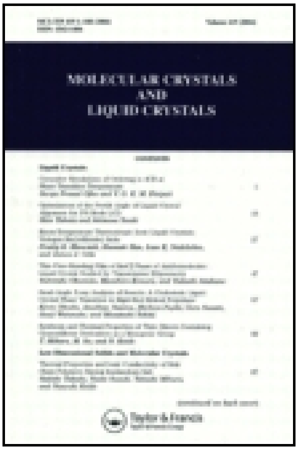

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Donors, Acceptors and the FOM Model

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DONORS, ACCEPTORS AND THE FOM MODEL

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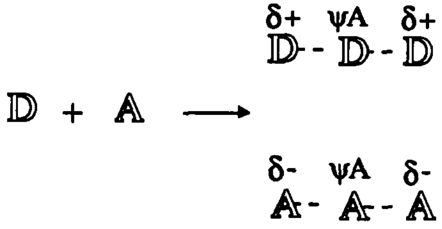
Abstract Electron donors and acceptors designed primarily for the formation of ferromagnetic organic metals (FOM) are described. The synthesis of molecules of trigonal symmetry which are either electron rich or electronegative as well as charge transfer complexes derived from them are described. The donor is a derivative of trimethylenemethane and the acceptor is 1,3,5-tris(tricyanovinyl)benzene.

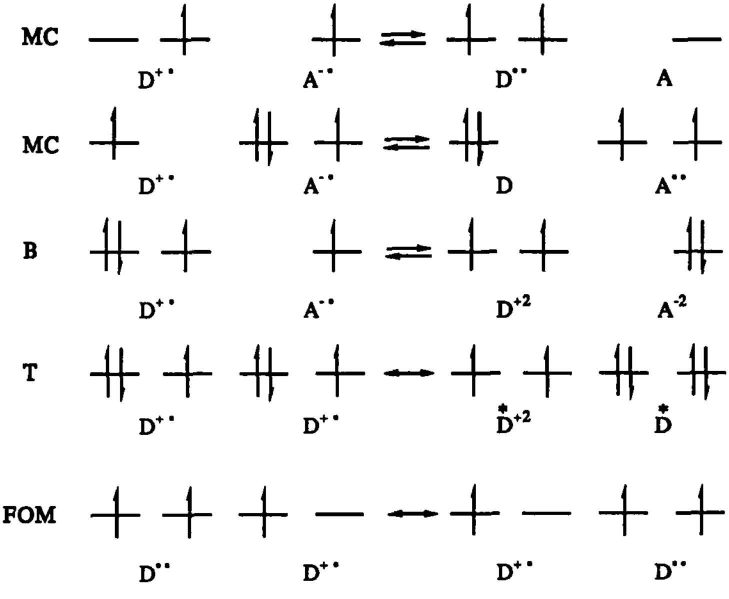
INTRODUCTION

Previous presentations in this symposium have dealt with all the different approaches to produce molecular and/or organic ferromagnetic solids[1]. Our work is based on a combination of concepts derived from the special type of charge transfer complexes which lead to organic metals and superconductors, and from the McConnell model for organic ferromagnets which was originally suggested for insulating or semiconducting charge transfer complexes. One major hurdle to be surmounted with previous approaches to organic ferromagnets employing charge transfer complexes is the problem of translating intramolecular, intradimer (a donor-acceptor pair) or intrastack ferromagnetic coupling to the *bulk*; i.e., there is no mechanism suggested to prevent two adjacent stacks from having an antiferromagnetic ordering of their electronic spins relative to each stack. Another important consideration, pointed out by Kinoshita and Callen[2], which previous models do not address, is the fact that ferromagnetism is a result of *extended interactions* much like those observed in electronic conduction bands of metals.

Contrary to all previous systems described in this symposium, the organic metals composed of charge transfer complexes have their donors and acceptors segregated into separate stacks and the molecules which make up the stacks bear a partial charge; i.e. the stacks are mixed valent[3] and charge and spin are *delocalized throughout the stack* on essentially a "supermolecular orbital" made up of molecular orbitals belonging to the individual donors and acceptors. A schematic representation is shown below:



As can be seen above, (ΨA means "pseudo acceptor") essentially every alternating molecule within a metallic stack is a "radical cation" and has a doublet spin multiplicity. We reasoned that if the "neutral" molecules within the stack were diradicals of triplet spin multiplicity, then by virtue of the fact that they are part of a metallic "band", the entire stack would be ferromagnetic[4] as shown schematically below in the line labeled "FOM".



The other lines in the diagram above correspond to various modifications of the McConnell model (MC, McConnell; B, Breslow; T, Torrance), as described earlier by Breslow[1]. Not shown in the scheme are the closed shell counterions in the last two lines

(T and FOM). However, calculations by Yamaguchi[5] on a particular $D^{\uparrow\uparrow}$ (HTTM, see below) indicate that the the FOM stacks may in fact be ferrimagnetic where the triplet spins and the doublets are antiferromagnetically coupled but, since the triplet has $S = 1$ and the doublet has $S = 1/2$, the result is a net magnetic moment for the stack, in direct analogy to the mixed metal coordination complexes of O. Kahn[1]. If Yamaguchi's calculated prediction were to be proved correct, then, in analogy to some of O. Kahn's systems[1], our FOM stacks could also be ferrimagnetically ordered with respect to each other and we would have a bulk organic ferrimagnet akin to Fe_3O_4.

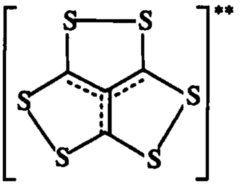
The major problem with the FOM model rests with the $D^{\uparrow\uparrow}$ species; it would have to be a ground state (or very close lying excited state) triplet neutral diradical[6]. In the past we proposed[4] approaches to the design of such molecules. It should be pointed out that the FOM model applies equally well to mixed valent stacks of acceptor molecules ($A^{\uparrow\uparrow}$ and $A^{\uparrow-}$ in place of $D^{\uparrow\uparrow}$ and $D^{\uparrow+}$). In this presentation, we disclose the preparation of the immediate precursor of hexathiotrimethylenemethane (HTTM, 1) and a new acceptor 1,3,5-nonacyanotrivinylbenzene.

RESULTS AND DISCUSSION

A key feature in the design of is the stabilization of $D^{\uparrow\uparrow}$ is a trimethylenemethane (TMM) skeleton. Having learned from tetrathiafulvalene that sulfur is an excellent substituent for the stabilization of open shell molecules, we opted for designing a special TMM, namely HTTM.

Hexathiotrimethylenemethane

Below we show the structure of HTTM (1) indicating the delocalized nature of its various potential oxidation states.



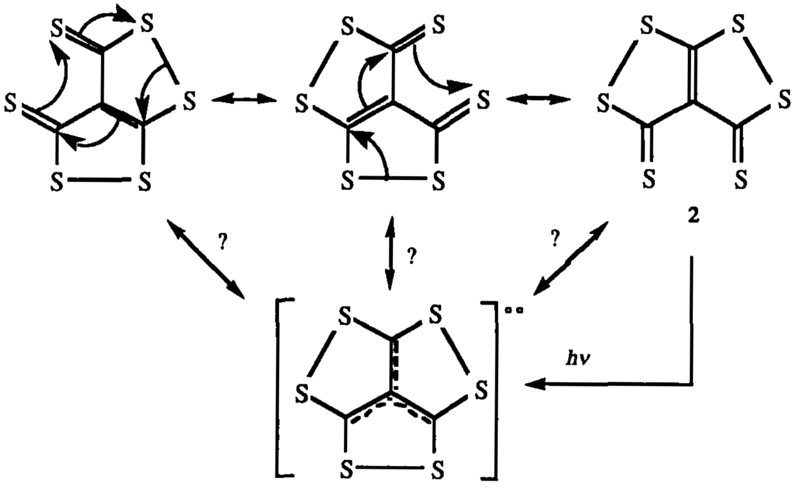
HTTM

*= +, -, •

1

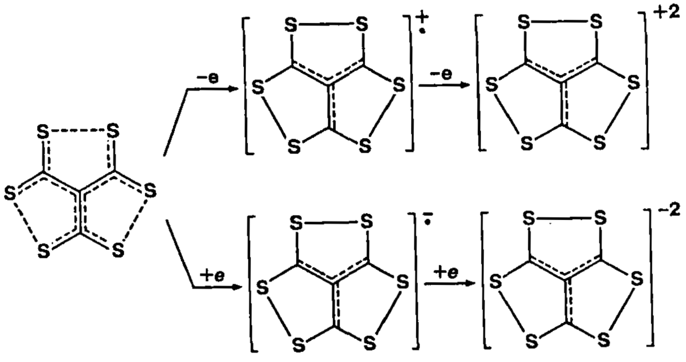
An important aspect of molecule **1** is that its periphery consists of chalcogen atoms, this feature is important to maximize interstack interactions and consequently lead to a three dimensionally interconnected solid, a prerequisite for the observation of ferromagnetism at ambient temperature.

A logical precursor to **1** would be the dithione **2**, a hypothetical molecule proposed by Gleiter to undergo degenerate rearrangements[7] as shown below.

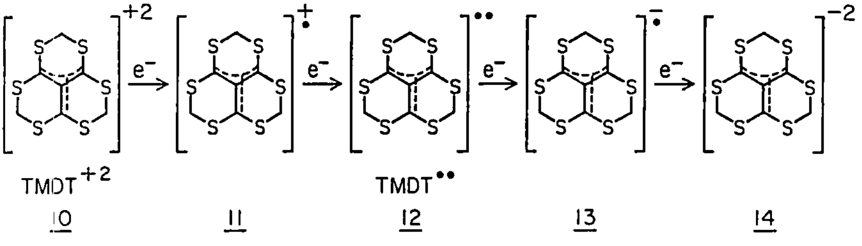


1

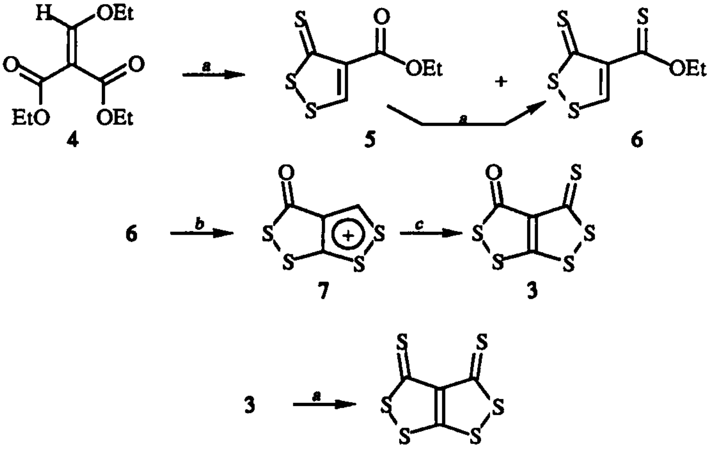
Compound **2** should also be interesting because 2^{++} and 2^{--} should be Hückel aromatic (14 π and 18 π electrons, respectively) and "Y aromatic" with a plethora of available oxidation states:



Dithione **2** should also be an excellent precursor to another D$^{\uparrow\uparrow}$, TMDT shown below.

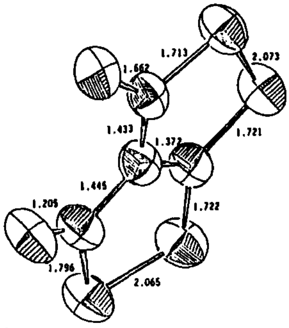


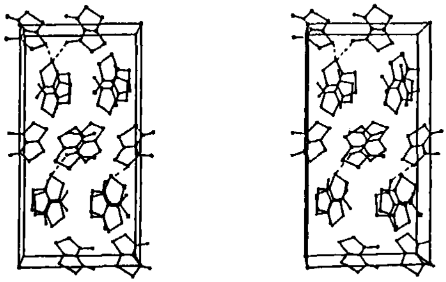
Several research groups have been attempting to prepare the tetrathiapentalene-dithione (TTP) **2** without success[8]. Here we report that the compound can be prepared by the synthetic approach shown in the Scheme below.



a, LR (Lawesson's Reagent)/toluene, reflux; *b*, ICl/CH_3CN, RT; *c*, S_8/pyr.

The key steps are the oxidative cyclization of the thionoester and the sulfuration of the dithiolium cation to produce the pentathio precursor **3**. The latter was a crystalline solid whose X-ray structure was recently determined[9]. The molecular structure and a stereoview of the molecular packing are shown in the figure below.





The bond distances and angles of the *planar* molecule are normal, the intramolecular O-S separation is 3.16 Å which is 0.16 Å shorter than the sum of O and S Van der Waals radii, yet the molecule is not distorted (planar molecule, no unusual bond angles); inplying an attractive and not repulsive transannular S-O interaction.

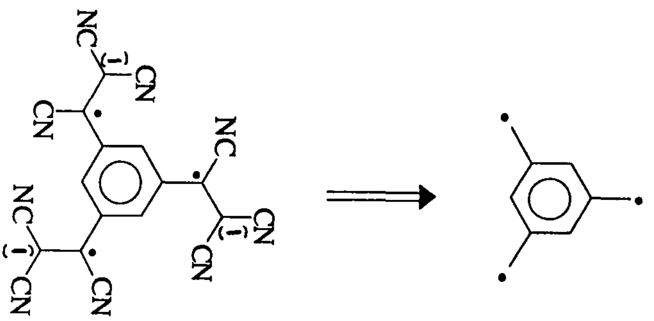
The molecules pack in such a way as to minimize the net bulk dipole moment; i.e. with the carbonyl bonds pointing in opposite directions. Not shown in the figure, above, are most of the short intermolecular contacts in all directions; however, the shortest intermolecular S-O contact is 2.88 Å and the shortest S-S contact is 3.087 Å, as shown by dotted lines in the figure.

Conversion of **3** to **2** was straightforward. The latter is a purple (by reflectance, brown by transmission) crystalline solid whose x-ray structure determination has, so far, eluded us. Method of synthesis, elemental analysis, ir, UV-vis and mass spectroscopies are all in agreement with the proposed structure. The compound proved to be too insoluble to test Gleiter's hypothesis[7] by ^{13}C NMR in solution and we have not yet had enough material for a CPMAS study.

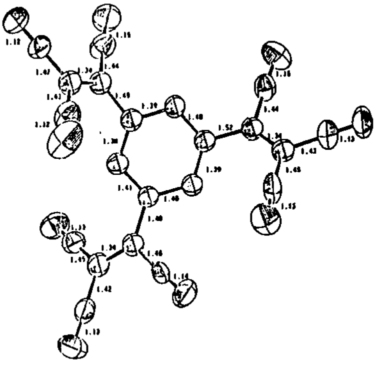
We are looking forward to obtaining larger amounts of **2** to study the oxidative ring closure to **1** (** = +,• or +,+) and to explore the uses of **1** as a component in organic ferromagnetic metals, organic metals and organic superconductors.

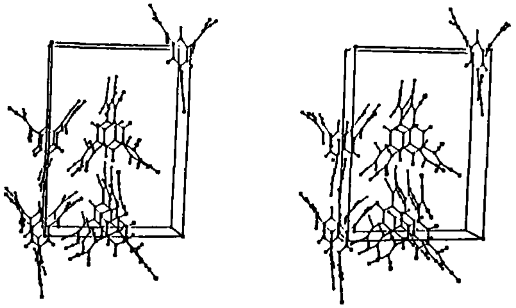
Nonacyanotrivinylbenzene

In the McConnell-Breslow model one requires donors and/or acceptors with trigonal symmetry. It has also been suggested that high spin molecules, if properly aligned, could give rise to ferromagnetism (Itoh, Iwamura[1]). With these thoughts in mind we designed the acceptor **4** and show below how it could be the precursor of a high spin triradical trianion



Its synthesis from 1,3,5-triformylbenzene as well as some of its physical properties have been presented by us[10] but its x-ray crystal structure was not. Depicted below are the molecular unit as well as a stereo view of the packing mode as recently determined[11].





The intramolecular bond distances and angles are normal. The interesting result is the twist of the tricyanovinyl groups relative to the plane of the benzene ring. Two tricyanovinyl groups point in the same direction and the third in an opposite direction.

We have combined our new acceptor with a number of donors. It gives charge transfer complexes with TTF and tetrakis(dimethylamino)ethylene. With the former, there is only a very weak interaction as determined by ir spectroscopy. With the latter, in terms of redox potentials, up to two electrons could be transferred from the donor to the acceptor. The esr spectrum shows a 7 Gauss wide line whose integration indicates that it corresponds to only 1% of the expected number of spins. The signal at 20K shows higher intensity than tha one at room temperature, implying Curie-Weiss behavior. We are looking forward to formation of charge transfer complexes with R. Breslow's donors[1] and to complete the preliminary work on the above charge transfer complexes of this acceptor.

SUMMARY

We have shown above how the FOM model is related to organic metals and how with the development of specially designed donors the model could be tested. The precursor to one of these donors, a tetrathiapentalenedithione was reported here for the first time as was the crystal structure of its immediate pentathio-precursor. The latter exhibits remarkably short intermolecular chalcogen-chalcogen contacts, and effect that bodes well for creating three dimensional molecular solids.

We have also shown above that the structure of 1,3,5-tris(tricyanovinyl)benzene) ("nonacyanotrivinylbenzene") is not planar in the neutral state and that the ensemble belongs to chiral space group, implying that the solid is ferroelectric. So far, this acceptor has not produced solids which are ferromagnetically coupled.

Acknowledgment

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6. It could also be a species $D^{\uparrow\uparrow++}$ (triplet dication) because the $D^{++}{\bullet}D^{+}$ stack would also be mixed valent and hence metallic; the problem in this case is the buildup of Coulomb interactions particularly as regards the counterions.
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9. C_4S_4O, M = 224.36, orthorhombic, Pbca, a = 9.691(1), b = 12.802(2), c = 24.316(4) Å, V = 3016.74 $Å^3$, Z = 16, D_c = 1.98 gcm^{-3}, D_m = 1.97 gcm^{-3}, λ (MoKα) = 0.71069 Å, μ = 13.98 cm^{-1}, F(000) = 4352, T = 295K, R = 7.3% for 2301 observed reflections.

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11. $C_{21}H_3N_9$, M = 381.32, orthorhombic, $P2_12_12_1$; a = 13.917(6), b = 18.666(8), c = 7.141(3) Å, V = 1855.05 Å^3, Z = 4, D_c = 1.36 gcm^{-3}, D_m = 1.37 gcm^{-3}, λ (MoKα) = 0.71069 Å, μ = 0.84 cm^{-1}, F(000) = 768, T = 295K, R = 5.0% for 718 observed reflections.