What's new in stable radical chemistry?

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Many kinds of radicals are stable enough to isolate, handle, and store without any special precautions. The diversity in molecular architectures of these *stable radicals* is sufficiently large that the common factors governing radical stability/persistence, geometric and electronic structure, association/dimerization preferences, and reactivity have generally not been well articulated or appreciated. This review provides a survey of the major classes of stable or persistent organic/organomain group radicals with a view to presenting a unified description of the interdependencies between radical molecular structure and properties.

1 Introduction

Radicals are *subvalent* compounds: they have one less bond than expected based on simple valency considerations. The highly reactive, often transient nature of radicals is a reflection of the fact that their major reactivity pathways—dimerization, hydrogen abstraction, disproportionation—are strongly favoured thermodynamically, and these reactions typically occur with little to no activation barrier.

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Many radicals exist whose properties defy the dogma espoused above. There are examples of molecules with unpaired electrons that have sufficiently long lifetimes to be observed by conventional spectroscopic methods. Other radicals can be isolated as pure compounds, and a few of these are even unreactive to air and water. The notion that radicals can be stable and isolable is still news to much of the chemical community, as evidenced by the continuing stream of publications trumpeting the discovery of new molecules that are radicals and yet can be isolated.[1,2] However, stable radicals have been recognized for just over a century, and some were in fact synthesized over 150 years ago. It is also evident that certain *kinds* of molecular architectures provide a versatile template that can support stability in open-shell molecules; there are *families* of stable radicals, many of which have been around for decades.

Much of the current interest in stable radicals probably arises from their status as "novelty acts" and, more substantially, from the fundamental structure and bonding issues that naturally arise with this class of compounds. However, there are many areas of chemistry that take advantage of the properties afforded by the specific combination of open-shell configuration and chemical stability. Firstly, stable radicals have long been used as reporter molecules to obtain structural, dynamic, and reactivity information using electron paramagnetic resonance (EPR) spectroscopy. Techniques such as spin labelling[3] and spin trapping[4] and, more recently, EPR imaging[5] can provide a wealth of information on systems into which stable radicals have been introduced. Second, there have been widespread efforts aimed at developing new materials with technologically relevant properties (magnetism, conductivity) for which stable radicals are excellent building blocks simply by virtue of having unpaired electrons.[6,7] Third, stable radicals do in fact have a very rich chemistry, but of a much more selective and controllable nature than the reactivity of reactive radicals. Certain kinds of stable radicals are widely used as (co)catalysts for the oxidation of alcohols to carbonyl compounds,[8] while other radicals are exploited for their ability to act as *anti*oxidants;[9] the transition metal coordination chemistry of radicals has been an active area of interest to inorganic chemists for three decades;[10–12] and polymer synthesis has received a significant boost from the development of stable-radical-mediated living radical polymerization processes.[13] Radical reactions are implicated in a huge range of biological processes, and stable radicals are often key players—from simple inorganic radicals such as NO and O_2 to tyrosyl[14,15] and flavin[16]-based radicals. Stable radicals have even been incorporated into the interior of golf balls (!),[17] demonstrating that the range of uses for these molecules is limited only by one's imagination.

Space limitations do not permit further discussion of these applied areas; instead, the vast array of applications in which stable radicals are employed provides a context for discussion of what kinds of stable radicals exist. More fundamentally, a number of reviews have appeared dealing with specific types of stable radicals, but the last broad-based review of organic stable radicals was Forrester *et al.*'s book published *nearly 40 years ago.*[18] A comprehensive review on *inorganic* main group element-based stable radicals appeared in 2003;[19] "organic" radicals—those based on C, N, O, and S, which, by and large, are the classes of radicals which are utilized in the applications described above—were deliberately excluded.

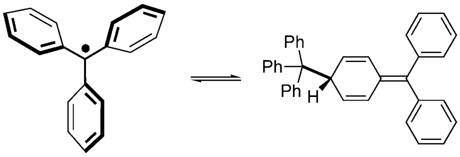
This Perspective focuses on organic (including "organomain group") stable radicals, and as such is complementary to the aforementioned 2003 review of inorganic-based radicals. The terms "stable" and "persistent" are used very subjectively within the genre; we adopt Ingold's pragmatic (but not universally followed) definition of a *stable radical* as one that can be isolated and handled as a pure compound, whereas radicals that are sufficiently long-lived to be observed using conventional spectroscopic methods but cannot be isolated are classified as *persistent.*[20] For the most part emphasis is placed on isolable radicals, although there is in realty a continuum of reactivity/stability, necessitating some discussion of radicals that qualify as persistent as a matter of context. The main emphasis of this Perspective is to highlight the relationships between molecular structure and stability/reactivity of the major classes of stable radicals. For space limitation reasons, radical ions[21] are not included, nor are di-, tri-, and polyradicals except in cases where the merger of two or more odd-electron fragments has important consequences for the gross electronic structure of the aggregate molecule. Space constraints also preclude discussion of the *synthesis* of all of these radicals. Finally, a few classes of radicals are given shorter treatment than they might otherwise deserve based on the overall volume of literature available. Space considerations are again a prime consideration, coupled with the fact that, for certain classes of radicals, there have been few or no new developments for over 25 years. Thus, discussions of some of the more venerable and well-studied stable radicals, *e.g.* phenoxyls, nitroxides, are summarized, and readers are referred to key reviews. Pyridinyl radicals will not be discussed because Kosower's 1983 review[22] is the definitive (and, so far, final) word on this subject.

2 Hydrocarbon-based radicals

2.1 Triphenylmethyl and related radicals

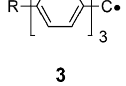
Gomberg's synthesis of the triphenylmethyl (trityl) radical **1** was a landmark discovery as it marked the beginning of organic free radical chemistry.[23] Despite the historical importance of these species, there has not been a general overview/review of triarylmethyl radicals. A historical account of the nearly 70-year controversy surrounding the nature of the triphenylmethyl dimer[24] is available, as is an essay concerning the question of why Gomberg never received the Nobel Prize for his seminal discovery.[25]

Triphenylmethyl **1** and its derivatives are best described as persistent rather than stable radicals: in dilute, carefully deoxygenated solution, **1** is in equilibrium with dimeric species **2** and the radical cannot be isolated. The dimer consists of a σ bond between the central carbon of one radical and a *para* carbon of another. The intradimer bond of **2** is weak, with a bond dissociation enthalpy of only ~11 kcal mol^{-1}.[26] Nonetheless, under anaerobic conditions, **1** is highly persistent, as are most of its simple substituted derivatives. This stability is ascribed largely to steric protection of the central carbon, where the bulk of the radical spin density is found, by the three phenyl groups which adopt a propellor conformation, with the rings twisted by ~30° with respect to the plane containing the central carbon and the three *ipso* phenyl carbons.[27,28] However, some spin density resides on the phenyl substituents, as evidenced by EPR spectroscopy.[26,29] As an odd alternant hydrocarbon, the π SOMO of **1** has atomic orbital contributions from every other carbon atom—in this case the *ortho* and *para* carbons in addition to the central (methine) C. The presence of spin on the phenyl rings, coupled with the steric problems associated with hexaphenylethane, provide a rationale for the formation of **2**. There is smaller, negative spin density on the *meta* (and *ipso*) carbons arising from spin polarization effects.



1 **2**

Heteroaromatic analogues of **1** in which one or more of the phenyl groups is replaced by, *e.g.*, pyridyl,[30] thienyl,[31] or benzotriaozlyl[32] do not show dramatically different stability from the parent compound. The tendency to dimerize can be attenuated and, in some cases, shut down through substituent effects. *Para* substitution on all three phenyl rings (*i.e.* **3**) renders these radicals monomeric, although still very air sensitive.[28,33] The perchlorinated triphenylmethyl **4** is not only stable but essentially chemically inert,[34] only undergoing reactions under extremely harsh conditions or outer sphere electron transfer. The main source of this extraordinary stability is the complete shielding of the central carbon by the six *ortho* chlorine atoms. The steric bulk increases the twist angle in the propeller-like structure to ~50°,[35] which renders these radicals even more localized than the unsubstituted species,[36] but the steric effects block any sort of dimerization or small molecule reactivity.



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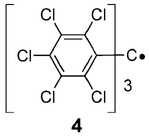
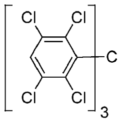


4

Radical **4** is the prototype of what has become a large number of polychlorinated triphenylmethyl (PTM) radical derivatives which display outstanding stability.[37] More recent work on partially chlorinated derivatives such as **5** and **6**—both of which are essentially as stable as **4**—reveals that not all of the chlorine substituents in **4** are necessary; the six chlorines in the *ortho* positions appear to be sufficient and necessary for radicals of this type to be exceptionally stable.[38] This feature is demonstrated by the relative stabilities of perchlorinated tris(thienyl)methyl radicals **7** and **8**.[39] The 2-thienyl derivative **7** only has three *ortho*-chlorine groups and is not particularly persistent, decomposing within minutes. In contrast, compound **8**, with the full complement of six *ortho* chlorines, enjoys comparable stability to that of **4**.



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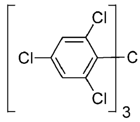

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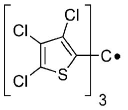

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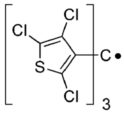
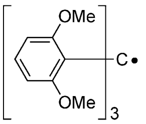


8

Ortho substituents other than chlorine can also attenuate the reactivity of triarylmethyls. The tris (2,6-dimethoxyphenyl) methyl radical **9** is monomeric and relatively unreactive to air, though it does react slowly with oxygen in solution to form an unusual peroxide.[40] Interestingly fused compound **10** is completely associated to form a presumed σ dimer of unknown structure.[41] Clearly the gain in resonance delocalization in **10** by enforcing a planar orientation of the phenyl groups is offset by the lack of steric barrier to radical dimerization.



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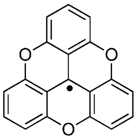
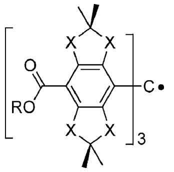


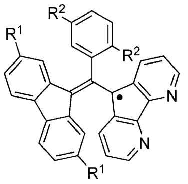
10

A family of heavily substituted triphenylmethyls **11** (X = O, S; R = Me, Na) have been studied as candidates for EPR imaging probes.[42,43] The complete substitution at all of the *ortho* carbons renders these quite persistent, although the ester derivatives degrade over a period of several days. The carboxylate-based radicals are, however, indefinitely stable and insensitive to oxygen. The spin distributions in these radicals were compared to that in the parent triphenylmethyl (**1**) through density functional theory calculations.[43] As is the case for the chlorinated radicals (see above), the increased twist angle of the aromatic groups leads to an *increase* in spin density at the methine carbon (from 0.56 in **1** to ~0.62 in derivatives of **11**) and a *decrease* in spin density on the aromatic carbons (~0.115 in **1** and 0.06–0.08 in **11**).



11

There has been some interest in employing suitably substituted triphenylmethyl radicals as paramagnetic ligands for metal complex chemistry. One such example is the series of compounds of structure **12**,[44] nitrogen-containing analogue of Koelsch's radical **13** (the latter being a long-known very stable hydrocarbon radical).[45] The bipyridine-like moiety present in **12** harkens to the possibility of forming metal complexes, but the results of preliminary studies to this end were inconclusive.



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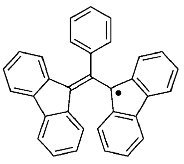
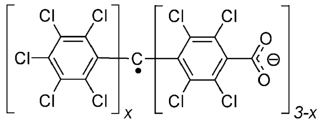


13

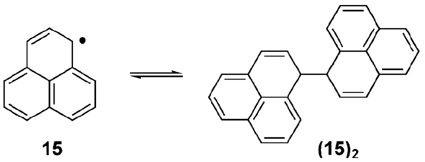
Perchlorinated triphenylmethyl radicals with one to three carboxylate groups in the *para* positions (**14**; $x = 0$–2)[46] are as stable as the parent perchlorinated triphenylmethyls. The possibility of linking these radicals *via* coordination or non-covalent interactions has been extensively explored by Veciana. The carboxylate groups bind to transition metals in discrete complexes[47] as well as metal-organic frameworks,[48] and can also be employed as supramolecular synthons in the generation of hydrogen bonded networks.[49] The extended structures based on these radicals exhibit interesting magnetic and nanoporous properties.



14

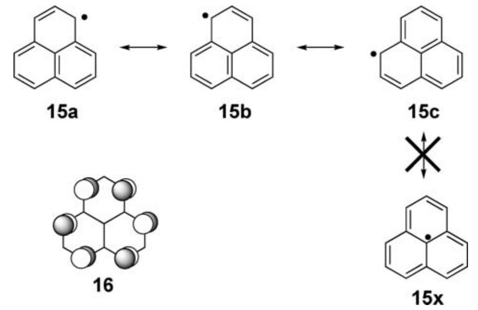
2.2 Phenalenyl and related radicals

The phenalenyl radical **15** was prepared by Reid[50] and independently detected by Calvin[51]; in both instances the radical was derived from phenalene oxidation. A number of simple derivatives have been generated[52,53] and the older literature has been reviewed.[54] Most of the early examples are very oxygen sensitive and in equilibrium with a σ-bound dimer $(\mathbf{15})_2$; the dimer decomposes further to form highly fused polycyclic aromatic hydrocarbons. Nonetheless, in dilute deoxygenated solutions most phenalenyl radicals persist indefinitely, despite the lack of an appreciable steric barrier to association. In this context phenalenyl radicals demonstrate the beneficial (from a stability perspective) consequences of electron delocalization in hydrocarbon-based radicals.



15 **$(15)_2$**

The spin density in **15** is predominantly found on the six α carbon atoms (three of the six resonance structures are depicted by **14a**, **14b**, and **14c**). The spin density at the three peripheral (β) carbons is much smaller and it arises from spin polarization effects. The spin distribution can be understood on the basis of the singly occupied molecular orbital (SOMO) **16**, a π orbital with coefficients only on the α carbon atoms. Importantly, the SOMO also suggests no spin density on the central carbon—this can also be understood in valence bond terminology, as resonance structure

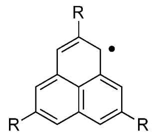


15a **15b** **15c** **16** **15x**

15x would consist of a methyl type radical inside an *antiaromatic* 12π periphery. Thus **15x** is not an appropriate representation of this radical.

In the past 20 years a number of new phenalenyl-based radicals have been reported. The body of experimental and computational data on a variety of substituted derivatives of **15** have led to significant new insights into the stability and association of these radicals. Most simple phenalenyls weakly and reversibly dimerize *via* σ bond formation.[53–55] High-level computational studies suggest a weak (bond dissociation enthalpy of ~16 kcal mol^{-1}) and long (d(CC) ~1.59 Å) intradimer bond. The calculated bond length is in excellent agreement with the only structurally characterized phenalenyl σ dimer—a spirobiphenalenyl derivative (see below) with a CC inter-radical bond of length 1.599 Å.[56]

Placement of *t*-butyl groups at the three β (2-, 5-, and 8-) carbons (**17**) effectively shuts down the σ dimerization pathway, resulting in an alternative dimeric structure, that of a π dimer $(\mathbf{17})_2$—a common fate for *many* flat, delocalized π-radicals (see subsequent sections). The first phenalenyl π dimer structure was reported by Nakasuji[57] and has been subsequently studied in some detail by Kochi.[55,58] The two radicals are stacked face-to-face approximately 3.2 Å apart—significantly less than the non-bonded π stacking distance of ~3.4 Å—and *antiparallel* with respect to one another to minimize steric interactions between R groups. As is the case with the more conventional σ dimer, π dimerization in solution is weak (~10–15 kcal mol^{-1}) and reversible. In addition to its distinct structural characteristics, the π dimer is evidenced in solution by long wavelength (~600 nm) electronic transitions that are absent in σ dimer structures; the dimer can also be detected by NMR and MS techniques.[59]



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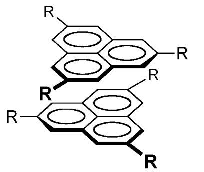
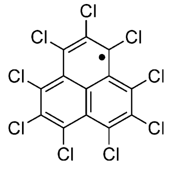


$(\mathbf{17})_2$

The nature of the bonding within the phenalenyl π dimer structure has received considerable attention (as have π dimers of many other radicals, see below). The dimer is held together by a two-electron "bond", but one in which the two orbitals involved in the bond are the delocalized π SOMOs **16** of the two radicals. The antiparallel arrangement of phenalenyl radicals in the dimer structure still permits direct overlap between the 2p orbitals of the α carbons which dominate the SOMO. As a result the orbital overlap is substantial, the spin pairing between two radicals is quite strong, and the dimer is diamagnetic at room temperature.[60] The electronic transition (see above) ascribed to the π dimer structure is a HOMO–LUMO transition involving the two linear combinations of the π-SOMOs.

Other substituents on the phenalenyl periphery such as chlorine (**18**)[61] or sulfur (**19**)[62] render phenalenyl radicals completely monomeric in solution. No structural information is available for **19**, but **18** is monomeric in the solid state, forming antiparallel columnar stacks separated by 3.78 Å; the rather long stacking repeat arises from the buckled nature of the phenalenyl skeleton, which in turn originates from repulsive interactions between *peri* chlorine substituents.



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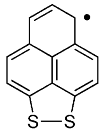
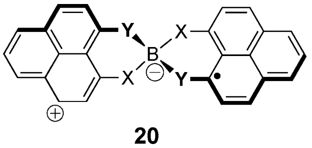


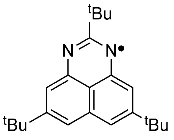
19

Haddon has developed an extensive series of phenalenyl-based radicals **20** (X, Y = O, NR; NR, NR; O, O) in which two phenalenyl moieties are attached to a tetrahedral boron center. These *formally* zwitterionic species have spin and charge delocalized over both phenalenyl moieties through a resonance-stabilized spiroconjugation mechanism.[63] These radicals are highly oxygen-sensitive but isolable in crystalline form, and display a diverse array of structures. A few of these are monomeric, with no evidence for association in the solid state.[64] Many possess a π dimer structure in which only one of the two phenalene rings of one molecule associates with a neighbouring molecule.[56,65] Some of the dimeric species have two different phases: a "diamagnetic π dimer" in which the spins involved are completely paired (*cf.* the π dimer of **17**) and the interplanar separation between π systems in the dimer is ~3.1 Å; and a "paramagnetic π dimer" consisting of significantly longer interplanar separations (3.3–3.4 Å) and incomplete spin pairing (based on magnetic measurements). The paramagnetic form dominates at room temperature, but upon cooling the dimers convert to their diamagnetic form. Other derivatives assemble into extended one-dimensional π stacks showing exceptionally high electrical conductivity,[66] and one spirobiphenalenyl can be crystallized in either a paramagnetic π dimer form or a σ dimer structure (see above) depending on the absence of light during the crystallization process.[56] All of these materials display very unusual solid state electrical and magnetic properties. From a more fundamental perspective, the rich variety (in some cases unprecedented) modes of association (and their lack of correlation with the size or nature of the substituents X and Y) is evidence that the interactions between radicals in these molecules is subtle indeed.



20

The phenalenyl skeleton has been subjected to heteroatom perturbation. 2,5,8-Tri-*tert*-butyl-1,3-diazaphenalenyl **21** was prepared by Nakasuji as a nitrogen-containing analogue of **17** (R = ^{t}Bu).[67] The former appears to decompose significantly more slowly in air than the latter. Detailed EPR and computational studies show the spin distribution in **21** to be predictably altered by the lower symmetry of this compound compared to **17**; the two nitrogens have substantially less spin density than the four remaining α carbons, whereas in **17** all six α carbons carry the same spin density. This desymmetrization of spin density appears to have consequences for the solid state structure of **21**, which adopts an antiparallel π dimer (**21**)$_2$ whose structure differs in important ways from (**17**)$_2$. The two radicals in (**21**)$_2$ are twisted by 60° relative to one another, as is the case for (**17**)$_2$. However, the two phenalenyl rings in (**21**)$_2$ are tilted with respect to each other, creating a *range* of atom–atom contact distances. The shortest of these distances is only 2.15 Å. The putative hexazaphenalenyl analogue **22**, for which spin density would reside dominantly on *nitrogen* (*cf.* **16**) does not appear to be accessible from the stable (closed shell) anion; electrochemical studies on the anion do not show any oxidation processes at all.[68]



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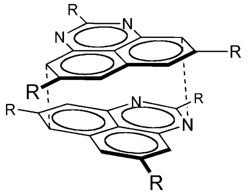
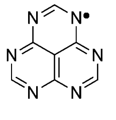
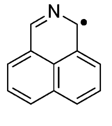


(21)$_2$



22

Rubin has introduced nitrogen atoms at the β positions of the phenalenyl skeleton. 2-Azaphenalenyl **23** possesses an electronic structure (as probed by EPR and computational studies) that is only modestly perturbed compared to the parent hydrocarbon radical.[69] To a first approximation this might be expected as the nitrogen atom in **23** does not occupy a site with very much spin density. However, some key differences arise in the dimerization behaviour: in solution **23** shows no tendency to dimerize at all whereas **15** does, despite the lack of steric protection in both and the otherwise general similarities in their electronic structures. Attempts to coordinate **23** to copper(II) leads to a monometallic complex containing a σ dimer of **23** bound as a bidentate ligand. A chlorinated version of the triazaphenalenyl **24** is stable and monomeric, although the synthesis of this radical requires care to avoid formation of an unusual CC *double* bonded dimer (**24**)$_2$.[70]



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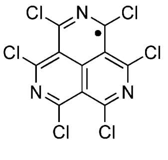

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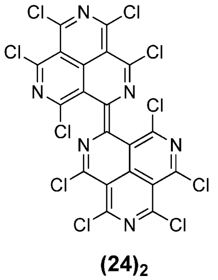
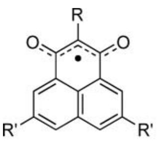


(24)$_2$

Nakasuji has prepared a series of of 'oxophenalenoxyl' radicals **25–27** which can be considered hybrids of phenalenyls and phenoxyl radicals.[71] These radicals appear to be qualitatively somewhat less stable than the phenalenyl radicals: derivatives of **25** with small R groups (R′ = H, CH_3) decompose in solution over a period of hours, while various *tert*-butyl substituted species are longer lived, though not indefinitely so, and all are oxygen sensitive. EPR and computational studies suggest that the introduction of the oxygen atoms significantly alters the spin distributions (represented for radicals **25–27** as **28–30** respectively; shaded and open circles represent positive and negative spin density respectively), which are distinctly non-phenalenoid in



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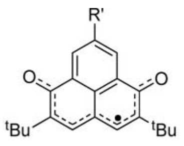

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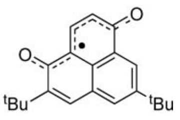

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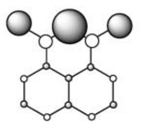

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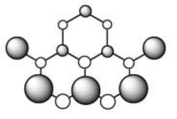

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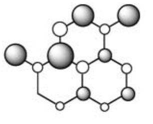

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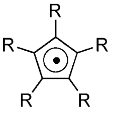
nature and less symmetrically distributed. In all three cases the spin density lies predominantly along a single conjugated bond path between the two oxygens.

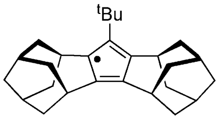
2.3 Cyclopentadienyl radicals

Substituted cyclopentadienyl [$Cp^{\bullet}$] radicals **31** enjoy varying degrees of stability. This is evident even with relatively small substituents: bis(pentamethyl-cyclopentadiene) dissociates at high temperatures (>360 K) in solution into pentamethylcyclopentadienyl radicals **31a**. Variable temperature EPR analyses reveal a very weak inter-ring (dimer) CC bond enthalpy of 19 kcal mol^{-1}.[72] Larger substituents such as phenyl **31b**[73,74] or isopropyl **31c**[75] render the resulting radicals isolable as monomeric (but highly air-sensitive) species. Structural and EPR studies on these compounds indicate that steric factors dominate the stabilization of these radicals, although hyperconjugation may also be prevalent in the pentaisopropyl compound **31c**. The pentakis(triisopropylsilylethynyl)-radical **31d** is intriguing because the steric bulk of the TIPS groups is relatively remote from the Cp ring; despite this structural feature, this radical is monomeric and *air stable* (unlike all other stable $Cp^{\bullet}$ radicals).[1] The only other isolable cyclopentadienyl radical is the bis-homoadamantyl-annelated compound **32**, whose stability derives from a combination of steric and conformational constraint effects.[76]



31a R = Me
31b R = Ar
31c R = ^{i}Pr
31d R = $C{\equiv}CSi^{i}Pr_3$

31



32

It is tempting to ascribe some of the stability of cyclopentadienyl radicals to delocalization of the spin around the five positions of the ring (as represented canonically by structure **31**). However, the fully delocalized, symmetric (D_{5h}) structure of the parent cyclopentadienyl radical is known to be unstable with respect to a first order Jahn–Teller distortion. Two possible distorted states both have C_{2v} symmetry (Fig. 1); one of these (B_1) is essentially a localized radical while the other (A_2) state can be described as an allyl-type radical.[77] The crystal structure of **31b** (R = Ph)[74] was not high enough in quality to be subjected to

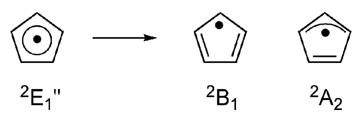
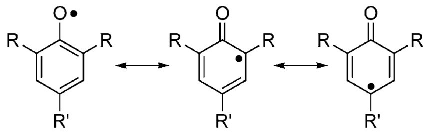


Fig. 1 Electronic states of the cyclopentadienyl radical before (left) and after (right) Jahn–Teller distortion.

detailed bond length analysis. Radical **31c**[75] consists of essentially (within experimental crystallographic error) symmetric (D_{5h}) Cp rings. However, this structure may represent a dynamic average because the barrier to interconversion between distorted structures is low and the magnitude of the distortion may just be within the crystallographic error limits. Interestingly, the X-ray structure of **32** shows a distinctly *localized* Cp ring: the two "double bonds" depicted in **32** average 1.385 Å, the two "single bonds" flanking the radical site are nearly identical at 1.45 Å and the remaining single bond is 1.48 Å. Computational studies accurately reproduce the X-ray structure and suggest that the radical is in a distorted $^2B_1$ state with the allyl moiety centered at the *t*-butyl substituent position, creating an essentially localized cyclopentadienyl radical.

2.4 Phenoxyl radicals

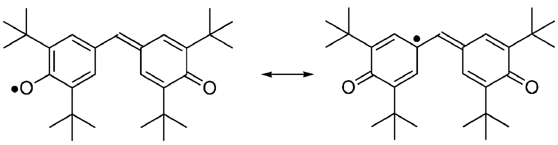
Phenoxyls **33** are a venerable class of radicals; a comprehensive, and still largely valid, review on their synthesis, properties, and chemistry appeared in 1967.[78] Ongoing interest in these radicals is largely focused on their chemical biology, *e.g.* studies on phenoxyl radicals engaged in hydrogen bonding[79] or coordinated to metal ions[12,80] as structural and functional models for tyrosyl radicals in living systems,[14,81] and the role of phenoxyl radicals and their corresponding phenols as antioxidants.[82] From a stability perspective, it has long been known that *ortho* and *para* substituents—particularly relatively bulky groups such as *tert*-butyl—are required for stability; in the absence of large groups radical reactivity patterns indicative of carbon-centered as well as oxygen-centered radicals emerge. This can be understood most simply by the canonical resonance structures shown in Fig. 2. High level computational studies indicate that the oxygen atom carries only marginally more spin density than the *ortho* and *para* carbon atoms.[83] Electron-rich aromatic groups attached as substituents to the *para* carbon (R′) can possess as much spin density as the phenoxyl residue itself.[84] Thus although these are nominally represented and described as oxygen-centered radicals, their reactivity and spin distributions suggest that they should alternatively be considered as carbon centered radicals.



33

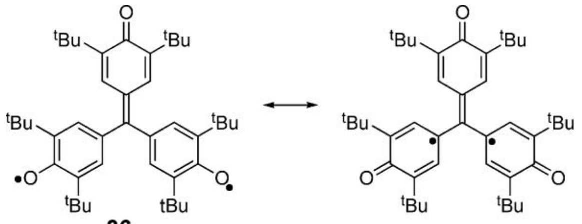
Fig. 2 Phenoxyl radical resonance structures.

The galvinoxyl radical **34** (Coppinger's radical[85]) merits special mention in this section. This species has attracted interest because of it exceptional stability (it can be isolated in pure form and is essentially insensitive to oxygen) and its unusual solid state magnetic properties.[86] Computational studies show that, like simple phenoxyls, there is substantial spin density on the *para* carbon atoms in **34**, leading to an alternate representation of galvinoxyl and related species[87] as delocalized allyl-type radicals **35**.[88]

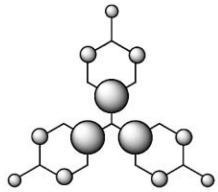


34 **35**

Closely related to **34** is "Yang's biradical" **36**,[89] a stable triplet (S = 1) diradical. The three benzenoid rings of this molecule are twisted by ~34° in a propellor-like arrangement,[90] similar to the structures of simple triarylmethyl radicals. The three "arms" of the diradical are structurally equivalent within experimental error. The spins are delocalized in a manner reminiscent of the spin distribution in phenoxyl monradicals; EPR and ENDOR studies as well as computational work[90] indicate that nearly 50% of the total spin density (shown in **38**) lies on the three carbons directly adjacent to the central carbon. Thus although **36** is canonically represented and often described as a phenoxyl-based diradical, resonance structure **37**—which is a more accurate representation of the spin density—suggests that Yang's biradical could alternatively be categorized as a delocalized version of trimethylenemethane **39**, the prototypical triplet organic biradical.[91]



36 **37**



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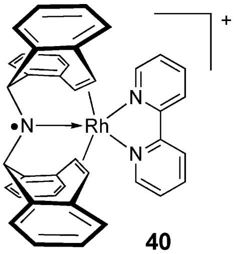
3 Radicals based on nitrogen and/or oxygen

Many of the most stable radical types have a substantial portion of spin density on nitrogen and/or oxygen. Simple inorganic radicals such as O_2, NO, and NO_2 can be viewed as prototypes of the many different organomain group radicals described in the sections to follow.

3.1 Aminyl radicals

Most simple aminyl radicals $[R_2N^\bullet]$ are short-lived species, rapidly dimerizing to hydrazines or undergoing other radical reaction pathways (H atom abstraction, disproportionation).[18,92] With only two substituents on the nitrogen atom, rendering aminyl radicals stable enough to be isolated requires extreme steric bulk: the perchlorodiphenylaminyl radical $[(C_6Cl_5)_2N^\bullet]$ can be isolated and is indefinitely air stable in the solid state, although in solution it abstracts hydrogen from toluene.[93] Grützmacher has cleverly designed a rhodium(I) amide complex which is oxidized not at the metal but instead at the amide center to afford an isolable cationic complex containing a coordinated aminyl radical **40**.[94]



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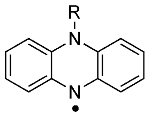
The stability of the aminyl center arises from a combination of steric effects and conformational constraints on the radical imposed by metal coordination and the design of the aminyl substituents.

Aminyl radicals tied into a cyclic, π-conjugated framework exhibit somewhat enhanced stability. There are several examples of isolable phenazinyl radicals **41**.[95] In all of these cases R ≠ H and the aromatic groups also have electron withdrawing (CN, NO_2) and/or bulky (^{t}Bu) substituents. Most stable phenazinyls are predominantly monomeric in solution at room temperature but associate upon cooling, most likely *via* π dimer formation. Crystal structures of several derivatives of **41** have been obtained, most of which show the radicals forming π-dimers or π-stacked structures in the solid state. Bulky substituents on either the aromatic periphery or on the trivalent nitrogen favour *antiparallel* cofacial π dimers (akin to the antiparallel structures seen for substituted phenalenyl radicals **17** and **21**) in which the dominant intermolecular (intradimer) contacts are between the two nitrogen atoms which carry most of the spin density. Interplanar separations are under 3.3 Å and the absorption spectra contain low energy absorption maxima not seen in the monomeric species—both features being evidence for strong electronic coupling in the π dimer structure. Interestingly, the related phenoxazinyls and phenothiazinyls (obtained by isolobal replacement of the NR group in **41** by O or S, respectively) are generally quite short-lived species except for derivatives **42**[96] and **43**[18] for which steric factors are a major stabilizing factor.



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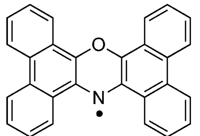

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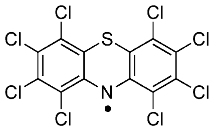

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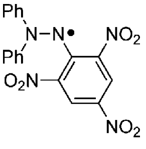
3.2 Hydrazyl radicals

N,*N*′-Diphenyl-*N*′-picrylhydrazyl (DPPH) **44** has been known for decades as a stable radical and as an EPR reference compound.[18] Interestingly, from a stability perspective, **44** is almost unique amongst hydrazyl radicals [$R_2NNR^•$]. In general, hydrazyl radicals are only persistent, and often are not very long-lived, in solution. For example, closely related analogues of **44** in which only the *p*-nitro or one of the *o*-nitro groups is removed are not stable, despite their otherwise close structural resemblance to DPPH. Stable hydrazyls benefit in part from strong electron withdrawing groups on the divalent nitrogen, presumably to enhance charge separated resonance contributions (Fig. 3). However, torsional twisting about the NN bond attenuates these affects and can localize the spin on the divalent nitrogen, rendering these radicals more like conventional aminyl radicals. There have been no significant new developments in fundamental hydrazyl chemistry for quite some time.



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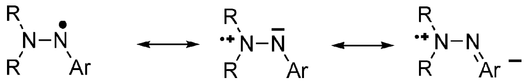
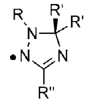


Fig. 3 Resonance structures for hydrazyl radicals.

A number of stable radical families contain the hydrazyl moiety built into a cyclic and/or delocalized skeleton. Constraining the hydrazyl group into a ring optimizes (enforces) π orbital overlap between the nitrogen (and possibly other) atoms. For example, dihydro-triazolyl radicals **45** are generally sufficiently stable enough to be isolated provided the R′ substituents are aromatic residues and R ≠ H. A few derivatives have been crystallographically characterized, all of which are monomeric in the solid state; temperature dependent solution studies also indicate that these radicals show no tendency to dimerize.[97] The spin distribution in these radicals (as probed by EPR, ENDOR, and NMR spectroscopy indicates some spin density) suggests that these are still mainly hydrazyl-like radicals, but with non-negligible spin density also on the imine nitrogen. In a similar vein, the benzotriazinyl radicals **46** have substantial spin density on all three nitrogen atoms as well as appreciable spin into the annelated benzene ring; notably the proton hyperfine coupling constants to the annelated ring protons are 2–3 times larger than the hfc's found on aromatic substituents (R,R′).[98,99]



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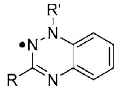

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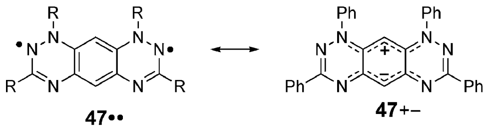
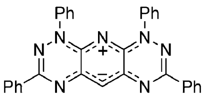
Delocalization of spin from the hydrazyl moiety into the annelated phenyl ring has consequences for systems in which two triazinyl rings are fused onto a common benzene spacer. Putative "diradical" **47**•• is EPR silent, has a well-behaved NMR spectrum, and displays unusual solvatochromism.[100] Computational studies point to a closed shell electronic structure best represented by a charge-separated, dual-cyanine-like ground state (**47**+-). Replacement of the central benzo unit by pyridine (**48**) does not alter the fundamental (closed shell) ground state electronic structure.[101]



47•• **47+−**



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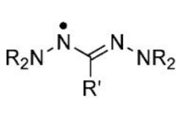
3.3 Resonance delocalized hydrazyls: tetraazapentadienyl, tetrazolinyl and verdazyl radicals

Conjugation of a hydrazyl radical with a second, closed shell RNNR$_2$ group permits the unpaired electron to be delocalized between two chemically equivalent subunits, *i.e.* a resonance-delocalized radical. Simple acyclic resonance-delocalized tetraazapentenyl radicals **49** can be isolated as monomeric radicals and show no tendency to associate in solution. However they decompose within days in solution in a complicated array of reactions, probably because of conformational flexibility problems which are known to plague the parent hydrazyls.[102] Tetrazolinyl radicals **50** can be regarded as cyclic analogues of **49** in which the two outermost nitrogen atoms are directly attached to one another.[103,104] The stability of these radicals appears to improve with electron withdrawing substituents (*e.g.* R = *p*-nitrophenyl) on the nitrogen atoms.[104]



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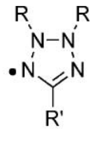

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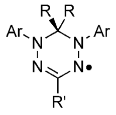
Verdazyl radicals are another class of resonance-delocalized hydrazyls. Verdazyls of general structure **51** were discovered over 40 years ago,[105] while closely related "6-oxoverdazyls" **52** were first synthesized in the 1980s.[98,106] Both classes of verdazyls are among the most robust of all stable radicals. There are dozens of derivatives *not* requiring steric bulk which can be isolated, stored, and handled without decomposition, and in addition verdazyls are air- and water-stable. Verdazyls of structure **51** have *N*-aromatic substituents, while oxoverdazyls **52** can be made with *N*-aryl or *N*-alkyl substituents. The latter show substituent-dependent stability; derivatives of **52** with R = Me show behaviour ranging from indefinitely stable to modestly (hours) persistent. Recently it has been shown that verdazyls with *N*-isopropyl groups are generally much more robust than their *N*-methyl counterparts.[107]



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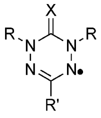

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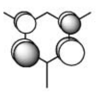
Verdazyls are 7π cyclic radicals with π SOMOs as shown in **53**; the nodal planes in this orbital prevent spin delocalization (but not polarization) onto the C-substituents. These radicals do not associate or dimerize, but Hicks has recently reported a ferrocene-bridged verdazyl diradical **54** which contains an *intramolecular* π dimer in the solid state.[108] The π dimer structure is not retained in solution, suggesting that the dimerization enthalpy is very low and the solid state structure may arise at least in part from intermolecular packing effects in the solid state.



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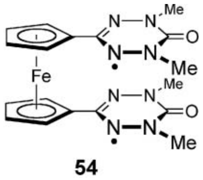

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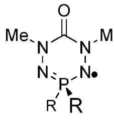
A few verdazyl radicals have been reported containing an inorganic element in place of one of the two skeletal carbon atoms, though their electronic structures suggest that they are not significantly different from their all-organic analogues **51** and **52**. Phosphaverdazyls **55**[109] and **56**[109,110] have electronic structures that are, for the most part, reminiscent of the parent systems. However, the few derivatives which have been studied are persistent for days in solution and the solid state but ultimately decay to diamagnetic products. A persistent, but highly air-sensitive, boron-containing verdazyl radical anion **57** has recently been reported.[111] It is not clear whether the negative charge plays a role in the higher reactivity of **57** compared to its isolobal counterpart **51**.



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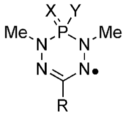

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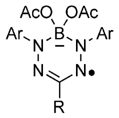

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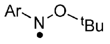
3.4 Oxoaminyl radicals

Oxoaminyl radicals [RNOR′]$^•$ are isoelectronic with hydrazyls [RNNR$_2$′]$^•$ and, like hydrazyls, are generally persistent but not isolable. As is the case with other acyclic radicals, the lack of conformational constraints facilitates electron localization on the divalent nitrogen, creating a more reactive aminyl-like radical. The few examples of isolable oxoaminyls have general structure **58** in which Ar is a very bulky aromatic group.[112]



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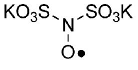
3.5 Nitroxide radicals

Nitroxides [R$_2$NO]$^•$ are easily the most well-known class of stable radicals. The first nitroxide—an "inorganic" derivative, Fremy's salt **59**—is over 150 years old, and the first "organic" nitroxide **60** was discovered very shortly after the triphenylmethyl radical at the beginning of the 20th century. Nitroxide chemistry has a long and rich history, and there are many, many derivatives which are stable with respect to air, water, dimerization, and other radical-based reactions. The versatility of these radicals is further enhanced by the fact that a fairly diverse range of organic chemistry can be carried out on remote sites of molecules carrying a nitroxide group without affecting the radical site itself. Nitroxide radical chemistry has been compiled in a number of books and reviews,[18,113] the most recent of which was Keana's review nearly 30 years ago.[114] The discussion below summarizes the salient features concerning nitroxide radical stability.



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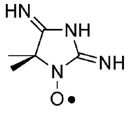

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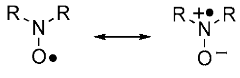
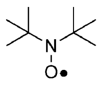
Nitroxides have substantial spin density on both N and O. Each possibility can be represented by one of two resonance structures **61** and **62**. In the language of molecular orbital theory, the electron resides in an NO π^* orbital, as does the spin in the relatively reactive oxoaminyls **58** (see above). It is interesting to contrast the stability of these two tautomers. Reactivity in the oxoaminyls,



61 **62**

as with other acyclic radicals, arises from the conformational flexibility which inhibits electron localization; twisting about the NO bond attenuates π overlap between N and O, thereby localizing the spin. The NO bond in nitroxide does not suffer from conformationally-driven destabilizing effects because the oxygen carries no substituent.

As mentioned above, there are many examples of isolable nitroxides. However there are also plenty of nitroxides that are not truly stable. Ultimately the stability (or lack thereof) of nitroxides depends on the nitrogen substituents; in all of the known nitroxide literature, symmetric nitroxide dimers of the type R_2NOONR_2 have never been observed, demonstrating the basic *inherent* stability of the $R_2NO^\bullet$ radical framework. Rather, it is the substituents which provide decomposition/reactivity pathways, for example, alkyl nitroxides in which there are α hydrogens can decompose to nitrones by transferring $H^\bullet$ to another nitroxide molecule, giving the hydroxylamine as a second decomposition product (*i.e.* disproportionation). Nitroxides with two quaternary carbon-based substituents are quite robust, *e.g.* di-*t*-butyl nitroxide **63** and TEMPO **64**. Several nitroxides of this sort are commercially available, often with a remote functional group suitable for modification for spin-labelling applications.



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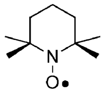

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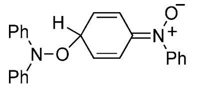
Nitroxides with simple π-conjugated substituents (alkenyl, phenyl) are generally not sufficiently stable to isolate. The delocalization of spin from the NO moiety onto the carbon-based π system creates new decomposition pathways, typically involving coupling of the oxygen center of one radical with the *para*-carbon atom of another (not unlike the dimerization mode for triphenylmethyl radicals). For example, diphenyl nitroxide initially dimerizes to form structure **65** *en route* to fragmenting to give **66** and diphenylamine. Substitution at the *para*-carbon positions shuts down this decomposition pathway and can render these radicals isolable. Multiple substitution at the *ortho* positions can also stabilize diaryl nitroxides, though in this case the substituents enforce twisting of the aromatic substituents out of the plane of the NO group, thereby limiting conjugation and spin density on the Ar groups.



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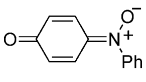

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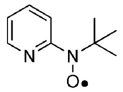
It should be noted that the decomposition rates of diaryl nitroxides vary greatly and the relationship between nitroxide structure—namely the substituents on nitrogen—and level of persistence/stability is not always clear. As one example, pyridine-based *t*-butyl nitroxide **67** cannot be isolated, but the bipyridine analogue **68** has recently been reported to be stable in solution and in pure form for months.[115]



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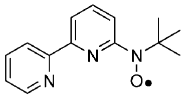

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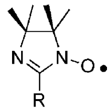
Nitroxide radicals in which the NO group is conjugated to a C=N moiety, so-called "imino nitroxides" **69**, are generally stable enough to be isolated and do not undergo the sorts of bimolecular decomposition reactions that plague other conjugated nitroxides.[116] EPR spectroscopy, neutron diffraction, and computational studies indicate spin on the nitroxide nitrogen is substantially larger than that on the imino nitrogen, though the latter nitrogen does possess substantial spin density.[116,117] Interestingly the sp^2 carbon does not contribute to the radical SOMO despite the lack of a nodal plane (*cf.* nitronyl nitroxides, see below) but does have some negative spin density from polarization effects. The coordination chemistry of these radicals has been explored extensively, predominantly in derivatives where an additional donor atom on the substituent R creates a chelating binding site involving the imine nitrogen.[118]



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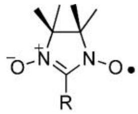
3.6 Nitronyl nitroxide radicals

α-Nitronyl nitroxides **70** are cyclic, resonance-delocalized nitroxides. Ullmann first reported nitronyl nitroxides nearly 40 years ago;[119] these radicals continue to receive a great deal of attention as building blocks for organic magnetic materials, but the fundamental aspects of their electronic structure were well-established early on and summarized in a 1991 review.[11] These radicals incorporate the necessary features for stability (*e.g.*, no α hydrogens) established for nitroxides, and can thus be made with a wide variety of R groups. The stability of nitronyl nitroxides generally rivals the most stable examples of nitroxides. The π SOMO (**71**) spans both NO groups and has a nodal plane passing through the central carbon atom; as a result the spin distribution is symmetrically disposed about the two NO groups and is not affected by the substituent R. EPR spectra are typically dominated by the five-line pattern generated by coupling to two equivalent nitrogen atoms, with *a*(N) values approximately half the typical values found for nitroxides.



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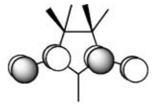

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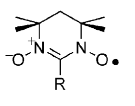
α-Nitronyl nitroxide radicals based on other structural templates are known. Rey has recently developed the synthesis of pyrimidinyl nitronyl nitroxides **72**,[120] whose electronic structures are generally quite similar to those of the more familiar imidazoline-based nitronyl nitroxides **70**. Benzannelated analogues **73** have not yet received much attention,[121] though recent experimental and computational studies indicate that there is at least partial delocalization of spin from the ONCNO moiety onto the annelated ring.[122]



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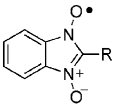

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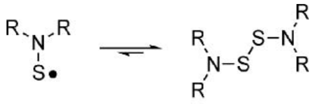
4 Radicals with spin density on nitrogen and sulfur: thiazyls

Heavy main group elements do not commonly support *inherently* stable radicals, *i.e.* radicals in which steric bulk is *not* required for stability. The lone and dramatic exception to this is sulfur, an element that has proven to be quite versatile in stable odd-electron compounds. Almost invariably the sulfur is divalent and catenated to itself and/or nitrogen, and normally other elements (usually carbon) figure into a π-conjugated framework. Collectively the body of work on thiazyl radicals is impressive in breadth and depth. Several reviews focusing on specific classes,[123] properties,[124] or applications[7] of thiazyl radicals are available. More general overviews[125] are somewhat dated—not because they were written very long ago but because there have been many new developments in this branch of stable radical chemistry.

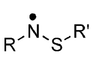
Given that oxygen and sulfur both belong to Group 16, one might expect to find analogous families of stable radicals in which S simply replaces O. This turns out not to be the case, as the differences in properties of the two chalcogens (sulfur is larger and more polarizable than oxygen) and the resulting E–N bond (polarized towards nitrogen ($S^{\delta+}N^{\delta-}$) instead of oxygen ($O^{\delta-}N^{\delta+}$)) produce far more differences than similarities. As a simple example, thionitroxides **74**—sulfur analogues of nitroxides—exist at room temperature mainly as their disulfide dimers **75**, although dissociation into moderately stable radicals takes place at elevated temperatures and the SS bond is a relatively weak one (ΔH_{diss} ~30 kcal mol^{-1}).[126]



74 **75**

4.1 Thioaminyl radicals

Thioaminyl radicals **76**—tautomers of thionitroxides and the sulfur analogues of oxoaminyls—have been extensively studied by Miura. Similarly to the thionitroxides, thioaminyls appear to enjoy a minimal level of persistence regardless of the substituent,[127] but reversibly form dimers which are assumed to be hydrazine-like species (*i.e.*, NN sigma bond formation).[128] Bulky substituents on the nitrogen center (*e.g.* triphenylmethyl,[129] substituted pyrenyl,[130] and particularly 2,4,6-trisubstituted phenyl[128,131]) are needed to make these radicals stable enough to be isolated. The role of the R′ group on sulfur is less well understood but typically is a substituted (hetero)aromatic. The most stable of these radicals are typically described as insensitive to oxygen. Related to these are aminyl radicals bearing two SR substituents. The few known acyclic derivatives (**77**) are long-lived (1 week) in solution and are not oxygen sensitive.[132] A number of cyclic analogues in which the SNS fragment is fused to a norbornane group (**78**) also show excellent persistence in solution, though none have been isolated as pure compounds.[133] Thioaminyl and related radicals are mainly nitrogen-centered, with lesser amounts of spin density on the sulfur and on any aromatic substituents that may be present. Variable temperature EPR studies reveal that derivatives of **78** reversibly dimerize in solution; the nature of the dimer is not known. A few studies of the decomposition behaviour of thioaminyls suggest that even the nominally "stable" species are thermally sensitive, decomposing to non-radical products at 80 °C in degassed benzene.[134] There are no reports of isolation of any $(RS)_2N^{\bullet}$ based radicals.



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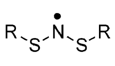

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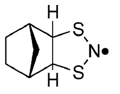

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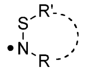
Kaszynski has explored cyclic thioaminyls **79** which can be viewed as derivatives of **76** in which R and R′ are part of a common ring system. In general these radicals do not exhibit enhanced stability compared to analogous acyclic species lacking in steric bulk. Sealed degassed samples of cyclic thioaminyls based on the biphenyl core **80** (R,R = H,H or –N=N–) decompose over several days to non-radical products,[135] while annelated thiadiazinyl radicals **81** are generally only persistent at low temperatures—although derivatives with perhalogenated benzannelated groups are stable enough to be isolated.[136] Computational studies indicate that the spin distributions in derivatives of **80** and **81** are remarkably similar to acyclic, *N*-aromatic thioaminyls in that they are predominantly nitrogen-centered radicals and the modest amount of spin delocalization tends to be on an aromatic group pendant to the nitrogen.



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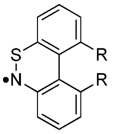

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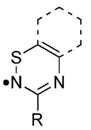

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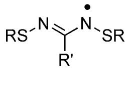
Radicals **82** are resonance-delocalized thioaminyls. A few of these derivatives have been detected as intermediates but do not appear to be very persistent.[137] The specific substrates did not posses bulky substituents, so in this regard the inability to isolate these radicals is in accord with simple thioaminyl stability. Oakley has described **83** as a resonance-stabilized analogue of **81**. This radical is air stable and has been isolated and structurally characterized in the solid state as a monomeric species. EPR and calculations indicate that the spin density is essentially equally shared among the four outer nitrogen atoms.[138]



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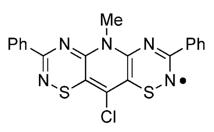
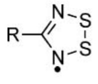


83

4.2 Dithiadiazolyl radicals

1,2,3,5-Dithiadiazolyl (DTDA) radicals **84** were among the first major class of heterocyclic thiazyl radicals to be discovered. They are indefinitely stable in oxygen-free solution and in the solid state, and are also extremely thermally stable—many are purified by high-temperature, high vacuum sublimation. These radicals can be viewed as resonance delocalized thioaminyls, *i.e.*, cyclic analogues of species **82** (see above), a notion which is supported by the symmetric spin distribution and π-SOMO **85**. Similarly to several other π radicals, this SOMO has a nodal plane which passes through the lone carbon, thereby precluding resonance interactions between the substituent R and the radical.



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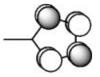

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In solution the radicals are in equilibrium with dimers, and all of the early derivatives of these radicals adopt π-dimeric structures in the solid state. The steric requirements of the substituent R lead to a number of different *kinds* of π dimer (Fig. 4). The 4-phenyl-1,2,3,5-DTDA structure adopts a *cis*-cofacially aligned structure (Fig. 4a), and notably was the first structurally characterized π-dimer of *any* radical;[139] many other derivatives with simple aromatic substituents also have this dimeric structure.[140–142] The closest contacts within the dimer are between sulfur atoms and are 3.0–3.1 Å, in between an SS covalent bond (~2.1 Å) and a van der Waals contact (3.6 Å). Other, mostly non-planar substituents (CF_3, Me, NMe_2, Cl, adamantyl) give rise to a cofacial but twisted π dimer structure (Fig. 4b) which still permits significant SOMO–SOMO overlap.[143] Semiempiricial calculations suggest small energetic differences between these two dimeric structures, and perhaps not surprisingly there are a few other associative modes seen in exceptional cases, *e.g.* Fig. 4c[140] and 4d.[144] A number of DTDA derivatives have been made which do not associate at all, most of which are based on fluorinated phenyl substituents.[145]

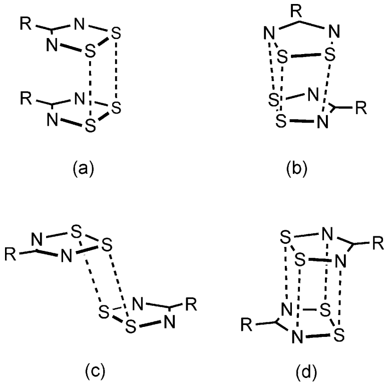
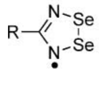


Fig. 4 Structural classification of dimers of **84**: (a) *cis*-cofacial, (b) twisted (gauche), (c) *trans*-antarafacial, (d) *trans*-cofacial. Adapted from ref. 7.

1,2,3,5-Diselenadiazolyl radicals **86**—the selenium variants of **84**—are also stable. In solution and the solid state these radicals associate, forming *cis*-cofacial π dimers (Fig. 4) almost exclusively.[140,146] The Se–Se contacts between radicals within the dimers are longer, ranging from 3.2–3.3 Å, though calculations suggest the intradimer binding energy is stronger than in the sulfur counterparts.[141] Two of these radicals adopt an unprecedented T-shaped dimeric structure **87**; strong orbital overlap between π SOMOs in a spiroconjugative manner **88** leads to complete spin pairing and a resulting diamagnetic dimer.



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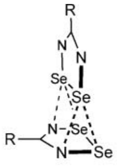

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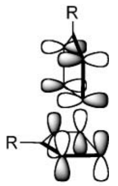

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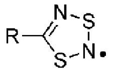
1,3,2,4-Dithiadiazolyls **89** are isomers of the 1,2,3,5-radicals.[147] The former are less stable thermodynamically than the latter, and the 1,3,2,4-isomers convert to the corresponding 1,2,3,5-derivatives in solution and in the solid state.[148] This rearrangement is bimolecular and has been proposed to proceed through an antiparallel π dimer intermediate **90** (Fig. 5). Bond rearrangement leads to a 1,2,3,5-dithiadiazolyl *trans*-antarafacial π dimer **91** (analogous to the structurally characterized dimer depicted in Fig. 5c) which can then dissociate into the 1,2,3,5-radicals. Spectroscopic evidence for **90** in solution has been put forth,[149] and the lone structurally characterized 1,3,2,4-dithiadiazolyl radical possesses exactly this π dimeric structure (the solid also slowly converts to the 1,2,3,5-isomer).[150]



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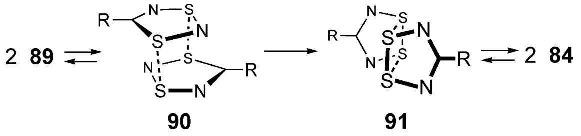
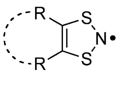


Fig. 5 Conversion of 1,3,2,4-dithiadiazolyl radicals **89** to 1,2,3,5-dithiadiazolyls **84**.

4.3 Dithiazolyl radicals

Like the dithiadiazolyl radicals described in the previous section, there are two isomers of radicals based on dithiazolyl (C_2NS_2) rings. Many early examples of 1,3,2-dithiazolyls **92** were studied by EPR[151] and several have since been structurally characterized. These radicals are stable in solution though somewhat reactive to air; solid forms of the radicals are indefinitely stable and typically air stable. In contrast, diselenadiazolyls **93** are rare and are unstable due to facile extrusion of nitrogen, leading to (nonradical) Se/C based rings.[152] Similar to the 1,2,3,5-dithiadiazolyls **84**, there is some diversity in the solid state structures of dithiazolyls, although in derivatives of **92** substituent/annelation electronic effects are more important because the radical π-SOMO **94** permits spin delocalization onto the rest of the molecule. Simple 4,5-disubstituted radicals adopt cofacial π-dimer structures **95** (R = CN,[153] CF_3[154]), whereas the benzannelated radical dimerizes in a centrosymmetric fashion **96**.[155,156] In both cases the characteristic intradimer distances are between sulfur atoms, between 3.1–3.2 Å. Other derivatives are monomeric in the solid state, *e.g.* **97** (X = CH or N)[157] and the benzobis(dithiazolyl) diradical **98**[158] (although interestingly, the radical cation of **98** forms a cofacial π dimer akin to **95**).[159]



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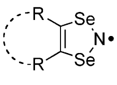

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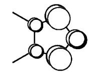

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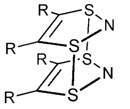

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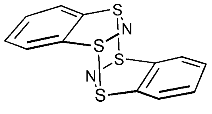

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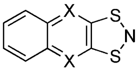

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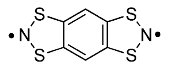
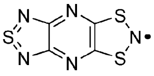


98

EPR[155] and computational[154] studies suggest that the enthalpy of dimerization is very low (in solution and the gas phase, respectively). The subtleties of intermolecular association energetics in these radicals leads in some cases to very unusual solid state properties. The structure of the tricyclic fused 1,3,2-dithiazolyl **99** is temperature-dependent:[160] at room temperature the radicals are monomeric and pack in evenly spaced π stacks, while the 150 K structure consists of cofacial π dimers. The transition between dimeric and monomeric structures is hysteretic in nature, *i.e.* the dimer-to-monomer (increasing temperature) transition temperature is about 190 K while the monomer-to-dimer (decreasing T) phase transition takes place at about 120 K. Thus in the temperature range between the two transition temperatures these radicals exhibit a form of solid-state bistability, *i.e.*, they can exist in either monomeric or dimeric form depending on sample history. Other 1,3,2-dithiazolyl derivatives **100**[161] and **101**[162,163] possess analogous temperature-dependent and cooperative (hysteretic) properties. The structural and mechanistic basis for this bistability has been elegantly delinated by Oakley.[163,164]



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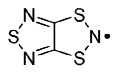

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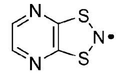

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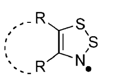
1,2,3-Dithiazolyl radicals **102** are isomers of the 1,3,2-derivatives. Early EPR studies were reported on a variety of benzo-fused derivatives but these radicals were only modestly persistent in solution. In the past decade many isolable 1,2,3-dithiadiazole compounds have been developed by Oakley. Structural richness once again appears in the solid state characteristics in these radicals: four "simple" substituted or annelated 1,2,3-dithiazolyls have been structurally characterized, and each one has a different solid state structure. The naphtho fused derivative **103** adopts the common cofacial π dimer structure,[165] tricyclic fused compound **104** exists as a cofacial but *antiparallel* (centrosymmetric) π dimer,[166] **105** has a twisted ('gauche') π dimer structure[167] similar to that seen in a few 1,2,3,5-dithiadiazolyl radicals (*cf.* Fig. 5b), and thiazole-substituted radical **106** is monomeric.[168] Finally, the seemingly subtle modification of replacing the thiadiazole fused ring in **100** by a benzo group, *i.e.* **107**, renders this radical persistent but not isolable.[169] In the three dimeric examples, the intradimer distances range from 3.0 to 3.3 Å, somewhat longer than in other thiazyl radical π dimers. EPR and computational studies show that the spin density in these radicals is quite a bit more delocalized, particularly in the fused ring compounds, so it is perhaps not surprising that the variety of structural possibilities is sensitive to the electronic (and steric) structure of each particular derivative. The few forays into selenium analogues of **102** that have been reported have not led to isolable radicals.[165]



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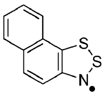

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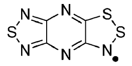

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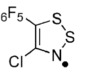

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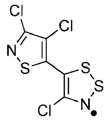

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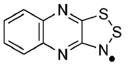
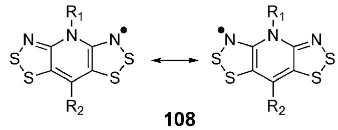


107

Oakley has also developed "dithiazolodithiazolyl", or resonance-delocalized 1,3,2-dithiazolyl, radicals **108** (R_1 = H, Me, Et, Pr; R_2 = H, Cl, Me, Ph). These highly delocalized radicals are generally monomeric in solution and the solid state.[170, 171] However, one derivative (R_1 = Me, R_2 = Ph) has short (<3.3 Å) intermolecular S–S contacts in the solid state but not between π stacked radicals. Instead the contact is a *lateral* one between neighbouring molecules lying side by side, leading to the suggestion that this intermolecular contact is an incipient S–S bond.[170] Pyrazine-based radical **109** also adopts an S–S σ bonded dimer β-[**109**]$_2$ in the solid state, with an even shorter *d*(SS) (2.82 Å).[172] Interestingly **109** can be obtained in a second crystalline phase which contains the first example of a thiazyl radical which dimerizes by σ bond formation between two *carbon* atoms, α-[**109**]$_2$. The CC dimer can be rationalized by the presence of substantial spin density on the carbon atoms that are part of the dimer bond. The same can, of course, be said about the sulfur atoms participating in the bond in the β phase structure.



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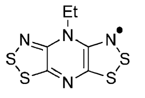

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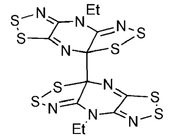
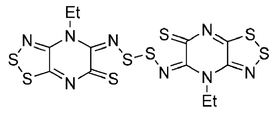
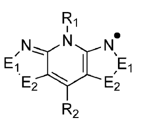


α-[109]$_2$



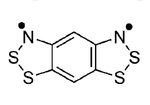
β-[109]$_2$

Very recently the family of resonance-delocalized 1,2,3-dithiazolyls has been expanded by replacement of some/all of the sulfur atoms by selenium. Unlike the selenium analogues of simple 1,2,3-dithiazolyls which are not isolable, examples of each of the resonance delocalized analogues **110–112** have been successfully isolated and characterized. Solid-state structures consist either of monomeric radicals or Se–Se σ bound dimers analogous to the structure of (β-**109**)$_2$.



110 E_1 = S, E_2 = Se
111 E_1 = Se, E_2 = S
112 E_1 = E_2 = Se

There is a variety of putative bis(1,2,3-dithiazolyl) "diradical" structures which are actually closed shell compounds. A triplet ground state is predicted for the (yet to be synthesized) diradical **113**, but the simple replacement of a central carbon atom by nitrogen produces **114** which has been shown (experimentally and computationally) to possess a zwitterionic ground state[173] analogous to "diradicals" **47** and **48**. Alternative "diradicals" created either by placing the nitrogens at the *para* positions of a central aromatic,[174] *e.g.*, **115**, or by connecting two C_2NS_2 rings by exocyclic double bonds,[175] *e.g.*, **116**—instead produce closed shell ground state *quinoidal* species.



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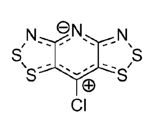

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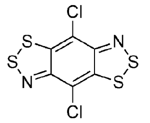

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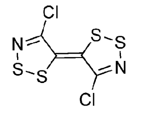
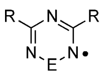


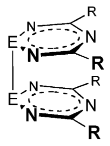
116

4.4 "Thiazinyl" radicals

Some of the earliest developments in heterocyclic C/S/N radical chemistry concerned six membered ring radicals. 1,2,4,6-thiatriazinyls **117** and their selenium analogues **118** are highly stable radicals, and both form cofacial π dimers **119** in the solid state.[176,177] In the dimer structures there is an appreciable bowing out of the rings within the dimer, such that the E–E distances (2.66 Å for E = S, 2.79 Å for E = Se) are considerably shorter than the distances between the other atom pairs, and also shorter than typical intradimer S–S distances in other thiazyl radicals (see above). This is partly a reflection of the spin distribution in these radicals, for which a substantial fraction of spin density is found on the chalcogen (as evidenced by the π SOMO **120**). Thus dimer structure **119** could be interpreted either as π dimer or a nascent SS σ bond.



117 E = S
118 E = Se



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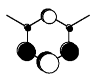
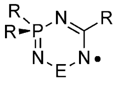
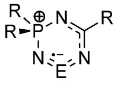


120

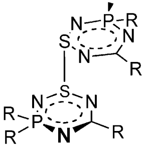
In the C_2N_3E rings described above, both EPR and computational studies indicate that all three nitrogen atoms carry nearly the same amount of spin.[176,178] Replacement of the ring carbon atoms in **117** and **118** by phosphorus leads to substantial changes in both spin and charge distribution. The phosphorus centers in phosphathiatriazinyls **121** (E = S) and **122** (E = Se) are accurately described as phosphonium cations, with the corresponding negative charge distributed over the remainder of the π conjugated part of the ring; spin density is particularly concentrated on the chalcogen and nitrogen adjacent to it and the phosphorus.[179,180] Consequently, the zwitterionic structure **123** is a better representation of the spin and charge density in these radicals. The solid state structures of the sulfur and selenium analogues differ: the former exists as an S–S bound antarafacial dimer **124** with an SS bond length (2.49 Å) only moderately longer than a covalent SS bond. In contrast the selenium radical dimerizes by a Se–N "bond" (1.99 Å; there is also a secondary Se–N contact at 3.1 Å, well within the van der Waals contact distance) to give **125**. The differences between these structural preferences have been ascribed to a subtle competition between homodimerization enthalpies and electrostatic (charge-transfer) driven associations brought on by the strong spin/charge polarization.[180] Thus **124** can be thought of as arising from radical SOMO–SOMO overlap, whereas **125** is the result of a formal redox disproportionation between two of radicals **122** followed by bond formation between Se^+ and N^- centers.



121 E = S
122 E = Se



123



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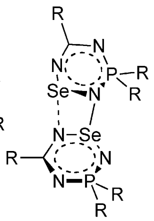
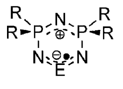
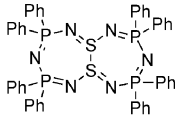


125

The all-heteroatom-based radicals **126**/**127** complete the series begun by the progression from **117**/**118** to **121**/**122**; as shown below, the cyclic P_2N_3E radicals are best represented as internal salts, with negative charge—and spin—confined to the NSN fragments.[180,181] The structure of the selenium variant **127** is not known, but the sulfur-based radical cannot be isolated as such and instead rearranges/dimerizes to form bicyclic fused structure **128**.[182] Subsequent work on intermolecular substituent scrambling in acyclic sulfur diimide radical anions $[\mathrm{RN{=}S{=}NR}]^{\bullet-}$ have provided a clear mechanistic basis for the dimerization/rearrangment of **116** to **128**.[183]

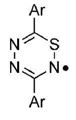


126 E = S
127 E = Se



128

Kaszynski has described attempts to prepare a different isomer of the thiatriazinyl ring **129**.[184] This radical does not appear to be very persistent, although the difficulties in generating the radical cloud the issue somewhat. There have been just a few reports of thiazyl radicals in rings with more than six atoms. Benzo-dithiadiazepinyls **130** have been identified spectroscopically but have eluded isolation.[185] Eight-membered ring radical **131** reversibly associates at low temperatures in solution. The EPR spectrum of this radical supports an internal salt formulation analogous to that described for **126** and **127**.[186] The EPR spectroscopy of this compound is further complicated by apparent conformational flexibility in solution.



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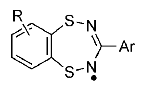

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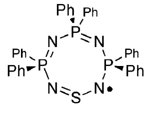

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5 Discussion

5.1 What makes stable radicals stable?

There are a number of molecular structural features which can contribute to radical stability, most of which have been appreciated to some extent for as long as stable radicals have been around. Steric protection—the incorporation of bulky substituents—is probably the most universally reliable means of providing kinetic and thermodynamic stability to an otherwise reactive moiety, and this remains a popular approach in stabilizing many kinds of radicals.[19] However, it should be noted that many of the "applications" which rely on stable radicals require the spin of the stable radical to interact with other molecules—chemically, magnetically, *etc.* In this context, using steric protection to stabilize radicals may ultimately be counterproductive, as the method for making the radical stable enough in the first place also prevents that radical from interacting with its environment.

Other stabilizing features can be described as purely electronic in origin. Virtually all stable radicals described here are π-radicals, which offers the possibility of the spin to be delocalized over any portion of the radical that is part of the same π system. Delocalization certainly seems to generally be an effective means of reducing reactivity, as the spreading of spin density over more atomic centers should dilute the amount of spin on any one atom, which in turn should correlate with attenuated reactivity at that site. The best example of radicals which are stabilized due to delocalization are the phenalenyl radicals (section 2.2) but many of the stable radicals described in this Perspective enjoy some degree of delocalization. It is also evident that *cyclic* π systems are generally superior to acyclic ones because π delocalization is maximized in the former. However, the notion that "more delocalization is better" is probably an oversimplification as it ignores the differential reactivity at different atomic centers. For example, spin density in many simple, stable, nitroxide radicals (section 3.5.) is "delocalized" only over the two heteroatoms, whereas spin delocalization onto N-aromatic groups in diaryl nitroxides actually *lowers* the nitroxide stability.

Many of the most stable of stable radicals are heteroatom-based. In particular, nitrogen, oxygen and sulfur are effective carriers of spin density in stable radicals. The origins of this are twofold. Firstly, these atoms can be described as "lone pair rich", a feature which produces lone pair repulsions when two or more these atoms are catenated. This effect is well-known to contribute to the anomalously low σ bond strengths in peroxides, hydrazines, and even F_2. The hypothetical *σ dimer* of a nitroxide radical—a peroxide-like species R_2NOONR_2—would consist of four consecutive lone-pair-rich atoms; the lone pair repulsions in this (unknown) molecule override any possible thermodynamic gain from the σ bond formation. Perhaps not coincidentally, these heteroatoms are all among the most electronegative, a feature that probably makes these kinds of radicals considerably less reactive to molecular oxygen—in contrast to nearly all of the carbon-centered radicals.

Other molecular structure–stability relationships have received somewhat less attention but are no less important. Obviously the spin distribution of a radical is a prime determinant of many of its properties. Far less frequently articulated is that the *charge* distribution can also play a major role as well. This facet of stable radical chemistry has in fact been articulated nicely to understand reactivity–association trends in (hetero)thiazinyl radicals (section 4.4) and can be at least superficially appreciated in radicals where resonance structures require formal charges (*e.g.* nitronyl nitroxides, section 3.6). However, in general there seems to be room for expansion on the *interplay* between spin and charge distribution in stable radical chemistry. In this context, the electronic (conjugative, inductive) effects of substituents should be expected to have a marked effect on radical stability. For some classes of stable radical there have not been many different derivatives from which substituent effects could be elucidated, but other less stable (persistent) radicals have been analysed in terms of donor or acceptor substituents (particularly when *both* donor and acceptor are present, *cf.* captodative stabilization[182]) and one would expect to be able to use substituent effects to optimize stability.

All of the preceding discussion concerning radical stability should be digested with two caveats concerning the word 'stability'. The subjectiveness of this term has already been alluded to. But stability, in addition to being a relative descriptor, is also a multi-faceted one: stability with respect to *what*? The molecules described in this Perspective show a broad range of relative stabilities with respect to the many reactions open to radicals—dimerization, hydrogen abstraction, disproportionation, oxidation–reduction, *etc.* From a practical perspective, Ingold's "put it in a bottle" concept is a useful working definition, but context is important too, for example, those interested in *in vivo* EPR imaging would not consider any radical which is air- or water-sensitive to be stable *enough.*

5.2 Concluding remarks

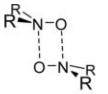
From Gomberg's seminal report of the triphenylmethyl radical at the turn of the 20th Century up to relatively recent times, essentially every new stable/persistent radical class was an accidental discovery which typically catalyzed fundamental research into the synthesis and properties of that class. In parallel—but not in *concert*—with these fundamental studies were the development of useful applications (*e.g.* spin labelling, organic and polymer chemistry) of stable radicals (usually nitroxides) which curiously did not involve much in the way of optimizing radical properties beyond stability.

In the past 20–25 years there has been an explosion on the number and variety of stable radicals. The diversity in molecular structures found in the array of stable radicals is impressive. One of the goals of this Perspective was to unite two general classes of stable radicals that are often treated separately from one another—the "organic" radicals found in sections 2 and 3 and the thiazyl based radicals from section 4, normally labelled as "inorganic" molecules. I hope that this review highlights the fact that the broad similarities between these compounds far outweigh their differences.

Concomitant with the growth of stable radical activity has been an evolution in the approach to making and studying them. This is by no means universal, but there is now a distinctly rational approach to synthesizing and examining new stable radicals. This is particularly true in some of the modern "applications" such as conducting and magnetic materials. Perhaps the future will bring even more of a rational approach to stable radical science and also an appreciation that these molecules are much more than esoteric species.

Note added in proof

A few stable but sterically unhindered nitroxides reversibly dimerize in solution and in the solid state. The solid state structures consist of centrosymmetric dimers of nitroxides, shown in **132**, with intermolecular N · · · O distances of *ca.* 2.28 Å. The structural aspects of these dimers are consistent with π-dimer formation.[187]



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Acknowledgements

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