

# Organic Magnets

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## Introduction

The notion of organic molecular materials showing metallic properties, such as electric conductivity or ferromagnetism, started several decades ago as a mere dream of some members of the chemical community. The goal was to create an assembly of organic molecules or macromolecules containing only light elements (C, H, N, O, S, etc.) and yet possessing the electron/hole mobility or spin alignment that is inherent in typical metals or their oxides and different from the isolated molecular materials. Organic molecular conductors initially were developed during the 1960s, but the first examples of organic molecular magnets took several more decades to be discovered, owing to the more subtle and complex structural and electronic aspects of these materials. The flurry of activity in this field can be traced to the widely held belief that even the most sophisticated properties can be rationally designed by a systematic modification of organic molecular structures. This motivation was further fueled by increased synthetic capabilities, especially for obtaining large organic molecules with suitable structures and topologies, and also by the spectacular progress of supramolecular chemistry for materials development witnessed in recent years. Also noteworthy is the pioneering work performed in the 1960s by several physical organic chemists who unraveled different ways of aligning spins within open-shell molecules (i.e., triplet diradicals, carbenes, etc.), working against nature's tendency to align them in an antiparallel manner. Magnetic interactions between unpaired electrons, located on the singly occupied molecular orbitals (SOMOs) of di- and polyradicals, or between the adjacent open-shell molecules in crystals, are a crucial issue in this evolving field. Thus, depending upon the symmetry, degeneracy, and topological characteristics of SOMOs and also on the mode of arrangement of the molecules in a crystal, the resulting interaction can align the neighboring spins parallel or antiparallel (see the introductory article by Miller and Epstein in this issue of *MRS Bulletin*).

Two aspects are to be considered in the development of strong magnetic proper-

ties in molecular materials. They are the spin-containing building blocks (i.e., free radicals and radical ions) and their coupling routes (mechanisms). In this article, we will briefly summarize the essence of both of these issues, which are important for the design of this class of materials and the understanding of their physical properties. We will also review some of the most important research results achieved worldwide in this rapidly developing area of research.

## Magnetic Interactions and Magnetic Ordering

Magnetic exchange interactions alone determine the magnetic behavior of organic compounds made of light elements at temperatures well above 0.1 K. Other kinds of magnetic interactions (such as hyperfine, dipolar, or spin-orbit interactions) can be considered negligible above this temperature in most organic materials. Consequently, magnetic organic systems may be described at zero applied magnetic field by the effective spin Hamiltonian approach that takes the form

$$H = -2 \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1)$$

where  $J_{ij}$  represents the effective exchange interaction parameter for magnetic centers  $i$  and  $j$  (the spin-containing building blocks), which have spin quantum numbers  $\mathbf{S}_i$  and  $\mathbf{S}_j$ , respectively, and the summation runs over all adjacent pairs of centers. The  $J_{ij}$  parameter is a scalar constant, often referred to as the *isotropic interaction parameter* or the *exchange coupling constant* between the two interacting magnetic centers. When  $J_{ij}$  is positive, the two spins tend to be parallel to each other in the ground state, and the interaction (or coupling) is called ferromagnetic. If  $J_{ij}$  is negative, the two spins tend to be antiparallel in the ground state and the interaction is called antiferromagnetic.

A ferromagnetic interaction will result if an orthogonal arrangement of SOMOs with a null overlap integral between such orbitals is produced. A paradigmatic example of an organic molecule showing a ferromagnetic coupling is diphenylcar-

bene, in which the two SOMOs having  $\sigma$  and  $\pi$  symmetries are intrinsically orthogonal (Figure 1).

On the other hand, if a nonzero overlap integral between the SOMOs of two neighboring units is produced, an antiparallel alignment is favored. However, if this kind of overlap is nil and yet a significant overlap of the SOMO with the next-highest occupied molecular orbital or with the next-lowest unoccupied molecular orbital is present, admixture of charge-transfer configurations with the ground state may take place, and a slight preference for the parallel alignment might occur. In fact, this type of kinetic exchange is a basis for the famous McConnell II mechanism postulated in the late 1960s.<sup>1</sup> McConnell also postulated another mechanism (the McConnell I mechanism, 1963) in which the kinetic exchange term is also operative.<sup>2</sup> This proposal explains a possible origin of the ferromagnetic interactions between close-packed odd-alternant hydrocarbon radicals and has been one of the seminal concepts in molecular magnetism. These radicals have a set of atoms (starred) with positive spin densities and another set of atoms (unstarred) with negative spin densities produced by the spin polarization phenomenon. In a first approximation, negative spin densities appear where the Hückel approximation predicts the existence of nodes in the SOMOs. Suppose we place one of these odd-alternant radicals on top of another so that those atoms with opposite spin densities face one another. Since spins on neighboring atoms of close-packed molecules tend to be antiparallel, the net spin on the first radical should tend to be parallel to the net spin of the second radical, leading to a ferromagnetic interaction. On the contrary, when the signs of the spins on facing atoms are the same, an antiferromagnetic coupling is produced. In Figure 2, an example of three different orientations of two close-packed benzyl radicals is given. Thus, for the relative orientations of Figures 2a and 2c, where the

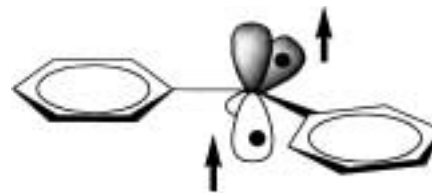


Figure 1. Simplified scheme of the singly occupied molecular orbitals (SOMOs) of diphenylcarbene, showing intramolecular ferromagnetic coupling of two spins.

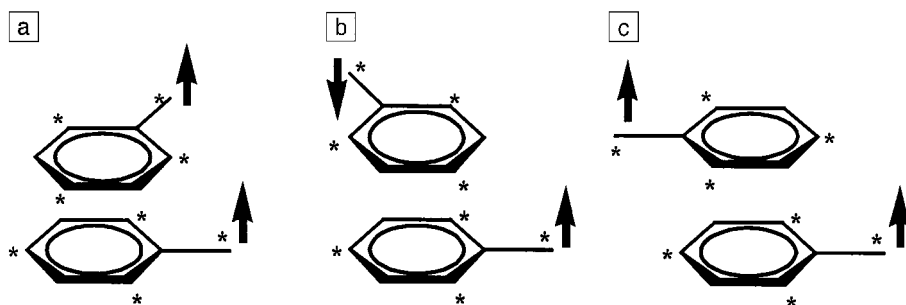


Figure 2. Different magnetic couplings (a), (b), and (c) for three distinct orientations of two parallel, close-packed benzyl radicals.

facing of atoms with positive (starred) and negative (unstarred) spin densities dominate, ferromagnetic couplings are produced. For the orientation of Figure 2b, in which the dominant contacts occur among atoms with the same sign of spins, an anti-ferromagnetic interaction is favored. The experimental support was found 20 years after McConnell's proposal by preparing and studying a series of positional isomers of a pair of diphenylcarbenes incorporated into a [2,2]-paracyclophane skeleton.<sup>3,4</sup>

Most organic magnetic materials exhibit paramagnetic behavior at high temperatures where the spins of the materials behave independently of each other. However, as the temperature is decreased, the exchange interactions become comparable with the thermal energy of the system, and the neighboring spins tend to align in accordance with the signs of their  $J_{ij}$  parameters. The correlation in the spin alignment is extended within small regions of the material, and short-range order is attained. For achieving bulk magnetic behavior, a further temperature decrease is required, so that the thermal energy is well below the smallest  $J_{ij}$  term in the material. Under these conditions, the spin ordering is established throughout the three dimensions of the material, and long-range magnetic ordering might be achieved, as in Figure 1 in the introductory article in this issue.

The spins in most organic free radicals are regarded as being of the Heisenberg type and therefore behave nearly isotropically. As a result, the exchange interaction fixes only the relative orientation of the spins. Any preferential orientation (or direction) of the interacting spins is not established with respect to the atomic framework of the material, since the energies of all possible directions are nearly identical. This explains why most organic ferromagnets behave as "soft" magnets, showing vanishing coercive fields in their hysteresis curves. A preferred direction for the spin alignment in an organic magnetic

material is achieved only if a source of magnetic anisotropy is present in the material. In purely organic compounds, the two main sources of anisotropy are spin-orbit couplings and magnetic dipolar interactions that both generally have a small magnitude.

### Molecular and Supramolecular Aspects of Organic Magnets

Both the structural and electronic characteristics of spin-containing building blocks and their relative orientations in space are of utmost importance in organic magnets.

#### Spin-Containing Building Blocks

When used as advanced materials, organic compounds are generally reputed to exhibit good correlation of their molecular structures with properties and to be tailor-made under mild laboratory conditions. They are, however, mechanically and thermally fragile. To make matters worse, most organic spin-containing molecules are reactive intermediates formed by various reaction processes called *homolytic bond cleavage*, *free-radical addition*, and *electron-transfer reactions*. For the purpose of developing molecular magnets, we have to tame them so that they may stay alive and not react with each other or with other reactive molecules in their surroundings.

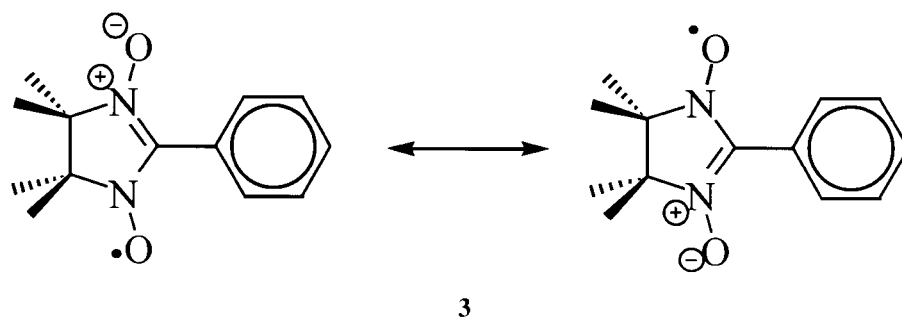


Chart 2.

Several strategies can increase the stability of organic free radicals kinetically and, to some extent, thermodynamically.<sup>5</sup> Steric shielding of the atoms having high spin densities by bulky atoms and groups is often employed. The methyl groups at the  $\alpha$  positions of aminoxyl radicals **1** (Chart 1) are typical examples. However,

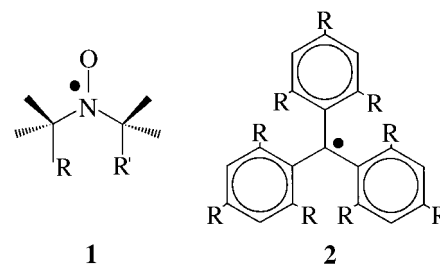


Chart 1.

steric shielding with large groups must be employed in moderation because the larger the shielding groups, the lower the chances of each spin-carrying site interacting magnetically with its neighbors. Many radicals with bulky groups such as **2** ( $R = \text{Cl}$ ) show quasi-ideal paramagnetic behaviors, evidencing the insignificance of the intermolecular magnetic interactions.<sup>6</sup> Another strategy is the replacement of the carbon radical center with an electronegative heteroatom, namely, the use of heteroatom-centered radicals. An extension of this strategy is to introduce both the electrical charges and unpaired electrons into a neutral molecule by a redox process including doping. Due to Coulombic repulsion between the charges of the same sign, the resulting radical ions are kept apart from each other, avoiding their dimerization and other reactions and thereby increasing their half-lives.

The phenyl derivative **3** (Chart 2) shows a certain degree of steric shielding, due to the bulkiness of the phenyl and the four

methyl groups, as well as considerable negative charges on the two oxygen atoms of the NO groups, where most of the unpaired electron spin is localized. Moreover, there is a  $\pi$  conjugation between the two NO groups. Other species most commonly appearing in the literature related to molecular magnetism are *tert*-butyl phenyl aminoxy (4), nitronyl aminoxy (5), galvinoxyl (6), phenoxy (7), 3-phenylverdazyl (8), 5-phenyldithiadiazolyl (9), and high-spin molecules derivable from diphenylcarbenes (10) (all shown in Chart 3), triarylmethyls (2), and several delocalized heterocyclic radical cations and anions.

All of these families of open-shell molecules have three outstanding characteristics in common<sup>7</sup> that differentiate them from compounds containing transition- or lanthanide-metal ions: (1) spin densities spread out over a large region of the molecules, (2) existence of regions with spin densities of opposite signs, and (3) generally low magnetic anisotropies.

### Assemblies of Spin-Containing Building Blocks

Since the magnetic properties of molecular materials are intimately related to the relative disposition of the spin-containing building blocks, we must pay attention to two important attributes: (1) distinction of

the different molecular arrangements present in the materials and the forces (bonds, intermolecular interactions, etc.) governing the relative arrangements, and (2) identification of the relative arrangements of neighboring molecules producing ferro- and antiferromagnetic interactions. Some basic principles and considerations are useful in understanding the magnetic properties of these materials.

According to an *Aufbau*-type principle of Kitaigorodskii's,<sup>8</sup> when molecular building blocks pack to form molecular crystals, the total energy of the crystal is at a minimum. This means that the strongest intermolecular contacts form first, and then the remaining contacts form according to their decreasing strengths. Thus, when building blocks can make either strong or weak intermolecular contacts, they prefer to form first certain crystalline motifs (discrete clusters, chains, ribbons, stacks, planes, etc.) with other molecular blocks, using the strongest interactions (coordinative, ionic, or hydrogen bonds, etc.). Then, the resulting crystalline motifs use the remaining weaker intermolecular forces ( $\pi$  stacking, van der Waals interactions, etc.) to complete the three-dimensional (3D) crystal packing. Thus, the first types of crystalline motifs are called *primary structures* and are expected

to exhibit shorter intermolecular distances through which, in some cases, intermolecular magnetic exchange interactions can be established. The primary structure of any molecular solid propagates in a 3D way by the spontaneous action of self-organization. The interactions responsible for self-organization are less specific, less directional, and are called *secondary*, *tertiary*, or *quaternary* structures of the crystal, according to their levels of structural complexity. Undoubtedly, the secondary and tertiary structures of a molecular solid are also important to its magnetic properties. In contrast, with the lower-level structural motifs, which are highly predictable, the design of the high-level structures (secondary, tertiary, or quaternary structures) and their influences on the macroscopic magnetic behavior of a given material must be left for the moment in most cases to serendipity.<sup>9</sup> For this reason, a total design of molecular solids with predetermined magnetic properties is still a dream that must wait for further progress in supramolecular chemistry.

It is important in molecular magnetism to distinguish between the structural dimension of a molecular solid and its magnetic dimension. Figure 3 shows schematic drawings of three ideal molecular solids with the same structural dimensions but differing magnetic dimensions due to the existence of different magnetic exchange pathways along the three directions of the solid (i.e.,  $J_1$ ,  $J_2$ , and  $J_3$ ). Solids with 3D ( $J_1 \sim J_2 \sim J_3$ ), 2D ( $J_1 \sim J_2 \gg J_3$ ), and 1D ( $J_1 \gg J_2 \sim J_3$ ) magnetic exchange interactions are shown in Figures 3a, 3b, and 3c, respectively. Figure 3d depicts another molecular solid that has a distinct structural dimensionality (dimers) and exhibits a zero magnetic dimensionality ( $J_1 \gg J_2 \sim J_3 \sim J_4$ ).

### Molecular Solids Showing Long-Range Magnetic Ordering

The first example of an organic bulk ferromagnet was reported in 1991 by Kinoshita et al. for crystals of the  $\beta$  phase of *p*-nitrophenyl nitronyl aminoxy radical 11 (Chart 4).<sup>10</sup> First evidence of long-range ferromagnetic order for this compound was achieved by ac susceptibility and heat-capacity measurements at low temperatures. The heat capacity shows a sharp peak at 0.60 K with a  $\lambda$  shape, indicating the presence of a magnetic phase transition. The entropy contained inside this peak nearly corresponds to that theoretically expected for a 3D magnetically ordered state. The ac susceptibility diverges around the same critical temperature  $T_c$  of 0.60 K, indicating that the ordered state is a ferromagnetic one. In ad-

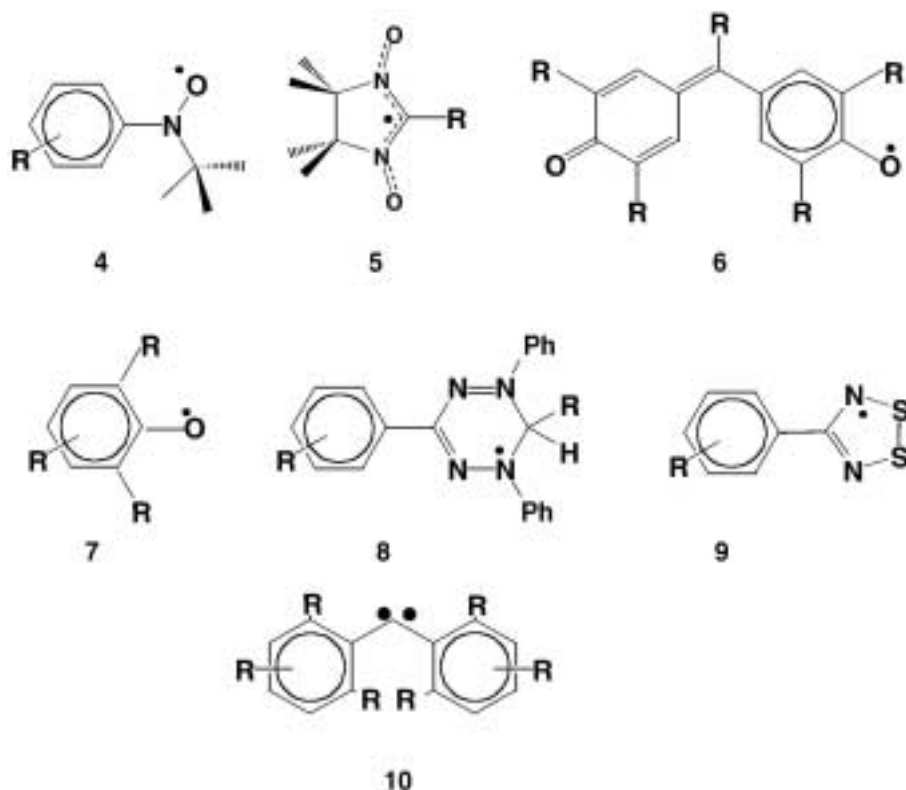


Chart 3.

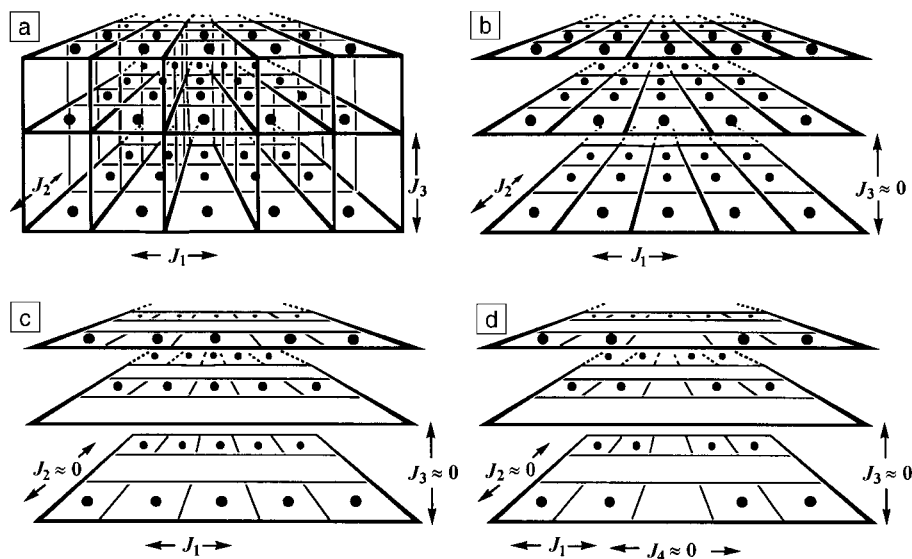


Figure 3. Schematic representation of four solids with different magnetic dimensionalities. (a)–(c) Solids with 3D ( $J_1 \sim J_2 \sim J_3$ ), 2D ( $J_1 \sim J_2 \gg J_3$ ), and 1D ( $J_1 \gg J_2 \sim J_3$ ) magnetic exchange interactions, respectively. (d) Another molecular solid that has a distinct structural dimensionality (dimers) and exhibits a zero magnetic dimensionality ( $J_1 \gg J_2 \sim J_3 \sim J_4$ ).

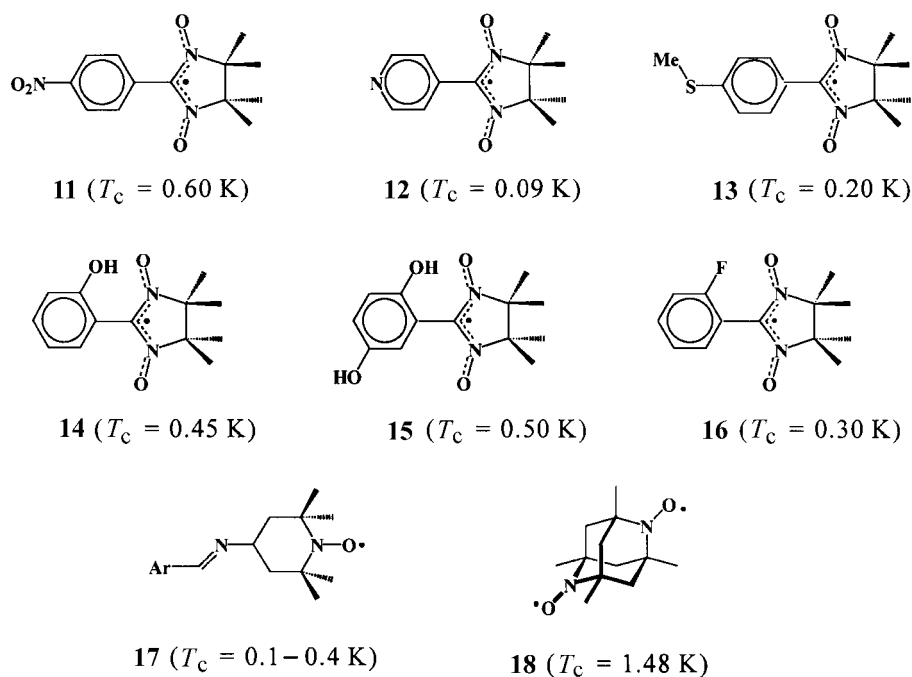


Chart 4.

dition, the magnetization curve below  $T_c$  shows a hysteresis loop, characteristic of a soft ferromagnet, that almost saturates at a field as low as 5 mT. Further insights into the ferromagnetic ordering state and the magnetic interaction mechanism were provided by experiments of zero-field muon spin rotation (ZF- $\mu^+$ SR), polarized neutron diffraction (PND), ferromagnetic

resonance, and the study of pressure and applied magnetic field effects on the transition temperature. Based on these experimental results and on theoretical calculations, the authors concluded that magnetic exchange interactions, rather than the magnetic dipolar interaction, dominate in determining the transition temperature. Moreover, they reported that

the anisotropy of the dipolar interaction determines the direction of the magnetic easy axis of this magnet along the crystallographic  $b$  axis. As a conclusion, the origin of this remarkable magnetic behavior is the particular molecular packing present in the orthorhombic  $\beta$  phase, in which the molecules are arranged following the pattern of a distorted diamondlike lattice. In accordance with this crystal packing, two distinct types of relative molecular arrangements exist; therefore, two different ferromagnetic exchange couplings ( $J$  and  $J'$ ) with different magnitudes form a 3D network of magnetic exchange paths. Thus,  $J$  is the coupling on the  $ac$  planes, where the molecules form a square-lattice arrangement, and  $J'$  is the exchange path, with a tetrahedral coordination that transmits the interaction along the  $b$  axis, their relative magnitude being  $J > J'$ . The importance of the relative arrangement of the molecules on the magnetic properties of the  $\beta$  phase of radical **11** is also supported by the completely different magnetic properties shown by other polymorphs of this radical:  $\alpha$  phase (monoclinic),  $\gamma$  phase (triclinic), and the  $\delta$  phase (monoclinic).<sup>10</sup>

Some other substituted nitronyl aminoxy radicals also order ferromagnetically (See 12–16 in Chart 4). The long-range ferromagnetic order of these compounds has been characterized mainly by the measurements of ac susceptibility and magnetization, and, in very few cases, by ZF- $\mu^+$ SR, PND, and heat-capacity experiments.<sup>11</sup>

Serendipity has played a key role in obtaining these organic magnets, since presently there is no way to control the 3D molecular packing that favors the appearance of ferromagnetic order. This assertion is illustrated by the fact that many of the examples have polymorphs that do not show bulk magnetic ordering. Efforts to control packing have been intensively done using crystal engineering tools, such as hydrogen bonds with phenyl nitronyl aminoxy radicals substituted by one or two OH groups. Depending on the number and position of the OH groups, the radicals form H-bonded primary structures that are zero-, one-, two-, or three-dimensional and show different magnetic interactions—either ferro- or antiferromagnetic.<sup>12</sup> Figure 4 shows the primary (chains) and secondary (sheets) structures of the 4-hydroxyphenyl nitronyl aminoxy radical, consisting of chains of molecules bonded by strong H bonds between NO and OH groups of neighboring molecules, which are additionally linked by other weak H bonds between NO and  $\text{CH}_3$  groups, forming molecular sheets. Remarkable is the fact that radicals within these planes are ferromagnetically cou-

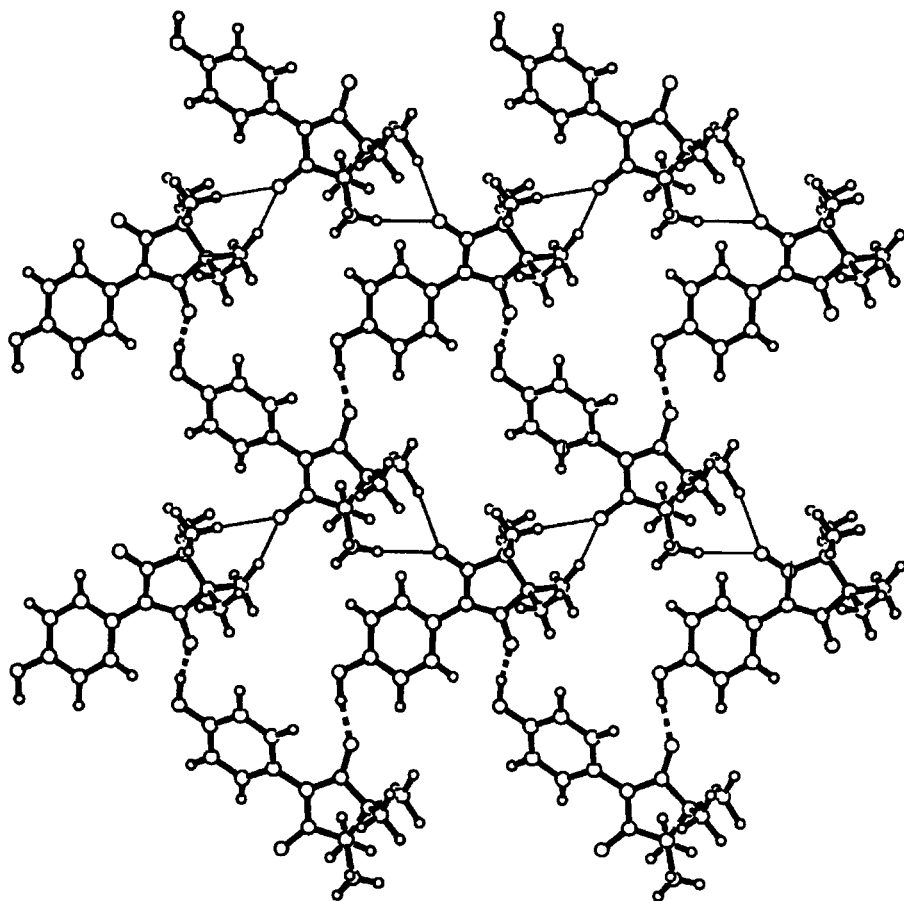


Figure 4. Projection along the *ab* plane of the primary structure of the 4-hydroxyphenyl nitronyl aminoxy radical.

pled to each other, yielding a system with a 2D magnetic dimensionality.

Other aminoxy-based organic radicals, such as the series of TEMPO derivatives **17** (Ar = C<sub>6</sub>H<sub>5</sub>, 4X-C<sub>6</sub>H<sub>4</sub>, 4-C<sub>6</sub>H<sub>5</sub>-C<sub>6</sub>H<sub>4</sub>, 4-MeS-C<sub>6</sub>H<sub>4</sub>, and 4-C<sub>6</sub>H<sub>5</sub>O-C<sub>6</sub>H<sub>4</sub>)<sup>13</sup> and the diaza-adamantane bisaminoxy **18**,<sup>14</sup> also show long-range ferromagnetic ordering.<sup>15</sup> The latter diradical exhibits the highest *T<sub>c</sub>* described for an aminoxy-based magnet, in which the magnetic exchange interactions involved are noteworthy. As dictated by the small magnetic anisotropy of this compound, no hysteresis can be observed. This diradical was pursued because of the orthogonal arrangement of its two SOMOs, which are mainly located on the two NO groups. This structural characteristic is provided by the rigid covalent framework of the diaza-adamantane skeleton and produces an intramolecular ferromagnetic coupling of the two unpaired electrons, as ascertained by electron spin resonance (ESR) studies in solution.<sup>16</sup> Two crystalline phases have been detected for the compound, but only

one of them—the *α* phase—is a bulk ferromagnet, in which the NO groups of the radicals are arranged intermolecularly in a head-to-tail manner along one direction, with the intramolecular interaction being perpendicular to this chain. PND studies revealed that the spin density is located mainly in the *π* orbitals of the nitrogen and oxygen atoms, although some spin was also detected on the contiguous CH<sub>2</sub> groups.<sup>17</sup> The alternation of the sign of spin density of the carbon atoms linking the two NO groups was taken to indicate that the intramolecular ferromagnetic coupling was a consequence of exchange through the weakly polarized carbon framework. Interestingly, in its crystals, the molecules of **18** (Chart 4) are not *D*<sub>2d</sub> symmetric, as a result of nonplanar conformation of the NO group, which therefore finds itself in a chiral (*C*<sub>2</sub>) situation.<sup>18</sup>

Ferromagnetic exchange interactions of aminoxy-based materials appear invariably small and, in our experience,<sup>15</sup> seem unlikely to give rise to high-*T<sub>c</sub>* materials. To increase the magnetic ordering tempera-

ture, one should look for spin-containing building blocks that promote stronger intermolecular ferromagnetic interactions or, alternatively, design building blocks so that they can interact strongly with neighboring units. Actually, the *T<sub>c</sub>* for long-range 3D ferromagnetic ordering is related to the average exchange coupling constant, *J<sub>av</sub>*, and the spin magnitude, *S*, in the mean-field approximation as

$$T_c = 2J_{av}zS(S + 1)/3k_B, \quad (2)$$

where *z* is the number of nearest-neighbor spins and *k<sub>B</sub>* is the Boltzmann constant. Thus, the use of molecules with spherical shapes, which increases the chances of interaction with many neighboring units, must produce, under favorable circumstances, an increase of *T<sub>c</sub>*. This seems to be the case, at least in part, for the charge-transfer salt [C<sub>60</sub>·TDAE] **19**, between C<sub>60</sub> and tetrakis(dimethylamino)ethylene (TDAE), exhibiting long-range magnetic ordering at 16.1 K,<sup>19</sup> which recently has been definitively proved to be ferromagnetic.<sup>20</sup> Many physical studies, including ZF-*μ*<sup>+</sup>SR, solid-state Raman, ESR, and proton nuclear magnetic resonance (<sup>1</sup>H-NMR) spectroscopies, as well as the study of pressure effects on the transition temperature, have been employed to shed light on the spin-coupling mechanism of this material, thus confirming the magnetic ordering. To date, charge-transfer salt **19** is the organic material exhibiting a ferromagnetic ordering with the highest *T<sub>c</sub>* ever reported. On the other hand, very few fullerene-based materials have been found to show relevant magnetic behavior. Thus, for example, TDAE adducts with C<sub>70</sub>, C<sub>84</sub>, C<sub>90</sub>, and C<sub>96</sub> do not show magnetic orderings above 4 K, and the same lack of ordering occurs when TDAE is replaced by other strong electron donors.

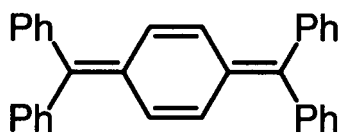
Initially, long-range ferromagnetic ordering was the unique target of many scientists looking for organic magnets. However, in recent years a few examples of weak ferromagnetic materials, such as the TEMPO derivative<sup>21</sup> and nitronyl aminoxy,<sup>22</sup> have been reported. In these cases, the canting of antiferromagnetically coupled spins was due to the absence of an inversion center between the interacting spins, yielding small net magnetizations. The ordering temperatures of these materials are very low because of the small antiferromagnetic exchange interactions involved. A recent approach to increasing such interactions consists of using organic radicals bearing heavier main group elements, such as P, S, and Se, in which more radially diffuse SOMOs and less sterically hindered structures would lead to stronger antifer-

romagnetic exchange interactions. Indeed, some sulfur nitrogen radicals of the dithiadiazolyl family have been reported to exhibit large antiferromagnetic couplings and, in a limiting case, they exhibit diamagnetism due to a complete cancellation of spins. There is one exception to this rule: the  $\beta$  phase of the  $p$ -NCC<sub>6</sub>F<sub>4</sub>CN<sub>2</sub>SSN radical **20** (Chart 5), which orders as a weak ferromagnet at 36 K as a result of spin canting. It is the organic compound with the highest ordering temperature reported to date.<sup>23</sup>

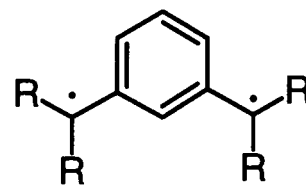
Finally, it is worth noting that no example of an organic material with long-range ferrimagnetic ordering has been reported. In principle, this type of magnet could be obtained by combining two different species, a high-spin molecule (discussed in the next section) and a free radical, which differ in their spin magnitudes and interact antiferromagnetically in the three directions of the solid. Although the concept involved in the design of a ferrimagnet is very simple, the lack of this type of material reveals that there is still much room to explore in this exciting field.

### High-Spin and Super-High-Spin Organic Molecules—Spin Alignment in Polyradicals

In good agreement with the fact that a Kekulé resonance structure can be drawn for the Thiele hydrocarbon **21** (Chart 6), it has a singlet ground state. On the contrary, no Kekulé resonance structure can be drawn for the Schlenk hydrocarbon **22**, which has a triplet ground state.<sup>24</sup> There are two reasons for this, illustrated here by the simpler analogue to **22**, *m*-benzoquinodimethane **23**. Two Hückel nonbonding molecular orbitals (NBMOs) of **23** have AO coefficients that

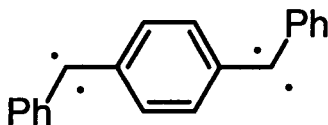
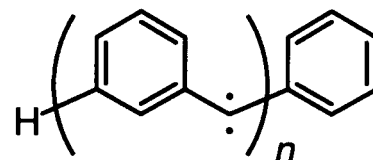


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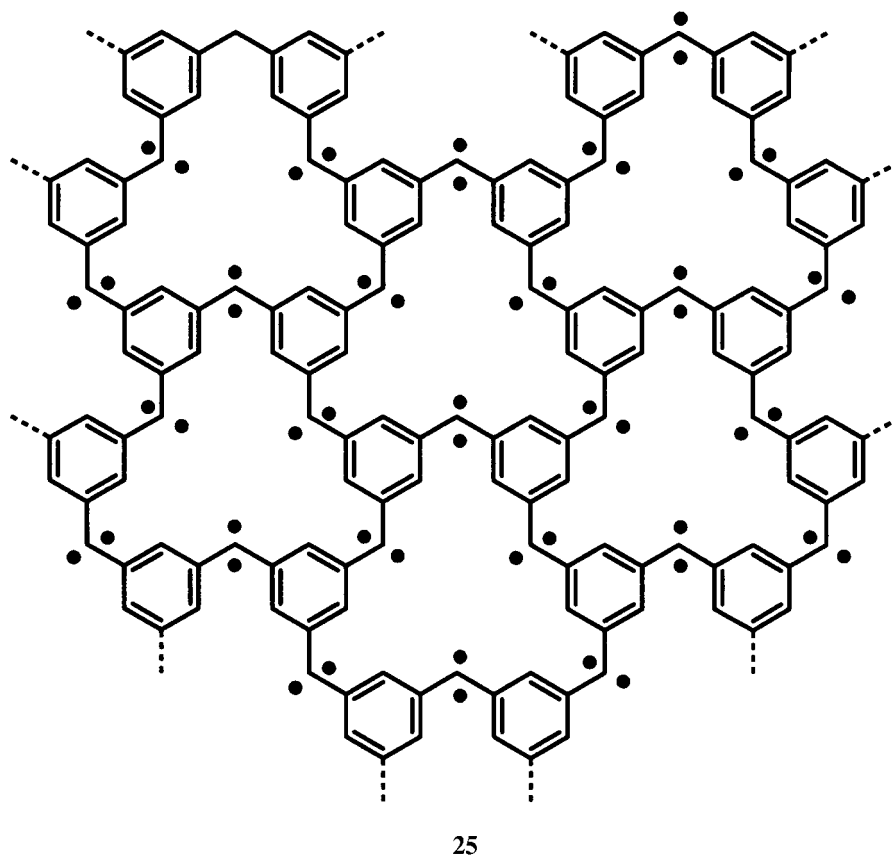


22 (R = Ph)

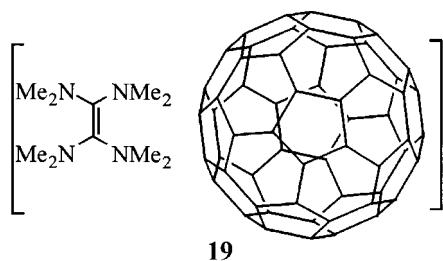
23 (R = H)

*p*-24

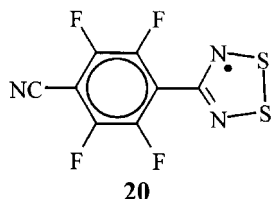
24



25



19



20

Chart 5.

Chart 6.

look like those in Figure 5a and are orthogonal to each other in the sense that the overall overlap integral is zero. According to Hund's rule, a triplet state can become thermodynamically more stable than a

singlet state when two high-lying orthogonal orbitals are degenerate, or nearly so, and carry two fewer electrons for forming a closed-shell structure. The Coulombic repulsion between the two electrons

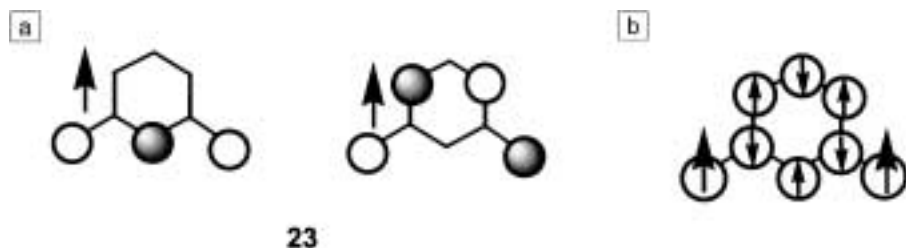


Figure 5. (a) Two Hückel nonbonding molecular orbitals and (b) polarization of the  $\pi$  electrons in *m*-benzoquinodimethane **23**.

would be minimized in the triplet, as dictated by Pauli's exclusion principle. Alternatively, the spins are polarized in **23**, as shown in Figure 5b, and the two spins are aligned in parallel in the ground state.<sup>25</sup>

### Non-Kekulé Hydrocarbons

Diradical **23** is a member of the non-Kekulé hydrocarbons, meaning that it lacks one bond and cannot be represented by a conventional resonance structure. Most non-Kekulé hydrocarbons are related to one of the two most basic units: trimethylenemethane (TMM) and tetramethylethane (TME) by resonance structures (Figure 6). In TMM, two orthogonal SOMOs (NBMOs) are coextensive in molecular space. This is called *nondisjoint*, and its ground state should be a triplet state, since the exchange interaction is large. In TME, the SOMOs can be chosen so that they do

not share any atoms. This is called *disjoint*, and singlet and triplet states are degenerate to a first approximation, since the exchange interaction is nil. Thus, not all non-Kekulé hydrocarbons have high-spin ground states,<sup>26</sup> only those related to TMM. The resonance structure of *m*-benzoquinodimethane related to TMM is also shown in Figure 6.

### One-Dimensional Array of Spins

In the early 1960s, *p*-phenylenedicarbene *p*-**24** and *m*-phenylenedicarbene **24** ( $n = 2$ ), a hybrid of the two examples of orthogonality of SOMOs—*m*-quinodimethane **23** and diphenylcarbene **10**—were demonstrated to have singlet and quintet ground states ( $S = 2$ ), respectively.<sup>26</sup> It was only in the early 1980s that the latter dicarbene was taken seriously and extended to linear tri-, tetra-, and pentacarbene **24** ( $n = 3, 4,$

and 5, respectively). These were established from their electron paramagnetic resonance fine structures and/or magnetization data to have  $S = 3, 4,$  and 5 ground states, respectively,<sup>28</sup> the highest-spin hydrocarbons known at that time. The linear structure can, in principle, be extended to poly(*m*-phenylenedicarbene)s **24** ( $n \rightarrow \infty$ ). In practice, however, a number of limitations exist in the linear structure. First, the kinetically active polycarbene are produced efficiently by irradiation of the corresponding diazo compounds in solid solutions and can be kept for days at liquid-helium temperature. However, it was expected that it would become more and more difficult to produce all of the carbene centers without fail and keep them intact in the real polymers **24** ( $n \rightarrow \infty$ ). A defect at a terminal site would be innocuous, that is,  $S$  would be lowered by 1. Once such a chemical defect is formed in the middle of the cross-conjugated main chain, the high spin multiplicity would be halved. Second, the linear polyketones, one of the precursors, become less and less soluble in typical organic solvents in which further chemical transformations must be carried out. Third, 1D alignment of spins is unstable from the point of view of statistical dynamics. Inversion of all of the second half of the one-dimensionally aligned electron spins would require an additional enthalpy of only  $2J$ , which is defined by the Heisenberg Hamiltonian (Equation 1) for the exchange energies between the neighboring spins  $S_i$  and  $S_{i+1}$ . Whereas the magnitude of the required enthalpy  $2J$  is independent of the length of the units, such inversion of all the second halves of the spins near the center of the one-dimensionally aligned electron spins would become more and more favorable in terms of entropy as the chain length increased. Thus, any magnetic linear chain including **24** is dictated to exhibit no spontaneous magnetization at finite temperature. All of these difficulties inherent in 1D structures might be overcome by 2D structures. Thus, inversion of all of the second halves of the one-dimensionally aligned  $n$  electron spins would require an additional enthalpy of  $2z'nJ$  (where  $z'$  is the number of nearest-neighbor spins on different chains) and becomes unfavorable.

Radical centers may reside on the side chain as pendants of conjugated polymer chains, such as polyacetylenes, poly(phenylacetylene)s, poly(diacetylene)s, and polyphenylenes. All efforts have yielded polyradicals that have either a stoichiometric number of spin centers (but the exchange coupling between the adjacent spins is too weak) or the polymers

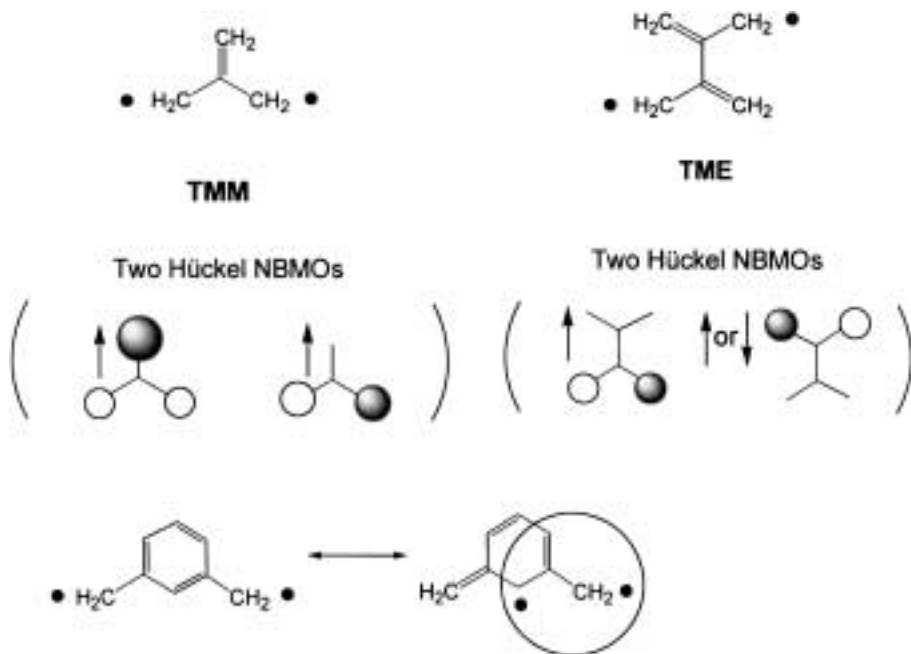


Figure 6. Two kinds of non-Kekulé hydrocarbons represented by trimethylenemethane (TMM) and tetramethylethane (TME).

carry only a fraction of unpaired electrons originally designed to give segments having average spin of about 5 at best.<sup>29</sup>

### Two-Dimensional Possibilities

Cleavage of the connectivity of the neighboring interaction by any defect can also be alleviated by an alternative interaction path in the 2D and 3D systems. Thus, the foregoing analyses dictate that we should design and construct polyradicals and polycarbenes in which a large number of the doublet and triplet centers are joined ferromagnetically in 2D and 3D network structures. A rigid structure would also help reduce the high reactivity of the unpaired electrons at the radical centers toward recombination and other modes of radical reactions. One of the possibilities is a network structure **25** proposed by Iwamura and co-workers as their long-range goal for the strongly magnetic super-high-spin polycarbenes.<sup>30</sup> This structure is obtained on paper by removing every third benzene ring from Mataga's network poly(trityl radical),<sup>31</sup> which in turn can be obtained by truncating every fourth carbon atom from a graphite network. The construction of such regular network structures would be the most formidable task of synthetic organic and polymer sciences to date. Therefore, branched-chain hexa- and nonacarbenes (**26** and **27**, respectively, in Chart 7) and a cyclic hexacarbene corresponding to unit structures contained in **25** were synthesized and studied by the temperature and field dependencies of their magnetization. In good agreement with the expectation, the

hexa- and nonacarbenes were found to have  $S = 6$  and  $9$  ground states, respectively.<sup>32</sup> The quantitative production and characterization of most reactive polycarbenes can be readily achieved as long as the precursor polydiazocompounds are isolated in matrices or organic solid solutions, photolyzed at cryogenic temperature, and studied at that temperature *in situ*. By using this method of taking the data both before and after photolysis, any error due to paramagnetic impurities can be subtracted, and the results will be more reliable.

In an extensive series of preparative work on poly(triarylmethyl)s, Rajca and co-workers pointed out that, whereas interruption of the exchange coupling by one defect at an inner site seriously decreases the spin quantum number in chains and dendritic skeletal structures, it is less vulnerable to a defect in macrocycles; they demonstrated that a dilute solution of dendritic macrocyclic pentamer **28** in THF- $d_8$  showed perfect paramagnetic behavior, with an average  $S = 10$  at 5 K or below. Theoretically, however,  $S = 12$  is expected for 24 ferromagnetically coupled electron spins in the high-spin ground state of this molecule. This discrepancy is associated with a small density of defects, estimated at 2% from a simple percolation model.<sup>33</sup> A poly(trityl radical) with this macrocyclic skeletal strategy promises an even higher average  $S$ , exceeding 30.

All super-high-spin polyradicals and polycarbenes exhibit the paramagnetism of large spin, that is,  $S \gg 1/2$ . When the temperature- and field-dependence of mag-

netization are analyzed in terms of the Brillouin function, either precise  $S$  values or average  $S$  values are obtained, depending on whether the sample is pure or a mixture of the components of different  $S$  values. Due to the lack of magnetic anisotropy and intermolecular ferromagnetic interaction, none of them exhibited single-molecule-magnetic behavior or a transition to a 3D magnet at finite temperature.

### Strategies for Stable Polyradicals

The general strategies for stabilizing the open-shell species described in the previous section can be applied to triplet diradicals and carbenes and their higher analogues with higher spin multiplicity. Steric protection and heteroatom substitution have been employed with success for stable perchlorinated triradicals with a quartet ground state.<sup>34</sup> Even triplet diphenylcarbene has been stabilized by polybromination at all the ortho- and para-positions. A tris(diazo) compound of this family gave upon photolysis in MTHF (2-methyltetrahydrofuran), a tricarbene that survived 140 K for 15 min. In solid solutions, this tricarbene has been proven to have an  $S = 3$  ground state.<sup>35</sup>

Radical centers of *m*-quinodimethane and 1,3,5-trimethylenebenzene can be replaced with aminoxyl radicals (**1**) that make triplet diradicals and quartet triradicals. Some of these (summarized in Chart 8) are crystalline solids and can be kept at ambient temperature under air.<sup>36</sup> However, the intermolecular exchange coupling is too small to effect macroscopic ordering of the spins at temperatures above 2 K.

Generation of *p*-doped radical centers in preconstructed oligomers and polymers has been successful. The two most unambiguous examples are a solution-stable trication **33** (Chart 9) that has a quartet ground state<sup>37</sup> by ESR/electron spin transient-nutation spectroscopy and a polymer **34** connecting a 2,5-bis(1,3-butadienyl)thiophene radical cation spin-bearing unit via an *m*-phenylene coupling unit that has an average  $S = 4.5$ .<sup>38</sup>

### Recourse to Metal Complexes with Organic Ligands Carrying Spin Centers for High-Dimensional Extended Structures

The 1D array of spins within a chain molecule is limited in practice to  $S = 5$  of pentacarbene **24** ( $n = 5$ ). Sano et al.<sup>39</sup> made 1:1 chain complexes **35** and **36** of Mn(hfac)<sub>2</sub> and Cu(hfac)<sub>2</sub>, respectively (where hfac is hexafluoroacetylacetonate), with di-(4-pyridyl)-diazomethane as bridging ligands in crystalline solids that are dilute paramagnets of  $S = 5/2$  and  $1/2$ , respectively. When photolyzed in a

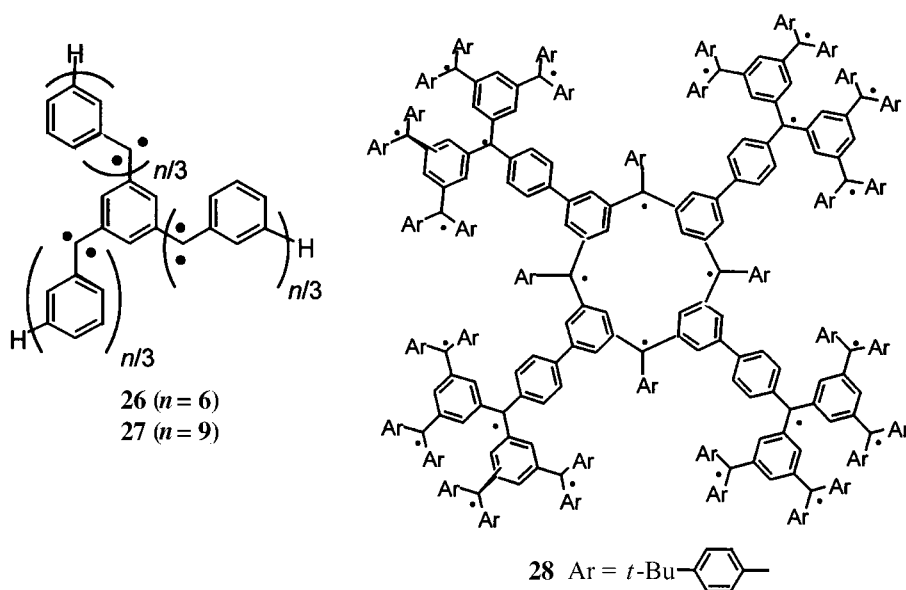
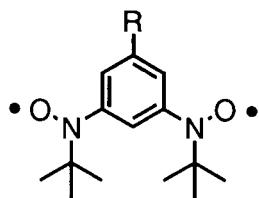
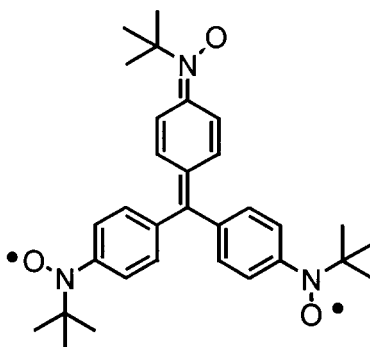


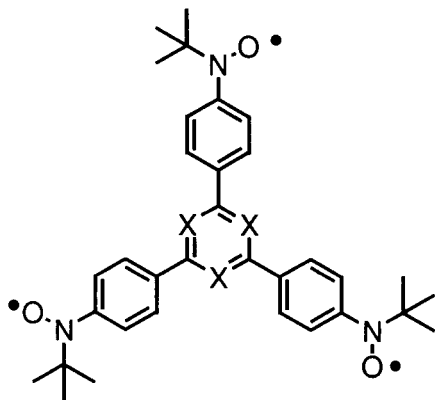
Chart 7.



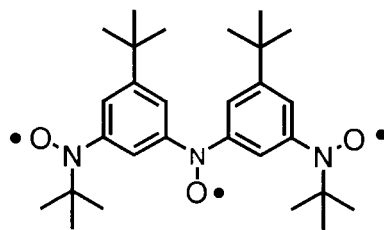
- 29H (R = H)  $J > 300$  K  
 29Cl (R = Cl)  $J > 300$  K  
 29Br (R = Br)  $J > 300$  K



- 30  $J = 205 \pm 5$  K



- 31C (X = CH)  $J = 6.8 \pm 0.1$  K  
 31N (X = N)  $J = 15.3, 11.8$  K



- 32  $J = 480 \pm 40$  K

Chart 8.

sample holder of a semiconducting quantum interference device magnetometer/susceptometer at cryogenic temperature, and the photoproducts studied *in situ*, the formation of ferri- and ferromagnetic chains **35C** and **36C**, having extended correlation lengths (corresponding to  $S = 325$  and  $33.5$  at  $5$  K and  $3$  K, respectively), was confirmed. Furthermore, since the carbene centers were fixed in the crystal lattice of the metal complexes, they were found to be stable up to  $220$  K.

In the case of the polyaminoxyl radicals in Chart 8, the aminoxyl oxygen atoms are sufficiently basic and serve as bridging ligands for magnetic metal ions. Trigonal triradicals **31C** formed with  $\text{Mn}(\text{hfac})_2$  a mixed ligand complex that has an extended honeycomb network structure and an ordering temperature of  $3.4$  K. This structure corresponds in connectivity to **25**. The 3D network complex formed with T-shaped trisaminoxyl radical **32** became a real magnet, with a  $T_c$  as high as  $46$  K.<sup>40</sup> In all of these metal complexes, both the

$3d$  spins of  $\text{Mn}(\text{II})$  and the  $2p$  spins of the organic ligands in ferrimagnetic coupling account for the observed magnetization. Thus, new preparative methods of synthetic or polymer chemistry for extended network structures would allow us to construct high- $T_c$  purely organic magnets. The magnetic metal ions have two functions: construction of extended network structures by coordinative bonds and strong exchange coupling through the bonds. Efforts are in progress to replace magnetic metal ions with nonmagnetic metal ions, and then to replace metal ions with nonmetal atoms, while keeping the network structures always intact.

### Future Possibilities

Future applications of organic magnets are based on a series of attributes described in Table I of the introductory article in this issue. Nevertheless, another important feature must be stressed: the enormous flexibility and power that organic synthesis and supramolecular

chemistry provide. Both characteristics will allow us to design new multiproperty organic materials in which magnetism is combined with another useful physical property such as electric conductivity or optical (e.g., luminescence, nonlinear optics, chirality), mechanical, and chemical activities. Major breakthroughs are likely in the study of this new type of multiproperty molecule-based magnetic materials. The control or tuning of magnetic properties will be made by synergism with other external stimuli such as photons, electrons, protons, temperature, pressure, and so on. Diradicals and dicarbenes will be studied as prototypes of tunable molecular-based magnetic materials. Production of strongly magnetic polycarbenes and their complexes by irradiation of diamagnetic or weakly paramagnetic precursors would serve as prototypes of nanoscale write-only memory.<sup>39</sup>

It is useful to comment here on magnetic bistability. This phenomenon is one of the fundamental underlying concepts for obtaining molecular electronic devices, such as nanoscale switching units, information storage media, and so on. This rare phenomenon is presented by a molecule or a molecular assembly existing under two stable (or metastable) electronic states in a given range of external parameters (temperature, pressure, etc). These states must be associated with a response function (magnetic or optical) that reveals the electronic state of the system. Matsuda and co-workers have been successful in designing diradicals that can cross over from a triplet state to a singlet state by using the intervening photochromic coupling unit (Figure 7).<sup>41</sup>

Recently, Awaga and co-workers reported the first example of a room-temperature molecular magnetic bistability in a thiazyl radical.<sup>42</sup> Thus, 1,3,5-trithia-2,4,6-triazapentalenyl **37** is an  $S = 1/2$  radical that exists in two crystalline phases that differ in their magnetic properties and may coexist at room temperature. Magnetic measurements and x-ray crystal-structure determinations indicate a first-order phase transition with a surprisingly wide hysteresis loop between the paramagnetic high-temperature phase and the diamagnetic low-temperature phase, with transition temperatures of  $T_{c\downarrow} = 230$  K and  $T_{c\uparrow} = 305$  K. Consequently, crystals of this organic radical exhibit room-temperature bistability in the magnetic properties, which confers a memory effect to the system that depends only on its thermal history. Discovery of new examples of room-temperature molecular magnetic bistable systems in which magnetic ordering occurs, instead of a diamagnetic-

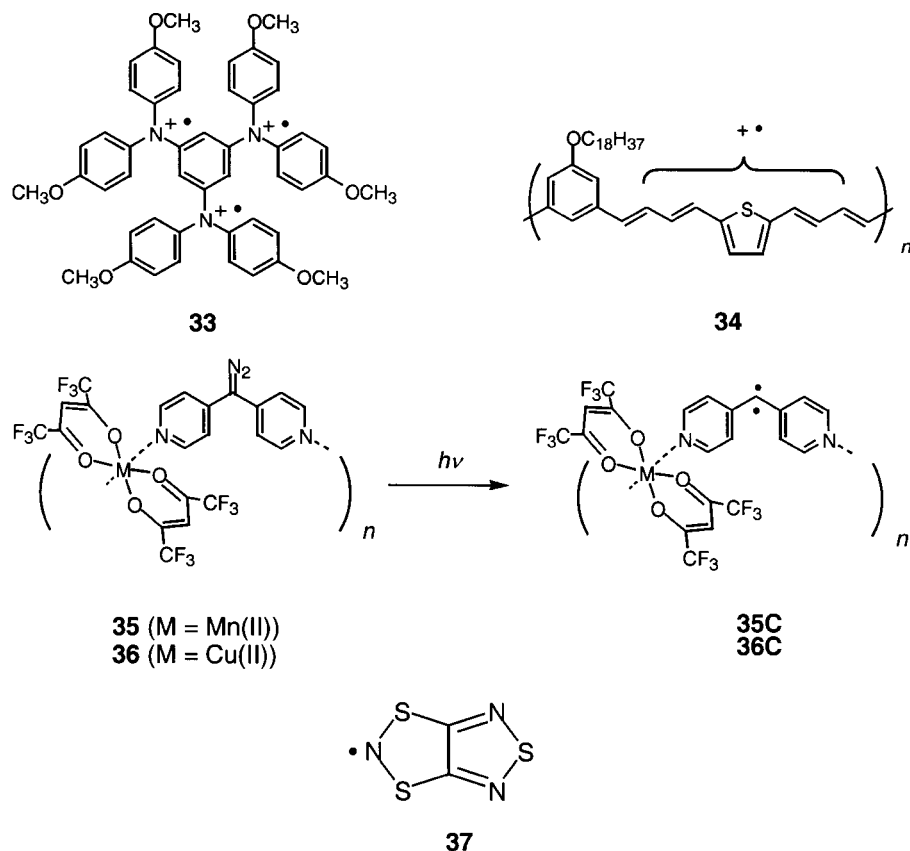


Chart 9.

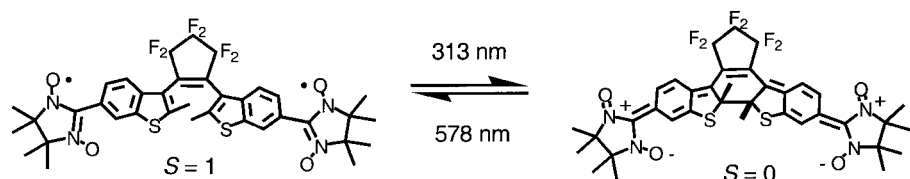


Figure 7. An example of the organic photochromic spin crossover system tunable by UV-visible light.

paramagnetic change, would be a challenge in this field, for which practical applications could be realized.

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**NEW!**

**MRS** Materials Research Society

**research tools seminars**

As a complement to the 2000 MRS Fall Meeting, the Materials Research Society (MRS) is pleased to introduce a NEW educational program called Research Tools Seminars.

To further integrate the MRS Exhibit with the technical meeting and provide you with an educational service, MRS has established an educational seminar series that focuses on the scientific basis and practical application of commercially available, state-of-the-art tools for materials research.

Held in the Exhibit Hall, Hynes Convention Center, each of the following seminars will describe a technical approach to meet a particular challenge, as embodied in commercially-available products or tools.

**TUESDAY, NOVEMBER 28**

2:30 pm-3:30 pm **When is a Microscope More Than a Microscope?**

THERMOMICROSCOPES • SUNNYVALE, CA

How scanning probes are used not only for topography imaging, but also to measure and quantify many specific materials properties at the nanoscale. Applications include polymers, semiconductors and biomaterials.

4:00 pm-5:00 pm **New Developments in Low Temperature Materials Characterization**

ADVANCED RESEARCH SYSTEMS, INC. • ALLENTOWN, PA

New cryostat designs and selection criteria for specific characterization techniques. Temperature range, control and stability issues are covered plus vibration reduction especially for scanning probe microscopy.

**WEDNESDAY, NOVEMBER 29**

10:30 am-11:30 am **Advanced Tools for Nanoscale Measurement of Electrical Properties of Materials**

DIGITAL INSTRUMENTS, VEECO METROLOGY GROUP • SANTA BARBARA, CA

2-dimensional, nanoscale mapping of tunnel and leakage currents, capacitance and spreading resistance on semiconductor materials and devices. Probe techniques plus sensitivity, signal-to-noise and data acquisition rate are covered.

2:30 pm-3:30 pm **Selecting the Right DC Sensitive Measurement Instrument for Your Material**

KEITHLEY INSTRUMENTS, INC. • SOLON, OH

Measurement techniques matter! Sources of noise and error for different resistivity materials are covered and optimum instrument designs are discussed.

4:00 pm-5:00 pm **Accurate Characterization of SiGe Hetero-junction Bipolar Transistors**

EVANS ANALYTICAL GROUP • EAST WINDSOR, NJ

Accurate near-surface chemical analysis and depth resolution using Dynamic Secondary Ion Mass Spectrometry. Illustrated on a high performance transistor for process development and troubleshooting.