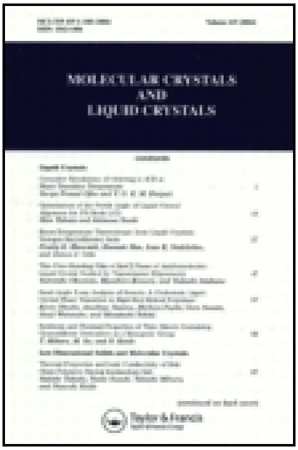

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Approaches to Organic Ferromagnets

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APPROACHES TO ORGANIC FERROMAGNETS

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Abstract Two species have been prepared as dications that exist in the ground triplet state. These can be used to explore one proposal for the production of organic ferromagnets.

INTRODUCTION

Cyclic compounds with 4n pi electrons are exotic species of considerable interest. Our early work focused on the energy content of these molecules. We suggested the word "antiaromaticity" to describe the finding that some of them were destabilized by conjugation.[1] The other interesting feature of these species is their electronic structure. When these species have C_3 or greater symmetry, the highest two electrons can occupy a degenerate pair of orbitals (in the simple HMO description) and the molecule can have a ground triplet state.

Our work and that of others has confirmed that such a 4 pi electron species as the cyclopentadienyl cation indeed exists as a ground state triplet molecule.[2] Thus we were intrigued by the suggestion that such species could play a key role in the preparation of organic ferromagnets.

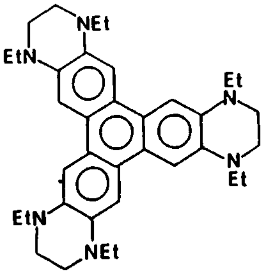
THE McCONNELL MODEL

In a brief discussion, Harden McConnell suggested that an ionic organic solid, consisting of a cation radical and an anion radical, could be ferromagnetic if charge transfer mixed the structure with a neutral state in which one of the neutral components was a ground state triplet molecule.[3] In the normal situation in which mixing occurs with a singlet state, this kind of interaction leads to antiferromagnetic ordering. We decided that this model deserved serious exploration.

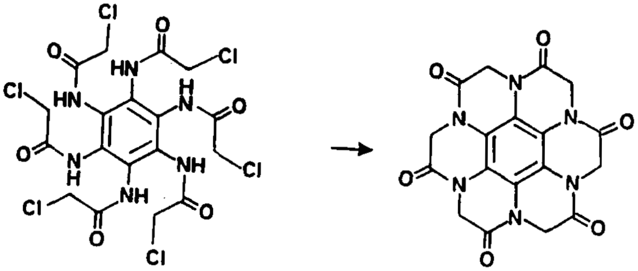
In its original formulation it seemed a problem, since donor-acceptor complexes with only partial charge transfer often exist in the solid state as separate donor and acceptor stacks. However, a version that seemed likely to work combines a cation radical with an anion radical but with their potentials matched so that forward charge transfer occurs. That is, they mix with a state represented by the dication and dianion. With the species at all times carrying at least a full charge one would expect an alternating structure in the solid state. Thus it seemed to us very attractive to look at dications with triplet ground states as a component of an organic ferromagnet.[4,5]

TRIPLET STATE DICATIONS

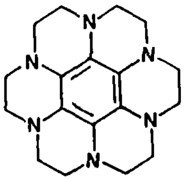
Wasserman had demonstrated that the dication derived from hexachlorobenzene was a ground state triplet, as expected from simple considerations.[6] The species is terribly unstable, and it is hard to imagine an electron acceptor that could generate it in a charge transfer interaction. However, with electron donor substituents such as amino groups we expected that the situation should be different. We prepared a benzene ring carrying six dimethylamino groups, but it was not easily oxidized to the dication.[7] Apparently the crowding of these groups twisted them so that they could not fully contribute to stabilizing the higher oxidation state of the benzene ring. However, we did devise the synthesis of a novel structure with threefold symmetry in which six nitrogen atoms are substituted on a triphenylene nucleus.[4] The species, which we nickname HET, could be oxidized quite readily to the cation radical and fairly readily to the dication. As expected, this dication showed a triplet ESR spectrum, and Curie Law studies indicated that the triplet state was the ground state. Interestingly, it was also possible to oxidize this system reversibly to the trication and even the tetracation.



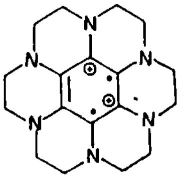
Very recently we have been able to prepare a nitrogen substituted simple benzene compound with similar properties.[8] We developed an improved synthesis of the very unstable hexaaminobenzene, and converted it to the completely cyclic compound that we call HOC. The synthesis involved a remarkably selective cyclization series.



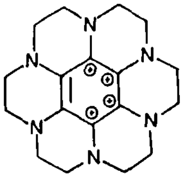
HOC oxidized extremely readily to its cation radical, and the oxidation to the dication involved almost the same potential as was required to make the dication of HET. The dication of HOC also showed a triplet ESR spectrum, and as expected the zero-field splitting parameter D was larger for this triplet state than it had been for the HET dication triplet state. Curie Law studies of the HOC dication over a limited temperature region indicated that it was a ground state triplet, but further work is needed with both HOC dication and HET dication to confirm this ground state assignment completely. Interestingly, HOC could also be electrochemically oxidized reversibly to the trication and also to the tetracation. In this latter species we have removed all four electrons from the degenerate pair of orbitals in the original molecule, converting the system from a derivative of benzene to a derivative of the benzene tetracation, that is from a 6 pi electron conjugated system to a 2 pi electron aromatic conjugated system (ignoring the electrons of the nitrogen atoms).



HOC



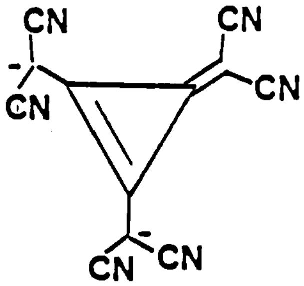
HOC^{2+}



HOC^{4+}

SALTS OF HOC AND HET THAT COULD BE FERROMAGNETIC

Of course the synthesis of these species, even if indeed the triplet dications are the ground states, is only part of the problem involved in testing the McConnell model. A suitable electron acceptor must be selected that can fully accept one electron from each of these neutral species, and partially accept a second electron so as to mix the cation radical and dication states of the donors. It seems that the electron acceptor should also have at least C_3 symmetry, so that the environment of the donors in the crystal could still have the correct symmetry for the triplet state to be the ground state. The best candidates so far seem to be a series of electron acceptors prepared by Fukunaga.[9] As an example, the reaction of malononitrile with tetrachlorocyclopropene yields a hexacyano compound that is a good electron acceptor. It readily forms the anion radical and easily picks up a second electron to form the dianion.



The solution potentials for this uptake of a second electron match very well with the solution potentials required to remove the second electron from HET or HOC. Thus this would seem to be an ideal partner in a test of the McConnell mechanism. However, simple solution potentials should not be perfect guides to the behavior of these species in the solid state, and one can make an argument that a somewhat weaker electron donor would be better. For this reason we have examined a number of other electron acceptors related to this hexacyano compound. It has not yet been possible to grow a single crystal of any of these species, so we cannot yet confirm the detailed solid state structure of the complexes. However, in two of the complexes that have been prepared so far antiferromagnetic ordering has been observed, not the desired ferromagnetism. When we can grow good crystals of such complexes and determine their solid state structures, we will be in a position to determine whether this approach to the McConnell model can indeed lead to the production of the first organic ferromagnetic materials.

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