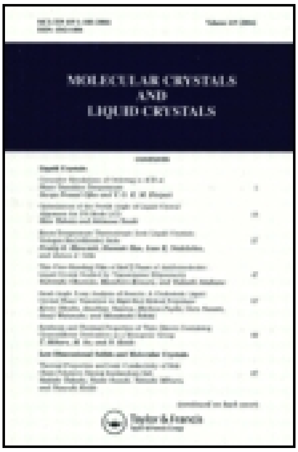

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Interrupted σ-Bonds in Organic Materials with Colligative Magnetic Properties

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INTERRUPTED σ-BONDS IN ORGANIC MATERIALS WITH COLLIGATIVE MAGNETIC PROPERTIES

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Abstract Solutions of tris(2,6-dimethoxyphenyl)methyl radical (**1**) and lithium salts form solids showing unusual magnetic behavior. The propeller-shaped radicals, with their tripods of nucleophilic oxygens, are preorganized polydentate ligands. By coordination with small alkali metal cations the radicals may stack, enforcing spin-spin interactions in extended chains of paramagnets. *Ab initio* calculations on a linear $H_3C{\cdot}Li^+{\cdot}CH_3$ model shows that high-spin (ferromagnetic) electron coupling is favored for a wide range of radical-Li^+ distances.

Keywords: organic ferromagnet, molecular magnet, triarylmethyl radical, diradical, triplet state, cryptand

INTRODUCTION

In 1985, we combined solutions of the stable free radical tris(2,6-dimethoxyphenyl)methyl (**1**) with solutions of lithium salts in order to study the spectroscopic consequences of complexation of these organic radicals with metal

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ions. Precipitates that formed upon mixing frequently gave unusual, intense ESR spectra. Some of the spectra were very broad, whereas others had considerable fine and hyperfine structure, and often *g*-shifts deviated markedly from the free electron value.[1] Failing to establish a structural basis for the surprising magnetic behavior of our precipitates by growing single crystals from the precipitated solids we hypothesized that colligative magnetic properties might be a possible explanation for our puzzling and highly variable phenomena.

Crystals of **1** behaved as a paramagnet following the Curie-Weiss law; the field dependence of the magnetization was linear. On the other hand, the magnetic susceptibility of the "salted" precipitates showed a field-dependent hysteresis, a classic signature of ferromagnetism. Hysteretic phenomena characterized by small saturation moments are to be regarded with suspicision. Nevertheless we were encouraged to pursue a rational approach to organic ferromagnets because of striking structural elements of the constituent radicals that quickly suggest extended structures with cooperative interactions between the isolated carbon based radicals.

Tris(2,6-dimethoxyphenyl)methyl (**1**), originally synthesized by J.C. Martin, is a remarkably robust organic free radical.[2] It is monomeric and air-stable presumably by virtue of the fact that in its D_3 propeller conformation the central carbon bearing the lone electron is protected from above and below by crowns of methoxy groups.[3] The principles developed in selective ion binding studies of polyether ligands[4] suggest that these methoxy groups can serve as binding sites for metal cations. Two radicals can "sandwich" a cation of appropriate size between them in a distorted octahedral pocket,[5,6] fixing their relative orientation. The spatial relationships in such controlled radical aggregation can, in turn, dictate intermolecular electron coupling[7,8] in "interrupted σ-bonds"—radical pairs or oligomers in which electron interactions are mediated by metal cations. An extended stack formed by this complexation mechanism would have at its core a linear array of one-electron carbon-centered *p*-orbitals interacting through metal ions.[9]

Figure 1 portrays these "interrupted σ-bonds" in radical pairs (**2**) or oligomers (**3**). CPK models, molecular mechanics calculations, UV-Vis studies and X-ray structures of **1** and related species (*vide infra*) support the metal ion-radical ether tripod binding model. An illustration of the disposition of a pair of radicals in a dimeric species such as **2** based on a reasonable ground state conformation of the monomer is shown in Figure 2.

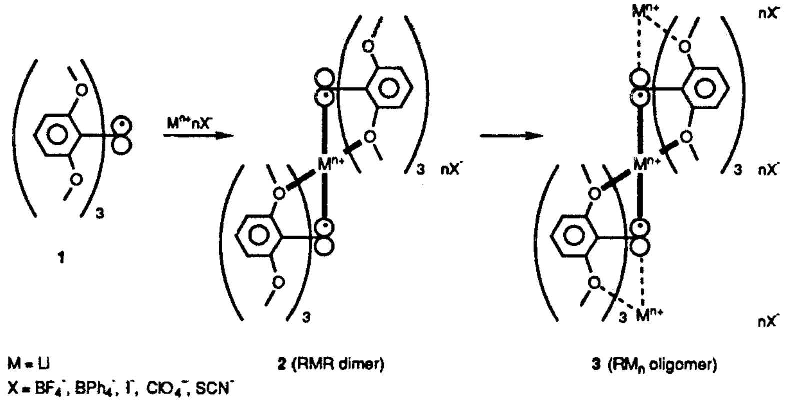


Figure 1. Schematic illustration of the dimeric and oligomeric association of tris(2,6-dimethoxyphenyl)methyl (1) with lithium cations.

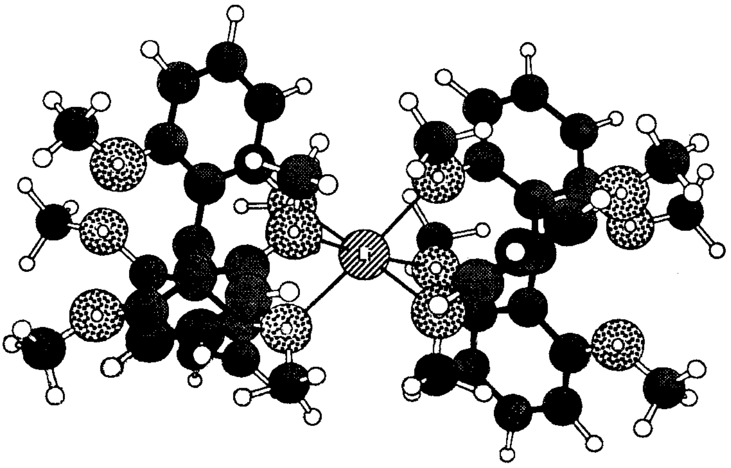


Figure 2. Optimized structure of the RMR dimer calculated by the molecular mechanics methods in PCModel. Here the individual radicals adopt a homochiral, staggered conformation.

In an isolated atom or molecule, a pair of electron spins may be coupled in a closed shell singlet, open shell singlet, or triplet state. In extended odd-electron systems, these three modes correspond, respectively, to diamagnetic, antiferromagnetic, and ferromagnetic coupling. In this work we seek to control magnetic interactions—specifically, the sign and magnitude of nearest neighbor exchange integrals—between pairs of simple paramagnets such as **1** through the use of metal ion complexation which will enforce well-defined spatial relationships during crystallization.[10] Such control could lead to organic materials with permanent magnetic moments. The quest for organic and molecular magnets[11,12] has grown so much in the last five years that an ACS symposium on the subject was held in 1989 the proceedings were published in a special edition of this journal,[13] yet to date there are only a few molecular substances that clearly exhibit long-range magnetic interactions, much less ferromagnetism.[14,15]

MAGNETIC SUSCEPTIBILITY

A hysteretic response[16] of the magnetization with respect to applied field was reproducibly observed in the blue-grey precipitates obtained when combining solutions of **1** and $LiBF_4$ under a nitrogen atmosphere. Measurements were carried out on a Quantum Design SQUID magnetometer. The saturation moment at 5K was 4 EMU/mol indicating that only a fraction of one percent of the material could have been ferromagnetic. The hysteresis persisted up to 100 K. The temperature dependence of the magnetization appears consistent with a Brillouin function.

In contrast to the salt-treated samples, radical **1** showed simple paramagnetism and lithium salts were diamagnetic thus suggesting that the observed ferromagnetism must somehow derive from the *combination* of the radical with the lithium salt. The tetrafluoroborate anion was replaced by the similar-sized perchlorate or iodide ions without qualitatively affecting the magnetic properties. This result indicated that the bulk behavior is not due to chemistry involving the counterion.

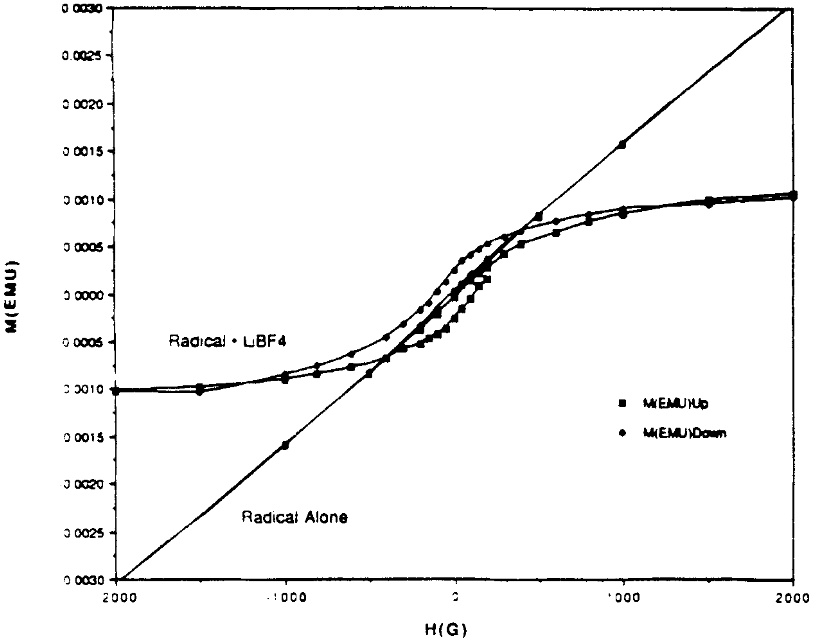
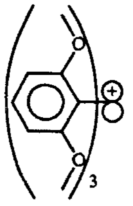


Figure 3. Plot of magnetization M (EMU) vs magnetic field strength H (Gauss) at 5K for radical **1** alone and for its complex with $LiBF_4$.

Despite the rigorous purification of all reagents and solvents employed in the synthesis of **1·LiBF4** it is difficult to emphatically rule out ferromagnetic contaminants in polycrystalline or amorphous materials. Martin's original synthesis used Cr(II) ion as the reducing agent; zinc works well too. We sought to avoid metals, such as Cr or Zn that could easily carry ferrous contaminants. Ultimately we reduced salts of the cation with ascorbic acid (vitamin C) in aqueous solutions; the neutral radical prepared in this way migrates into a nonpolar organic solvent layer, where it is easily separated and isolated. Atomic emission photometry showed iron at the level of the background in all samples regardless of their magnetic susceptibility.

We subsequently synthesized tris(2-methoxy-4,6-dimethylphenyl)methyl (**3**), an oxygen sensitive radical. Precipitates formed on combination with lithium were diamagnetic. This result reinforces the notion that the ferromagnetism seen in **1·LiBF4** is unique to a radical which can bind metals on both faces and is not simply due to an artifact such as iron particle production by reduction of adventitious iron salts.



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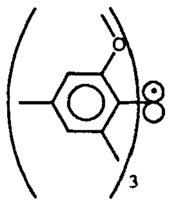

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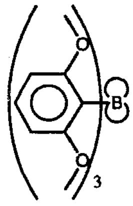


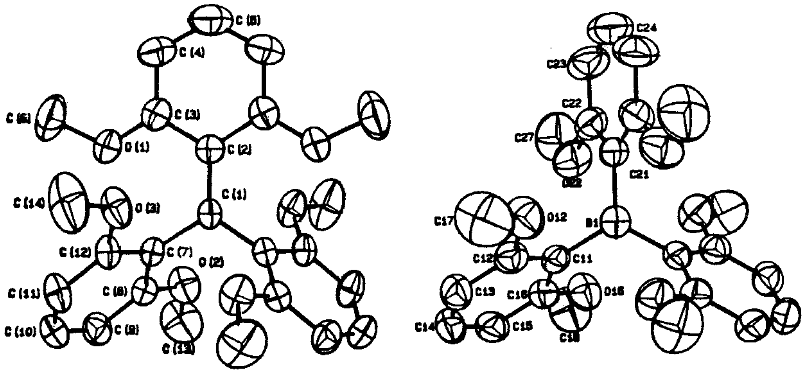
6

X-RAY DIFFRACTION STUDIES OF THE BINDING SITE

To date we have not obtained single crystals of metal complexes of **1**. Our efforts have in part been frustrated by the fact that Li^+ appears to catalyze the oxidation of the radicals and the persistent cation **4** in solution inhibits the crystal growth process. Consequently, we have focused on characterizations of the binding site via diffraction studies of the uncomplexed monomeric species and some close structural analogues.[17]

Brick-red monoclinic prisms of **1** were obtained by evaporation of an ether solution. In contrast to the solution conformation as assessed by ESR,[2] the radicals adopt an unusual conformation in the solid state. One aryl ring is twisted out of the central methyl carbon plane by only 12° while the other two rings are twisted by 61° (Figure 4). This structure represents a point well along the way to the transition state for the two-ring flip racemization pathway[18] and its large deviation from the D_3 ground state is unprecedented for triaryl-X propellers. Crystals of **1** are difficult to obtain reproducibly and we believe that they represent a kinetically stable solid state structure which may be far from the relaxed solution conformation.

The ether tripod binding site is poorly represented by the crystal structure of the radical, because of the dissymmetric twists of the rings. A more realistic picture of the binding site is provided by the crystal structure of the corresponding cation tetrafluoroborate salt (**4**·BF_4). In contrast to radical **1**, cation **4** is not crystallographically planar—the crystals are triclinic—but nevertheless the conformation is approximately D_3 with all the rings similarly twisted out of the plane defined by the central methyl carbon substituents. The crystal structure is shown in Figure 5 alongside the MMP2 calculated structure of the radical. The average distance between the oxygen atoms is 3.9 Å which defines a pocket that could form half of an octahedral binding site for small cations. This distance can be varied substantially over a small range of energies by adjusting the torsion angles of the constituent aryl rings.



1 **6**

Figure 4. View normal to the least squares plane of **1** and **6**.

Prompted by complications introduced by the oxidation chemistry of radical **1**, we synthesized a diamagnetic redox inactive structural analogue. This compound, borane **6**, is a white solid which is easily handled in the absence of Bronsted acids. It also has an approximate D_3 structure in the solid state (Figure 4). The combined structural evidence points to an anomalous solid state structure for **1**.[19]

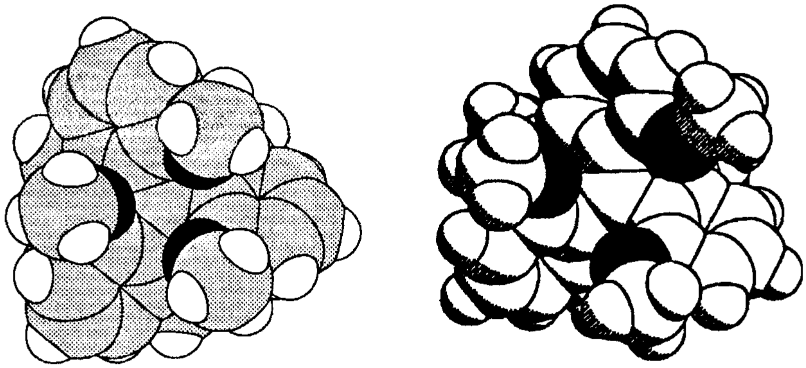


Figure 5. (a) MMP2 ground state conformation of **1** and (b) X-ray structure of **4** (from **4•BF4**).

AB INITIO MODELING

Multiconfigurational self-consistent field calculations with configuration interaction (MCSCF-CI) are generally necessary to properly represent the behavior of diradicals. It is particularly challenging to correctly position the relative energies of singlet and triplet states of such systems.[4] However, with simple single-reference theory such as that available in the Gaussian86 program[20], we have made preliminary attempts to assess the sign and magnitude of magnetic interactions between our lithium coupled radicals. We have examined and compared the total and one-electron frontier orbital energies of calculated singlet and triplet states for the simplest model system, $H_3C{\bullet}Li^+{\bullet}CH_3$.

Requisite for the positive exchange interaction between a pair of electrons is their occupancy in a pair of degenerate or near-degenerate orbitals. The linear interaction of two carbon *p*-orbitals on radical centers, communicating via the 2*s* and 2*p* orbital set of a lithium cation, can be described by a simple qualitative interaction diagram, shown below. For "stretched" ethane, with the radicals separated by ca. 5 Å, the symmetric (f_1) and antisymmetric (f_2) combinations of carbon 2*p* orbitals are nearly equi-energetic. The lithium 2*s* orbital can then mix with f_1 to form A_{1g} bonding and antibonding orbitals. If lithium only contributed an *s* orbital, like the hydrogen in the C-C protonated ethane ion $(H_3C\cdot\cdot H\cdot\cdot CH_3)^+$, the orbital pattern would resemble that for an allyl fragment with an ascending ladder of three orbital levels,[21] and a singlet ground state (GS) would be expected. However, the $2p_z$ orbital on lithium, while energetically less well matched to carbon than the $2s$, benefits from better overlap with the antisymmetric f_2 orbital combination, resulting in split A_{2u} bonding/antibonding levels. If the f_1-Li $2s$ and f_2-Li $2p_z$ interactions are competitive, molecular orbitals A_{1g} and A_{2u} will remain close in energy as the methyls converge on the lithium cation. Except for the orbital contributions from Li, the A_{1g} and A_{2u} orbitals shown below occupy the same regions of space; thus if they are degenerate or nearly so, electron repulsion should favor a triplet, or ferromagnetically coupled spin state. Such a situation would be an accidental example of a superexchange-coupled triplet, where the orbital level degeneracy was fortuitously maintained by competing bonding effects, not by the symmetry properties of the system.

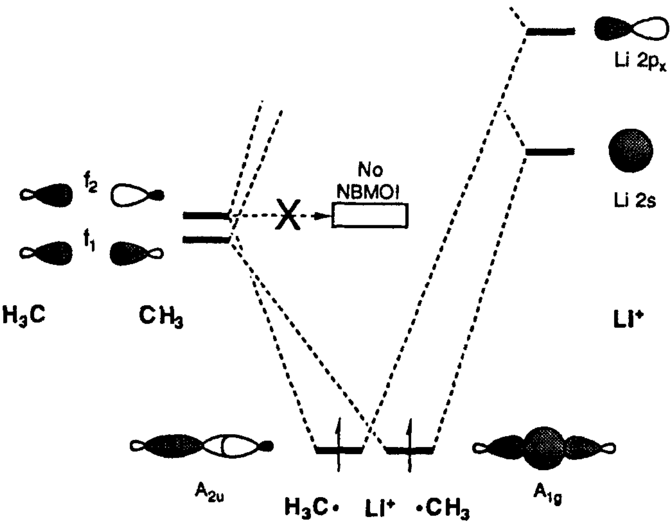


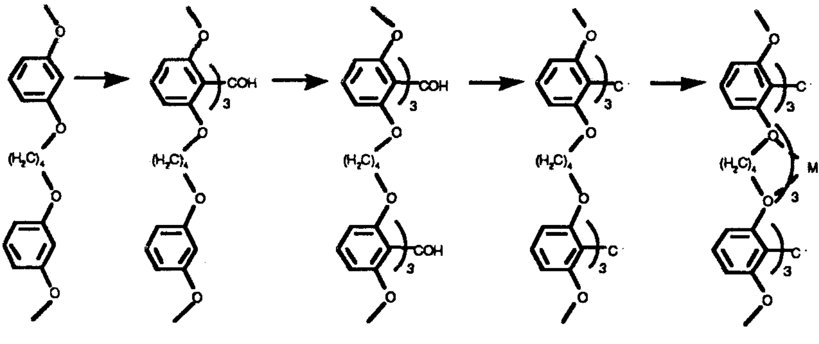
Figure 6. Qualitative MO diagram schematically indicating the coincidental near-degeneracies from mixing a pair of C_{2p} orbitals with a Li$_{2p_z}$ orbital and a Li$_{2s}$ orbital.

Ab initio calculations on $H_3C{\bullet}Li^+{\bullet}CH_3$, a model metal-mediated radical pair, suggests that the triplet-coupled state lies low in energy, perhaps low enough to be the ground state. It is notable that in the UHF wavefunctions (3-21G and 6-31G* basis sets) for the triplet state of this model, the one-electron energies of the A_{2u} and A_{1g} molecular orbitals stay within 0.015 H of each other from $r_{CLi}=\infty$ to 2.0 Å; they are nearly degenerate at the optimized distance, and remarkably, the A_{2u} orbital falls *below* the A_{1g} at closer approaches. Geometry differences between singlet and triplet optimized structures are small, and vibrational analysis on the triplet shows that the linear form is a local minimum. The system is calculated to be bound, relative to separated CH_3 + CH_3 + Li^+, by roughly 28 Kcal/mol.

We have begun MCSCF calculations using the GAMESS[22] program on the $H_3C{\bullet}Li^+{\bullet}CH_3$ system and the related but simpler four-electron case of linear $H{\bullet}Li^+{\bullet}H$, an "interrupted" hydrogen molecule. Initial results place the singlet and triplet states of both these systems very close in energy, with the triplet always lying just slightly lower. These calculations avoid the spin-contamination problems which inevitably arise with the UHF method. We expect to complete CASSCF (Complete Active Space SCF) analysis with a polarized basis set for the $H_3C{\bullet}Li^+{\bullet}CH_3$ model system.

OUTLOOK

By isolating the functional diradical unit (**2**) of our proposed polymeric chains, the intrastack electronic coupling can be studied, varied empirically, and analyzed in terms of current theory of diradicals. In progress is the synthesis of a diradical complexant in which a pair of radicals of the type **1** are covalently linked through methylene bridges (Figure 7). The polycyclic compound **7** resembles the cryptands which have distorted octahedral oxygen pockets that are bi-capped with nitrogen atoms.[23] The [2.2.2]cryptand and its benzannelated analogues bind a wide variety of cations.[24] Species **7** is also reminiscent of spherands[25] which are hosts comprised of tethered aryl ethers.



7 **8**

Figure 7. Schematic synthesis of diradical **7** and complex **8**.

The propeller-shaped triarylmethyl radicals in the complexant **7** may adopt homochiral or heterochiral relationships to one another. CPK models can be constructed of either conformation; they are both flexible and the size of the interior cavity is easily varied by changing the pitch of the constituent triarylmethyl propellers. This degree of freedom in the molecular architecture of **7** may render the nucleophilic pocket a general host for cationic guests. A variety of complexes **8** will be prepared from diradical **7** and metal cations. Structural and spectroscopic investigations of these isolated "interrupted σ-bonds" will inform our understanding of the $C{\bullet}M^{+}{\bullet}C$ orbital interactions.

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