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Organic Diradicals and Polyradicals: From Spin Coupling to Magnetism?

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Contents

1. Introduction

Diradicals and polyradicals are molecules that possess two or more weakly interacting "unpaired" electrons, each formally associated with different atomic centers in a molecule. Diradicals are common intermediates of chemical reactions and have received perpetual attention over the years.[1-3] Triradicals, tetraradicals, and higher radicals are relatively rare, and until several years ago, only a few of them were known.[4,5]

Di- and polyradicals are a class of molecules that are especially relevant to a multidisciplinary frontier of science concerned with weak interatomic/intermolecular interactions in large systems. Many interesting phenomena in condensed matter are associated with weak interactions between electrons and/or nuclei leading to a characteristic state (e.g., with a long-range order, frozen disorder, etc.) in macroscopic or mesoscopic ensembles.[6-8] Thus, for an ambient temperature superconductor, magnet, etc., the characteristic energy of the interaction leading to order should be ~1 kcal/mol, that is, $\geq RT$ at ambient temperature. These interactions are quite weak compared to the typical bond dissociation energy of 10^2 kcal/mol.

Andrzej Rajca was born in Walbrzych, Poland, in 1959. He graduated from Politechnika Wroclawska (Poland) in 1981 (M.S.). In 1982, he joined Laren M. Tolbert's group at Kentucky (Ph.D. 1985). Subsequently, he was a Miller Fellow and Lecturer with Andrew Streitwieser at Berkeley (1985–1988). Before he joined the University of Nebraska chemistry faculty in 1992, he was on the faculty at Kansas State University, where he was awarded a Camille and Henry Dreyfus Teacher–Scholar Award.

"The molecular approach" to studying such macroscopic and mesoscopic phenomena consists of the following sequence: (1) a small molecule with simple electronic structure with two weakly interacting entities (e.g., unpaired electrons), (2) a larger molecule with several interacting entities, (3) mesoscopic-size molecule with added complexities, (4) assembly of molecules to supramolecular clusters, monomolecular layers, or bulk solids. Study of organic di- and polyradicals in relation to magnetism is one of many examples of this approach.[9] Other examples are found in model studies for molecular recognition, hydrogen bonding in biological structures, etc.[10] The goals of such an approach, through rational design and synthesis of molecules, molecular ensembles, films, etc., are to prepare materials with superior properties compared to their existing "natural" or "conventional" counterparts and to gain better insight to the most complex systems.

This review is focused on molecules with two or more "unpaired" electrons on carbon and other first row elements; the transition metal organometallics are excluded. The other organic molecules with "unpaired" electrons, which are relevant to interactions between "unpaired" electrons such as carbenes, nitrenes, and certain ions, are briefly mentioned in section 11.

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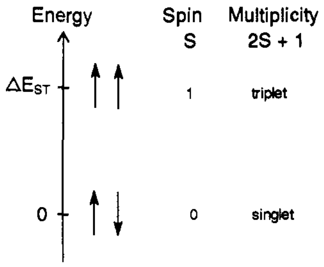
Qualitatively, weakly interacting "unpaired" electrons suggest presence of near-degenerate low-lying electronic states of different spin for di- and polyradicals. Determining the spin of the ground and low-lying excited states, as well as the energy gaps between the low-lying states, is the primary goal of the experimental measurements. The energy gaps and spin can be interpreted in terms of spin coupling between the "unpaired" electrons. Application of "the molecular approach" should lead to insight about spin coupling in meso- and macroscopic size structures.

Because many interesting phenomena in magnetism rely on the competition between the interaction involving a large number of magnetic moments (typically, associated with spins of "unpaired" electrons) and thermal motion, di- and polyradicals with spin couplings, which are comparable or larger than kT in the accessible temperature range, are particularly relevant. Furthermore, the special role of ferromagnetic spin coupling in bonding and magnetism implies importance of di- and polyradicals with high-spin ground states.

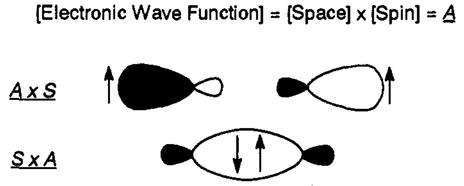
2. Spin Coupling and Chemical Bond

For a pair of electrons, their total spin (S) can be either $S = 1$ ("parallel spins") or $S = 0$ ("antiparallel spins"); in terms of spin multiplicity, $2S + 1$, these spin values correspond to triplet and singlet, respectively. In regard to the lowest energy state, the reference can be made to either ferromagnetic ($S = 1$) or antiferromagnetic ($S = 0$) spin coupling. The energy difference between the singlet and triplet states (ΔE_{ST}) measures the strength of the spin coupling. (Spin–orbit coupling effects are neglected.) Thus, a chemical bond may be viewed as an extreme case of antiferromagnetic coupling, and ΔE_{ST} can be a measure of the bond strength.[11] It is challenging to achieve and understand a strong ferromagnetic coupling, which is antithesis to bonding.



The case of antiferromagnetic coupling

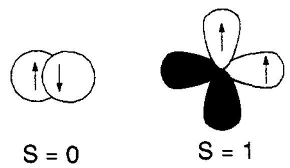
The origin for preponderance of antiferromagnetic coupling (chemical bonding) is well established.[12] Because electrons are indistinguishable particles with spin, $S = {}^1/_2$, the electronic wave function must be antisymmetric (A), that is, interchanging coordinates of any pair of electrons should not change the probability for finding an electron, but does change the sign of the wave function. Typically, it is a good approximation to write electronic wave function as product of the two parts, *space* and *spin*, each part either symmetric (S) or antisymmetric (A). The antisymmetric product, *space* × *spin*, may be either $A \times S$ or $S \times A$. For two electrons and two nuclei, i.e., a chemical bond, these two products correspond to triplet ("parallel" spin, $S = 1$) and singlet ("antiparallel" spin, $S = 0$) functions; for $S = 0$, the symmetry of the spatial part leads to large probability for finding an electron between the nuclei. This symmetric spatial part of the wave function can be approximately illustrated by a Hartree–Fock σ-bonding orbital in H_2. The spatial part of the $S = 1$ wave function possesses a node between the nuclei, similarly to the σ-antibonding orbital in H_2.



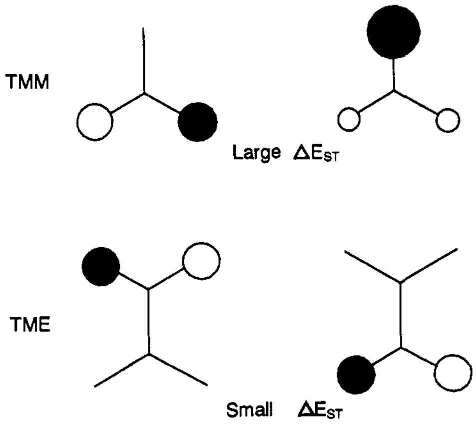
Therefore, the spin preference, $S = 0$ vs $S = 1$, is associated with the distribution of electrons with respect to nuclei; thus, electrostatics, not the magnetic interactions between the magnetic moments of electrons, determines the spin of the lowest energy state (ground state).[13] For H_2, the ground state is singlet ($S = 0$) at all internuclear separations; this is not only the result of the above simplistic analysis of symmetry of the exact two-electron wave function but also the result of rigorous mathematical proof for kinetic/electrostatic energy Hamiltonian for H_2 as well.[14]

Singlet ground states are found in an overwhelming majority of nonmetallic molecules; however, for systems with more than two electrons, $S = 1$ ground states are possible in rare cases. Examples are C (atomic carbon), O_2, CH_2 (carbene), etc.[2,15]

The preference for $S = 0$ vs $S = 1$ ground state can be illustrated by applying the above symmetry arguments to a simple two-orbital two-electron model. When no restrictions are placed upon the orbitals, they overlap in phase; the spatial part of the two-orbital wave function is symmetric and the $S = 0$ ground state results, i.e., hydrogen atoms forming a chemical bond in H_2 (two 1s orbitals). When the orbitals are restricted to being orthogonal, they will overlap out-of-phase; the spatial part of the two-orbital wave function will possess a node and the $S = 1$ ground state will be obtained, i.e., in C (two 2p orbitals).



Triplet ground state for C, which possesses half-occupied degenerate atomic orbitals, is a manifestation of Hund's rule.[16] The extension of the rule to molecules with half-occupied degenerate molecular orbitals (MO) appears straightforward because MO's can be made orthogonal.[17] Examples of such an extension is found in those diradicals, where a pair of half-occupied near-degenerate (or degenerate) nonbonding MO's (NBMO's) must have their lobes coincide significantly (non-disjoint MO's). In fact, very strong ferromagnetic coupling may be obtained in such diradicals, with ΔE_{ST} on the order of 10 kcal/mol. The complication is that, for some diradicals, the half-occupied NBMO's can be selected in such a way that their lobes coincide to very small extent (disjoint MO's). In those cases, the exchange integral is small and, consequently, the spin coupling is small (the $S = 0$ and $S = 1$ are near degenerate).[18] The examples are provided by two π-conjugated diradicals, trimethylenemethane (TMM) and tetramethylenethane (TME).



When the interaction between the pair of selected MO's is small because of their disjoint nature or difference in energy (e.g., TME), interaction between other MO's, including unoccupied ones, should be taken into account; that is, electron correlation (e.g., with respect to restricted Hartree–Fock MO's) may become important. Then, predictions of the ground state, $S = 1$ vs $S = 0$, are problematic; the problem is further discussed in section 5.

Finally, it can be shown that symmetry properties of the wave function allow one to write a spin-coupling Hamiltonian for spins $\mathbf{S}_1$ and $\mathbf{S}_2$ as

$$H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2 \qquad (2.1)$$

The negative sign and factor of 2 are one of the traditional choices,[19] e.g., $J > 0$, $S_1 = S_2 = {}^1/_2$, corresponds to the $S = 1$ ground state which is separated by an energy gap of $2J$ from the $S = 0$ excited state ($\Delta E_{ST} = 2J$). Equation 2.1 is frequently referred to as Heisenberg (or Heisenberg–Dirac) Hamiltonian. Its derivation is straightforward for $S_1 = S_2 = {}^1/_2$ and orthogonal orbitals.[20]

3. Spin Coupling and Organic Magnetism

Most recent research on organic di- and polyradicals is also tailored toward discovery of novel magnetic materials and understanding important aspects of magnetism. While comprehensive discussion of magnetism is beyond the scope of this article, selected issues relevant to organic radicals are mentioned.

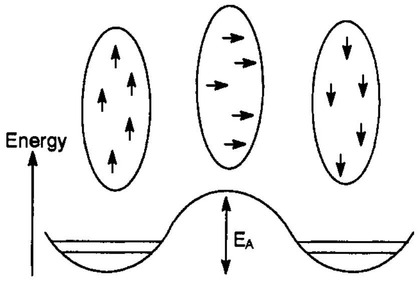
Many interesting magnetic phenomena involve spin coupling of a macroscopic number of electron spins (and other interactions), in competition with thermal excitations. An example is ferromagnetically ordered material below Curie temperature, T_C, which possess many important features, including ferromagnetic spin coupling (e.g., pairwise "parallel spins") and spontaneous magnetization (e.g., net number of "parallel spins"). Consideration of thermal energy versus pairwise spin coupling with spin-coupling constant "J" (for example, eq 2.1) gives an order of magnitude estimate for T_C; that is, $kT_C \approx J$.[21] However, the sufficient strength of ferromagnetic spin coupling is merely one of the prerequisites for ferromagnetism. Consideration of spin ensembles with predominantly ferromagnetic coupling but with either maximum or zero spontaneous magnetizations indicates that ferromagnetism at $T > 0$ is not possible for a one-dimensional (1D) chain of spins.[22] In two- and three-dimensional (2D and 3D) spin ensembles ferromagnetism is possible; however, in 2D, this prediction is highly model dependent and T_C's tend to be lower.[23]

Intramolecular ferromagnetic spin coupling is exceptionally large (compared to transition metal dimers) for some organic diradicals. If such large ferromagnetic couplings can be maintained in polyradicals with 2D or, most likely, 3D-extended structures, then bulk organic magnets with high T_C (ambient temperature) are achievable. Examples of suitable structures are highly cross-linked polymers; in 1968, Mataga proposed some relevant 2D structures.[24] A combination of high T_C and very low density of unpaired electrons would be unusual; dilute alloy ferromagnets, e.g., 0.1% Fe in Pd, has rather low T_C.[25]

Another option is to use mono-, di-, and polyradicals as components of molecular or macromolecular solids. Unfortunately, the intermolecular ferromagnetic spin couplings discovered to date are rather weak, with some exceptions.[26,27] The first organic ferromagnet, which is based upon neutral organic monoradicals, possesses very low T_C (0.60 K).[28-30]

Interesting magnetic phenomena in systems which contain a mesoscopic number of spins (e.g., nanometer-size magnetic particles) are of both fundamental and technological interest.[31] Recent examples are theoretical prediction and experimental confirmation for quantum mechanical tunneling of magnetization through magnetic anisotropy barrier on a mesoscopic scale.[32]

Mesoscopic organic polyradicals are promising targets because their size can be rigorously controlled by organic synthesis. Furthermore, their anisotropy barriers can be more easily evaluated because of the negligible spin–orbit coupling effects for nonlinear three-coordinate carbon-based radicals.[33] Consideration of classical magnetic dipole–dipole interaction gives the shape anisotropy barrier (E_A) as follows:



When attempting to invert magnetization in nanometer-size elongated-shape "ferromagnetic" particles, the intermediate configuration has a relatively high proportion of the unfavorable side-by-side vs a low proportion of the favorable head-to-tail dipole orientations. Besides the more elongated shape, other factors should increase E_A:[34]

$$E_A \propto (\text{number of unpaired electrons})(\text{unpaired electron density})^2 \qquad (3.1)$$

Application of organic polyradicals to interesting problems in magnetism of solids poses an obvious synthetic challenge, especially when the 2D and 3D structures are needed in some cases. Most importantly, strong ferromagnetic spin coupling found in diradicals must be maintained in their higher homologues.

4. Measurement of Electron Spin Coupling: What Is the Ground State and by How Much?

As discussed in section 2, spin coupling in a diradical may be described by Heisenberg Hamiltonian, $H = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$ (eq 2.1), where "J" is spin-coupling constant. The ground-state total spin (S) is $S = 1$ for $J > 0$ (ferromagnetic coupling) and $S = 0$ for $J < 0$ (antiferromagnetic coupling); the energy difference between the two states is $\Delta E_{\mathrm{ST}} = 2J$. Extension of this approach to spin coupling in polyradical is straightforward by summing over all important pairwise interactions, $H = -2\sum J_{ij}S_iS_j$ within Heisenberg or other Hamiltonian.[35]

The measurement of J falls into three categories: $|J| \ll kT$, $|J| \approx kT$, and $|J| \gg kT$. The most important method of measurement of J relies on detecting the relative thermally induced populations of the states of different spin; when $J \approx kT$, the changes in populations between different spin states will be the most pronounced and, therefore, the J will be determined with the greatest accuracy.

The temperature range of most spectroscopic and magnetic measurements is limited by, on the one side, difficulty in attaining temperatures in the neighborhood of absolute zero and, on the other side, instability of polyradicals. Typically, temperatures between 2 and 300 K are readily accessible; in terms of energy per mole, $0.004 < RT < 0.600$ kcal/mol.

A. Bulk Magnetization and Susceptibility

Bulk magnetization (M), which is an average (thermal) magnetic moment of the sample, can be determined using nonspectroscopic methods.[36] Most recently, magnetometers based upon SQUIDs (superconducting quantum interference device) have gained popularity because of their sensitivity.[37] M is typically measured as a function of temperature (T) and applied static magnetic field (H); static magnetic susceptibility χ is calculated as $\chi = M/H$.

When the measurement is carried out in an oscillating H, dynamic (differential) χ is measured directly as $\chi = \mathrm{d}M/\mathrm{d}H$, which is a complex, frequency-dependent quantity; for frequency that is low compared to the relaxation times, the differential χ is real and identical to the static χ. For anisotropic substances both static and dynamic χ are tensors.[36]

In the following text, it is assumed that both M and χ refer to the paramagnetic component; e.g., the measured M or χ have other components negligible or substracted.[38]

a. Intramolecular Interactions, $|J| \gg kT$ or $|J| \ll kT$

For di- and polyradicals with either very strong or very weak spin coupling, $|J| \gg kT$ or $|J| \ll kT$, population of the ground state is independent of temperature. Spin values are determined by perturbing population of the m_s sublevels in the ground state with either magnetic field (H) or temperature. For polyradicals with "n" unpaired electrons, the following total values of spin for the ground state are obtained: (a) strong antiferromagnetic coupling, $-J \gg kT$, $S = 0$ (n = even) and $S = 1/2$ (n = odd), (b) strong ferromagnetic coupling, $J \gg kT$, $S = n/2$, (c) very weak coupling either ferro- or antiferromagnetic, $|J| \ll kT$, $S = 1/2$.

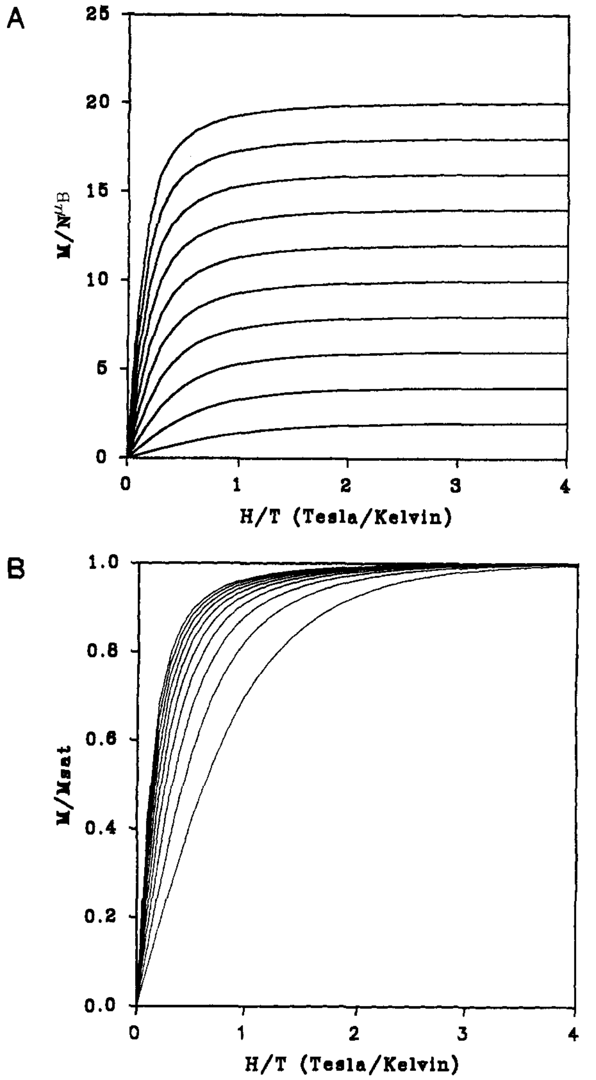


Figure 1. (A) Magnetization in Bohr magnetons (μ_{B}) per polyradical vs H/T; solid curves correspond to S = 1–10 and (B) Brillouin functions, $M/M_{\mathrm{sat}} = B_S(x)$, plotted vs H/T for S = 1–10.

Spin values are best determined by measuring M as a function of H at very low temperatures; thus, the population of the m_s sublevels is affected by H. In other words, the degree of spin allignment induced by H as opposed to the thermal disorder is examined. Qualitatively, the higher the spin of the polyradical, the greater is degree of alignment at a given H and T. Quantitatively, the M vs H/T is given by[36]

$$M = Ng\mu_{\mathrm{B}}SB_S(x) \tag{4.1}$$

where $B_S(x)$ is the Brillouin function for spin S (Figure 1), $B_S(x) = [(2S + 1)/2S]\coth(S + 1/2)x - (1/2S)\coth(x/2)$, and $x = g\mu_{\mathrm{B}}H/kT$.

For larger values of x, i.e., H/T, the Brillouin function, $B_S(x) \approx 1$; this corresponds to the alignment of all spins with the field, that is, "all" molecules are in the lowest energy m_s sublevel. The magnetization attains its maximum value (saturation), which is $M_{\mathrm{sat}} = Ng\mu_{\mathrm{B}}S$. Given the experimental M vs H/T data, which show substantial saturation, M_{sat} and S can be obtained by a numerical two-parameter fit to eq 4.1, even if the amount of polyradical is unknown. Alternatively, if the amount of the polyradical is known, S may be obtained by a one-parameter fit to eq 4.1 or, less accurately, calculated from M_{sat}. The data is usually shown as magnetization, M vs H/T, or "normalized" magnetization (equivalent to Brillouin function), M/M_{sat} vs H/T (Figure 1B). The reliability of the value of S depends on number of the fitting parameters, their interdependence, and the H/T range; the type of the Brillouin plot used to display the results as in Figure 1 (A vs B) is irrelevant.

$B_S(x)$ for large values of S show very similar curvature. Only approximate values of large S may be obtained by the above procedures, if the amount of polyradical is unknown. In the more favorable case, where the amount of radical is known, all experimental errors in measurement of M_{sat} have to be less than $(1/2S)100\%$ to obtain the spin, $S \pm {}^1/_2$, e.g., for $S = 10$ - less than 5%. Finally, in the limit of infinite S, Brillouin function (eq 4.1) becomes Langevin function.[39]

Polyradicals with $S = 0$ and large $|J|$ should be investigated using other techniques; for all other polyradicals with extreme values of "J", magnetization follows the Brillouin functions with appropriate values of S. For odd-electron $S = {}^1/_2$ polyradicals, distinction between the strong antiferromagnetic and uncoupled (weakly coupled) polyradical is made by evaluating M_{sat}, that is, the amount of polyradical should be determined independently.

When polyradicals with different values of S are present in the sample, M does not follow any Brillouin function.[40] M for a polyradical with spin, S, is related to the product, $S{*}B_S(x)$, which, in the limit of small and large H/T, is related to $S(S + 1)$ and S, respectively. Consequently, addition of magnetizations, $M_1 = \text{const}_1{*}S_1{*}B_{S1}(x)$ and $M_2 = \text{const}_2{*}S_2{*}B_{S2}(x)$, for any pair of polyradicals with different spins ($S_1 \neq S_2$), cannot be related to the product $S{*}B_S(x)$. For example, for an equimolar mixture of two polyradicals with different spins, $S_1 \neq S_2$, molar magnetization follows Brillouin functions corresponding to $S' = [(1 + 2A)^{1/2} - 1]$, where $A = S_1(S_1 + 1) + S_2(S_2 + 1)$, at small H/T and $S'' = (S_1 + S_2)/2$ at large H/T, i.e., there is a crossover from the larger, S', to smaller, S'', function with increasing H/T. Analogous results are easily obtained for mixtures of more than two-spin systems.

Spin values can also be determined by thermally perturbing population of the m_s sublevels. In the limit of small H/T, eq 4.1 can be shown to give rise to simple Curie plot (eq 4.2).[36]

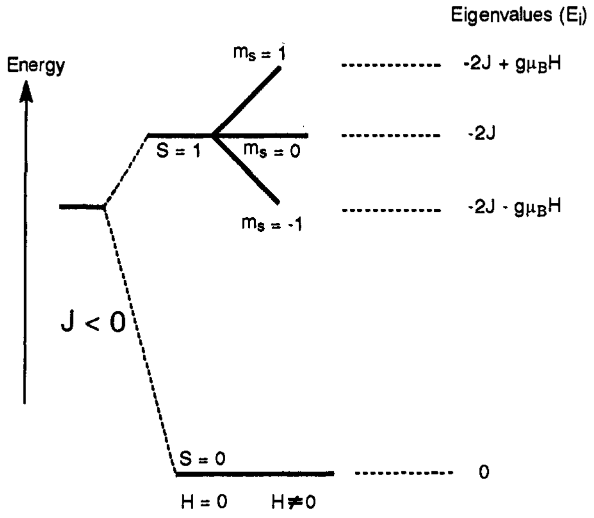
$$\chi = Ng^2\mu_B{}^2S(S + 1)/3kT \qquad (4.2)$$

In connection with eq 4.2, the susceptibility data are frequently plotted as χT vs T; S for polyradical is obtained from the value of χT. Alternatively, an effective magnetic moment ($\mu_{eff} = 2.84(\chi T)^{1/2}$) can be defined. The amount of polyradical must be known accurately, and for isolated polyradical, one data point might be sufficient to determine value of S.

b. Intramolecular Interactions, $J \approx kT$

For weakly coupled (small J's or $J \approx kT$) polyradicals, it is possible to perturb population of both the m_s sublevels and the ground vs excited states of different spin using variable H and T. Therefore, Brillouin functions (eq 4.1) and Curie plots (eq 4.2) are not applicable; more general equations, which include eqs 4.1 and 4.2 as special cases, should be used. The derivation is outlined below, using a diradical as an example.

Scheme 1



(1) Write Hamiltonian (Heisenberg, Ising, XY, etc.); Heisenberg is used here

$$H = g\mu_BS_zH_z - 2J\boldsymbol{S}_1\boldsymbol{S}_2 \qquad (4.3)$$

(2) Find eigenvalues corresponding to the total spin, $S = S_1 + S_2$, and magnetic quantum number, $m_s = S, S - 1, ..., -S$. The solution of the Hamiltonian (eq 4.3) for a pair of spins, S_1 and S_2, can be written as[36]

$$E(S,m_s) = g\mu_Bm_sH_z - J[S(S + 1) - S_1(S_1 + 1) - S_2(S_2 + 1)] \qquad (4.4)$$

In this example, $S_1 = S_2 = {}^1/_2$ and $S = 0$, 1 and $m_s = 1, 0, -1$, and for $J < 0$, the energy diagram shown in Scheme 1 is obtained.

(3) Calculate partition function [$Z = \sum\exp(-E_i/kT)$] where E_i are eigenvalues from eq 4.4 (relative to the $S = 0$ energy level, Scheme 1):

$$Z = 1 + \exp(2J/kT)[1 + 2\cosh(g\mu_BH/kT)] \qquad (4.5)$$

(4) Calculate magnetization ($M = NkT(\delta \ln Z/\delta H)_T$) for 1 mol of diradical:

$$M = 2Ng\mu_B \sinh(g\mu_BH/kT)/[\exp(-2J/kT) + 1 + 2\cosh(g\mu_BH/kT)] \qquad (4.6)$$

(5) Calculate static magnetic susceptibility ($\chi = M/H$). χ is typically measured at low magnetic fields (small H) or at high temperature (large T); i.e., H/T is small. Therefore, the following approximations for hyperbolic functions, $\sinh(x) \approx x$ and $\cosh(x) \approx 1$, are appropriate. Thus, χ for 1 mol of diradical is

$$\chi = 2Ng^2\mu_B{}^2/3kT[1 + ({}^1/_3)\exp(-2J/kT)]^{-1} \qquad (4.7)$$

This is a well-known Bleaney–Bowers expression.[41] Equation 4.7 should be treated as an approximate version of eq 4.6, especially, at low temperatures; at $T \approx 2$ K and for $J = 0$, the χT from eq 4.7 is too high by ~1% at $H = 0.5$ T and ~10% at $H = 2$ T.

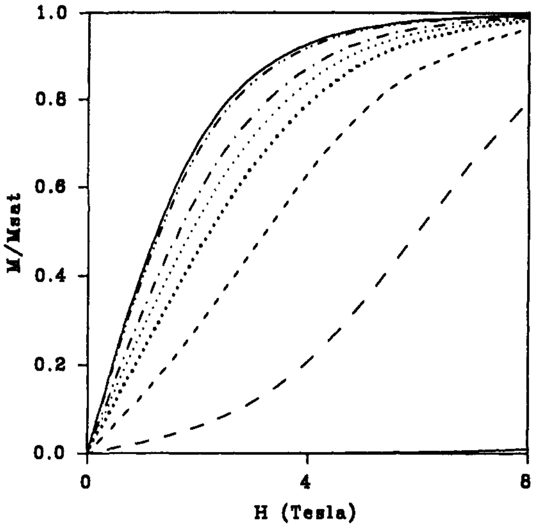


Figure 2. Plot of normalized magnetization, M/M_{sat} vs magnetic field, H, at temperature, $T = 2$ K using eq 4.6. The curves from left to right correspond to a diradical with J/k = 200, 2, 0, −0.5, −1, −2, −4, −10 K.

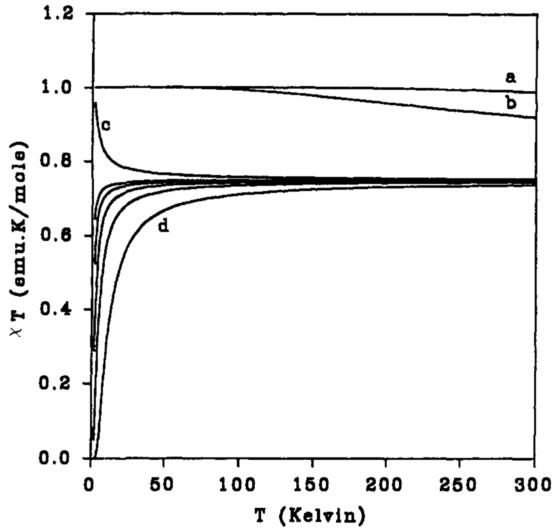


Figure 3. Plot of the product of magnetic susceptibility and temperature vs temperature (χT vs T). χ is obtained from eq 4.7; the curves correspond to the following values of J/k (Kelvin): (a) 500, (b) 200, (c) 2, (d) −10, and −4, −2, −1, −0.5. J/k = 500 K corresponds to $J \approx 1$ kcal/mol.

Equations 4.6 and 4.7 are quite sensitive to the magnitude of $J < 0$, i.e., antiferromagnetic interactions (Figures 2 and 3). In particular, sigmoidal shape of the M vs H plot (eq 4.6) at very low T for small antiferromagnetic coupling is quite characteristic. For ferromagnetic interactions, the sensitivity of the curvature to the values of J is very small; however, plotting eq 4.6 at different temperatures somewhat improves the situation.

The limiting values of J, i.e., $J = 0$, $J = +\infty$, $J = -\infty$, correspond to noninteracting doublets, isolated triplet ground state, and isolated singlet ground state, respectively. In the first two cases, eq 4.6 is equivalent to the magnetization obtained using the $S = {}^1/_2$ and $S = 1$ Brillouin functions (eq 4.1).

Equations such as 4.7 and its analogues are widely used for fitting of the experimental data for transition metal clusters;[36] copper dimers, which are counterparts of organic diradicals, are among the most thoroughly studied transition metal compounds.[42] Both types of the Hamiltonian and connectivity should be explored. For example, for tetraradical (four $S = {}^1/_2$ centers), the equations analogous to eq 4.7 are distinctly different for colinear, triangular, square, "butterfly", or tetrahedral connectivity of the radical centers.[35] Interpretations of the magnetic interactions, based upon eq 4.7 and its analogues, are very sensitive to the quality of the magnetic data. Proper calibration of the instrument and accurate weight, purity, and correction for diamagnetism of the sample and the sample holder are important.[43]

c. Intermolecular Interactions

On the one hand, intermolecular magnetic interactions complicate the study of spin coupling in organic di- and polyradicals. On the other hand, they are a prerequisite for designing molecular solids (and films) with interesting bulk magnetic properties. Both intra- and intermolecular magnetic interactions are present in the solids and, in some instances, in dilute frozen solutions. Typically, such interactions are antiferromagnetic and should decrease with dilution. Many models of intermolecular interactions are available.[44] The simplest of all is a mean-field correction, which is implemented by adding an additional fitting parameter, θ; θ is introduced either self-consistently to eq 4.6 or by replacing T with $T - \theta$ everywhere, except for the J-containing exponent in eqs 4.6 and 4.7.[44] For example, eq 4.6 with mean-field correction is

$$M = 2Ng\mu_B \sinh(g\mu_B H/k(T-\theta))/[\exp(-2J/kT) + 1 + 2\cosh(g\mu_B H/k(T-\theta))] \quad (4.8)$$

In addition to the mean-field model, other models are frequently used such as linear chains with various degrees of alternation, 2D networks, oligomers, etc.[36]

As an example, we consider the extreme case of a linear Heisenberg chain, e.g., antiferromagnetically J-coupled pairs of triplet diradicals.[45] For readily accessible magnetic fields ($H < 6$ T), the curvatures of the M vs H and MT vs T plots are similar (but not identical) for intramolecular (a pair of $S = {}^1/_2$ spins) and intermolecular (a pair of $S = 1$ spins) interaction. Unequivocal distinction between these two cases is possible when very large H and very low T are available. Magnetic fields, which are comparable in energy to J, cause crossing of the m_s sublevels for different total spin values (e.g., $S = 2, 1, 0$). Therefore, at $T < -J/k$, distinct changes of curvature in the M vs H plot will be seen, which correspond to the level crossings where the $m_s = -1$ and $m_s = -2$ sublevels become the lowest in energy. The resultant M vs H plot consists of one- and two-segment sigmoidal curves for inter- and intramolecular interactions, respectively (Figure 4). For a pure, stable diradical, which sample weight can be determined accurately, distinction between the two models is straightforward for many values of J, e.g., at high temperature, χT (emu K mol^{-1}) per mole of diradical should be 0.75 and 1.00 for the intramolecular singlet–triplet model and intermolecular dimer of triplets model, respectively. However, presence of impurities (e.g., arising from partial association of diradicals) may severely complicate the analysis.

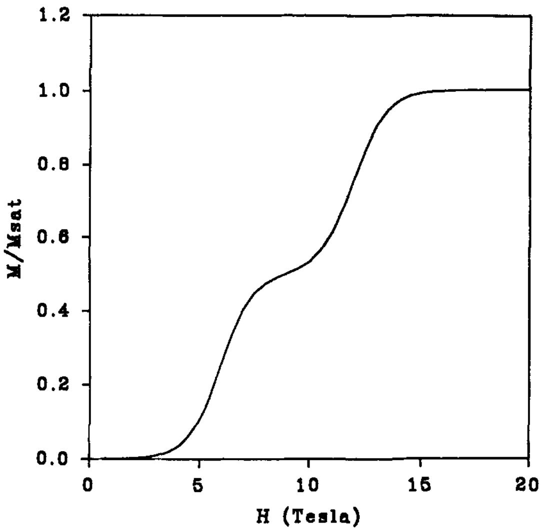


Figure 4. Plot of normalized magnetization, M/M_{sat} vs magnetic field, H, at temperature, $T = 1$ K for $J/k = -4.0$ K for an intermolecular antiferromagnetic interaction (J) within an isolated pair of two high-spin ($S = 1$) diradicals. M for one mole of diradical: $M = Ng\mu_B\{[\exp(z)\sinh(x) + \exp(3z)(\sinh(x) + 2\sinh(2x))]/[1 + \exp(z)(1 + 2\cosh(x)) + \exp(3z)(1 + 2\cosh(x) + 2\cosh(2x))]\}$ where $z = 2J/kT$ and $x = g\mu_B H/kT$.

B. ESR Spectroscopy

ESR spectroscopy had a crucial role in the discovery of a triplet excited state ($S = 1$). It is a common tool for study of $S > 0$ states in di- and polyradicals.[46-48]

Because the intensity (I) of the ESR signal is related to magnetic susceptibility (χ) as $\chi = A_{const}I$, ESR spectroscopy may be used similarly to the bulk magnetic measurements, as described above.[48,49] However, quantitative ESR measurements (spin counting) are rare because determination of A_{const}, which may be routine for $S = {}^1/_2$, is difficult for $S > {}^1/_2$.[50] Typical ESR measurements involve temperature perturbation of either m_s sublevels in high-spin polyradicals or population of the ground vs excited states of different spin. In the first case, $I \propto 1/T$, which is analogous to eq 4.2, is followed, and in the second case, $I \propto 1/T[1 + ({}^1/_3)\exp(-2J/kT)]^{-1}$, which is analogous to eq 4.7, is followed for a diradical. (For $S > 1$, equations similar to 4.7 can be derived.) Thus, when I vs $1/T$ follows the straight line at cryogenic temperatures, the ground state (typically, high spin) is separated by either a very large or a very small energy gap (compared to kT) from the excited states. If the curvature in the I vs $1/T$ plot is detected, then, the gap between the ground and excited states is comparable to kT and can be obtained from the fit equations analogous to eq 4.7. Thus, as discussed previously by Berson,[51] elucidation of the spin states using I vs $1/T$ dependence is ambiguous in many diradicals. Furthermore, even if the curvature in the I vs $1/T$ is detected, it is almost always assumed to originate in intramolecular spin coupling.[52] Such interpretations can be confirmed by dilution experiments.[53]

One of the attributes of ESR spectroscopy is electron–electron dipolar coupling that provides characteristic spectral pattern.[51] (Other terms in spin Hamiltonian, such as g anisotropy and A anisotropy, are less important for most high spin organic polyradicals.) Typically, spectra are obtained in dilute, rigid media, where polyradicals are randomly oriented with the respect to external magnetic field (e.g., frozen solution). However, even partial orientation of the molecules may improve spectral resolution.[54] The transitions are typically observed between the neighboring m_s sublevels ($\Delta m_s = 1$) but, the formally forbidden, weak transitions between more distant m_s sublevels ($\Delta m_s = 2, 3$) are sometimes detected. Because the number of m_s sublevels is $2S + 1$ (spin multiplicity), these $\Delta m_s = 2, 3$ (half-field, third-field) transitions are of great value to demonstrate the detection of a spin state with $S \geq 1$ and $S \geq {}^3/_2$, respectively. Dipolar couplings, which are characterized by two parameters, D and E (sometimes, $E/hc = 0$), will affect all observable Δm_s transitions; at least for $E/hc = 0$ and small $|D/hc|$, the spectral patterns from dipolar couplings in $\Delta m_s = n$ for spin $= S$ and $\Delta m_s = n + 1$ for spin $= (S + {}^1/_2)$ transitions appear similar.[55] More rigorously, computer simulations of ESR spectra, with D, E, and S (spin) among several parameters, allow for determination of spin states of the observed species.[47] In particular, a spectrum of a thermally populated $S > 0$ excited state can be detected.[56]

C. Other Methods for Determination of Spin States

Magnetic susceptibility (χ) can also be estimated using either contact shift or susceptibility shift, as detected by solution NMR spectroscopy.[57] Distinction between the contact shift and susceptibility shift and knowledge of the amount (concentration) of the polyradical must be accurate.

Contact shift originates in hyperfine electron–nuclear coupling (A), which splits NMR transition; for one unpaired electron, two NMR lines are shifted by $+({}^1/_2)A$ and $-({}^1/_2)A$ from their position in the absence of the hyperfine coupling. Typically, the electron spin–lattice relaxation times are shorter by several orders of magnitude, compared to h/A, and the two lines collapse into one at the chemical shift which is weighted by Boltzman population of the electron m_s sublevels. The measurement of this shift (contact shift) compared to the appropriate diamagnetic reference reveals the relative population of the electron m_s sublevels at a given magnetic field (H) and temperature (T). For a polyradical with spin, S, this contact shift is[58]

$$\Delta H/H = -[g^2\mu_B^2 S(S + 1)/3kT][2\pi A/\gamma_N h g\mu_B] \quad (4.9)$$

The expression in the first square bracket corresponds to eq 4.2 for magnetic susceptibility. Similar to the eqs 4.7 vs 4.2, an equation for the contact shift in a weakly coupled diradical is obtained by substituting $S = 1$ in eq 4.9 and multiplying eq 4.9 by an additional factor, $[1 + ({}^1/_3)\exp(-2J/kT)]$. Such an equation may be particularly useful for determination of the spin coupling in singlet ground state diradicals because of favorable NMR line widths.[59] NMR line widths that are too broad are one of the limitations for measurement of contact shifts. Small hyperfine coupling (spin density) at the observed nucleus, small γ_N (^{2}H is better than ^{1}H), fast electron spin–spin exchange (e.g., higher concentration and temperature, solvent with unpaired electrons) are among the factors sharpening the paramagnetic NMR lines.

Contact shifts allow for determination of spin densities in polyradicals.[60] Also, impurities in samples of polyradicals may be quantified, which is important for other types of measurements.

Susceptibility shift arises because the NMR chemical shift for a given nucleus (i.e., the effective magnetic field at the nucleus at a given frequency) depends not only on microscopic environment of the nucleus but also bulk properties of the sample such as its magnetic susceptibility, shape, orientation with the respect to the applied magnetic field, etc.[57] This is the basis for Evan's method for measurement of bulk magnetic susceptibility.[61] Evans method is widely used by inorganic chemists to determine μ_{eff} for transition metal complexes in solution; recently, it was applied to unstable polyradicals.[62] For a sample, which is contained in narrow tube parallel to the external magnetic field (modern high-field NMR spectrometer), magnetic susceptibility (χ_m in emu/g) is determined from the following equation[61]

$$\chi_m = 3\Delta\delta/(4\pi c) + \chi_o + \chi_o(d_o - d_s)/c \qquad (4.10)$$

where "c" is concentration (in g/mL), χ_o is diamagnetic susceptibility of the solvent, and $\Delta\delta$ is the chemical shift difference (measured for solvent or inert reference) between the solution (density, d_s) and pure solvent (density, d_o). The third term in eq 4.10 can be omitted with negligible error for highly paramagnetic compounds.[61] $\Delta\delta$ should be corrected for the presence of other diamagnetic solutes and the contact shift of the solvent (or the reference) should be negligible. For example, $\Delta\delta$ for diradical dianion **59** (R = H) in Me_2O is significantly less than expected because of substantial contact shift.[63]

Typically, an assembly of two concentric tubes is used. The concentration of the solution should be sufficient to obtain easily measurable $\Delta\delta$, but not too excessive, in order to avoid large NMR line broadening. The concentration should be known exactly at the temperature of the measurement;[62] for variable-temperature measurements, it is convenient to use a solvent with its density as a function of temperature known.[64]

For polyradicals with $|J| \ll kT$, ESR or EPR spectroscopy can be applied to estimate electron–electron spin coupling in the ways similar to those found in NMR spectroscopy for determination of nuclear–nuclear spin coupling. The important distinction between electron–electron and its nuclear counterparts is that the exchange mechanism is preponderant for the former and rare for the later.[65]

For a symmetrical diradical, diradical, X···X, with unpaired electrons localized on nuclei X with a hyperfine coupling A, small $|J|$ may be estimated by comparison to A. There are two limiting cases for J and A expressed in identical units: $J < A$ where the A-spaced multiplet from a single X is observed, and $J > A$ where the (A/2)-spaced multiplet from two identical X's is found.[66] For some diradicals, these two limiting cases are attainable by changing temperature.[67] The range of $|J|$ is limited by small values of A, e.g., $A \approx 40$ MHz for ^{14}N in a localized nitroxide, which is equivalent to kT at $T = 0.002$ K.

For a nonsymmetrical diradical, X···Y, where two sites for unpaired electrons have significantly different g values, it may be possible measure $|J|$ directly as an additional multiplet in the hyperfine splitting in the solution EPR spectrum;[68] this is in analogy to the detection of an AB multiplet in the routine NMR spectroscopy. (Isotropic g value in EPR is an analogue of the NMR chemical shift in solution.) So far this method was applied to "diradicals", where one of the unpaired electrons was localized at a transition metal.[68] Because the g values are so similar for C-, N-, and O-centered unpaired electrons (g = 2.002–2.005, i.e., spread of several Gauss at X band), it may be difficult to extend this method to organic polyradicals; perhaps, very high field EPR spectroscopy may be helpful in exploring this possibility.[69]

Heat capacity (C), which is related to the partition function (Z)

$$C = \delta[RT^2(\delta \ln Z/\delta T)]/\delta T \qquad (4.11)$$

can be used similar to bulk magnetic measurements. Expression for C as a function of T, H, and spin coupling parameters is derived similarly as outlined for magnetization, M.[36] This magnetic contribution to heat capacity is obtained experimentally by substracting the lattice contribution (phonons) from the total heat capacity. This procedure is more reliable when (1) an isostructural but nonmagnetic compound is available to estimate the lattice contribution and/or (2) the measurement is carried out at very low temperatures ($T < 4$ K) to minimize the lattice contribution. Therefore, the measurements of C are most suitable for weakly coupled di- and polyradicals (small J). Care should be taken to distinguish between different models of spin coupling.[36]

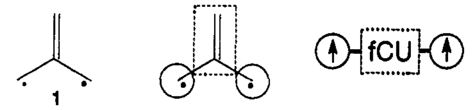
Chemically induced dynamic nuclear polarization (CIDNP), electron nuclear double resonance (ENDOR), and neutron scattering are among other methods that may be useful for determination of spin states in polyradicals.[70]

5. Diradicals

A. Simple Diradicals: Ferromagnetic vs Antiferromagnetic Coupling Units

The simplest π-conjugated diradical is trimethylenemethane (**1**), first observed by Dowd.[78] Spectroscopic studies suggest a triplet ground state, and ab initio calculations for **1** predict the singlet–triplet energy gap, $\Delta E_{ST} \approx 15$ kcal/mol.[74,75] **1** may be thought as two methyl radicals connected to the same end of ethylene (1,1-connection). Alternatively, two methyl radicals may be formally connected to the opposite ends of ethylene (1,2-connection) to give butadiene, which is, of course, singlet ground state with $\Delta E_{ST} = -74.3$ kcal/mol.[76] The ethylene moiety acts as a strong ferromagnetic and strong antiferromagnetic coupling unit when 1,1- and 1,2-connected, respectively; that is, connectivity (topology) determines the type of spin coupling (bonding).[77] The concept of spin coupling unit (bridge) is widely used in both organic diradicals and metal complexes.[5a,78,79]

Strong ferromagnetic coupling may also be achieved via a benzene moiety. Spectroscopic studies of m-benzoquinodimethane (**3**) by Migirdicyan, Platz, Berson, and their co-workers suggest triplet ground state and ab initio calculations predict $\Delta E_{ST} \approx 10$ kcal/mol.[80,81] Its *para* and *ortho* isomers **4** and **5** are ground-state singlets.[82] Antiferromagnetic coupling units tend



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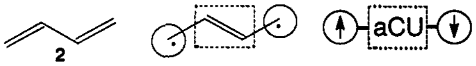

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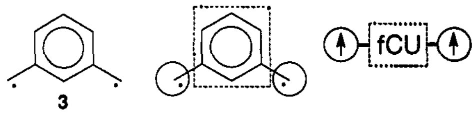

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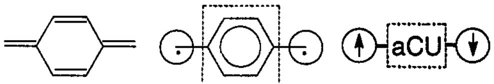

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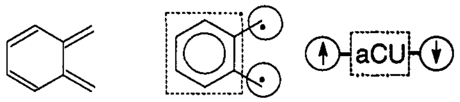

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to be more effective, compared to their ferromagnetic counterparts.

The presence (non-Kekule structures) vs absence (Kekule structures) of important open-shell resonance structures suggests strong ferromagnetic vs strong antiferromagnetic coupling for diradicals with one coupling unit.[83]

The strength of the ferromagnetic coupling is also elucidated by the MO theory as outlined by Borden and Davidson.[18] Both 1 and 3 possess a pair of half-occupied nonbonding MO's (degenerate or near degenerate). These MO's may be orthogonal and have to coincide at one or more atomic sites (non-disjoint MO's); this leads to the strong ferromagnetic coupling (section 2).[18]

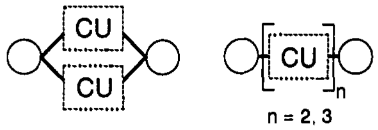
Another approach is to invoke the concept of spin polarization within either valence bond (VB) or MO theory;[84] in the latter case, UHF method or limited electron correlation are used. Heuristically, spin densities at the adjacent atomic centers in π-conjugated system prefer opposite signs, α and β, which correspond to antiferromagnetic coupling for nonorthogonal 2p orbitals. Such spin "polarization" should lead to the $\alpha\beta\alpha\beta\alpha\beta$ pattern in alternate systems. If the number of α sites (n_α, "arrows up") is greater compared to β sites (n_β, "arrows down"), the net spin S results. According to Ovchinnikov[85]

$$S = (n_\alpha - n_\beta)/2 \tag{5.1}$$

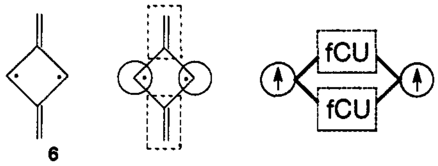
Counting "arrows up" and "arrows down" in 1 and 3 shows that both diradicals should be $S = 1$. Another way to apply eq 5.1 is to count the number of atomic centers between the sites with "unpaired" electrons in one of the important resonance structures; if this number is odd, as in 1 and 3, these "unpaired" electrons are ferromagnetically coupled. Unfortunately, eq 5.1 does not address the strength of spin coupling.

The concept of spin coupling unit may be extended into diradicals with multiple coupling units. Such units may be connected either parallel or sequentially. It is expected that the former will not weaken spin coupling and the later will lead to a weak spin coupling.

Spectroscopic studies of dimethylenecyclobutadiene (6), which is an example of ferromagnetic coupling via two parallel coupling units, suggest a triplet ground



state;[86] ΔE_{ST} from semiempirical calculations is comparable to that found for a single-coupling unit analogue, 1.[86b] This is in agreement with theory; 6 possesses non-disjoint half-occupied MO's and application of eq 5.1 gives $S = 1$. An example for antiferromagnetic coupling, which is an analogue of 6, is benzene; $\Delta E_{ST} \approx -90$ kcal/mol implies stronger antiferromagnetic coupling compared to butadiene.[87]



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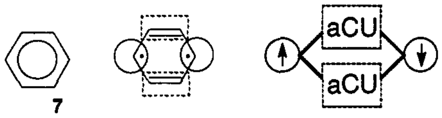

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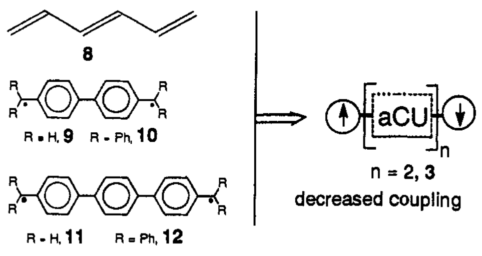
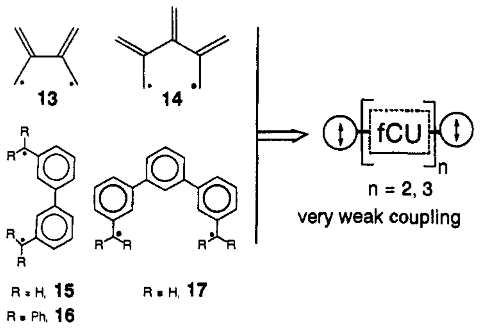
π-Conjugation in polyenes, which is an example for antiferromagnetic coupling through sequentially connected coupling units, has been thoroughly studied over the years.[88] Decrease of $-\Delta E_{ST}$ upon addition of one coupling unit is moderate, e.g., from 74.3 for butadiene to 60.2 kcal/mol for hexatriene.[76b] Derivatives of diradicals based upon the sequential 1,4-connection of one, two, and three benzene units are singlet ground states;[89] for 12, $\Delta E_{ST} \approx 1$ kcal/mol was found by the observation of a thermal population of a triplet state, using ESR spectroscopy.[90a]

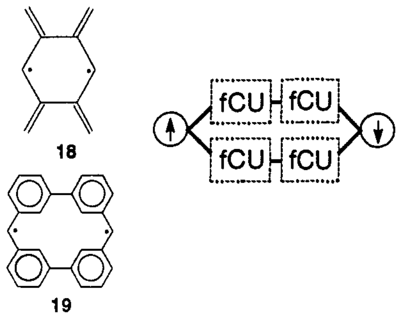
The sequential connection of ferromagnetic coupling units such as 1,1-connected ethylenes or 1,3-connected benzenes corresponds to diradicals 13–17. Among those diradicals, 13, 16, and their derivatives are known. 13 is a ground state triplet according to ESR spectroscopic studies.[91] Ab initio calculations support this assignment of the ground state and predict $\Delta E_{ST} \approx 1$ kcal/mol; however, for a "planar" structure, the singlet ground state is calculated.[92] Similarly, weak ferromagnetic coupling is claimed in 16; ESR Curie studies on impure samples in a rather narrow temperature range give $\Delta E_{ST} \approx 0.3$ kcal/mol.[90] Thus, coupling is weak for two sequentially connected ferromagnetic coupling units.

The nature of this weak coupling, i.e., ferromagnetic vs antiferromagnetic, is difficult to predict because, as for most weak interactions, slight structural or medium changes may matter. For diradicals with sequentially connected ferromagnetic coupling units, the half-occupied nonbonding MO's may be chosen in such a way that they do not coincide at any of the atomic centers (disjoint MO's). Exchange interaction between these two MO's is small, leading to weak spin coupling (section 2). Therefore, other small interactions (between other MO's), such as those accounted for by electron correlation, may have a significant effect; in many instances, these interactions favor singlet ground states. Equation 5.1 predicts a singlet ground state and a triplet ground state for diradicals with two and three sequential ferromagnetic coupling units, respectively.

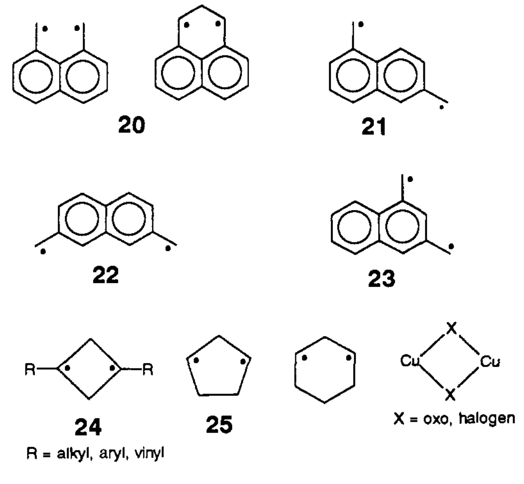




The sequential and parallel connectivity of ferromagnetic coupling units are also found in a single diradical. Examples are 18 and 19. Solid-state NMR spectroscopy of matrix-isolated 18 establishes its singlet ground state with $-\Delta E_{ST} > 1$ kcal/mol.[93] This is in agreement with ab initio calculations on 18 ($\Delta E_{ST} \approx -5$ kcal/mol[94a]) and "planarized" 13.[92,94] Diradical 19, for which molecular models suggest an approximately planar structure, is unknown; is it a singlet ground state?



Diradicals based upon other ferromagnetic coupling units, presumably weaker than ethylene and benzene, are known, e.g., the naphthalene moiety (20–23) and methylene (24 and 25).[95,96] In the naphthalene-based diradicals 20–23, eq 5.1 provides a simple guide where to attach the groups with unpaired electrons in order to control spin coupling. Similarly, numerous other diradicals based upon homologues of naphthalene (anthracene, phenanthrene, etc.) can be designed.

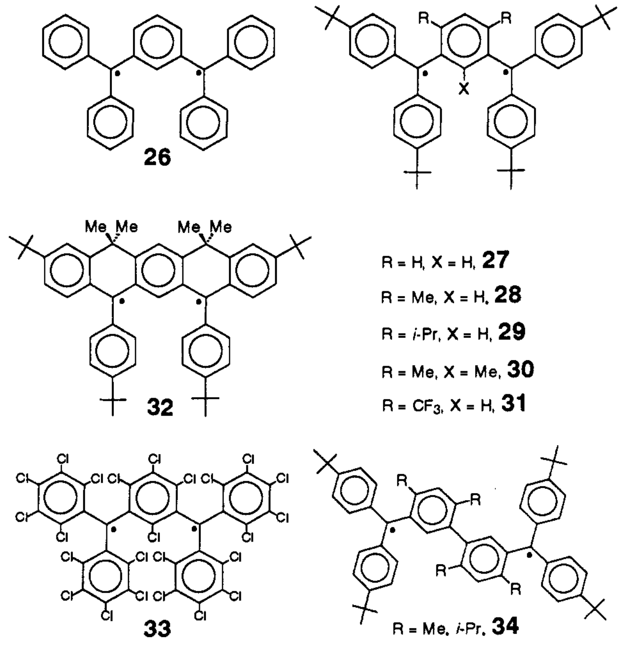


Dougherty has recently reviewed methylene-based diradicals 24 and 25.[5a] Strength of their ferromagnetic spin coupling decreases as the C–(CH$_2$)–C angle increases.[97] This is reminiscent of analogous angle dependence in copper dimers.[42,98]

Dowd proposed nonalternant diradicals containing a cyclopentadienyl moiety.[99] Ab initio calculations on cyclopentadienyltrimethylenemethane (CPTMM) reveal a $^3B_2$ triplet ground state, which is approximately described as a cyclopentadienyl and methyl radicals 1,1-connected to ethylene.[99b] Because cyclopentadienyl can be viewed as a "spin diluted" methyl radical, ΔE_{ST} for CPTMM, which is a few kilocalories per mole, is less than ΔE_{ST} for 1.

B. Stable Diradicals: Steric Shielding, Heteroatom Perturbation, Multiple Coupling Units

Because stable monoradicals are known, the simplest design for stable diradicals is to couple two stable monoradicals via a spin coupling unit. 1,3-Connection of benzene with two phenylmethyl moieties corresponds to Schlenk hydrocarbon 26,[100–102] which is almost completely oligomerized at ambient temperature. Heating, followed by rapid cooling, of oligomerized 26 in toluene gives an ESR spectrum at 77 K; Curie studies above 77 K suggest that a minor species possesses triplet ground state.[103] Triphenylmethyl is almost completely associated in solution; the dimer CC bond is between the triphenylmethyl site in one radical and *para* position in the benzene ring of the other radical. Therefore, steric shielding of sites *para* with respect to triarylmethyl sites for unpaired electron in 26 should improve stability of polyarylmethyl diradicals.[100,101]



All diradicals 27–33 show intense triplet ESR spectra in frozen solutions; only small amounts of doublet

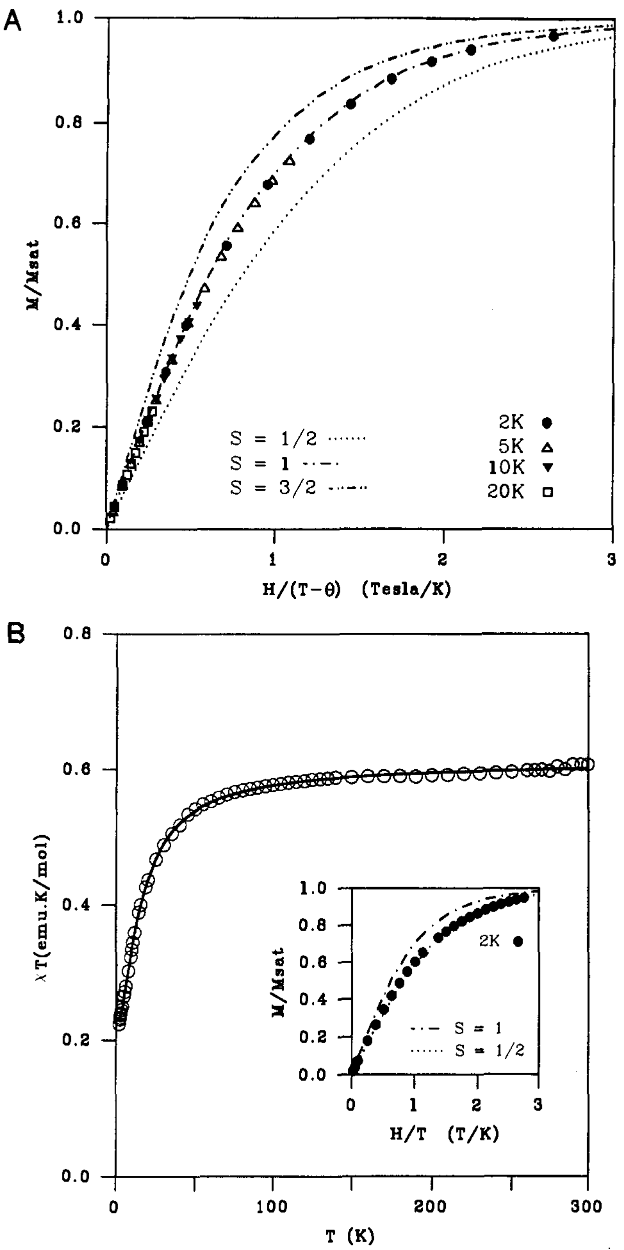


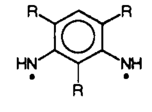
Figure 5. SQUID data for diradical 28. (A) Solution of 28 in 2-MeTHF: Plot of normalized magnetization, M/M_{sat} vs $H/(T - \theta)$, compared to the $S = {}^1/_2, 1, {}^3/_2$ Brillouin functions (eq 4.1); $\theta = -0.09$ K.[40] (B) Solid 28: χT vs T plot at $H = 0.5$ Tesla with fit using a model of pair of two antiferromagnetically coupled $S = 1$ diradicals with partial dimerization to monoradicals. (Strong intramolecular ferromagnetic and weak intermolecular antiferromagnetic couplings.) Magnetization (M) and susceptibility ($\chi = M/H$) is calculated from the following equation (analogous to eq 4.6 and equation in caption of Figure 4): $M = Ng\mu_B\,\alpha\{[\exp(z)\sinh(x) + \exp(3z)(\sinh(x) + 2\sinh(2x))]/[1 + \exp(z)(1 + 2\cosh(x)) + \exp(3z)(1 + 2\cosh(x) + 2\cosh(2x))]\} + Ng\mu_B(1 - \alpha)[\sinh(x)/(2 + 2\cosh(x))]$ where $z = 2J/kT$ and $x = g\mu_B H/kT$. $J/k \approx -7$ K and $\alpha \approx 0.4$ are intermolecular spin-coupling constant between diradicals and fraction of diradical in the sample, respectively. Insert shows M/M_{sat} vs H/T plot less contribution from diradical, which is very small at $T = 2$ K and $H < 5.5$ T. Satisfactory fit to the $S = {}^1/_2$ Brillouin function is obtained as expected for monoradicals (dimerized diradicals).

impurities (with the exception of 31) are found.[104-106] In conjunction with electrochemical studies at ambient temperature, this indicates their thermal stability and lack of significant association in solution. Furthermore, 33 is stable in air. Diradicals 32 and 33 are isolated as pure solids; magnetic susceptibility studies up to ambient temperature give μ_{eff} close to the theoretical value of 2.83 μ_B for $S = 1$ state. Similar studies on 28–30 are complicated by the presence of $S = {}^1/_2$ impurities, predominantly arising from partial association of diradicals in the solid state;[106] magnetic susceptibility data for 28 and 30 are best fit with intermolecular antiferromagnetic interaction between two $S = 1$ diradicals (dimer), which possess strong intramolecular ferromagnetic coupling.[106b] Magnetization studies of 28 (Figure 5) and 29 in frozen THF (2-MeTHF) at 2, 5, and 10 K indicate good fit to a $S = 1$ Brillouin curve and show a constant magnetic moment between 3 and 80 K. A very weak antiferromagnetic interactions are seen below 3 K ($\theta \approx -0.1$ K); because a $S = 1$ Brillouin curve is followed, these weak interactions are intermolecular (section 4).[106b]

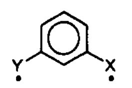
Steric hindrance in diradicals 28–30 and 33 inevitably leads to substantial out-of-plane distortion. Because ferromagnetic coupling remains strong (i.e., $\Delta E_{ST} > 1$ kcal/mol) in these diradicals, 1,3-connected benzene is a good ferromagnetic coupling unit.[56b]

Sterically hindered derivatives of 16 such as 34 are also obtained.[107] Magnetic studies, M vs H and MT vs T, rule out a singlet ground state with $-\Delta E_{ST} > 0.004$ kcal/mol, and the observation of a triplet ESR spectrum implies some degree of spin coupling. Although the singlet ground state with very small spin coupling is possible, the best fitting to eq 4.8 suggests triplet ground states with $\Delta E_{ST} \approx 0.04$ kcal/mol (R = Me) and $\Delta E_{ST} \approx 0.004$ kcal/mol (R = i-Pr). Thus, spin coupling is quite weak in these systems.[107b]

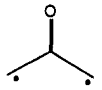
Many stable diradicals contain heteroatoms. Heteroatom-containing spin sites may be attached to a strong ferromagnetic coupling unit such as 1,3-connected benzene or 1,1-connected ethylene. For example, ESR spectroscopic studies suggest triplet ground states for 35 and 36 (X = CH_2, Y = O).[51,108] Ab initio calculations give a triplet ground state with $\Delta E_{ST} \approx 10$ kcal/mol for 36 (X = Y = O);[81a] i.e., similar to the all-carbon counterpart, 3. Analogous perturbation in 1,1-connected ethylene systems diminishes ferromagnetic coupling; e.g., calculations suggest that 37 is a triplet ground state with very small ΔE_{ST} and alkyl-substituted derivatives of 37 are ground-state singlets.[109] This is in agreement with ESR spectroscopic studies on diradicals 38 and 39; that is, derivatives with the most electron-withdrawing substituents (and oxo) are ESR silent.[110,111] Although 40 (X = CH_2, Y = O) is a triplet ground state according to ESR spectroscopic studies and ab initio calculations,[86b,c] double substitution with oxygen (X = Y = O) is predicted to give singlet ground state.[86c,112] Different behavior of the benzene and ethylene coupling unit can be explained in terms of MO theory;[113] the defining structural factors appear to be aromaticity of benzene and strength of C=O vs C=C bond. Berson and co-workers found that heteroatom-substituted diradicals 41 (X = O, S) which are derivatives of 13, are singlet ground states.[114] Their all-carbon analogues 41 (X = $C(Me)_2$) and 42 are triplet ground states.[115,116] Ab initio MO calculations suggest that, for diradicals 41 (X = O, NH, CH_2, $C(Me)_2$) and 42, the sign and magnitude of ΔE_{ST}'s might be related to the square of energy gap between the NBMO's.[92a]



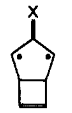
35
R = H, F



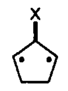
36
X = CH$_2$, Y = O
X = Y = O



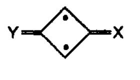
37



38
X = C(Ph)$_2$, CH(Ph), C(CN)Ph, CH(CN), C(CN)$_2$, O



39
X = C(Me)$_2$, C(SOMe)$_2$, C(SO$_2$Ph)$_2$

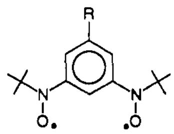


40
X = CH$_2$, Y = O
X = Y = O

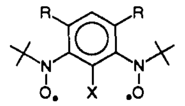
41
X = C(Me)$_2$, S, O

42

Di-*tert*-butyl nitroxide is an air-stable free radical, which is commercially available. 1,3-Connection of two nitroxide moieties to benzene gives diradical **43**;[117,118] magnetic studies find triplet ground state with $\Delta E_{ST} >$ 1 kcal/mol.[118] A frozen solution of dinitroxide **44**, which is an analogue of **30**, is studied by ESR spectroscopy in the cryogenic temperature range. Temperature dependence of ESR intensity is interpreted in terms of intramolecular antiferromagnetic coupling; i.e., a singlet ground state with a thermally populated triplet excited state.[119] Magnetic susceptibility studies of methoxy-substituted dinitroxide **45**, either in solid state or polymer matrix, indicate singlet ground state. The fact that the antiferromagnetic coupling is intramolecular is further confirmed by examination of an X-ray-determined structure; large intermolecular distances between the sites with large spin density are found.[120]



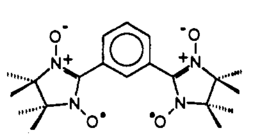
R = H, *t*-Bu, **43**



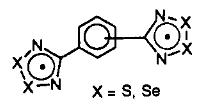
R = Me, X = Me, **44**
R = OMe, X = H, **45**

Because spin density is localized on nitroxide moiety (approximately equally on oxygen and nitrogen) in π-conjugated nitroxides,[121] spin coupling is weaker for π-conjugated dinitroxides, e.g., **43**–**45**, compared to their carbon counterparts (section 5.C). Other weakly coupled diradicals, e.g., **46** and **47**, are formally obtained by connecting different heteroatom-based monoradicals to ferromagnetic coupling units. Stable, but weakly coupled diradicals, containing several coupling units are known, e.g., **48**–**51**; only weak coupling ($\Delta E_{ST} <$ 0.1 kcal/mol) is found for these diradicals.[122-126] In particular, spin coupling through three coupling units, fCU–aCU–fCU and fCU–fCU–fCU should be very weak; therefore, factors other than connectivity (coupling units) are likely to affect it significantly, especially in nonplanar systems (sections 2, 5.A, and 5.C).

Dinitroxide **49** gives bulk ferromagnet with T_c = 1.48 K.[29]

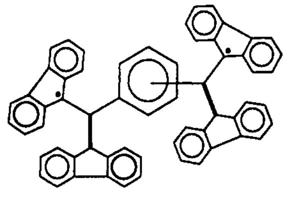


46

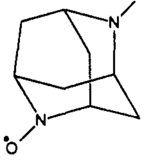


X = S, Se

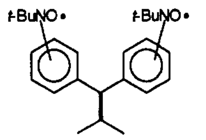
47



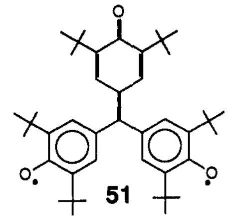
48



49



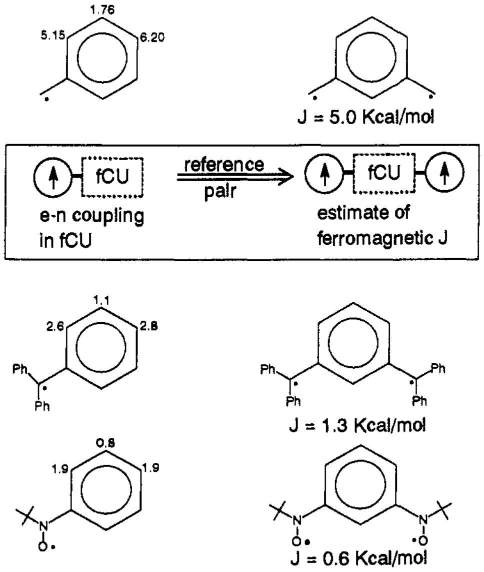
50



51

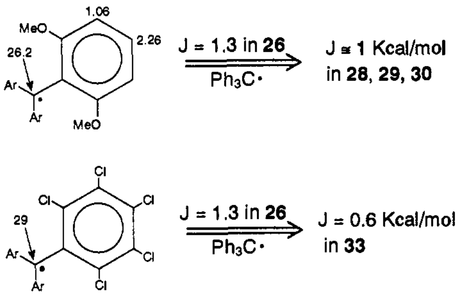
C. Quantitative Usage of Spin-Coupling Units

In the preceding discussion, we used spin-coupling units to rationalize qualitatively the type and strength of spin coupling in diradicals. Now we attempt a more quantitative approach to strong ferromagnetic coupling in diradicals based upon 1,3-connected benzene as ferromagnetic coupling unit. We conjecture that, within the 1,3-connected benzene series, the existing experimental and computational data on spin-coupling constant J (or $\Delta E_{ST} = 2J$) for such diradicals may be related to electron–nuclear (e–n) couplings (spin densities) in the corresponding monoradicals,[49] which formally contain the spin coupling unit of interest: $J \propto$ (spin density in ferromagnetic coupling unit)^2.[127]



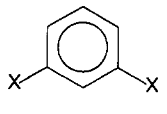
Comparison of electron–proton coupling constants in the benzene rings of benzyl,[128a] triphenylmethyl,[128b] and *tert*-butylphenyl nitroxide[128c] gives the following ratio of spin densities associated with one benzene ring: 20:10:7. Therefore, if the result of ab initio calculation for spin coupling for **3**, J = 5.0 kcal/mol, is correct, then, the predicted J for **26** and **43** are $5 \times (10/20)^2 \approx 1.3$ and $5 \times (7/20)^2 \approx 0.6$ kcal/mol, respectively.

J values for sterically hindered analogues of polyarylmethyl diradical **26** may be estimated considering electron–^{13}C and electron–proton coupling constants for triphenylmethyl, tris(2,6-dimethoxyphenyl)methyl, and perchlorotriphenylmethyl.[128de] As far as out-of-plane twisting caused by steric hindrance is concerned, tris(2,6-dimethoxyphenyl)methyl provides a conservative model for estimating J for alkyl-substituted diradicals **27–30**; among those, **30** is likely to be most twisted but, presumably, less than the model monoradical. Perchlorotriphenylmethyl should be a good model for diradical **33**. Notably, the ^{13}C-coupling increases in increments of about 3 G between monoradicals. This suggests that the spin density (and electron–proton coupling constants) in their benzene rings decreases by similar increments.[128e] Extrapolation of the electron–proton coupling constants from triphenylmethyl to the other two model monoradicals gives the following J values: (1) diradicals **27–30**, $1.3 > J > 1.0$ kcal/mol, and (2) diradical **33**, $J \approx 0.6$ kcal/mol.



Ortho substitution with Me or OMe groups in *tert*-butylaryl mononitroxides drastically decreases (more than factor of 2) electron–proton coupling constants from the already low values for the parent *tert*-butylphenyl nitroxide.[128f] Consequently, spin coupling through 1,3-connected benzene, which is ferromagnetic coupling unit for dinitroxides **44** and **45**, should be very small ($J < 0.1$ kcal/mol); therefore, other interactions may become comparable in strength and control the spin coupling.

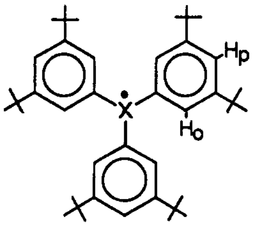
Next, the effect of heteroatom perturbation of J is reexamined; in place of diradicals **3**, **35**, and **36**, the following pairs of diradicals are compared using electron-proton coupling constants for the corresponding monoradicals.[128g-j]



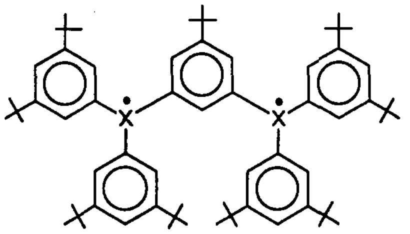
$X = Ph_2\dot{C}$ vs $Ph_2\dot{N}^{+}$
$X = Ph\dot{C}H$ vs $Ph\dot{N}$
$X = \dot{C}H_2$ vs $\dot{O}$

In this particular series of diradicals, it is predicted that the ferromagnetic coupling in each heteroatom-based diradical is, at least, as strong as in its hydrocarbon counterpart; this is in agreement with calculations on the parent systems. However, stable and strongly ferromagnetically coupled ($J > 0.5$ kcal/mol) polyarylaminium systems may be difficult to achieve because a stabilizing *para* substitution with MeO or Cl groups causes a precipitous decrease in the electron–proton coupling; e.g., from triphenylaminium to tris(4-methoxyphenyl)aminium by factor of 2.

For systems containing heavy elements such as Si and Ge, perturbation of J in diradicals, with 1,3-connected benzene as coupling unit, are examined by using the following monoradicals.[128k]



X	Ho (Gauss)	Hp (Gauss)	estimate of J (Kcal/mol)
C	2.58	2.80	1.3
Si	0.95	1.17	0.2
Ge	0.60	0.95	0.1



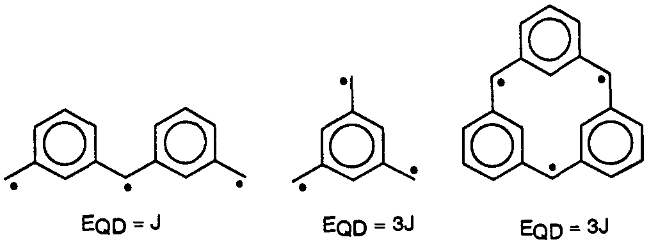
J for the all-carbon diradical should be identical to **26**, which is estimated at 1.3 kcal/mol. J for the Si and Ge analogues is predicted to be 0.20 and 0.10 kcal/mol, respectively; should these diradicals be prepared, their $\Delta E_{ST} = 2J = 0.4$ and $2J = 0.2$ kcal/mol are well suited for standard ESR spectroscopic and magnetic susceptibility measurements.

6. Tri- and Tetraradicals

Strength of the spin coupling (J) in many diradicals can be obtained by experiment, calculation, and empirical estimate. One of the key questions is whether strong spin coupling can be maintained in extended systems with more than two sites for unpaired electrons, e.g., is "J" constant within a homologous series di-, tri-, tetra-, and polyradicals?[129]

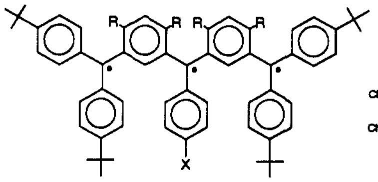
A. Triradicals

Triradicals are relatively rare compared to diradicals. Systems with potentially strong ferromagnetic coupling, which are homologous to *m*-benzoquinodimethane, fall into three categories: (1) two 1,3-connected benzenes in a "linear" arrangement, (2) 1,3,5-connected benzene, and (3) three 1,3-connected benzenes in a "closed loop" arrangement.

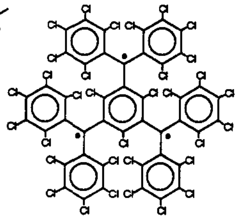


Assuming that a coupling constant J is associated with ferromagnetic ($J > 0$) spin coupling through each 1,3-connectivity in benzene, application of Heisenberg Hamiltonian (section 4) reveals that the energy gap between the ground quartet and lowest excited doublet state is much smaller ($\Delta E_{QD} = J$) for the "linear" topology, compared to $\Delta E_{QD} = 3J$ for the other two cases.[35] (Coupling constants may be different for the second and third topologies.) These energy gaps should be compared to $\Delta E_{ST} = 2J$ in a diradical. Therefore, "linear" triradicals are relatively susceptible to thermal population of the lowest excited states and can be used to measure strong ferromagnetic couplings.

The representative examples for the first topology are polyarylmethyl triradicals **52**–**55**, and trinitroxide **56**; all possess $S = {}^3/_2$ ground states in either solid state or frozen solution.



R = H, X = t-Bu, **52**
R = Me, X = t-Bu, **53**
R = i-Pr, X = t-Bu, **54**
R = i-Pr, X = Ph, **55**



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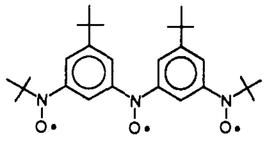

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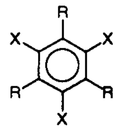


58

R = $(Ph\text{-}Ph)_2\dot{C}$, X = H
R = $Ph_2\dot{N}^+$, X = H
R = galvinoxyl, X = H
R = nitronylnitroxide, X = H
R = t-butylnitroxide, X = H, OMe
R = Ph_2NN, X = CN

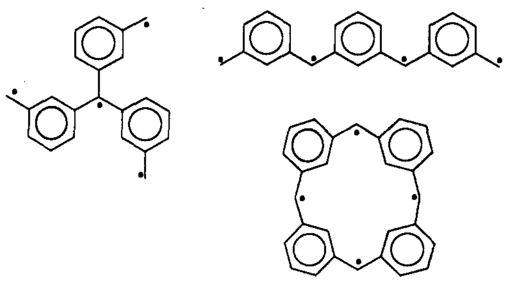
According to ESR spectroscopy, the "linear" polyarylmethyl triradicals **52**–**55** show negligible thermal population of the low-spin excited states at 100 K; triradical **54** also shows similar behavior at ambient temperature, according to the χ vs T magnetic susceptibility data.[55] Therefore, $\Delta E_{QD} = J > 1$ kcal/mol is in agreement with our empirical estimate for $J \approx 1.3$ kcal/mol and experimental results ($2J > 1$ kcal/mol) in the homologous diradical **29** (section 5). The data indicate that strong ferromagnetic coupling is maintained, although the out-of-plane twisting for the π-conjugated system in **54** is likely to be substantial.

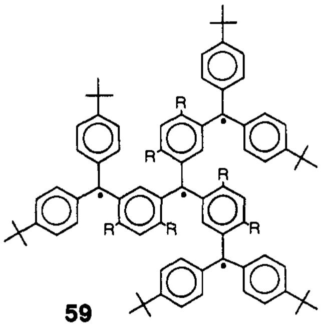
Fitting of the χ vs T data for trinitroxide **56** to the equation analogous to eq 4.7 (for "linear" triradical with the nearest-neighbor interactions only) gives $J \approx 0.5$ kcal/mol, which is the same as the quartet–doublet energy gap. Consequently, a substantial population of the $S = {}^1/_2$ excited state is found at ambient temperature.[118] The experimental $J \approx 0.5$ kcal/mol is in agreement with the empirical estimate of $J \approx 0.6$ kcal/mol and experimental studies ($2J > 1$ kcal/mol) for a homologous dinitroxide (section 5).

Several examples of triradicals **57**–**58** pertaining to the second topology have been reported; quartet states are detected in all cases.[130–133] In the case of a recent perchlorinated triradical **57**, it is found that quartet is a ground state by a significant margin. This implies $\Delta E_{QD} = 3J > 1$ kcal/mol for **57**, which is in agreement with the empirical estimate of $J \approx 0.6$ kcal/mol and experimental studies ($2J > 1$ kcal/mol) for the related diradical **33**. The steric hindrance is so severe in **57** that propeller isomers can be isolated.[132] Propeller isomerism implies out-of-plane distortion; notably, strong ferromagnetic coupling is maintained in this inert triradical.

B. Tetraradicals

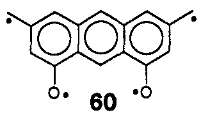
Several high-spin tetraradicals have been reported so far.[52,55,56] Systems with potential for strong ferromagnetic coupling, which are homologous to *m*-benzoquinodimethane, fall into three limiting categories: (1) "star-branched", (2) "linear", and (3) "closed loop". (Replacement of 1,3- with 1,3,5-connected benzenes may give an entry into multiradicals.) Among the three topologies only "star-branched" tetraradicals are known. ESR spectroscopy and magnetization studies suggest quintet ground states ($S = 2$) for tetraradicals **59**. The most sterically hindered tetraradical **59** (R = *i*-Pr) is obtained as a stable solid at ambient temperature; magnetic studies, which are complicated by impurities, do not indicate appreciable thermal population of low-spin excited states. The strong ferromagnetic coupling is still present, in spite of probable severe out-of-plane distortion of π-conjugated system.





59

R = H, Me, i-Pr



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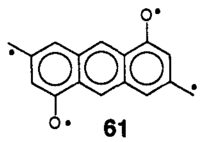

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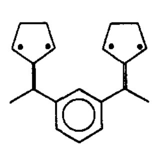

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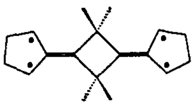

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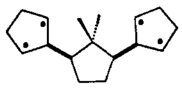

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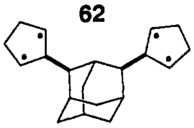


65

Application of eq 5.1 to naphthalene, anthracene, and other polycyclic aromatics reveals a plethora of possible ferromagnetic coupling units for tetraradicals. The only known example belongs to the first high-spin tetraradical **60**, which was reported in 1983 by the Berson group. ESR and UV–vis spectroscopic studies are best interpreted in terms of quintet ground state ($S = 2$) with strong ferromagnetic coupling. The other isomer **61** possesses either nearly degenerate triplet/

singlet ground/excited states, or it is a ground state triplet by a large margin.[134]

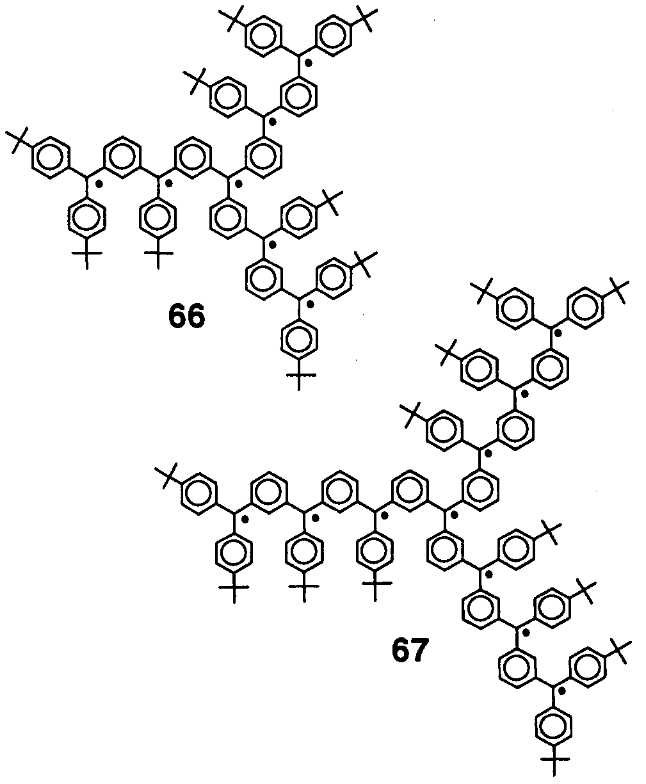
The Dougherty group has reported generation and ESR studies for series of tetraradicals **62**–**65**, which can be considered as a pair of $S = 1$ TMM's linked with 1,3-connected benzene or methylenes as spin-coupling units. ESR spectroscopy suggests quintet ground states ($S = 2$) for all tetraradicals, except for adamantane-based tetraradical **65**, which is assigned singlet ground state by following the ESR signal intensity during generation of tetraradical. A model based upon two-site Heisenberg Hamiltonian is used to correlate the calculated ΔE_{ST} in "localized" diradicals with the triplet–quintet energy gaps (ΔE_{TQ}) in the corresponding delocalized tetraradicals, that is, J in a tetraradical is scaled by $(^1/_3)^2$, compared to a diradical, because only $^1/_3$ of total spin of trimethylenemethane moiety is affecting the ferromagnetic coupling unit. The following ΔE_{TQ}'s are obtained: 2.2, 0.38, and 0.20 kcal/mol for **62**, **63**, and **64**, respectively; the last value is in excellent agreement with the ESR spectroscopic Curie studies.[56] The results suggest that these ferromagnetic coupling units retain their effectiveness upon different substitution. An elegant ESR study on the effect of steric hindrance on spin coupling in derivatives of **62** have appeared recently.[56b]

Very weakly coupled tetraradicals based upon stable radical moieties are also known.[71a,135]

7. Star-Branched and Dendritic Polyradicals. Toward Nanometer-Size Single Molecule Organic Magnetic Particle

A. Star-Branched Hepta- and Decaradicals

Homologation of "star-branched" topology for tetraradical **59** (R = H) allows for design of heptaradical **66** and decaradical **67**.[136] ESR and NMR spectroscopies at high temperatures (100 and 140 K) indicate dominant presence of the $S = {}^7/_2$ heptaradical and $S = 5$ decaradical. The absence of a large amount of other paramagnetic species (thermal population of low spin excited states) suggests that both polyradicals possess high-spin ground states with strong ferromagnetic coupling. Magnetic susceptibility studies give constant magnetic moment for both polyradicals between 100 and 10 K, which excludes intermediate strengths of spin coupling; an onset of weak antiferromagnetic interactions is observed at $T < 10$ K. Similar weak antiferromagnetic interactions are observed in the homologous high-spin di- and tetraradicals. Magnetization data for **66** and **67** are best fit to a model assumming intermolecular antiferromagnetic interactions and a probability "p" ($p < 1$) for having an unpaired at each triarylmethyl site (eq 8.1 and Figure 6); $p = 0.93$ (**66**) and $p = 0.95$ (**65**). (This probability times 100% gives yield per site for unpaired electrons.)



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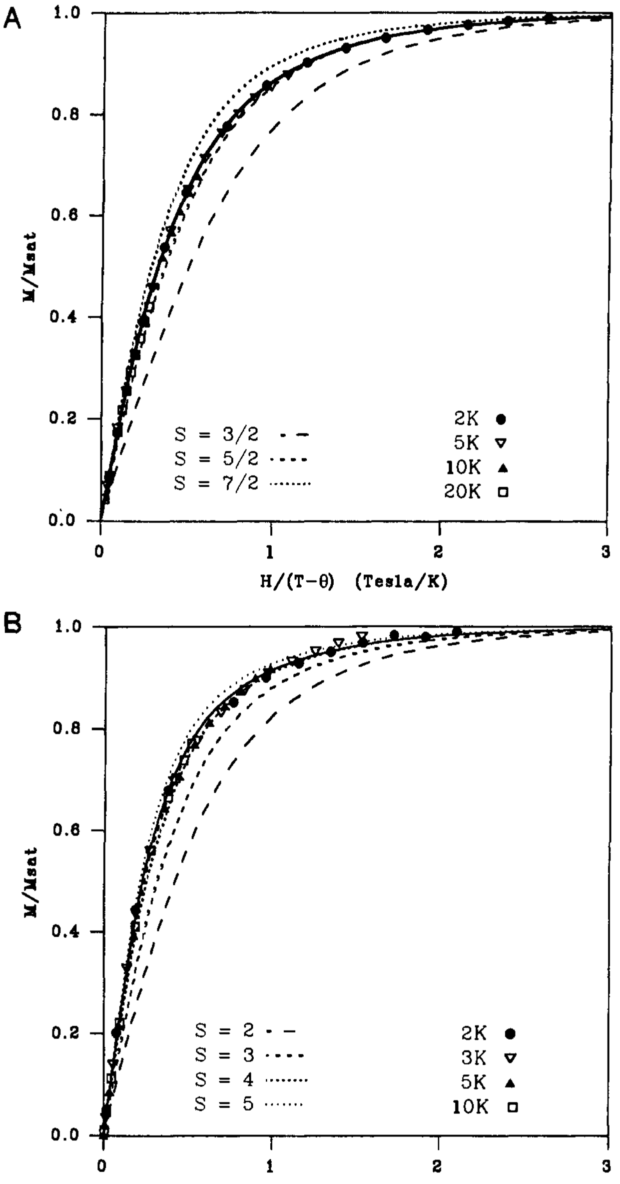
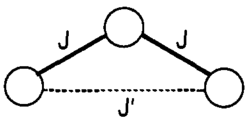


Figure 6. Plots of normalized magnetization, M/M_{sat} vs $H/(T-\theta)$; solid and intercepted lines correspond to fits (eq 8.1, method A) and Brillouin function (eq 4.1) plots, respectively:[40] (A) heptaradical **66** in 2-MeTHF, $p = 0.93$, $\theta = -0.1$ K, and (B) decaradical **67** in THF, $p = 0.95$, $\theta = -0.6$ K.

The high-spin ground states for **66** and **67** can be further confirmed by considering the possibility of intramolecular antiferromagnetic coupling between molecular branches. Because such coupling is through space, it is expected to be weak. An illustrative model is provided by three-spin systems with two coupling constants, strong ferromagnetic $J \gg 0$ and weak antiferromagnetic $J' < 0$.

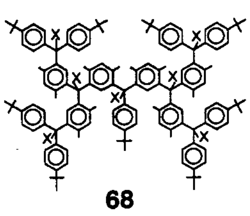


The energy levels for the model with Heisenberg Hamiltonian and three $^{1}/_{2}$ spins are: 0 ($S = ^{3}/_{2}$), $J + 2J'$ ($S = ^{1}/_{2}$), and $3J$ ($S = ^{1}/_{2}$).[35b] The decrease of energy gap between high- and low-spin states due to antiferromagnetic interactions is $2J'$; thus, as long as $|J| > |2J'|$, the ground state is high spin. Therefore, the observed weak antiferromagnetic interactions are not likely to originate from through-space interactions between branches of the same molecule.

Zero-field splitting parameters ($|D/hc|$) in the ESR spectra of decaradical **67** and its lower homologues are inversely proportional to spin (S), i.e., $D \propto$ constant + $1/S$; also, this reflects proportionality of $|D/hc|$ to volume. One of the practical consequences of this relationship is that the spectral widths ($2D$, $4D$, $6D$, $12D$, and $18D$) remain approximately constant while the number of allowed transitions greatly increases in the series of di-, tri-, tetra-, hepta-, and decaradicals; **67** is at the limit of usefulness of conventional continuous-wave ESR spectroscopy (randomly oriented media).

B. Dendritic Polyradicals with 7, 15, and 31 Sites for Ferromagnetically Coupled Electrons

Homologation of "linear" topology for triradical **53** allows for synthesis of dendritic heptaradical **68**, pentadecaradical **69**, and 31-radical **70**.[40,137] Hepta-, pentadeca-, and 31-ethers, which are precursors to these polyradicals, are characterized using mass spectrometry; NMR spectroscopy suggests complex conformational equilibria for these molecules. Consequently, ESR spectra of the corresponding polyradicals show broad single peaks, except for **68**, for which shoulders might be discerned. The ESR spectral width is significantly decreasing from triradical **53** to pentadecaradical **69**; this might suggest an increasingly isotropic spatial relationship of the radical sites in sterically hindered dendrimers; e.g., folding into "three-dimensional" shapes such as "barbells".[137]



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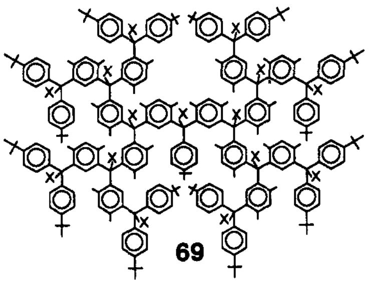

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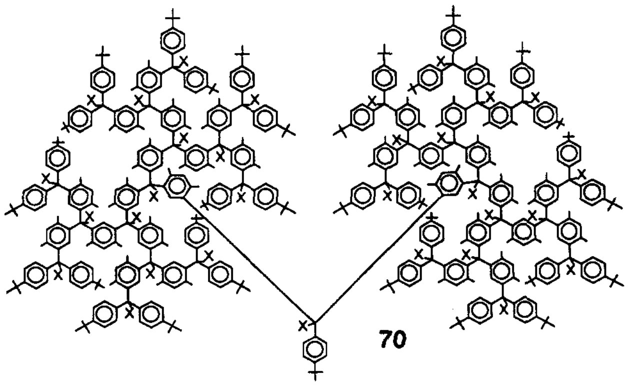

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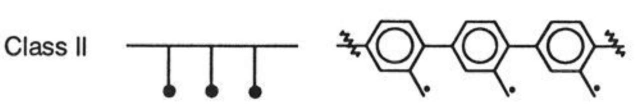
Magnetization data are obtained in the 2–80 K temperature range and at magnetic fields up to 5.5 T. Both temperature and field dependence of magnetization are interpreted in terms of mixture of spin systems with different values of spin (S) with weak intersystem antiferromagnetic interactions (mean-field parameter, $-\theta \approx 0.6$ K ≈ 0.001 kcal/mol). The "average" spin is about ~ 3, $\sim ^{7}/_{2}$, and $\sim ^{5}/_{2}$ for **68**, **69**, and **70**, respectively. However, no single Brillouin function can be fit to these data. One of the possible explanations is that defects, which are failures to generate an unpaired electron at some of the triarylmethyl sites, produce mixtures of the spin systems for each polyradical. Assuming equal probability for finding an unpaired electron at each triarylmethyl site, p, the following p are obtained: 0.94 (**68**), 0.8 (**69**), $\sim$0.8 (**70**). The yield per site for unpaired electrons, $p \times 100\%$, is good. However, spin coupling in multisite polyradicals such as **69** and **70** is extremely sensitive to defects and, although, 80% of unpaired electrons are generated, spin coupling is largely interrupted.[40]

8. Defects and Spin Coupling

All methods for generation of unpaired electrons in polyradicals rely on chemical, photochemical, or electrochemical reactions that are carried out to generate all unpaired electrons from a suitable precursor. Because the yields of such reactions are not quantitative, for polyradicals with a dozen or more unpaired electrons, there is a significant probability for formation of polyradicals with one or more unpaired electrons missing. The important questions are what is the effect of such defects is on the spin coupling and can very high spin systems be obtained in the presence of defects?

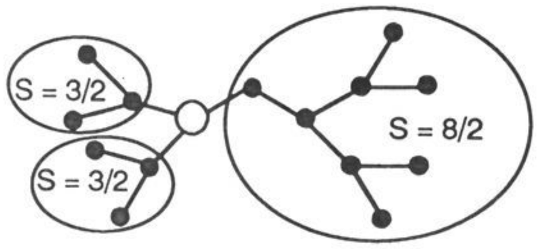
A. Spin-Coupling Path

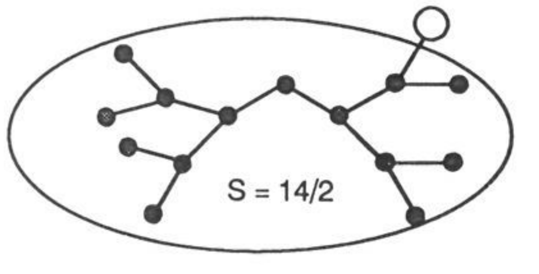
Spin-coupled systems may be viewed as systems containing "localized" *spin sites* which are linked via the *coupling units* (section 5). When considering spin coupling throughout the systems with more than two sites, it is useful to define, in the best resonance structure for π-conjugated polyradical, spin *coupling path* as the array of atoms (orbitals) between any pair of spin sites, which are spin coupled. Two limiting cases with regard to their spin-coupling paths between a pair of non-nearest-neighbor sites are as follows: class I, an additional site is formally included in the path; class II, no additional spin sites are formally included in the path. When the spin sites are represented with dots and the intervening atoms as bars, the following simple graphs can be obtained.



Among all polyradicals known to date, class I high-spin polyradicals show stronger spin coupling compared to the class II polyradicals. The important difference between the two classes is the effect of defects; in a class I spin system, a single defect may disrupt the strong spin coupling but, in class II, the coupling, which is already weak in defect-free systems, may be further weaken.

Dendritic polyradicals are an example of a class I system. Their ferromagnetic coupling path includes both 1,3-connected benzenes and the arylmethyl radical centers. Consequently, the failure to generate one of the unpaired electrons, i.e., having an sp^3-hybridized carbon at one of the arylmethyl sites as a defect, may interrupt the strong ferromagnetic coupling and drastically lower the spin value for the polyradical. Defects at the inner sites are especially detrimental; for example, in pentadecaradical **69** one such defect divides the polyradical into "uncoupled" parts with significantly lower spin; e.g., three parts with $S = {}^3/_2$, ${}^3/_2$, and ${}^8/_2$. Defects at the peripheral sites are relatively innocuous. Notably, about half of the spin sites in dendritic polyradicals such as **69**–**70** are peripheral, a much more favorable situation compared to linear chain polyradicals.[138]





In the presence of defects, polyradicals may consist of many spin systems with different spin values. Magnetic data for such samples are not straightforward to interpret; e.g., magnetization data do not adhere to any single Brillouin function (section 4).[40]

The following model may be used for class I polyradicals with defects. Random occupation by an unpaired electron of each site with probability p is assumed; $p \times 100\%$ is the yield per center for generation of unpaired electrons. The probabilities, N_s^{k}, for finding an s electron spin system ($S = s/2$) in a polyradical molecule with k sites are used as weighing factors for the Brillouin functions, $B_{s/2}$; thus, magnetization per mole of polyradical, M, is

$$M = Ng\mu_{\mathrm{B}}(N_1{}^{\mathrm{k}}B_{1/2} + N_2{}^{\mathrm{k}}B_{2/2} + \ldots + N_{(k-1)}{}^{\mathrm{k}}B_{(k-1)/2} + N_K{}^{\mathrm{k}}B_{k/2}) \quad (8.1)$$

N_s^{k} can be evaluated by two different methods (A and B).

Method A. For polyradicals with p close to 1 (90+% yield per site), polyradicals with a small number of defects will dominate the sample. Probability of finding a polyradical with k sites and j defects is $({}^k_j)p^{(k-j)}(1 - p)^j$; for example, heptaradicals with 0, 1, 2, 3, and 4 defects for $p = 0.93$ will account for essentially whole sample: $p^7 + 7p^6(1 - p) + 21p^5(1 - p)^2 + 35p^4(1 - p)^3 + 35p^3(1 - p)^4 = 0.99998$. For each polyradical with j defects, all configurations for defects are enumerated, and numbers of spin systems with $S = k/2$, $(k - 1)/2$, ..., ${}^2/_2$, ${}^1/_2$ are found. In order to obtain N_s^{k}, the each number of the spin systems with $S = s/2$ for polyradical with j defects is multiplied by $p^{(k-j)}(1 - p)^j$ and the products are added with respect to j.[40]

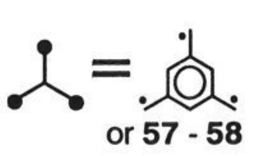
Method B. For polyradicals with small or intermediate values of p, method A may become exceedingly laborious as thousands of spin systems in polyradicals with large number defects may need to be enumerated. A more direct method to find N_s^{k} is illustrated, using a polyradical with linear connectivity. Probability for having s sites occupied and g sites unoccupied is $p^s(1 - p)^g$; in a k site chain, there is $k - s - 1$ ways to distribute s site spin systems, which are flanked by an empty site at each end. There are two ways to distribute s site spin systems, which are at the end of the chain and are flanked by only one empty site. Therefore, for linear k site chain:

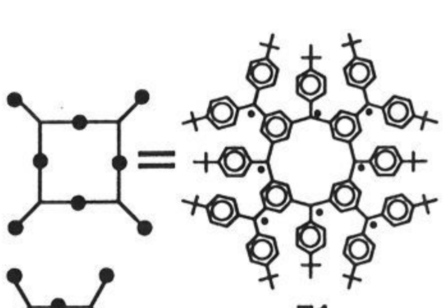
$$N_s^{\mathrm{k}} = (k - s - 1)p^s(1 - p)^2 + 2p^s(1 - p) \quad (8.2)$$

Efforts toward high-spin polymers, based upon linear connectivity in class I and II systems, may be futile, unless the following issues are addressed first: (1) development of highly efficient methods for generation of radical centers, i.e., even better than the carbanion method for polyarylmethyls[55] and (2) search for class II strongly coupled spin system.

B. Multiple Coupling Paths

Another approach to the problem of defects may rely on the class I systems with multiple spin-coupling paths. A simple connectivity is "closed loop" (ring), where two paths exist. For high-spin systems, interesting examples are structures based upon triradicals **57**–**58** and macrocyclic calixarenes, which correspond to 1,3-connected polyarylmethanes.[139] Such connectivities are oblivious to one defect; two defects may interrupt their coupling paths. We label such polyradicals as 1-proof. (Linear and branched connectivities are 0-proof in this terminology.) Annelation of "closed loops" gives extended networks and lattices with greater resistance to





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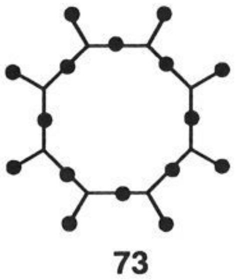

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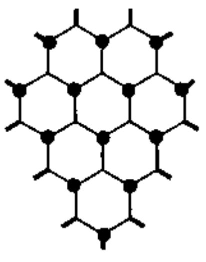
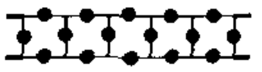
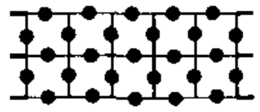
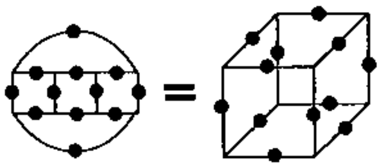
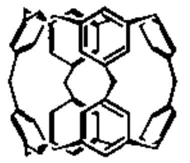
defects. The Mataga polymer[24] may be represented as a hexagonal 2D lattice and is 5-proof. Multiply stranded connectivities based upon annulated calix[4]arenes offer less resilience to defects: 2-strand is **1**-proof, and 3- and oligo-strand is 2-proof. 2-Strand can be modified by closure into a closed loop with 3-proof connectivity. The smallest 2-strand loop, based upon **1**,3,5-connected benzene as coupling unit, corresponds to O_h symmetric cubooctahedrane, a $C_{60}H_{48}$ parent hydrocarbon. Another way to describe this cage is as two calix[4]arenes, one at the bottom and one at the top, with four additional CH_2 linkers. A plethora of other less-symmetric cages are possible by closure of various strands of calixarenes.


Mataga polymer


2-Strand

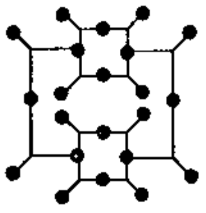

3-Strand


Cubooctahedral cage


$C_{60}H_{48}$

In the $C_{60}H_{48}$ cage, **12** benzhydryl CH_2's are potential sites for unpaired electrons; the corresponding polyradical, which would have benzene rings twisted by 90° out-of-plane in each benzhydryl moiety, would be an interesting test for 3D π conjugation and for the mechanism of ferromagnetic spin coupling.

An intermediate approach, which is a compromise between the synthetic efficiency of dendrimers and resistance to defects of closed loops, is embodied in homologation of **71** into polyradicals **74** and **75**, which may be referred to as "hypercyclomers". All the above polyradicals are **1**-proof; for polyradicals **71**, **74**, and **75** with two defects, spin coupling is interrupted in about 21%, 10%, and 4% of each homologue, respectively. This is unlike in 0-proof dendritic structures where the analogous percentages are approximately 75% for all homologues.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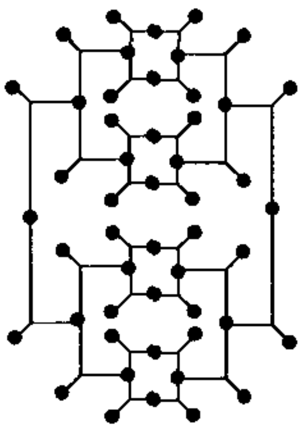
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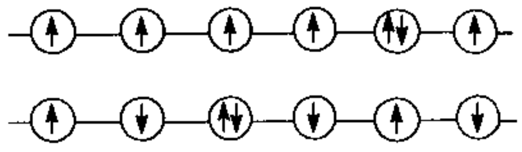
9. Polyradical Polyanions: Spin Coupling vs Electron Delocalization

As far as the currently available evidence suggests, spin coupling in polyarylmethyl high-spin polyradicals may be described by a model based upon Heisenberg Hamiltonian and localized spin sites. As a test for electron localization, addition of one or more electrons to a polyradical to form polyradical polyanions are considered. Each additional electron corresponds to an extra negative charge. Will the charge/spin be localized or delocalized? How is spin coupling between the remaining "unpaired" electrons affected by the negative charge?

From a more general point of view, understanding of the factors involved in spin coupling in polyradicals should permit a rational design of spin-coupled structures. An interesting example for such design are structures for electron transfer (or electrical conductivity), i.e., the question is whether the type and magnitude of spin coupling is related to aptitude for electron transfer.[140] For example, two extreme cases of the strongly antiferromagnetically and ferromagnetically coupled chains (or networks) of spins can be considered. As one or more electrons are added to the chain, will the type and magnitude of the spin coupling between the electron spins along the chain be preserved? Will the added electron(s) delocalize over the chain or tend to localize, that is, how is electron transfer affected by the ferro- vs antiferromagnetic spin coupling along the pathway?



The simplest system possesses two sites, e.g., a diradical, which after addition of an electron becomes radical anion. Several radical anions, which are derived from diradicals with strong antiferromagnetic coupling, have been studied. Examples are semiquinone radical anions,[141a] Wurster's salts,[141b] and their all-carbon analogues, which are topologically related to **4**.[79] ESR studies of the last two examples show spin/charge delocalization on the ESR time scale.[79,141]

Radical anion and radical cation of perchlorinated **10** are also found delocalized on the ESR time scale by Ballester and co-workers. Notably, perchlorobiphenyl shows 87° out-of-plane twisting in solid state. This severe steric hindrance dramatically weakens antiferromagnetic coupling in the related diradical ($|J| <$ ^{13}C hyperfine coupling) but does not appear to affect significantly the electron delocalization.[142]

Radical anion, which corresponds to diradical **27** with a strong ferromagnetic coupling, is localized on the ESR time scale.[79] Similar results hold upon extension of conjugation, that is, analysis of zero-field splitting parameters for diradical anions and diradical dianions, which correspond to tri- and tetraradicals **52**–**54** and **59**, indicates spin/charge localization on the ESR time scale. Furthermore, Curie plots of the ESR $\Delta m_s = 2$ signal intensity in the 10–80 K range suggest triplet ground states.[143a]

Results, which are obtained for the radical ions of perchlorinated **10**, suggest that steric hindrance should not significantly contribute to the observed electron localization in polyradical polyanions corresponding to **27**, **52**–**54**, and **59**. Consequently, the electron delocalization vs localization in radical ions may originate in antiferromagnetic vs ferromagnetic spin coupling in the related polyradicals.[143b] Important tests, which await experimental realization, are radical ions based upon diradicals with coupling through two or more ferromagnetic coupling units such as **34**.[144]

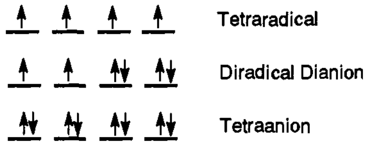
Spectroscopy of more complex radical ions, which are studied by the Miller and the Nelson groups, is reminiscent of inorganic mixed-valence complexes.[145,146a] Another interesting example is a spiro-conjugated radical anion prepared by Maslak and co-workers;[146b] its delocalization on the ESR time scale can be related to antiferromagnetic spin coupling in a related spiro-conjugated tetraradical.[5a]

Because the electron-coupling part of the theory is very similar for both electron transfer and energy transfer, it is not surprising that the energy transfer between porphyrins and other electrophores, which are linked via 1,3-, 1,2-, and 1,4-connected benzene-based bridges, is the slowest for the 1,3-case.[147] The relationship between the spin coupling and electron delocalization is also found in some models for magnetism, e.g., there is an isomorphism between a two-level quantum mechanical system and the Ising model. In particular, adjacent antiparallel spins in the Ising model correspond to tunneling between two spatial states (in analogy to electron transfer in radical anion).[23]

The search for the systems with extremely fast electron-transfer rates may not be the most important task; as Nature teaches us, it is far more important to be able to control the rate of the electron transfer. The spin-coupled di- and polyradical systems should provide novel opportunities in this field.

10. Insight into the Electronic Structure Associated with High Spin via Population of Nonbonding MO's

Most of the high-spin polyradicals studied to date are characterized by half-occupied nonbonding (NB) molecular orbitals (MO). Full NBMO occupation corresponds to polyanions; their intermediate occupations corresponds to polyradical polyanions.[79] Because population of NBMOs should not significantly change bonding, an insight into the electronic structure of polyradicals should be obtained by study of the related polyradical polyanions and diamagnetic polyanions.[148]



NMR, UV–vis, and electrochemical studies for the series of carbo polyanions, which are related to tris(4-*tert*-butylphenyl)methyl and polyradicals **27**, **59** (R = H), and **67** are primarily considered.[79] Arylmethyl carbons in these mono-, di-, tetra-, and decaanions possess large negative charge as evidenced by upfield ^{13}C NMR chemical shifts; notably, the chemical shift range is only a few parts per million. Because similar clustering of ^{13}C NMR resonances is observed for other carbons bearing substantial negative charge, it is concluded that extension of conjugation in this series does not perturb the electron density distribution.[79]

UV–vis spectra for the above polyanions and their selected alkyl-substituted derivatives (more sterically hindered) show a strong absorption, $\lambda_{max} \approx 500$ nm.[79,144] Molar absorptivities, which are determined for selected mono-, di-, tetra-, and decaanions, are found to be proportional to the number of arylmethyl fragments (molecular charge).[79]

Cyclic voltammetry and various pulse techniques reveal two, three, and four reversible oxidations at about −1.3 V for dianions, trianions, and tetraanions, respectively.[149] For example, consecutive three oxidations of trianion give radical dianion, diradical anion, and triradical. Further oxidation of polyradicals occurs at much more positive potentials (>1 V). The potential range between polyanion and polyradical is 0.2, 0.4, and 0.5 V for dianions, trianions, and tetraanions. Although these potential differences are small compared to most π-conjugated systems, they are about 1 order of magnitude more than the predicted values for completely independent arylmethyl anions.[79,144]

The above evidence suggests that 1,3-connected polyarylmethyl-based polyanions may be viewed as ensembles of weakly interacting arylmethyls. Such an electron localization is also found in the related polyradical polyanions (preceding section). Therefore, similar conclusions should apply to the corresponding polyradicals; in particular, the "localized spin" spin-coupling models such as Heisenberg Hamiltonian and related models, should be adequate. It is reasonable to conclude that the values of "J" in the series di-, tri-, tetra-, and higher radicals are either constant or show very slow decrease.

Presumably, the electronic structure, which is associated with electron localization on arylmethyl fragments in 1,3-connected polyarylmethyls, may also apply to other strongly coupled high-spin systems.

11. High-Spin Organic Ions and Polycarbenes

The discussion of the spin coupling would not be complete without at least mentioning carbenes, nitrenes, ions, and other molecules capable of possessing high-spin ground states. Polycarbenes have repeatedly been reviewed in recent years.[4,150]

Iwamura, Itoh, and their co-workers have prepared and characterized high-spin polycarbenes with up to nine carbene centers ($S = 9$) in matrix.[151] Truly remarkable features of these spin systems are the paucity of defects, due to efficiency of the photochemical generation of polycarbenes from their diazo precursors, and possibility for manifestation of magnetic anisotropy on a slow time scale at the molecular level.[151] Several examples of other di- and polycarbenes, and their nitrene analogues have been studied to elucidate the factors affecting spin coupling.[152–154]

First triplet states of antiaromatic ions were detected by ESR spectroscopy in early 1960s.[155] Among derivatives of cyclopentadienyl cations, benzene dications, and benzene dianions both singlet and triplet ground states were found; the spin of the ground state is affected by both substituents and medium.[154,155] Such molecules played an important role in Breslow's pioneering experimental attempts toward an organic ferromagnet.[156,157]

Many selected $S = {}^{1}/_{2}$ radical anions and radical cations are stable at ambient temperatures and/or on air; they are readily prepared by one-electron reduction or oxidation of appropriate precursors.[141,142] Polarons in some electrically conducting n- or p-doped polymers can also be considered as radical ions.[158] Such radical ions are promising building blocks for stable "polyradical" species with both high and low spin. Their stability and generation of "unpaired" electrons via redox processes, which may be thermodynamically controlled, should have advantages in preparation of extended structures with very small density of defects.

For biselectrophoric molecules,[159] which are obtained by linking two anthracene radical anions via short alkyl chain bridges or two naphthalene radical anions via 1,3-connected benzene bridges, or related examples, triplet states are detected by ESR spectroscopy.[159a–c] Topology of the bridging by alkyl chain appears to be important.[159a] Also, in mixtures of di-, tri-, and tetraanions of di-, tri-, and tetra(9,10-anthrylenes), triplet, quartet, and quintet states were detected in frozen a 2-MeTHF solution at T = 150 K using ESR spectroscopy.[160] In most of the above examples, it is not clear what is the spin of the ground state and how it is effected by ion pairing.[161,162]

High-spin states ($S \approx 2.5$) wee also found in a p-doped polymer, which before doping consisted of short polyene chains linked via 1,3-connected benzene bridges; the magnetization measurements were carried out down to T = 2 K.[163]

Interpretation of spectroscopic and magnetic data in the radical ion systems may potentially be complicated by disproportionation equilibria, e.g., for a triplet ground-state pair of radical ions in equilibrium with singlet dianion and singlet neutral species.[162]

12. Conclusions and Perspectives

In the past decade significant progress toward understanding of spin coupling in di- and polyradicals has been made. High-spin polyradicals (strong ferromagnetic coupling) are most interesting because selected π-conjugated hydrocarbon di- and polyradicals are among species with strongest ferromagnetic couplings to date. Although π-conjugated systems are traditionally viewed as examples of delocalized bonding, high-spin 1,3-connected arylmethyl polyradicals are highly localized as indicated by studies of polyradicals, polyanions, and polyradical polyanions; that is, extension of their conjugation and moderate out-of-plane distortion do not lead to a major change in electronic structure. This suggests that such polyradicals may be viewed as ensembles of arylmethyl monoradicals; consequently, simplistic concepts such as spin sites, coupling units, and coupling paths, in conjunction with simple spin-coupling models, are useful in elucidation of spin coupling.

Weak spin coupling in π-conjugated di- and polyradicals is far less understood; in particular, factors other than molecular connectivity, which is a dominant contributor in strong spin coupling, may be decisive.

Qualitative determination of spin coupling in homologous high-spin polyradicals and their localized electronic structure suggest that strong ferromagnetic spin coupling (J) should be maintained in mesoscopic-size or extended structures. Preparation of very high spin polyradicals requires a careful design of molecular connectivity to minimize impact of defects and further development of ultra-high yield methods for generation of polyradicals. Although some interesting magnetic phenomena are not restricted by dimensionality, long-range ferromagnetic order implies spin coupling in at least two dimensions. Rational organic synthesis of extended two- and three-dimensional extended structures, with repetitive macrocyclic ring closures, will be challenging.

Further insight into a relationship between spin coupling and electron transfer using polyradicals may be gained and, ultimately, better understanding of phenomena associated with electrical conductivity may result. From a broader perspective, it should be emphasized that both magnetism and superconductivity are unsolved problems and understanding a known relationship between them may be critical to the solution.

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References

(1) Recent reviews on diradicals: (a, photochemistry) Johnston, L. J. *Chem. Rev.* **1993**, *93*, 251; Wilson, R. M.; Schnapp, K. A. *Chem. Rev.* **1993**, *93*, 223; (b, tetramethylenes in polymerizations) Hall, H. K., Jr.; Padias, A. B. *Acc. Chem. Res.* **1990**, *23*, 3; (c, flexible triplet diradicals) Doubleday, C., Jr.; Turro, N. J.; Wang, J.-F. *Acc. Chem. Res.* **1989**, *22*, 199; (d, 1,5-diradicals from photoexcited ketones) Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83; (e, trapping of triplet diradicals with oxygen) Adam, W.; Grabowski, S.; Wilson, R. M. *Acc. Chem. Res.* **1990**, *23*, 165; (f, photoionization mass and photoelectron spectroscopy) Blush, J. A.; Clauberg, H.; Kohn, D. W.; Minsek, D. W.; Zhang, X.; Chen, P. *Acc. Chem. Res.* **1992**, *25*, 385; (g, optical studies of 1,6- and shorter polymethylenes) Johnston, L. J.; Scaiano, J. C. *Chem. Rev.* **1989**, *89*, 521.

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

(3) Meyers, A. G.; Dragovich, P. S.; Kuo, E. Y. *J. Am. Chem. Soc.* **1992**, *114*, 9369. Koga, N.; Morokuma, K. *J. Am. Chem. Soc.* **1991**, *113*, 1907.

(4) (a) Iwamura, H.; Koga, N. *Acc. Chem. Res.* **1993**, *26*, 346. (b) Iwamura, H. *Adv. Phys. Org. Chem.* **1990**, *26*, 179.

(5) (a) Dougherty, D. A. *Acc. Chem. Res.* **1991**, *24*, 88. (b) Buchachenko, A. L. *Russ. Chem. Rev.* **1990**, *59*, 307.

(6) *Ferromagnetic Materials*, Bushow, K. H. J., Wohlfarth, E. P., Eds.; North-Holland: Amsterdam, 1980–1990; Vols. 1–5.

(7) Fisher, K. H.; Hertz, J. A. *Spin Glasses*; Cambridge University Press: Cambridge, 1991.

(8) Tilley, D. R.; Tilley, J. *Superfluidity and Superconductivity*; Hilger: Bristol, 1986.

(9) International conferences on molecular magnetic materials: (a) *Proceedings of the Symposium on Ferromagnetic and High Spin Molecular Based Materials*, 197th National Meeting of the American Chemical Society, Dallas, TX, Spring 1989; American Chemical Society: Washington, DC, 1989. Miller, J. S., Dougherty, D. A., Eds. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 1–562. (b) Gatteshi, D., Kahn, O., Miller, J. S., Palacio, F., Eds. *Magnetic Molecular Materials*; Kluwer: Dordrecht, 1991. (c) *Proceedings of the International Symposium on Chemistry and Physics of Molecular-Based Magnetic Materials*, Iwamura, H., Miller, J. S., Eds. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 1–360; **1993**, *233*, 1–366. (d, recent reviews) Caneshi, A.; Gatteshi, D.; Sessoli, R.; Rey, P. *Acc. Chem. Res.* **1989**, *22*, 392. Miller, J. S.; Epstein, A. J.; Reiff, W. M. *Chem. Rev.* **1988**, *88*, 201. (e, recent leading reference) Stumpf, H. O.; Ouahab, L.; Pei, Y.; Grandjean, D.; Kahn, O. *Science* **1993**, *261*, 447.

(10) Seto, C. T.; Mathias, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 1321. Seto, C. T.; Whitesides, G. M. *J. Am. Chem. Soc.* **1993**, *115*, 1330. Chang, Y.-L.; West, M.-A.; Fowler, F. W.; Lauher, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 5991.

(11) Singlet–triplet energy difference and covalent bond strength (Michl, J. *Acc. Chem. Res.* **1990**, *23*, 127) for systems with more than two electrons, ΔE_{ST}, as a measure of bonding, should be taken between appropriate states. Also, see refs 99b and 113.

(12) Pauli principle: Merzbacher, E. *Quantum Mechanics*; Wiley: New York, 1970; pp 508–516.

(13) Virial theorem: ref 12; p 168.

(14) (a) Kinetic/electrostatic energy Hamiltonian for H_2: Herring, C. *Magnetism*; Rado, G. T., Suhl, H., Eds.; Academic: New York, 1966; Vols. IIB and IV. (b) In the Heitler–London approximation, the expression for the singlet–triplet energy difference in H_2 incorrectly predicts the triplet state to fall below the singlet at large internuclear distances because of the neglect of electron correlation: Heitler, W.; London, F. *Z. Phys.* **1927**, *44*, 455.

(15) For example, CH_2: Schaefer, H. F., III *Science* **1986**, *231*, 1100.

(16) Hund, F. *Z. Phys.* **1925**, *33*, 345.

(17) Hartree–Fock eigenfunctions (Slater determinant): ref 12; pp 535–540.

(18) Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1977**, *99*, 4587.

(19) Heisenberg Hamiltonian: Heisenberg, W. *Z. Phys.* **1928**, *49*, 619. Dirac, P. A. M. *Proc. R. Soc. London* **1929**, *123*, 714. Reference 12, p 528.

(20) Feynmann, R. P. *Statistical Mechanics*; Benjamin/Cummings: Reading, 1972, Chapter 7. McWeeny, R. *Spins in Chemistry*; Academic: New York, 1970; p 29.

(21) White, R. M. *Quantum Theory of Magnetism*; Springer-Verlag: New York, 1983.

(22) Chandler, D. *Introduction to Modern Statistical Mechanics*; Oxford: New York, 1987.

(23) (a) Mattis, D. C. *Theory of Magnetism II*; Springer-Verlag: Berlin, 1985. (b) Experiments on Fe thin films: Bader, S. D.; Moog, E. R. *J. Appl. Phys.* **1987**, *61*, 3729.

(24) Mataga, N. *Theor. Chim. Acta* **1968**, *10*, 372.

(25) Ferromagnetism in dilute metal alloys (giant moment): Mydosh, J. A.; Nieuwenhuys, G. J. In *Ferromagnetic Materials*; Wohlfarth, E. P., Ed.; Elsevier: New York, 1980; Vol. I, Chapter 2, p 71.

(26) Analysis ferromagnetic spin coupling between molecular units: Kollmar, C.; Kahn, O. *Acc. Chem. Res.* **1993**, *26*, 259. McConnell, H. M. *J. Chem. Phys.* **1963**, *39*, 1910. McConnell, H. M. *Proc. Robert A. Welch Found. Conf. Chem. Res.* **1967**, *11*, 144.

(27) Example for exceptionally strong intermolecular ferromagnetic coupling: Inoue, K.; Iwamura, H. *Chem. Phys. Lett.* **1993**, *207*, 551.

(28) Tamura, M.; Nakazawa, Y.; Shiomi, D.; Nozawa, K.; Hosokoshi, Y.; Ishikawa, M.; Takahashi, M.; Kinoshita, M. *Chem. Phys. Lett.* **1991**, *186*, 401.

(29) Chiarelli, R.; Novak, A.; Rassat, J. L. *Nature* **1993**, *363*, 147. Chiarelli, R.; Rassat, A.; Rey, P. *J. Chem. Soc., Chem. Commun.* **1992**, 1081.

(30) For fullerene derivatives with interesting magnetic properties, see: Allemand, P.-M.; Khemani, K. C.; Koch, A.; Wudl, F.; Holczer, K.; Donovan, S.; Gruner, G.; Thompson, J. D. *Science* **1991**, *253*, 301. Tanaka, K.; Zakhidov, A. A.; Yoshizawa, K.; Okahara, K.; Yamabe, T.; Yakushi, K.; Kikuchi, K.; Suzuki, S.; Ikemoto, I.; Achiba, Y. *Phys. Lett. A* **1992**, *164*, 221.

(31) Problem of optically "transparent" magnetic materials: Ziolo, R. F.; Giannelis, E. P.; Weinstein, B. A.; O'Horo, M. P.; Ganguly, B. N.; Mehrotra, V.; Russell, M. W.; Huffman, D. R. *Science* **1992**, *257*, 219.

(32) Superparamagnetic relaxation and quantum tunneling in small magnetic particles: Bucher, J. P.; Douglass, D. C.; Bloomfield, L. A. *Phys. Rev. Lett.* **1991**, *66*, 3052. Awschalom, D. D.; DiVincenzo, D. P.; Smyth, J. F. *Science* **1992**, *258*, 414.

(33) Spin–orbit coupling in molecules: Khudyakov, I. V.; Serebrennikov, Y. A.; Turro, N. J. *Chem. Rev.* **1993**, *93*, 537. Richards, W. G.; Trivedi, H. P.; Cooper, D. L. *Spin-Orbit Coupling in Molecules*; Clarendon: Oxford, 1981.

(34) Craik, D. J.; Tebble, R. S. *Ferromagnetism and Ferromagnetic Domains*; North-Holland and Wiley: New York, 1965. Osborn, J. A. *Phys. Rev.* **1945**, *67*, 351.

(35) Analysis of magnetic data on clusters: (a) Belorizky, E.; Fries, P. H. *J. Chim. Phys.* **1993**, *90*, 1077. (b) Sinn, E. *Coord. Chem. Rev.* **1970**, *5*, 313.

(36) Carlin, R. L. *Magnetochemistry*; Springer-Verlag: Berlin, 1986.

(37) Example of an integrated SQUID: Awschalom, D. D.; McCord, M. A.; Grinstein, G. *Phys. Rev. Lett.* **1990**, *65*, 783.

(38) Reference 36, p 16.

(39) Zeiger, H. J.; Pratt, G. W. *Magnetic Interactions in Solids*; Oxford: Oxford, 1973; p 92.

(40) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 10688.

(41) Bleaney, B.; Bowers, K. D. *Proc. R. Soc. London A* **1952**, 214.

(42) Cairns, C. J.; Bush, D. H. *Coord. Chem. Rev.* **1986**, *69*, 1.

(43) Reference 36, Chapter 11.

(44) Bino, A.; Johnston, D. C.; Goshorn, D. P.; Halbert, T. R.; Stiefel, E. I. *Science* **1988**, *241*, 1479.

(45) Shiomi, D.; Katori, H. A.; Goto, T.; Sawa, H.; Kato, R.; Tamura, M.; Kinoshita, M. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 109.

(46) Wasserman, E.; Snyder, L. C.; Yager, W. A. *J. Chem. Phys.* **1964**, *41*, 1763.

(47) Teki, Y.; Takui, T.; Itoh, K. *J. Chem. Phys.* **1988**, *88*, 6134. Teki, Y.; Takui, T.; Yagi, H.; Itoh, K. *J. Chem. Phys.* **1985**, *83*, 539. Iwasaki, M. *J. Magn. Reson.* **1974**, *16*, 417.

(48) Wertz, J. E.; Bolton, J. R. *Electron Spin Resonance*; Chapman: New York, 1986.

(49) The ESR signal intensity for organic radicals is related to paramagnetic susceptibility (no corrections for diamagnetism are needed).

(50) Example of EPR spin counting for $S > {}^1/_2$: Juarez-Garcia, C.; Hendrich, M. P.; Holman, T. R.; Que, L.; Munck, E. *J. Am. Chem. Soc.* **1991**, *113*, 518.

(51) Berson, J. A. In *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: 1988; Vol. II, Chapter 10.

(52) Standley, K. J.; Vaughan, R. A. *Electron Spin Relaxation Phenomena in Solids*; Plenum Press: New York, 1969. Reference 48, Chapter 9.

(53) (a) Both magnetization and paramagnetic susceptibility, which are related to ESR intensity (ref 49), show similar temperature dependence for intra- and intermolecular spin coupling (section 4.A). (b) Achievement of spin equilibrium, especially for photochemically generated di- and polyradicals radicals in frozen matrices at low temperatures, is important: Bush, L. C.; Heath, R. B.; Berson, J. A. *J. Am. Chem. Soc.* **1993**, *115*, 9830.

(54) ESR spectroscopy in oriented media: Yagi, M.; Uchida, K. S.; Higuchi, J. *J. Magn. Res.* **1987**, *71*, 303. Neumann, R.; Hugerat, M.; Micheli, S.; Natt, A.; Bernitz, M.; Levanon, H. *Chem. Phys. Lett.* **1991**, *182*, 249.

(55) Rajca, A.; Utamapanya, S. *J. Am. Chem. Soc.* **1993**, *115*, 2396.

(56) (a) Jacobs, J. S.; Shultz, D. A.; Jain, R.; Novak, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1993**, *115*, 1744. Novak, J. A.; Jain, R.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 7618. (b) Silverman, S. K.; Dougherty, D. A. *J. Phys. Chem.* **1993**, *97*, 13273.

(57) (a) LaMar, G. N.; Horrocks, D.; Holm, R. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973. (b) Recent review on paramagnetic NMR: Westlund, P.-O. In *Nuclear Magnetic Resonance*; The Royal Society of Chemistry: London, 1991; Vol. 20, Chapter 14, pp 452–496.

(58) Reference 57a, p 11.

(59) Cotton, F. A.; Chen, H.; Daniels, L. M.; Feng, X. *J. Am. Chem. Soc.* **1992**, *114*, 8980. Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915.

(60) NMR spectroscopy of organic radicals: Kreilick, R. W. In ref 57a, Chapter 15.

(61) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. Live, D. H.; Chan, S. I. *Anal. Chem.* **1970**, *42*, 791.

(62) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5890.

(63) Reference 57a, p 624; unpublished data from this laboratory.

(64) Ostfeld, D.; Cohen, I. A. *J. Chem. Educ.* **1972**, *49*, 829.

(65) Proton–proton exchange couplings: Zilm, K. W.; Heinekey, D. M.; Millar, J. M.; Payne, N. G.; Demou, P. *J. Am. Chem. Soc.* **1989**, *111*, 3088. Jones, D. H.; Labinger, J. A.; Weitekamp, D. P. *J. Am. Chem. Soc.* **1989**, *111*, 3087.

(66) Reference 48, p 250.

(67) Andrews, M. P.; Cordes, A. W.; Douglass, D. C.; Fleming, R. M.; Glarum, S. H.; Haddon, R. C.; Marsh, P.; Oakley, R. T.; Palstra, T. T. M.; Schneemeyer, L. F.; Trucks, G. W.; Tycko, R.; Waszczak, J. V.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, *113*, 3559. Cordes, A. W.; Haddon, R. C.; Oakley, R. T.; Schneemeyer, L. F.; Waszczak, J. V.; Young, K. M.; Zimmerman, N. M. *J. Am. Chem. Soc.* **1991**, *113*, 582.

(68) Long-range intramolecular electron–electron exchange interaction was recently reviewed: Eaton, G. R.; Eaton, S. S. *Acc. Chem. Res.* **1988**, *21*, 107.

(69) High-field EPR: Barra, A. L.; Brunel, L. C.; Robert, J. B. *Chem. Phys. Lett.* **1990**, *165*, 107. The high field would decrease the $|J|/\Delta g$ ratios, extend the accessible range of $|J|$ (may even be up to $|J| \approx kT$), and therefore, improve the chances of detection of AB multiplets. Variable-field superconducting magnets up to 7 T are readily available. The following example illustrates the difficulties. For EPR spectroscopy at 3 T = 30 000 G, Δg of 0.002 translates into 30 G; thus, for $|J| = 30\,000$ G $= kT$ at $T \approx 4$ K, $|J|/\Delta g = 10^3$ and the intensity for the outer wings of the AB multiplet, in analogy to the AB multiplet in NMR spectroscopy, will be smaller by about 6–7 orders of magnitude compared to the inner part. When the experiment is carried out at the temperatures where kT is comparable to $|J|$, the sign of J can be determined from relative intensities of the high- and low-field resonances. Thus, the detection will be difficult but not impossible.

(70) (a) CIDNP in diradicals: Closs, G. L. *Adv. Magn. Reson.* **1974**, *7*, 157. Closs, G. L. *J. Am. Chem. Soc.* **1971**, *93*, 1346. (b) J in polymethylene diradicals from variable-field EPR by detection of time-dependent emissive or absorptive polarization: Forbes, M. D. E. *J. Am. Chem. Soc.* **1993**, *115*, 1613.

(71) (a) ENDOR on tetragalvinoxyl: Kirste, B.; Grimm, M.; Kurreck, H. *J. Am. Chem. Soc.* **1989**, *111*, 108. (b) Spin density by ENDOR and related techniques: Okamoto, M.; Teki, Y.; Takui, T.;

Kinoshita, T.; Itoh, K. *Chem. Phys. Lett.* **1990**, *173*, 265. Takui, T.; Kita, S.; Ichikawa, S.; Teki, Y.; Kinoshita, T.; Itoh, K. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 67.

(72) Polarized neutron diffraction: Ressouche, E.; Boucherle, J.-X.; Gillon, B.; Rey, P.; Schweizer, J. *J. Am. Chem. Soc.* **1993**, *115*, 3610.

(73) Reviews on TMM: Dowd, P. *Acc. Chem. Res.* **1970**, *5*, 242. Berson, J. A. In ref 2, p 151. Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446. Borden, W. T. In ref 2, p 1.

(74) TMM: (a, ESR spectroscopy) Dowd, P. *J. Am. Chem. Soc.* **1966**, *88*, 2587. Baseman, R. J.; Pratt, D. W.; Chow, M.; Dowd, P. *J. Am. Chem. Soc.* **1976**, *98*, 5726. (b, IR spectroscopy) *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 119.

(75) TMM (ab initio calculations): Dixon, D. A.; Dunning, T. A.; Eades, R. A.; Kleier, D. A. *J. Am. Chem. Soc.* **1981**, *103*, 2878.

(76) (a) A weak peak at 3.22 eV in electron impact spectrum of butadiene is assigned to a transition from the ground state to ^3B_u state: Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, pp 54–55. (b) An analogous transition to ^3B_u state in hexatriene is found at 2.61 eV: Hudson, B. S.; Kohler, B. E.; Schulten, K. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982; Vol. 6, p 86.

(77) (a) Longuet-Higgins, H. C.; Rector, C. W.; Platt, J. R. *J. Chem. Phys.* **1950**, *18*, 1174. Gimarc, B. M.; Ott, J. J. *J. Am. Chem. Soc.* **1986**, *108*, 4298. Ott, J. J.; Gimarc, B. M. *J. Am. Chem. Soc.* **1986**, *108*, 4303. (b) Connectivity of a heteroatom may affect π-conjugation (and ΔE_{ST}), e.g., in allyl: Bordwell, F. G.; Ji, G.-Z.; Zhang, X. *J. Org. Chem.* **1991**, *56*, 5254. Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459. Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1984**, *106*, 2513. Rajca, A.; Streitwieser, A. *Organometallics* **1988**, *7*, 2215.

(78) McConnell, H. M. *J. Chem. Phys.* **1960**, *33*, 115. Iwamura, H. *Pure Appl. Chem.* **1993**, *65*, 57.

(79) Utamapanya, S.; Rajca, A. *J. Am. Chem. Soc.* **1991**, *113*, 9242.

(80) (a) Review on *m*-quinodimethane and quinoids: ref 51. (b) Rule, M.; Matlin, A. R.; Seeger, D. E.; Hilinski, E. F.; Dougherty, D. A.; Berson, J. A. *Tetrahedron* **1982**, *38*, 787. Goodman, J. L.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5409. Wright, B. B.; Platz, M. *J. Am. Chem. Soc.* **1983**, *105*, 628. Fluorescence spectrum: Migirdicyan, E.; Baudet, J. *J. Am. Chem. Soc.* **1975**, *97*, 7400.

(81) Ab initio calculations on *m*-benzoquinodimethane and *m*-quinone: (a) Fort, R. C., Jr.; Getty, S. J.; Hrovat, D. A.; Lahti, P. M.; Borden, W. T. *J. Am. Chem. Soc.* **1992**, *114*, 7549. (b) Kato, S.; Morokuma, K.; Feller, D.; Davidson, E. R.; Borden, W. T. *J. Am. Chem. Soc.* **1983**, *105*, 1791.

(82) *The Chemistry of Quinoid Compounds*; Patai, S., Rappaport, Z., Eds.; Wiley: New York, 1988.

(83) Numerous authors have used this reasoning.

(84) Spin polarization: ref 48, Chapter 6. Borden, W. T. In ref 2, Chapter 1.

(85) Ovchinnikov, A. A. *Theor. Chim. Acta* **1978**, *47*, 497. Misurkin, I. A.; Ovchinnikov, A. A. *Russ. Chem. Rev.* (*Engl. Trans.*) **1977**, *46*, 967.

(86) Dimethylenecyclobutane-1,3-diyl: (a) Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 1774. Snyder, G. J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1989**, *111*, 3927. (b) Dowd, P.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 2788. (c) Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1989**, *111*, 3773. (d) Pranata, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 1621.

(87) A transition from the ground state to $^3B_{1u}$ excited state corresponds to a peak at 3.9 eV in the electron-impact spectrum of benzene, which is in agreement with phosphorescence spectroscopy: Hudson, B. S.; Ziegler, L. D. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1982, Vol. 5, p 70–74, 118–119.

(88) Conjugation in (a) polyenes: Said, M.; Maynau, D.; Malrieu, J.-P.; Bach, M.-A. G. *J. Am. Chem. Soc.* **1984**, *106*, 571. Reference 76, Vol. 6. (b) Other extended systems: Mullen, K. *Pure Appl. Chem.* **1993**, *65*, 89.

(89) Chichibabin hydrocarbon and its derivatives: Platz, M. S. In Ref 2, Chapter 5. Montgomery, L. K.; Huffman, J. C.; Jurczak, E. A.; Grendze, M. P. *J. Am. Chem. Soc.* **1986**, *108*, 6004. Sugimoto, T.; Sakaguchi, M.; Ando, H.; Tanaka, T.; Yoshida, Z.; Yamauchi, J.; Kai, Y.; Kanehisa, N.; Kasai, N. *J. Am. Chem. Soc.* **1992**, *114*, 1893. Lichtblau, A.; Hausen, H.-D.; Schwarz, W.; Kaim, W. *J. Phys. Chem.* **1993**, *32*, 73.

(90) Mueller hydrocarbon and Schlenk II hydrocarbon: (a) Schmidt, R.; Brauer, H.-D. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 506. (b) Schmidt, R.; Brauer, H.-D. *Z. Natorforsch.* **1972**, *B27*, 1363.

(91) TME, ESR spectroscopy: Dowd, P. *J. Am. Chem. Soc.* **1970**, *92*, 1066. Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1986**, *108*, 7416. Dowd, P.; Chang, W.; Partian, C. J.; Zhang, W. *J. Phys. Chem.* **1993**, *97*, 13408.

(92) TME, ab initio calculations: (a) Nash, J. J.; Dowd, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 10071. (b) Nachtigall, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4743; **1993**, *115*, 270. (c) Reference 18.

(93) 1,2,4,5-Tetramethylenebenzene: (a, singlet ground state) Reynolds, J. H.; Berson, J. A.; Kumashiro, K. K.; Duchamp, J. C.; Zilm, K. W.; Rubello, A.; Vogel, P. *J. Am. Chem. Soc.* **1992**, *114*, 763. Reynolds, J. H.; Berson, J. A.; Scaiano, J. C.; Berinstain, A. B. *J. Am. Chem. Soc.* **1992**, *114*, 5866. (b, triplet ground state) Roth, W. R.; Langer, R.; Bartmann, M.; Stevermann, B.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Muller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 256. Roth, W. R.; Langer, R.; Ebbrecht, T.; Beitat, A.; Lennartz, H.-W. *Chem. Ber.* **1991**, *124*, 2751.

(94) (a) Du, P.; Hrovat, D. A.; Borden, W. T.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 5072. (b) Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 2273, 4362. Lahti, P. M.; Ichimura, A. S.; Berson, J. A. *J. Org. Chem.* **1989**, *54*, 958.

(95) (a) Muller, J.-F.; Muller, D.; Dewey, H. J.; Michl, J. *J. Am. Chem. Soc.* **1978**, *100*, 1629. Fisher, J. J.; Michl, J. *J. Am. Chem. Soc.* **1987**, *109*, 583. (b) Naphthoquinodimethanes by photolysis of bis(chloromethyl)naphthalenes: Biewer, M. C.; Biehn, C. R.; Platz, M. S.; Despres, A.; Migirdicyan, E. *J. Am. Chem. Soc.* **1991**, *113*, 616. Haider, K.; Platz, M. S.; Despres, A.; Lejeune, V.; Migirdicyan, E.; Bally, T.; Haselbach, E. *J. Am. Chem. Soc.* **1988**, *110*, 2318.

(96) (a) Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1975**, *97*, 3857. Buchwalter, S. L.; Closs, G. L. *J. Am. Chem. Soc.* **1979**, *101*, 4688. (b) Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356. Jain, R.; Snyder, G. J. *J. Am. Chem. Soc.* **1984**, *106*, 7294.

(97) Sherill, C. D.; Seidl, E. T.; Schaefer, H. F., III. *J. Phys. Chem.* **1992**, *96*, 3712. Goldberg, A. H.; Dougherty, D. A. *J. Am. Chem. Soc.* **1983**, *105*, 284. Doubleday, C., Jr.; McIver, J. W., Jr.; Page, M. *J. Am. Chem. Soc.* **1982**, *104*, 6533. Pranata, J.; Dougherty, D. A. *J. Phys. Org. Chem.* **1989**, *2*, 161. Conrad, M.; Pitzer, R.; Schaefer, H. F., III. *J. Am. Chem. Soc.* **1979**, *101*, 2245.

(98) Although typical mechanisms for nuclear spin–spin couplings do not involve exchange, the comparison between geminal nuclear spin–spin coupling constants and their electron counterparts in methylene-based diradicals is tempting. Geminal $^{13}C-^{13}C$ coupling constants: Krivdin, L. B.; Della, E. W. *Progress in NMR Spectroscopy*; 1991; Vol. 23, pp 301–610. Vicinal $^1H-^1H$ coupling constants: Barfield, M.; Smith, W. B. *J. Am. Chem. Soc.* **1992**, *114*, 1574.

(99) Cyclopentadienyltrimethylenemethanes: (a) Dowd, P. *Tetrahedron Lett.* **1991**, *32*, 445. Herdnon, W. C.; Ellzey, M. L. *Tetrahedron Lett.* **1991**, *32*, 1399. (b) Nachtigall, P.; Dowd, P.; Jordan, K. D. *J. Am. Chem. Soc.* **1992**, *114*, 4747.

(100) Reviews of triarylmethyls: (a) Sholle, V. D.; Rozantsev, E. G. *Russ. Chem. Rev.* **1973**, *42*, 1011. McBride, J. M. *Tetrahedron* **1974**, *30*, 2009. (b) Ballester, M. *Acc. Chem. Res.* **1985**, *18*, 380.

(101) Triarylmethyl radicals by electrocyclic reactions: Porter, N. A.; Hogenkamp, D. J.; Khouri, F. F. *J. Am. Chem. Soc.* **1990**, *112*, 2402.

(102) Schlenk hydrocarbon I: Schlenk, W.; Brauns, M. *Chem. Ber.* **1915**, *48*, 661, 716.

(103) Kothe, G.; Denkel, K.-H.; Summermann, W. *Angew. Chem., Int. Ed. Engl.* **1970**, *9*, 906. Lockhurst, G. R.; Pedulli, G. F. *J. Chem. Soc. B* **1971**, 329.

(104) Rajca, A.; Utamapanya, S. *J. Org. Chem.* **1992**, *57*, 1760.

(105) Veciana, J.; Rovira, C.; Crespo, M. I.; Armet, O.; Domingo, V. M.; Palacio, F. *J. Am. Chem. Soc.* **1991**, *113*, 2552.

(106) (a) Rajca, A.; Utamapanya, S.; Xu, J. *J. Am. Chem. Soc.* **1991**, *113*, 9235. (b) Rajca, A.; Utampanya, S.; Xu, J. Work in progress; ground states of **27**, **30**, and **31** in frozen solutions are being determined.

(107) (a) Rajca, A.; Utamapanya, S.; Smithhisler, D. *J. Org. Chem.* **1993**, *58*, 5650. (b) Magnetic and ESR studies on an unsubstituted derivative of **34** (R = H) in THF/2-MeTHF indicate singlet ground state: Rajca, A.; Rajca, S. Unpublished results.

(108) Bis-aza derivatives of *m*-benzoquinodimethane: Schaffer, M.; Platz, M. S. *Tetrahedron Lett.* **1989**, *30*, 1225. Haider, K. W.; Migirdicyan, E.; Platz, M. S.; Soundarajan, N.; Despres, A. *Mol. Cryst. Liq. Cryst.* **1989**, *176*, 85.

(109) Coolidge, M. B.; Yamashita, K.; Morokuma, K.; Borden, W. T. *J. Am. Chem. Soc.* **1990**, *112*, 1751.

(110) Hirano, T.; Kumagai, T.; Miyashi, T. *J. Org. Chem.* **1992**, *57*, 876. Hirano, T.; Kumagai, T.; Miyashi, T.; Akiyama, K.; Ikegami, Y. *J. Org. Chem.* **1991**, *56*, 1907.

(111) Platz, M. S.; McBride, J. M.; Little, R. D.; Harrison, J. J.; Shaw, A.; Potter, S. E.; Berson, J. A. *J. Am. Chem. Soc.* **1976**, *98*, 5725.

(112) (a) Planar 2,4-dioxocyclobutane-1,3-diyl, PPP CI calculations: Gleiter, R.; Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1969**, *8*, 214. (b) A reviewer has pointed out that assignment of diradical **40** (X = CH_2, Y = O) as the carrier of the EPR signal is extremely tentative (ref 86b).

(113) Borden, W. T. *Mol. Cryst. Liq. Cryst.* **1993**, *232*, 195.

(114) Greenberg, M. M.; Blackstock, S. C.; Berson, J. A.; Merrill, R. A.; Duchamp, J. C.; Zilm, K. W. *J. Am. Chem. Soc.* **1991**, *113*, 2318. Zilm, K. W.; Merrill, R. A.; Webb, G. G.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1989**, *111*, 1533. Zilm, K. W.; Merrill, R. A.; Greenberg, M. M.; Berson, J. A. *J. Am. Chem. Soc.* **1987**, *109*, 1567. Stone, K. J.; Greenberg, M. M.; Goodman, J. L.; Peters, K. S.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 8088. Du, P.; Hrovat, D. A.; Borden, W. T. *J. Am. Chem. Soc.* **1986**, *108*, 8086.

(115) Roth, W. R.; Kowalczik, U.; Maier, G.; Reisenauer, H. P.; Sustmann, R.; Muller, W. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1285.

(116) Dowd, P.; Chang, W.; Paik, Y. H. *J. Am. Chem. Soc.* **1987**, *109*, 5284.

(117) Calder, A.; Forrester, A. R.; James, P. G.; Luckhurst, G. R. *J. Am. Chem. Soc.* **1969**, *91*, 3724.

(118) Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 4238.

(119) Dvolaitzky, M.; Chiarelli, R.; Rassat, A. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 180.

(120) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1993**, *115*, 874.

(121) Forrester, A. R.; Hay, J. M.; Thomson, R. H. *Organic Chemistry of Stable Free Radicals*; Academic: London, 1968.

(122) (a) Nitronyl nitroxide-based: Reference 45. (b) Verdazyl-based: Reference 60.

(123) Tukada, H. *J. Am. Chem. Soc.* **1991**, *113*, 8991. Tukada, H.; Mutai, K. *Tetrahedron Lett.* **1992**, 6665.

(124) Matsumoto, T.; Ishida, T.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 9952. Matsumoto, T.; Koga, N.; Iwamura, H. *J. Am. Chem. Soc.* **1992**, *114*, 5448.

(125) (a) Nonconjugated di- and polynitroxides: Keana, J. F. W. *Chem. Rev.* **1978**, *78*, 37. (b) Ullman diradical: Alies, F.; Luneau, D.; Laugier, J.; Rey, P. *J. Phys. Chem.* **1993**, *97*, 2922.

(126) Tris(3,5-di-*tert*-butyl-4-oxophenylene)methane: Bock, H.; John, A.; Havlas, Z.; Bats, J. W. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 416.

(127) Assuming that attachment of the second identical site with unpaired electron to the formal coupling unit in the monoradical (to form diradical) increases the spin densities in the coupling unit by the same factor within the series, this conjecture is equivalent to the following: $J \propto$ (spin density in ferromagnetic unit of diradical)^2. According to the studies of the related dianions and radical anions, the diradicals, on the basis of a 1,3-connected benzene coupling unit, should possess a localized electronic structure (sections 9 and 10); thus, such diradicals can be viewed as ensembles of two "monoradicals" interacting in the coupling unit. (For **3** and its derivatives, the non-disjoint half-occupied NBMO's, which describe a major portion of spin density and exchange interaction, can be made predominantly coincident over the 1,3-connected benzene coupling unit.)

(128) Electron–nuclear coupling constants for monoradicals: (a, benzyl) Carrington, A.; Smith, I. C. P. *Mol. Phys.* **1965**, *9*, 137. Reference 121, p 58. (b, triphenylmethyl) Reference 121, p 60. Reference 128d. (c, *tert*-butylphenyl nitroxide) Reference 121, p 202. (d, tris(2,6-dimethoxyphenyl)methyl) Sabacky, M. J.; Johnson, C. S., Jr.; Smith, R. G.; Gutowsky, H. S.; Martin, J. C. *J. Am. Chem. Soc.* **1967**, *89*, 2054. (e, perchlorotriphenylmethyl) Falle, H. R.; Luckhurst, G. R.; Horsfield, A.; Ballester, M. *J. Chem. Phys.* **1969**, *50*, 258. Pyramidalization at the triaarylmethyl carbon may affect electron-^{13}C coupling. (f, sterically hindered alkylarylnitroxides) Jakobsen, H. J.; Torsell, K. *Tetrahedron Lett.* **1970**, 5003. Jacobsen, H. J.; Petersen, T. E.; Torsell, K. *Tetrahedron Lett.* **1971**, 2913. Calder, A.; Forrester, A. R.; Emsley, J. W.; Luckhurst, G. R.; Storey, R. A. *Mol. Phys.* **1970**, *18*, 481. Reference 121, pp 202–203. (g, triphenylaminium) van Willigen, H. *J. Am. Chem. Soc.* **1967**, *89*, 2229. Reference 121, Chapter 6. (h, diarylamino radicals) Reference 121, p 114. (i, diarylmethyls) Reference 121, p 59. (j, phenoxyls) Reference 121, p 289. (k, triarylsilyls) Lim, W.-L.; Rhodes, C. J. *J. Chem. Soc., Chem. Commun.* **1991**, 1228. Sakurai, H.; Umino, K.; Sagiyama, H. *J. Am. Chem. Soc.* **1980**, *102*, 6837. Gynane, M. J. S.; Lappert, M. F.; Riley, P. I.; Riviere, P.; Riviere-Baudet, M. *J. Organomet. Chem.* **1980**, *202*, 5.

(129) Ivanov, C. I.; Tyutyulkov, N.; Karabunarliev, S. *J. Magn. Mater.* **1990**, *92*, 171, and references therein. Li, J.; Tang, A. *Chem. Phys. Lett.* **1990**, *170*, 359.

(130) (a) Yoshizawa, K.; Chano, A.; Ito, A.; Tanaka, K.; Yamabe, T.; Fujita, H.; Yamauchi, J.; Shiro, M. *J. Am. Chem. Soc.* **1992**, *114*, 5994. The reported stability of this triaminium-based triradical contrasts with propensity of triphenylaminium toward dimerization (ref 121, Chapter 6). Triarylphosphonium-based radicals are reported even less stable: Culcasi, M.; Berchadsky, Y.; Gronchi, G.; Tordo, P. *J. Org. Chem.* **1991**, *56*, 3537. (b) Weissman, S. I.; Kothe, G. *J. Am. Chem. Soc.* **1975**, *97*, 2538.

(131) Brickmann, J.; Kothe, G. *J. Chem. Phys.* **1973**, *59*, 2807. Kothe, G.; Ohmes, E.; Brickmann, J.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1971**, *10*, 938. Schmauss, G.; Baumgartel, H.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1965**, *4*, 596.

(132) Veciana, J.; Rovira, C.; Ventosa, N.; Crespo, M. I.; Palacio, F. *J. Am. Chem. Soc.* **1993**, *115*, 57.

(133) Kanno, F.; Inoue, K.; Koga, N.; Iwamura, H. *J. Phys. Chem.* **1993**, *97*, 13267.

(134) Seeger, D. E.; Berson, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5144; 5146. Seeger, D. E.; Lahti, P. M.; Rossi, A. R.; Berson, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 1251.

(135) Carilla, J.; Julia, L.; Riera, J.; Brillas, E.; Garrido, J. A.; Labarta, A.; Alcala, R. *J. Am. Chem. Soc.* **1991**, *113*, 8281.

(136) Rajca, A.; Utamapanya, S.; Thayumanavan, S. *J. Am. Chem. Soc.* **1992**, *114*, 1884.

(137) Rajca, A.; Utamapanya, S. *Liq. Cryst. Mol. Cryst.* **1993**, *232*, 305.

(138) Utamapanya, S.; Kakegawa, H.; Bryant, L.; Rajca, A. *Chem. Mater.* **1993**, *5*, 1053.

(139) Vicens, J., Bohmer, V., Eds. *Calixarenes*; Kluwer: Dordrecht, 1991.

(140) (a) The question of electron transfer rate vs spin coupling was mainly raised for weakly antiferromagnetically coupled radical pairs, i.e., two-orbital two-electron model: Bertrand, P. *Chem. Phys. Lett.* **1985**, *113*, 104. Kaberkorn, R.; Michel-Beyerle, M. E.; Marcus, R. A. *Proc. Natl. Acad. Sci. U.S.A.* **1979**, *76*, 4185. Marcus, R. A. *Chem. Phys. Lett.* **1987**, *133*, 471. (b) There is a vast quantity of literature concerning spin coupling and electron transfer via non-π-conjugated linkages, e.g.: Closs, G. L.; Forbes, M. D.; Piotrowiak, P. *J. Am. Chem. Soc.* **1992**, *114*, 3285. Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

(141) (a) Semiquinones: Reference 121, p 292–293. For a recent application to construct organometallic high-spin species, see: Adams, D. M.; Rheingold, A. L.; Dei, A.; Hendrickson, D. N. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 391. (b) Wurster salts: Reference 121, Chapter 6.

(142) Radical anion and radical cation of chichibabin perchlorocarbon: Ballester, M.; Pascual, I. *Tetrahedron Lett.* **1985**, *26*, 5589. Ballester, M.; Castaner, J.; Riera, J.; Pascual, I. *J. Am. Chem. Soc.* **1984**, *106*, 3365.

(143) (a) Utamapanya, S.; Rajca, A. In preparation. (b) It is tempting to conjecture that electron-transfer rate (k_{el}) is extremely sensitive to the sign of J, e.g., k_{el} vs J plot might be represented by a sigmoidal curve.

(144) Radical anion of TME in the gas phase: Lee, J.; Chou, P. K.; Dowd, P.; Grabowski, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 7902.

(145) (a) Almlof, J. E.; Feyereisen, M. W.; Jozefiak, T. J.; Miller, L. L. *J. Am. Chem. Soc.* **1990**, *112*, 1206. Jozefiak, T. H.; Almlof, J. E.; Feyereisen, M. W.; Miller, L. L. *J. Am. Chem. Soc.* **1989**, *111*, 4105. (b) Yang, B.; Liu, L.; Katz, T. J.; Liberko, C. A.; Miller, L. L. *J. Am. Chem. Soc.* **1991**, *113*, 8993.

(146) (a) Nelsen, S. F.; Thompson-Colon, J. A.; Kaftory, M. *J. Am. Chem. Soc.* **1989**, *111*, 2809. (b) Maslak, P.; Augustine, M. P.; Burkey, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5359.

(147) Triplet and singlet energy transfer: Gust, D.; Moore, T. A.; Moore, A. L.; Devadoss, C.; Liddell, P. A.; Hermant, R.; Nieman, R. A.; Demanche, L. J.; DeGraziano, J. M.; Gouni, I. *J. Am. Chem. Soc.* **1992**, *114*, 3590.

(148) Rajca, A. *J. Am. Chem. Soc.* **1990**, *112*, 5889.

(149) All potentials are with respect to the ferrocene/ferrocenium couple in THF/tetrabutylammonium perchlorate at 0.51 V.

(150) Review on carbenes, Sander, W.; Bucher, G.; Wierlacher, S. *Chem. Rev.* **1993**, *93*, 1583.

(151) Nakamura, N.; Inoue, K.; Iwamura, H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 872. Nakamura, N.; Inoue, K.; Iwamura, H.; Fujioka, T.; Sawaki, Y. *J. Am. Chem. Soc.* **1992**, *114*, 1484. Fujita, I.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K.; Miko, F.; Sawaki, Y.; Iwamura, H.; Izuoka, A.; Sugawara, T. *J. Am. Chem. Soc.* **1990**, *112*, 4074. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1984**, *106*, 6449. Sugawara, T.; Bandow, S.; Kimura, K.; Iwamura, H.; Itoh, K. *J. Am. Chem. Soc.* **1986**, *108*, 368. Takui, T.; Itoh, K. *Chem. Phys. Lett.* **1973**, *19*, 120. Itoh, K. *Chem. Phys. Lett.* **1967**, *1*, 235. Wasserman, E.; Murray, R. W.; Yager, W. A.; Trozzolo, A. M.; Smolinsky, G. *J. Am. Chem. Soc.* **1967**, *89*, 5076.

(152) Murata, S.; Iwamura, H. *J. Am. Chem. Soc.* **1991**, *113*, 5547.

(153) Matsushita, M.; Nakamura, T.; Momose, T.; Shida, T.; Teki, Y.; Takui, T.; Kinoshita, T.; Itoh, K. *J. Am. Chem. Soc.* **1992**, *114*, 7470, and ref 23 therein.

(154) Ling, C.; Minato, M.; Lahti, P. M.; van Willigen, H. *J. Am. Chem. Soc.* **1992**, *114*, 9959.

(155) (a) Jesse, R. E.; Biloen, P.; van Voorst, J. D. W.; Hoijtink, G. J. *Mol. Phys.* **1963**, *6*, 633. Hexachlorobenzene dication: Wasserman, E.; Hutton, R. S.; Kuck, V. J.; Chandross, E. A. *J. Am. Chem. Soc.* **1974**, *96*, 1965. Coronene dication: Krusic, P. J.; Wasserman, E. *J. Am. Chem. Soc.* **1991**, *113*, 2322. Coronene dianion: Glasbeek, M.; van Voorst, J. D. W.; Hoijtink, G. J. *J. Chem. Phys.* **1966**, *45*, 1852. Pentaphenylcyclopentadienyl cation: Breslow, R.; Chang, H. W.; Yager, W. A. *J. Am. Chem. Soc.* **1963**, *85*, 203. (b) Recent theoretical studies: Krogh-Jespersen, K. *J. Am. Chem. Soc.* **1991**, *113*, 417. Sygula, A.; Rabideau, P. W. *J. Am. Chem. Soc.* **1991**, *113*, 7797.

(156) For leading references, see: Breslow, R.; Maslak, P.; Thomaides, J. S. *J. Am. Chem. Soc.* **1984**, *106*, 6453. Thomaides, J. S.; Maslak, P.; Breslow, R. *J. Am. Chem. Soc.* **1988**, *110*, 3970.

(157) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927.

(158) Polarons: *Handbook for Conducting Polymers*, Skotheim, T. A., Ed.; Dekker: New York, 1986; Vols. 1 and 2. Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Am. Chem. Soc.* **1992**, *114*, 2440.

(159) (a) Radical anions of alkyl-linked bis(anthracenes): Becker, B.; Bohnen, A.; Ehrenfreund, M.; Wohlfarth, W.; Sakata, Y.; Huber, W.; Mullen, K. *J. Am. Chem. Soc.* **1991**, *113*, 1121. (b) Trioxytriangulene: Allinson, G.; Bushby, R. J.; Paillaud, J.-L.; Oduwole, D.; Sales, K. *J. Am. Chem. Soc.* **1993**, *115*, 2062. (c) Radical anion of 1,3-phenylene-linked bis(naphthalenes): Tukada, H. *Mol. Cryst. Liq. Cryst.* **1993**, *233*, 9. (d) Gregorious, H.; Baumgarten, M.; Reuter, R.; Tyutyulkov, N.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1653.

(160) Oligo(9,10-anthrylenes) polyanions: Baumgarten, M.; Muller, U.; Bohnen, A.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 448.

(161) Ion pairing: Streitwieser, A. *Acc. Chem. Res.* **1984**, *17*, 353.

(162) Ion pairing in radical anions: Szwarc, M. *Prog. Phys. Org. Chem.* **1968**, *6*, 323.

(163) Kaisaki, D. A.; Chang, W.; Dougherty, D. A. *J. Am. Chem. Soc.* **1991**, *113*, 2764.