Studies of Organic Di-, Oligo-, and Polyradicals by Means of Their Bulk Magnetic Properties

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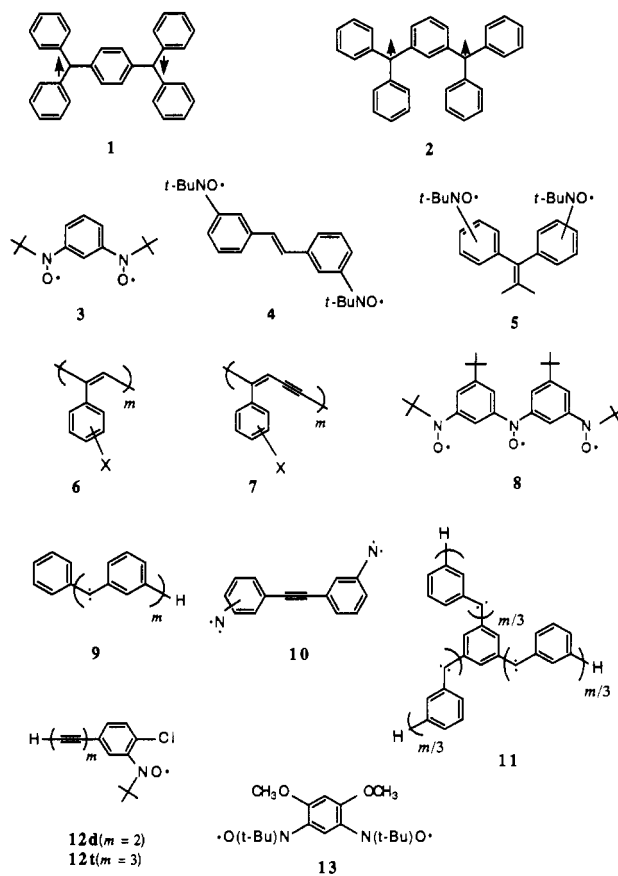
Electronic Structure of Organic Di-, Oligo-, and Polyradicals

In stark contrast to typical organic molecules having closed-shell electronic structures, free radicals have one or more unpaired electrons. The alignment of electron spins becomes the point at issue when there is an interaction between two unpaired electrons as in diradicals[1] and radical pairs.[2] The Coulombic repulsion between electrons lifts the zeroth-order degeneracy and gives rise to singlet and triplet states of different total energy for these chemical entities. It is the singlet state that is usually more stable, as described by the Heitler-London spin exchange between spins of opposite sign in chemical bonds. Chichibabin's hydrocarbon 1 with a singlet ground state is a classical example of such diradicals.[3] When the interacting spins are in orthogonal orbitals, however, the triplet states may be favored. The presence of the half-filled orthogonal orbitals is dictated by symmetry and can be achieved for organic molecular systems in two ways: by geometrical and topological symmetry.[4] One-centered diradicals, such as carbenes and nitrenes, are examples of the former. In π-conjugated diradicals, the intervening π-electrons are polarized, and therefore, if the periodicity of the spin polarization is in phase, the parallel alignment of the two spins can become favored. Schlenk's hydrocarbon 2 has a triplet ground state and is the first representative of such non-Kekulé hydrocarbons.[3,5] On the basis of these considerations, a number of di-, tri-, tetra-, and polyradicals with high-spin ground states have been designed, prepared, and characterized. These molecules are of importance in widening our understanding of covalent bonds and chemical reactions and for designing organic molecular magnetic materials.[4]

Since an assembly of these free radicals is paramagnetic, we have carried out a series of magnetization/magnetic susceptibility measurements on them and have found that these classical techniques afford a number of important results that are difficult to obtain otherwise or are complementary to EPR data. This

Account presents the highlights of the findings from our laboratories.

Molecular Paramagnetism and Instrumentation

Let us consider a paramagnetic substance that contains, in a unit volume, weight, or mole, N magnetic atoms, ions, or molecules, each of which has a magnetic moment M.[6] Since paramagnetism is a bulk property of unordered spins, they do not show any spontaneous

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(1) Borden, W. T., Ed. *Diradicals*; Wiley: New York, 1982; Chapter 1.

(2) Lepley, A. R., Closs, G. L., Eds. *Chemically Induced Magnetic Polarization*; Wiley: New York, 1973.

(3) Platz, M. S. In *Diradicals*; Borden, W. T., Ed.; Wiley: New York, 1982; Chapter 8.

(4) (a) Itoh, K. *Chem. Phys. Lett.* 1967, *1*, 235. (b) Mataga, N. *Theor. Chim. Acta* 1968, *10*, 372. (c) Iwamura, H. *Pure Appl. Chem.* 1986, *58*, 187. (d) Iwamura, H. *Pure Appl. Chem.* 1987, *59*, 1595. (e) Iwamura, H. *Adv. Phys. Org. Chem.* 1990, *26*, 179. (f) Dougherty, D. A. *Acc. Chem. Res.* 1991, *24*, 88.

(5) (a) Schlenk, W.; Brauns, M. *Ber. Dtsch. Chem. Ges.* 1915, *48*, 661. (b) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Engl.* 1970, *9*, 906.

(6) Weiss, A.; Witte, H. *Magnetochemie*; Verlag Chemie: Weinheim, 1973. Carlin, R. L. *Magnetochemistry*; Springer: New York, 1986.
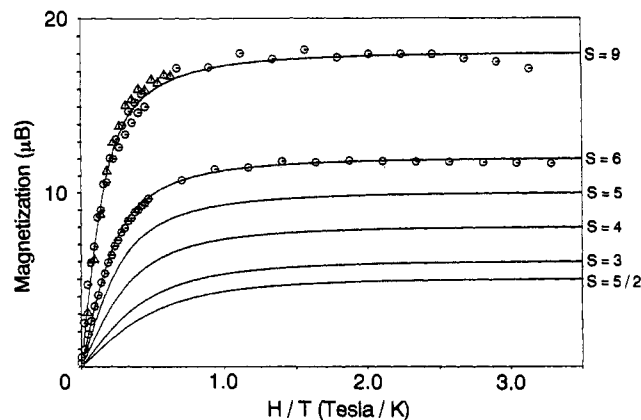
Figure 1. Plots of M/μ_B vs H/T for typical paramagnetic species. Curves are the Brillouin functions for various S values. The magnetizations at 2.1 K for $11(n=6)$ ($S = 6$) and those at 2.1 (O) and 10.0 ($\triangle$) K for $11(n=9)$ ($S = 9$) are also included (ref 8c).

Figure 2. A schematic drawing of a Faraday magnetic balance installed with a quartz light guide.

magnetization ($I = 0$) in the absence of an external magnetic field. At a sufficiently low temperature in a strong external magnetic field, the spins may order, and therefore, the magnetization I_S is given by eq 1:

$$I_S = NM = NgS\mu_B \qquad (1)$$

where S is the quantum number of total angular momentum in general but in particular is that of spin angular momentum for typical organic compounds that have negligible spin orbit coupling. μ_B is the Bohr magneton. Since the electron spins undergo thermal vibration at a finite temperature, their direction also fluctuates. The energy of this vibration at T K is on the order of kT, which is about 9.8×10^{-22} cal at room temperature. The potential energy of the magnetic moment, $M = 1\mu_B$, in the external magnetic field H of 1 M A m^{-1} (=1.26 T) amounts to 2.9×10^{-24} cal. This value is 2 orders of magnitude smaller than kT at room temperature. Therefore, the alignment of an assembly of electron spins with respect to the direction of H is dictated by the Boltzmann distribution of them among the spin sublevels $S_Z = -S, -(S - 1), ..., (S - 1), S$. As H is increased and T is lowered, the spins start to align in the direction parallel to H and the average magnetization I gradually increases from 0 eventually to I_S. Typical plots of I or M vs H/T shown in Figure 1 are dependent only on gS and are described analytically by the Brillouin function.

Note that I is linearly proportional to H/T when the latter is small. The paramagnetic susceptibility χ per cubic centimeter, gram, or mole defined by eq 2 is inversely proportional to T.

$$\chi = I/H = C/T = Ng^2S(S + 1)\mu_B^2/3kT \qquad (2)$$

This relation is called Curie's law, and the proportionality constant C is a Curie constant that should be 0.37 and 1.0 K emu/mol for $S = {}^1/_2$ and 1, respectively. For a species in degenerate singlet and triplet states, C should be 0.75 K emu/mol.

In reference to a classical-mechanical expression for the magnetic moment, the measured χ data are often expressed in terms of the effective magnetic moment μ_{eff} defined by eq 3:

$$\mu_{eff} = (3\chi kT/N)^{1/2} = g\mu_B[S(S + 1)]^{1/2} \qquad (3)$$
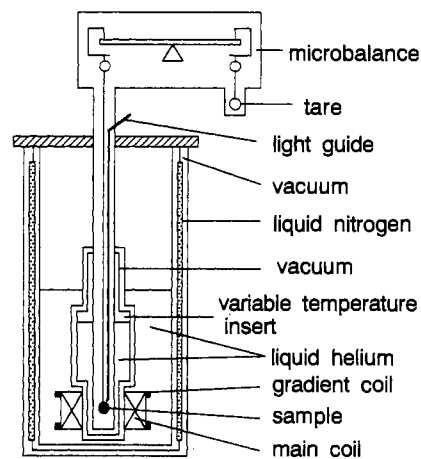
A diradical with a degenerate singlet/triplet state has

a μ_{eff} value of 2.45 μ_B and should clearly be distinguished from 2.83 μ_B for a ground triplet species.

The above relations apply to an assembly of independent spins. Any deviation from eqs 2 and 3 suggests the occurrence of cooperative magnetic phenomena, i.e., ferro-, antiferro-, ferri-, meta-, mictomagnetism, etc. Negative and positive intercepts of the inverse χ vs temperature plots extrapolated to 0 K are indicative of the ferro- and antiferromagnetic interactions, respectively. As the temperature is lowered, the μ_{eff} will start to deviate from the horizontal line upward for the ferro- and downward for the antiferromagnetic interaction (see Figures 3, 5, and 6). A molecular field treatment of the magnetic susceptibility of such systems above the spin-ordering temperature (T_C) leads to a Curie–Weiss expression for which T is replaced with $(T - \theta)$ in eq 2. Here a sample with dominant ferro- or antiferromagnetic interaction has the Weiss temperature $\theta > 0$ or $\theta < 0$, respectively. More rigorous treatment of the long-range order can be obtained by one-, two-, or three-dimensional Heisenberg models.[7]

A Faraday magnetic balance and a SQUID susceptometer/magnetometer have been used in our laboratories. The former was installed with a quartz light guide through which UV–vis light of selected wavelengths can be introduced from outside onto a sample in a quartz sample basket suspended in the superconducting solenoid (≤ 7 T) (Figure 2).[8] *Reactive intermediates* were thus generated photochemically at cryogenic temperature, e.g., 4.2 K, and subjected to the magnetic measurements *in situ*. Reliable data free from any paramagnetic impurity are obtained by taking the difference before and after the photolysis.

The magnetic force F experienced by a paramagnetic sample in an external magnetic field H and field gradient $\partial H/\partial z$ is detected with an electronic balance as an increase in weight (eq 4):

$$F = N\chi H \, \partial H/\partial z \qquad (4)$$

The increase in the weight ($F/980$ g) of a typical organic free radical, e.g., bis(p-methoxyphenyl)nitroxide ($S =$

(7) Palacio, F. In *Magnetic Molecular Materials*; Gatteschi, D., Kahn, O., Miller, J. S., Palacio, F., Eds.; Kluwer Acad. Pub.: Dordrecht, 1991; Chapter 1.
(8) (a) Nakamura, N.; Inoue, K.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 1484. (b) Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.*, in press. (c) Iwamura, H. *Pure Appl. Chem.* **1993**, *65*, 57.

$^1/_2$ and 5 mg), at $\partial H/\partial z = 500$ G/cm and $H = 1.0$ T amounts to 3.92 mg at 10 K.

Magnetic Properties of Organic Di-, Oligo-, and Polyradical Molecules

Diradicals. When topology is appropriate,[4] namely, a second radical center is placed in phase with the spin polarization of the intervening π-electrons due to the first radical center, and vice versa, the π-conjugated diradicals may have triplet ground states. A *m*-phenylene unit is such an example in that the doublet and triplet spins as well as polarons attached to its two ends have a strong tendency to align in parallel. Dinitroxide 3,[9] a diverdazyl,[10] a bis(1-oxido-3-oxy-2-imidazoline),[11] and chloro- and hydrocarbons[12,13] analogous to 2 have been demonstrated to have triplet ground states by their Curie constants of 1.0 K emu/mol and μ_{eff} of 2.83 μ_B. When the topology is inappropriate for aligning the spins in parallel, a singlet state may become the ground state. Since the first excited triplet state is often thermally accessible, the energy gap ($2J$) between the two states can be determined as in bis(galvinoxyl) ($2J = -970$ cal/mol)[14] and dinitroxide 4 (-38 cal/mol).[9c]

Determination of the Energy Gap between the Ground and Excited States of Diradicals.[15] Delineation of the intramolecular magnetic coupling between the radical centers in persistent dinitroxides 5 is a subject of considerable interest, since structures 5 constitute lower vinylogs of the dimer units of potentially very high-spin poly(phenylacetylene)s 6[16] and poly(phenyldiacetylene)s 7.[17] The knowledge of the sign and magnitude of the coupling in the dimer units is instrumental for designing the site of the radical centers X to be introduced on the phenyl rings of the polymers. The p,p', m,p', and m,m' isomers of 5 might also be considered to be related in connectivity to trimethylenemethane (TMM), tetramethyleneethane (TME), and pentamethylenepropane (PMP), respectively. The ground spin states of the latter two are still subjects of some controversy in theoretical and physical organic chemistry.[1,18]

Polycrystalline samples of isomeric 5 were studied on a SQUID susceptometer in the temperature range 5–300 K. The results are expressed in terms of μ_{eff} vs temperature plots in Figure 3. The μ_{eff} values approaching 2.45 μ_B at room temperature are strongly
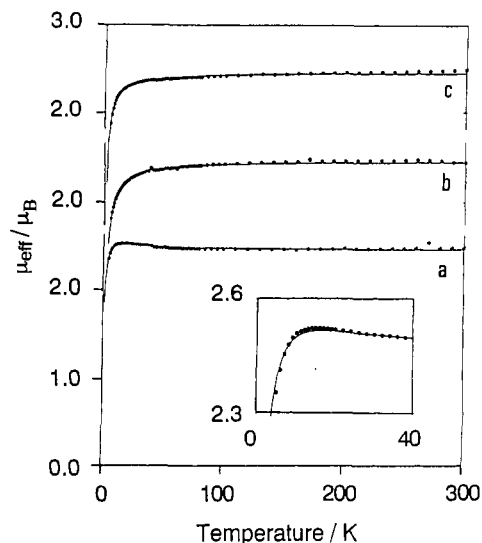
(9) (a) Mukai, K.; Nagai, H.; Ishizu, K. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 2381. (b) Ishida, K.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238. (c) Watanabe, T.; Iwamura, H. *Abstracts of Papers*, 21st Symp. Structural Org. Chem., Tsukuba, October 1989.
(10) Azuma, N.; Ishizu, K.; Mukai, K. *J. Chem. Phys.* **1974**, *61*, 2294.
(11) Ullman, E. F.; Osiecki, J. H.; Boocock, D. G. B.; Darcy, R. *J. J. Am. Chem. Soc.* **1972**, *94*, 7049.
(12) (a) Veciana, J.; Rovira, C.; Armet, O.; Domingo, V. H.; Crespo, M. I.; Palacio, F. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 77. (b) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552. (c) Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57.
(13) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1992**, *114*, 1884.
(14) Mukai, K.; Sakamoto, J. *Chem. Phys.* **1978**, *68*, 1432.
(15) (a) Matsumoto, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 5448. (b) Matsumoto, T.; Ishida, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952.
(16) Fujii, A.; Ishida, T.; Koga, N.; Iwamura, H. *Macromolecules* **1991**, *24*, 1077. Koga, N.; Inoue, K.; Sasagawa, N.; Iwamura, H. *Mater. Res. Soc. Symp. Proc.* **1990**, *173*, 3949.
(17) Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 9803.
(18) Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416.

Figure 3. Plots of μ_{eff}/μ_B vs temperature for (a) p,p'-, (b) m,p'-, and (c) m,m'-dinitroxides 5 (ref 15). Reprinted with permission from ref 15a. Copyright 1992 American Chemical Society.
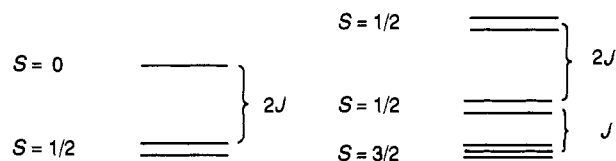

Figure 4. The energy diagram for ferromagnetically interacting two and linear three spins (S_A/S_B and $S_A/S_B/S_C$, respectively).

indicative of near degeneracy of singlet and triplet states in all three isomers at ambient temperature. Sharp decreases in the μ_{eff} values at the lowest temperature represent the antiferromagnetic coupling between the diradical molecules and were taken into account by a Weiss field approximation. The presence of a maximum at 16 K in the plot for the p,p'-5 (Figure 3a) corresponds to an increased population of a triplet relative to a singlet at these temperatures, showing that a triplet should be the ground state of the p,p' isomer of 5. Gradual decreases of the μ_{eff} values in the intermediate temperature range in m,p'- and m,m'-5 (Figures 3b and 3c, respectively) are suggested to be due to weak intraradical antiferromagnetic interaction.

For a system consisting of a pair of singlet and triplet states in equilibrium separated by an energy gap of $2J$ as shown in Figure 4, the behavior of χ with respect to T can be described by a modified Bleaney–Bowers equation (eq 5):[19]

$$\chi = P\frac{2Ng^2\mu_B^2}{k(T-\theta)[3 + \exp(-2J/kT)]} \tag{5}$$

where N is the number of spins per unit weight, g is the isotropic Landé factor, θ is the Weiss temperature, and P is a purity factor of the diradical. Equation 5 was fitted to the experimental μ_{eff} vs temperature data in Figure 3, and the parameters obtained were refined by a least-squares method to give the results summarized in Table I. Thus, the radical centers on the phenyl rings in 1,1-diphenylethylenes 5 were found to couple ferromagnetically in the p,p' isomer and antiferromagnetically in the m,p' and m,m' isomers. Parallel results were obtained from an EPR study of the corresponding

(19) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London* **1952**, *A214*, 451.

Table I. Energy Gaps between the Singlet and High-Spin States in Isomeric Dinitroxides 5 and the Corresponding Dinitrenes

	5		nitrenes
	ΔE_{S-T} (=2J), cal/mol	θ, K	ΔE_{S-Q} (=6J), cal/mol
p,p'	30.3	-2.0	$\gg$0
m,p'	-9.7	-2.0	-120
m,m'	-5.1	-2.1	-75

dinitrenes and are also included in Table I. Topology is concluded to play a more important role than the kind of radical center in controlling the high-spin vs low-spin ground states of π-conjugated diradicals.

The coupling in polyradicals 6 and 7 is predicted to be ferromagnetic only when radical centers X, e.g., $N(t$-Bu)O$^{\bullet}$, are all at the para positions. Even in these cases, however, the interaction among the neighboring X's should not be very strong relative to kT at ambient temperature. Antiferromagnetic interaction found in the m,p' and m,m' topology also suggests that the ground states of TME and PMP may be singlet with a singlet–triplet energy gap of small magnitude. Whereas it is dangerous to put too much emphasis on this conclusion based on topological analogy from the enlarged π-systems 5, it is clear that measurements of absolute μ_{eff} values and their variation in a wide temperature range should be a useful method for distinguishing between a triplet ground state and nearly degenerate singlet/triplet state in general and solving the controversy in TME and PMP in particular.

Triradicals. A tris(verdazyl) and tris(1-oxido-3-oxy-2-imidazoline) have been studied, with inconclusive results on the degree of intraradical coupling.[20] When di- and triradicals have triplet and quartet ground states, respectively, it is very often the case that large energy gaps do not allow the population of the lower spin states thermally as in a persistent 1,3,5-benzene-triyltris(arylmethyl radical) in a quartet ground state.[12a,c] When the energy gap of such a molecule is somewhat narrowed and on the order of a few hundred calories/mole, the value can be determined as exemplified below.

Determination of the Energy Gap between the Ground and Excited States in Triradicals.[9b] The temperature dependence of χ and μ_{eff} of trinitroxide 8 in the range 2–300 K is shown in Figure 5. As the temperature was increased, the moment of 8 increased from 1.05 μ_B at 2 K, reached a maximum of 3.53 μ_B at ca. 140 K, and gradually decreased to 3.43 μ_B at 300 K. The latter decrease is due to the thermal population of the spins from a quartet state to excited doublet states. The suppression at lower temperature is due to intermolecular antiferromagnetic coupling.

The magnetic interaction in a linear triradical system such as 8 can be described as consisting of two consecutive interactions of magnitude J between the neighboring spin sites S_A/S_B and S_B/S_C, with intramolecular coupling (J') between the two terminal radicals S_C/S_A negligibly small.[21] The energy levels of such systems are depicted in Figure 4. The temperature dependence of molar susceptibility is given by an equation similar to eq 5 but containing the Boltzmann
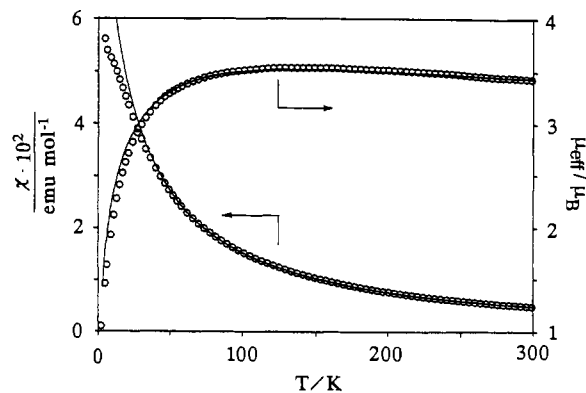
(20) Dulog, L.; Kim, J. S. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 415.
(21) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791. Ivanov, C. I.; Tyutyulkov, N. N.; Karabunarliev, S. *J. Magn. Magn. Mater.* **1990**, *92*, 171.

Figure 5. The temperature dependences of the magnetic susceptibility χ and the effective magnetic moment μ_{eff} of trinitroxide 8 in the range 2–300 K (ref 9b).

distribution among the three states instead of the two. Best fit parameters were $\theta = -19 \pm 2$ K and $J = 480 \pm 35$ cal/mol. The latter value corresponds also to the energy gap between the quartet and the lower doublet state.

The intramolecular magnetic coupling through the m-phenylene unit proved to be strongly ferromagnetic, suggesting that the perturbation due to the introduction of heteroatoms is smaller.[22-24] On the other hand, since the spins of aromatic nitroxides are much more localized and the spin polarization on the phenyl rings is considerably attenuated, the energy gap between the ground quintet and the first excited doublet states was somewhat narrowed. As a result, a measure for the ferromagnetic coupling through the m-phenylene unit could be obtained.

Tetraradicals, Higher Oligoradicals, and Dinitrenes. A perchlorinated persistent tetraradical with a pair of triplets due to the ferro- and antiferromagnetic m-phenylene and m,m'-stilbenediyl couplers has been reported.[25] A series consisting of a hydrocarbon poly-(arylmethyl) tetraradical ($S = 2$), heptaradical ($S = ^7/_2$), and decaradical ($S = 5$) has been reported by Rajca and co-workers.[26] While EPR fine structures are analyzed satisfactorily, the magnetization data from SQUID correspond to S values slightly lower than the theoretical values, suggesting the contribution of antiferromagnetic interaction. Reactive dinitrenes 10 have been generated and studied *in situ* by susceptometry/magnetometry; o,m'- and m,p'-10 proved to be generated with quintet ground states.[27,28] Dougherty and co-workers studied a poly(m-phenyleneoctatet-raene) derivative doped with AsF$_5$ on a SQUID magnetometer to find that the generated polarons couple ferromagnetically to form a segment in which $S > 2$.[29]

(22) Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.
(23) Tukada, H.; Mutai, K.; Iwamura, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1159.
(24) Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251.
(25) Carilla, J.; Julia, L.; Riera, J.; Brillas, E.; Garrido, J. A.; Labarta, A.; Alcala, R. *J. Am. Chem. Soc.* **1991**, *113*, 8281.
(26) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890. Rajca, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **1992**, *114*, 1884.
(27) Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 1266. Iwamura, H.; Murata, S. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 33. Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *114*, 5547.
(28) Sasaki, S.; Iwamura, H. *Chem. Lett.* **1992**, 1759.
(29) Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764.

Tetracarbenes and Higher Analogues. Determination of the Ground-State Spin Multiplicities. Poly(m-phenylenecarbene)s 9 were conceived by combining the two concepts for constructing high-spin organic molecules; triplet one-center diradical units are joined through a topologically robust ferromagnetic m-phenylene coupler. In 1984, we studied for the first time the magnetization of elusive reactive intermediates such as 9(n=4) frozen in crystals and in solid solutions.[30] It was produced by photolysis of the corresponding tetradiazo compound in a Faraday magnetic balance (Figure 2) at cryogenic temperature. By fitting of the Brillouin function to the observed I vs H/T data (Figure 1), the spin quantum number was determined as $S = 4$. The nonet ground state of 9(n=4) thus determined is even greater than those of typical 3d transition metal ions ($S \leq {}^5/_2$) and 4f lanthanides ($S \leq {}^7/_2$).

In order to realize the long-range order at finite temperature, it is desirable to increase the dimension of structure 9. Setting two-dimensional "starburst" or honeycomb-like π-systems as an ultimate goal, we have studied a pseudo-two-dimensional structure 11.[8] The magnetization data obtained for 11(n=6) at 2.1 K and nonacarbene 11(n=9) at 2.1 and 10.0 K are presented together with those of other typical paramagnetic samples in Figure 1. Least-squares analyses gave $S = 6.0$ and $S = 9.0$, respectively, the highest spins ever reported for purely organic molecules.[8] Note that the increase in weight of an 80-μg sample of 11(n=9) on a Faraday magnetic balance with $\partial H/\partial z = 5$ T/m and $H = 1.0$ T was as much as 2.35 mg. There was also a sign of partial blocking of rotation of the magnetic moment in solid solution at 4.2 K.[8c]

Magnetic Properties Pertinent to Crystalline States

Long-Range Spin Order in Crystals of Organic Radicals. The interaction between adjacent free radical molecules becomes more and more antiferromagnetic as the overlap between the singly occupied orbitals (SOMO) increases.[1,2] Diamagnetic dimers are sometimes formed in the extreme. The examples given in Figures 3 and 5 are in line with this general trend. In a few exceptional cases where the interaction of the two SOMOs is effectively orthogonal or positive spin density on one π-conjugated radical molecule faces negative spin density on another, such interradical interaction can become ferromagnetic.[31] These possibilities have been tested by model dimers[32] and by controlling the stacking orientation of diphenylcarbene derivatives in crystals.[33]

The temperature dependences of the observed μ_{eff} values of crystalline diacetylenic nitroxide 12d and triacetylenic nitroxide 12t form a striking contrast in that they show antiferro- and ferromagnetic interac-
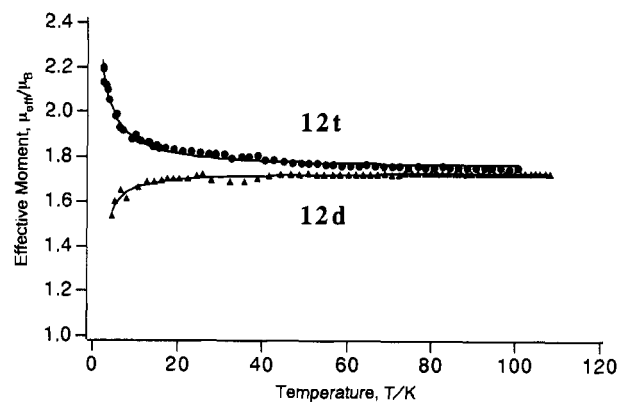

Figure 6. The temperature dependences of the effective magnetic moment μ_{eff} of di- and triacetylenic nitroxides (12d and 12t, respectively) (ref 34).

tions, respectively, at cryogenic temperature (Figure 6).[34] Whereas the data of 12d are interpreted in terms of a dimer model in which J(intradimer) = -2.4 cal/mol and θ(interdimer) = -0.2 K, in good agreement with the X-ray crystal structure, those of 12t are compatible with a one-dimensional Heisenberg model in which $J = +2.9$ cal/mol. It is not yet clear in this example if the ferromagnetic state is realized at lower temperature.[34] The β-phase crystals of a 2-(p-nitrophenyl)-1-oxido-3-oxy-4,4,5,5-tetramethyl-2-imidazoline showed similar magnetic susceptibility/magnetization behaviors and did undergo transition into a ferromagnetic state at 0.6 K.[35]

Magnetic Interaction in a Diradical in Neat Crystals vs in Solid Solution. 2,4-Dimethoxy-m-phenylenebis(N-$tert$-butylnitroxide) (13) gave a limiting μ_{eff} value of 2.45 μ_B at room temperature, in line with a degenerate singlet and triplet state.[36] As the temperature was decreased, the μ_{eff} values for a microcrystalline sample started to decrease appreciably at ca. 50 K and then decreased more sharply. The data were interpreted in terms of a singlet/triplet model (eq 5) in which $2J = -147$ cal/mol; the ground state is decidedly a singlet. Similar plots for a sample diluted in PVC film (2 mol %) remained constant in the range 45–300 K and decreased slightly at the lower temperature to give $2J = -13.9$ cal/mol; the triplet lies slightly above the ground singlet state.

The X-ray crystal structure of 13 revealed that the $tert$-butylnitroxide moieties are considerably out of the m-phenylene plane (by 65.1° and 75.3°) and in syn-conformation. Since there is no interradical distance shorter than 7.04 Å between the neighboring molecules, the formation of a dimer is ruled out. Thus, the strong antiferromagnetic coupling in the crystalline state appears to be intramolecular. Lower π-spin polarization on the m-phenylene ring and a possible antiferromagnetic through-space interaction between the spins rather localized on the nitroxide radicals at a distance of 5.74 Å may be responsible for the nonferromagnetic coupling in 13. In PVC solutions, 13 is presumed to take another

(30) Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H. *J. Am. Chem. Soc.* **1984**, *106*, 6449. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *108*, 368.

(31) (a) McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. (b) Yamaguchi, K.; Toyoda, Y.; Fueno, T. *Chem. Phys. Lett.* **1989**, *159*, 459.

(32) Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1985**, *107*, 1786. Izuoka, A.; Murata, S.; Sugawara, T.; Iwamura, H. *J. Am. Chem. Soc.* **1987**, *109*, 2631.

(33) Sugawara, T.; Murata, S.; Kimura, K.; Iwamura, H.; Sugawara, Y.; Iwasaki, H. *J. Am. Chem. Soc.* **1985**, *107*, 5293. Sugawara, T.; Tukada, H.; Izuoka, A.; Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1986**, *108*, 4272.

(34) Inoue, K.; Iwamura, H. *Adv. Mater.* **1992**, *4*, 801.

(35) Kinohsita, M.; Turek, P.; Tamura, M.; Nozawa, K.; Shiomi, D.; Nakazawa, U.; Ishikawa, M.; Takahashi, M.; Awaga, K.; Inabe, T.; Maruyama, Y. *Chem. Lett.* **1991**, 1225. Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

(36) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 847.

conformation, i.e., a more planar or *anti* form, in which such antiferromagnetic coupling is less effective. In short, the 4,6-dimethoxy-1,3-phenylene unit is not a ferromagnetic coupler; the two nitroxide groups are coupled in an antiferromagnetic fashion strongly in crystals and weakly in solid solutions. Much care should be taken in the proper choice of a combination of spins and ferromagnetic couplers for designing high-spin polymers.

Conclusion

Our understanding of the mode of coupling of unpaired electrons in organic di-, oligo-, and polyradicals and their magnetic properties has been deepened with the aid of magnetization/magnetic susceptibility studies. These methods are also instrumental in finding subtle interradical interactions and characterizing radicals with very large magnetic moments.

EPR spectroscopy is often used for detecting triplet and higher spin species and studying their electronic states. However, there are some limitations in this method. Firstly, since EPR fine structures are averaged out due to exchange narrowing for neat radical samples, high-spin species have to be diluted in solid solutions or in mixed crystals. It is difficult to study interradical interactions and long-range orders of the spins. Sec-

ondly, the principal axis of the zero-field tensor must be oriented with respect to the external magnetic field for analyzing the zfs parameters. Otherwise, complex powder patterns are obtained. A third limitation is the EPR spectral intensity, which is usually determined only in reference to that of a standard sample. Even when a linear intensity vs $1/T$ relation is obtained on the basis of an EPR version of eq 5, it is rather difficult to differentiate between triplet ground states with and without a low-lying excited singlet state.[4e,37]

The magnetization/magnetic susceptibility method is not without drawbacks. Since the magnetic properties of an assembly of molecules as a whole are measured, high homogeneity of the paramagnetic samples to be examined is required. This method can nonetheless provide essential information complementary to the results of EPR spectroscopy, thereby aiding the design, synthesis, and characterization of organic di-, tri-, tetra-, and polyradicals with high-spin ground states.

(37) Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: New York, 1988; Vol. 2, pp 462–469.