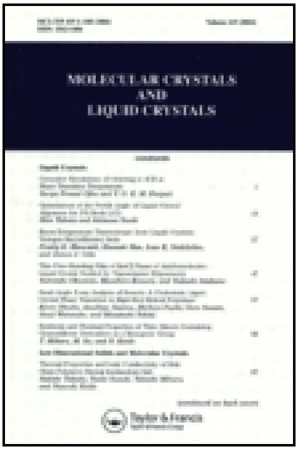

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4n PI ELECTRON TRIPLET SPECIES AND THEIR POTENTIAL USE IN ORGANIC FERROMAGNETS

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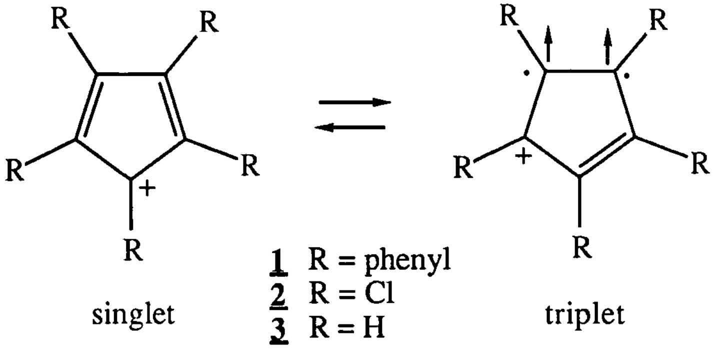
Abstract Antiaromatic cyclic conjugated molecules with 4n pi electrons and three-fold symmetry can have triplet ground states, but they may also distort to lower the singlet state below the triplet. Such distortion can be spontaneous, so the species are never true triplet ground state species, or distortion may be induced by a disymmetric environment. For instance, in crystalline solids an otherwise stable triplet species may adopt a singlet ground state because the environment within the crystal does not have the required three-fold symmetry.

There are several theories suggesting that ferromagnetic organic materials might result if a ground state triplet species is one component of the material. We have been able to prepare a number of stable triplet species relevant to this area. The requirements for a triplet ground state, and for ferromagnetic interactions, are discussed.

INTRODUCTION: TRIPLETS

Cyclic conjugated systems with 4n pi electrons, where n is an integer, are of interest for at least two reasons. First of all, they may be antiaromatic[1]. The cyclic conjugation does not convey aromatic stability on them, and some systems are actually destabilized by the conjugation. This is perhaps their most unusual property. However, in some cases they also exist as ground state triplet species[2]. This is not a cause of their thermodynamic stability; if they have triplet ground states they are thermodynamically more stable than they would be in the corresponding singlet states. However, it violates the simple assumption that molecules will make all the pi bonds possible by interaction of neighboring p orbitals. This assumption is of course violated in O_2, and for the same reason as in the organic triplet ground state species. If a molecule must place its highest two bonding electrons into a pair of degenerate orbitals, the physics behind Hund's Rule dictates that the two electrons preferentially go into different orbitals, and with unpaired spins.

The reality is not always so simple. Degeneracy of orbitals results from high symmetry, and this symmetry may be broken. For instance, distortion will lower the energy of one of the two degenerate orbitals while raising the other. This would be destabilizing for the triplet, since the overall rise in energy more than compensates for the decrease, but it will stabilize the singlet (Jahn-Teller effect). Thus in some cases a predicted triplet ground state molecule may actually exist as a singlet, with the triplet as a low lying excited state.



1 R = phenyl
2 R = Cl
3 R = H

An example of this is the pentaphenylcyclopentadienyl cation 1, one of the first species examined[3] with 4n pi electrons in a cyclic conjugated ring and the potential for five-fold symmetry (symmetry three-fold or greater is normally required for the orbital degeneracy that can produce triplets). A typical triplet ESR spectrum was seen, but its intensity did not follow the Curie law as it should for a ground state species. This law, that I·T is constant over temperature, is a good test for ground state triplets although it can have problems (*vide infra*). Instead, the intensity of the triplet spectrum increased with higher temperature, indicating that the triplet species was about a kcal/mole above the ground state[4].

The results were actually more detailed than that, and indicated a very interesting general situation for such measurements. The temperature *vs.* intensity plot was curved, indicating that there were several species present with different promotion energies required to reach the triplet state. This is because triplet ESR spectra are normally taken on frozen solid solutions.

The species in such a solid do not equilibrate their environments, and generally they can have a range of environments with varying symmetries. The pentaphenylcyclopentadienyl cation 1 may well have an intrinsic tendency to distort, so its ground state is probably intrinsically a singlet, but distortion will also be promoted by an unsymmetrical environment. Thus such environmentally induced distortion must always be considered. It is one of the reasons that the species are normally examined as solid solutions rather than as crystalline solids; a crystal will only rarely have the correct symmetry to prevent induced distortion. Ignoring this problem has led to some curious mistakes in the literature (*vide infra*).

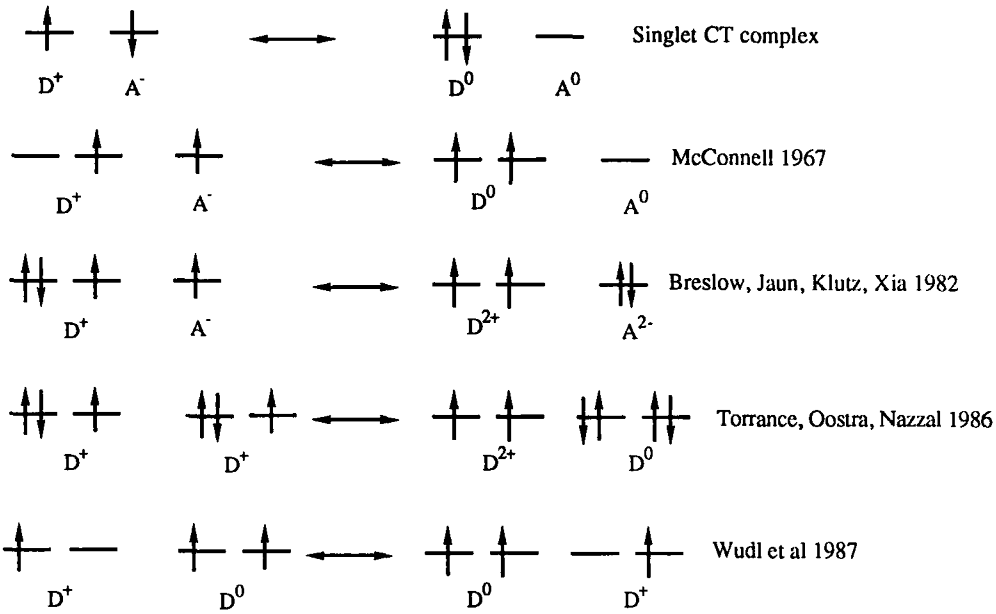
We found that the pentachlorocyclopentadienyl cation 2 showed a triplet ESR spectrum that followed the Curie law, suggesting that it was a ground-state triplet species[5]. Unfortunately, the Curie law behavior is not definitive in either direction. As mentioned above, deviations may reflect environmental distortions, but intensities that follow the Curie law only indicate that the triplet is either the ground state or a very low lying excited state. With measurements at low temperature one can have confidence that the promotion energy from singlet to triplet is very small, but not necessarily that it is negative. Unsubstituted cyclopentadienyl cation itself 3 also showed a triplet spectrum that follows the Curie law, suggesting that this triplet is also the ground state[6].

INTRODUCTION: ORGANIC FERROMAGNETS

Harden McConnell pointed out that ground state triplet molecules might be used to construct organic ferromagnets. His specific proposal[7] involved charge transfer interaction between a triplet state neutral donor molecule and a singlet state acceptor molecule. The charge-transferred diradical state would still be a triplet, so the spins on the two species would be parallel as in a ferromagnet. Similar interaction should correlate all the spins in the solid. We proposed[8] a simple modification of this scheme in which a cation radical was the donor and the charge-transferred dication species was the triplet, but the idea was the same. Our version seemed like something that we could approach experimentally. More recently Torrance has proposed a model for ferromagnetism in which the cation radical alone is ferromagnetically aligned because the ground state mixes with a charge transferred excited state involving the triplet dication[9].

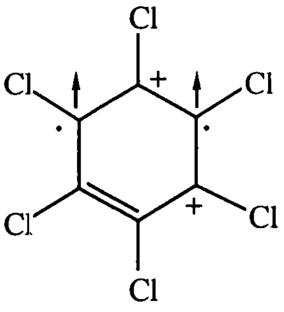
Wudl has proposed using the cation radical and triplet dication in a different way: doping the cation radical with triplet dication so that electron delocalization through the stack correlates the spins ferromagnetically[10]. These ideas are summarized in Scheme 1.

Scheme 1



TRIPLET DICATIONS

The requirement to test all of these schemes is a cation radical whose corresponding dication is a triplet ground-state species. In addition, in the McConnell and Breslow schemes a suitable charge-transfer partner is needed, while in the Torrance and Wudl schemes self-stacking of the cation radical is needed. [All these schemes would also really require additional sideways interactions, since ferromagnetism is not expected to be possible in only one dimension.] Thus we set out many years ago to synthesize examples of the key component: a cation radical whose dication was a ground-state triplet.



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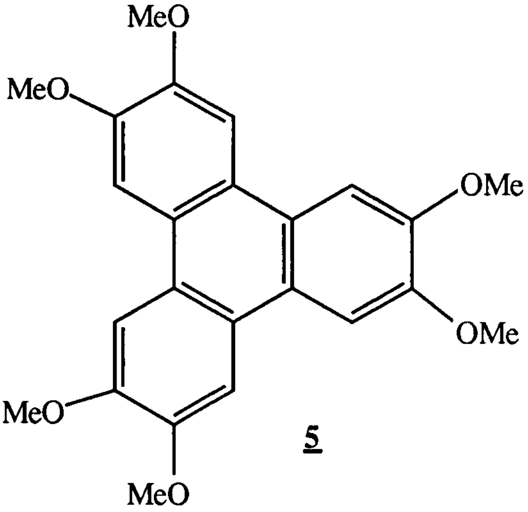
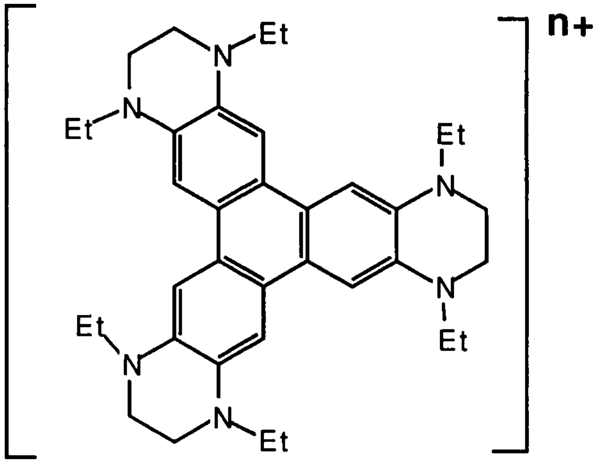


5

Hexachlorobenzene dication 4 had been prepared by Wasserman et al and shown to be a triplet[11], but it is chemically too unstable (as is its monocation radical) to have much promise for the preparation of stable ferromagnets. Hexamethoxytriphenylene 5 had also been prepared as the cation radical and dication[12]. The latter showed a triplet spectrum[12], and we determined[13] that the spectrum follows the Curie law so the triplet is probably the ground state. However, the oxidation potential for converting the monocation to the dication is so high that we despaired of finding suitable acceptors for the charge-transfer schemes. Thus we prepared derivatives of the much more easily oxidized hexaaminotriphenylene system 6[14-17]. The system was not known, but a good synthetic scheme was devised.

We found that various derivatives of this system were easily oxidized to cation radicals and to dications. The dications were examined in the ESR as solid solutions and showed triplet spectra that followed the Curie law. Thus they seemed ideal for testing our version of the McConnell charge-transfer scheme.



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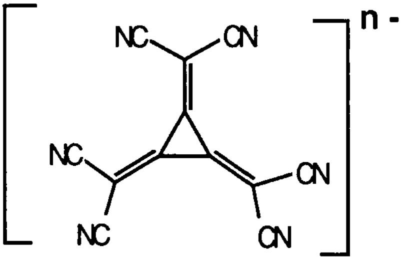

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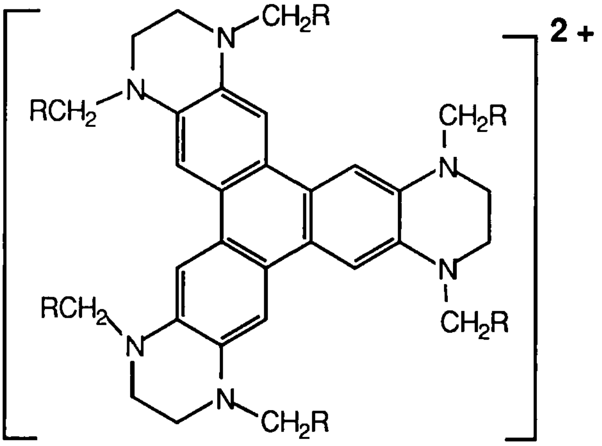
We selected the very interesting anion radical 7 prepared by Fukunaga[18] as the electron acceptor. The hexacyano derivative 7 could be reduced to the dianion at a potential that was a good match for the potentials available in our hexaaminotriphenylene derivatives. The infrared spectra of appropriate complexes indicated that the hexaethyl derivative of 6 was too good a donor, since the CN stretch of the complex corresponded to the dianion of 7[17]. With CH_2CF_3 substituents the donor 6 was not reducing enough, since 7 showed the spectrum of the monoanion. However, with CH_2CF_2H groups on the donor a mixed valence charge transfer complex was formed. The cyano stretch in the infrared was broad, and centered between the positions for monoanion and for dianion[17]. Thus this compound in principle met the requirements for ferromagnetism.

Magnetic susceptibility measurements[17] showed that the systems were not ferromagnetically coupled, but instead they were antiferromagnetic. There are several reasonable explanations (besides the possibility that the theoretical model is wrong): 1) The dication may not be a true ground-state triplet, either because the Curie law test is not adequate proof or because the species is distorted in the charge-transfer complex (the anion was chosen to have three-fold symmetry to avoid this problem, but we have not yet obtained crystals that let us see whether the geometric environment is distorted). 2) The system is designed to be one-dimensional, and there may be inadequate two- and three-dimensional interactions to permit bulk ferromagnetism. 3) There may be bonding interactions that lead to level splitting and electron pairing.



R = CF_3, R = CHF_2, R = t-Bu, R = adamantyl

The proposition that radical species A and B could interact ferromagnetically in a mixed stack, by charge transfer, requires that they not directly bond to each other. Bonding interaction will cause a splitting of degenerate levels and spin pairing to the singlet state (Fig. 2). To prevent this we have made some derivatives of **6** with bulky substituents on the nitrogens[19]. These should increase the spacing between donor and acceptor molecules, and decrease the strength of any bonding interactions. We are still evaluating their properties and applications.

It is critical that the triplet state be as stable as possible relative to the excited singlet state, so that the triplet species will remain the ground state in spite of environmental distortions. Since it is expected that the energy advantage of triplets over singlets will be greater in smaller systems, we wanted to examine some derivatives of benzene dication. As mentioned, the dication of hexachlorobenzene is indeed a triplet, but not a very stable species. We hoped that electron donor groups would stabilize it to the point at which the benzene dication would be a species with normal chemical properties. This idea was successful.

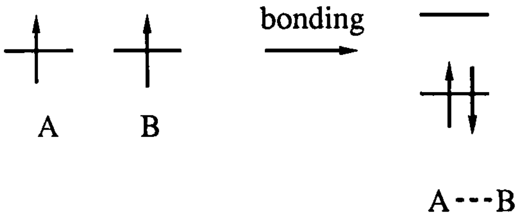
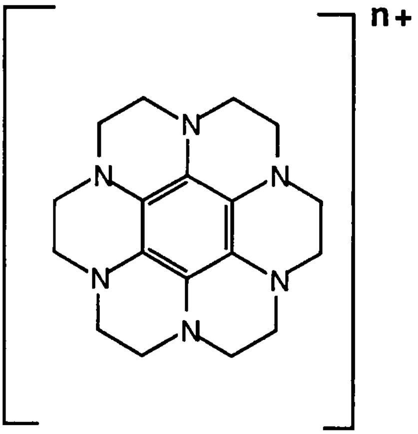


Figure 2

We examined the oxidation of hexakis(dimethylamino)benzene to its dication[19], but concluded that the severe twisting of the substituents out of conjugation with the ring made this an unattractive prospect. Recently Mislow has studied this system further[20]. He finds that the dimethylamino groups are indeed strongly twisted, but that the unstable dication can be prepared.

A more attractive compound is a hexaaminobenzene with ethano bridges between the nitrogens. We prepared this compound -- hexaazaoctadecahydrocoronene **8** -- and called it HOC[21,22]. Recently Miller has repeated our preparation and done his own studies on the system[23]. For obscure reasons he chooses to call it HAOC, but it is the same compound **8** that we made and originally abbreviated HOC.

We found that HOC is readily oxidized to the cation radical and fairly easily oxidized to the dication[21,22]. As with the hexaaminotriphenylenes, we saw that HOC could even be oxidized to the trication and to the tetracation, although we did not fully characterize these species[21,22]. The dication is the derivative that has the potential to be a ground-state triplet, so we concentrated efforts on it. It gave a triplet spectrum with the expected features, although in some preparations the spectrum is rather weak. We found that in one solvent it followed the Curie law, but in another medium it seemed that the triplet state was 0.9 kcal/mole above a ground singlet state[22]. With an iodide counterion the singlet was so stabilized that the triplet ESR spectrum of HOC^{2+} was not even visible[22].



HOC (**8**) ,n = 0
n = 0, 1, 2, 3, 4

Miller and coworkers at DuPont have also examined HOC^{2+}, and have published a paper purporting to show that the species is a singlet, not a triplet[23]. The ESR spectra were done on characterized crystalline salts of HOC^{2+}, not on solid solutions. Of course in a crystal the symmetry will most likely be distorted; this is why such spectra are normally done on frozen solutions. However, both their results and ours certainly indicate that if HOC^{2+} is a ground-state triplet it distorts very easily to the singlet state. That this is the actual situation is indicated by the finding of E. Wasserman, also at DuPont, that the triplet ESR of HOC^{2+} in frozen solutions can be seen even at liquid helium temperature[24]. At this temperature only a ground state triplet, or one very close to the ground state, would be visible.

Symmetry is not an artifact, but distortion can be. Thus at the current time the most reasonable interpretation is that HOC^{2+} is a ground-state triplet species, but easily distorted. The distortion occurs most obviously when the dication pairs with counterions, as in the crystal or in solvents that permit ion association. Then the bulk of the population of HOC^{2+} is present as an environmentally distorted singlet, but some is free of distortion and presents itself as a triplet even at 4° K. Such a mixed system will present the I·T profile of a ground state singlet, since as the temperature is raised more and more of the various distorted species will show triplet signals. However, even though the dication is probably a ground state triplet the easy distortion makes the HOC system an unattractive prospect for the construction of ferromagnets.

The distortion of HOC^{2+} apparently involves a decrease of its six-fold symmetry to two-fold, judging from the crystal structures published by Miller[23]. It is an interesting feature that six-fold symmetry contains both the three-fold symmetry required for orbital degeneracy, to produce a triplet, and the two-fold symmetry that splits the degeneracy and leads to a singlet state. Thus some other derivatives of benzene with only three-fold symmetry are perhaps more interesting.

We have described the preparation of compounds **9** and **10**, each with three nitrogens and three other weaker electron donor atoms[22]. Two electron oxidation of the oxygen compound **9** produced a triplet ESR spectrum, and Curie law studies suggest that this is a ground state triplet. Further work will be required to characterize it fully, and establish its potential for application in the models for ferromagnetism described earlier. We have also prepared compound **11**, with bulky substituents that can decrease bonding orbital overlap in a stack[25]. Its dication shows a triplet spectrum that also follows the Curie law. It remains to be seen whether these systems can be successfully incorporated into organic ferromagnetic materials.

SUMMARY

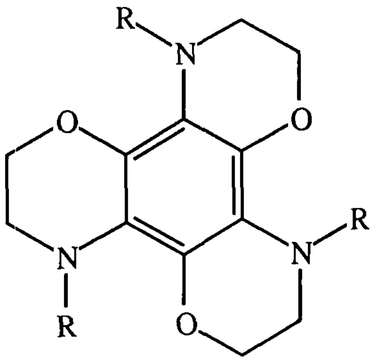
1. Cyclic conjugated systems with 4n pi electrons in a ring can exist as ground state triplet species if they have three-fold or greater symmetry.

2. Distortion to singlet ground state species may reflect the intrinsic properties of the molecules, but distortion may also be environmentally induced.

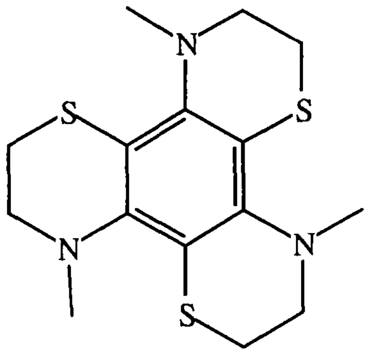
3. Environmental distortion is particularly likely in crystalline solids, with their high interaction energy and symmetry that will normally be less than three-fold.

4. Several schemes have been proposed for incorporating triplet ground state species into solid materials so as to achieve an organic ferromagnet.

5. The antiferromagnetic coupling observed in some of these systems has several possible explanations, which guide further work.



9 R = Me
11 R = neopentyl



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ACKNOWLEDGEMENTS

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