preparation of **43** (Figure 47D).³⁵ The indirect evidence for exchange narrowing due to aggregation of 20 mM **43** in THF- d_8 is from correlation between mean-field parameter $\theta = -0.05 - (-0.5)$ K, a measure of intermolecular antiferromagnetic exchange couplings, derived from M/M_{sat} vs $H/(T - \theta)$ magnetization data (as well as χT vs T plots at low temperatures) and the line-widths in the EPR spectra; that is, the narrower EPR spectra correspond to the greater value of $|\theta|$.³⁵

Conclusion

Over 120 years after Gomberg's discovery of triarylmethyl radicals, research on stable radicals continues to surprise us by the multitude discoveries of new properties and applications in diverse fields of science and technology. More recently, stable, and thermally robust high-spin di- and triradicals, with nearly planar π -systems, have emerged as the new frontier in organic radicals. When properly designed, such radicals possess large energy gaps (vs. thermal energy) separating the high-spin ground state and low-spin excited state. Thus, these radicals may possess relatively large populations of their high-spin ground state at room temperature, and their properties related to paramagnetism, scale with the factor of $S(S + 1)$, where the total spin quantum number S corresponds to the high-spin ground state. This implies scaling with approximately n^2 , where n is the number of "unpaired" electrons, for many properties, including relaxivity of MRI contrast agents, dynamic nuclear polarization (DNP), etc., assuming that other controlling factors can be optimized too.

Thermal robustness enables preparation of interesting thin films via evaporation, thus facilitating their potential applications in electronics and spintronics. One example of such high-spin diradical, so far, is a good electrical conductor – contrary to expectations.

Two relations are established:

- (1) between DFT computed singlet triplet energy gap (ΔE_{ST}) in a subset of 12 diradicals and SHI, which is the difference in energy of electrons in HOMO vs. SOMO in the corresponding one electron reduced $S = \frac{1}{2}$ species (mostly radical anions),
- (2) between 17 experimental pairwise exchange coupling constants J/k (e.g., equal to the half of the ΔE_{ST} in a diradical) in nitronyl nitroxide based high-spin di- or triradicals vs. hyperfine coupling constants in the corresponding monoradicals.

Both relations may allow us to identify outliers, which may correspond to radicals where J/k is not measured or computed with sufficient accuracy, e.g., because of the large magnitude of

experimental J/k .

Double helical (or helical) high-spin di- and polyradicals, in which spin density is delocalized over the chiral π -system, have been barely explored. Notably, the sole example of such high-spin diradical possesses alternant π -system with Kekulé resonance form. Finally, derivatives of triangulene diradical provide stable high-spin diradicals with singlet triplet energy gaps, estimated as a few kcal mol⁻¹, which are comparable to the previously reported persistent but air sensitive planar aminyl diradicals.

We hope this review provides critical analyses that may contribute to the development of new magnetically and thermally ultra-robust high-spin radicals, which may contribute to ever emerging applications.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENTS

We thank all the former Rajca group students and postdoctoral associates who contributed to the research on high-spin molecules, and whose names appear in the references. We thank Dr. Maren Pink (Indiana University) for quarter-of-century-long collaboration and her re-refinement of X-ray structure of diradical **32**. We would like to thank the NSF Chemistry Division and the National

Institutes of Health for the support of our research on stable radicals under the following grant numbers: CHE-1665256, CHE-1955349, CHE-2247170, NIGMS R01GM124310-01, and NIBIB R01EB019950-01A1.

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Andrzej Rajca was born in Poland where he graduated from Politechnika Wroclawska in 1981 with M.S. degree. In 1982, he joined Laren Tolbert's group at University of Kentucky (Ph.D. 1985). Subsequently, he did three-year postdoctoral research as a Miller Fellow and Lecturer with Andrew Streitwieser at Berkeley. Now he is a professor at University of Nebraska-Lincoln. Current research in his group is focused on stable radicals and thermally robust high-spin polyradicals with applications ranging from biomedicine and biophysics to organic materials.

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