

## STABLE $4n$ PI ELECTRON TRIPLET MOLECULES

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**Abstract** - Cyclic  $4n$  pi electron conjugated systems with  $C_3$  or greater symmetry can have triplet ground states. If stable examples of such systems can be prepared they can serve as the most important components of ferromagnetic organic compounds, a hitherto unknown class of substances. The theory of how triplets can be used to prepare ferromagnets is outlined. Synthetic approaches to stable triplets, and to the ferromagnetic systems themselves, are also described.

### INTRODUCTION

Cyclic conjugated systems with  $4n$  pi electrons, in which  $n$  is an integer, are unusual for at least three reasons. First of all they are not strongly stabilized by conjugation, in contrast to aromatic  $4n+2$  systems. In some cases they may indeed be destabilized by conjugation, leading to the phenomenon we have called "antiaromaticity" (Ref. 1). Secondly they may exhibit paratropic ring currents, which can be detected in the NMR by a shielding of protons outside the ring (Ref. 2). Perhaps most interesting of all,  $4n$  pi electron molecules can sometimes exist as ground state triplets, with less than the full spin pairing needed to maximize the number of pi bonds in the molecule. They thus violate one of the most elementary tenets of chemistry, the principle of maximum bonding.

A number of systems have been examined over the years which have appropriate symmetry and  $4n$  pi electrons and which have been shown to exist at least to some extent as triplets. The simplest of these, which has been shown to exist as a ground state triplet, is cyclopentadienyl cation (1),  $C_5H_5^+$  (Ref. 3, 4 & 5). A salt of this cation, prepared from 5-bromocyclopentadiene and  $SbF_5$ , showed a typical triplet esr spectrum, with  $D$  having a value of  $0.1865 \pm 0.0005$  cm<sup>-1</sup> and  $E$  being 0 (<0.001). The zero value of  $E$  indicates that the triplet molecule being examined has plain polygonal symmetry, as expected for this species. The rather large  $D$  value indicates that the two unpaired electrons are on the average fairly close, as is expected for this small molecule. As will be seen below, in larger systems the  $D$  value diminishes.

Not all systems with  $4n$  pi electrons have the potential to have triplet ground states. Only if they have  $C_3$  or greater symmetry does one expect degeneracies in some orbitals with half occupancy of a degenerate orbital pair. This leads to spin unpairing and the single occupancy of each orbital. However, even a molecule which could have this symmetry need not adopt it if distortions are readily available. Instead the possible degeneracy of the orbitals can be split by Jahn-Teller distortion, which will stabilize the singlet state relative to the triplet since the paired electrons of the singlet can both go into the orbital whose energy has been lowered by distortion (Fig. 1).

Of course the above is only a description in simplified molecular orbital terms. The 4 pi electrons of  $C_5H_5^+$  triplet in Fig. 1 have been considered in terms of a single electronic configuration (1,1,2,3) but a better quantum

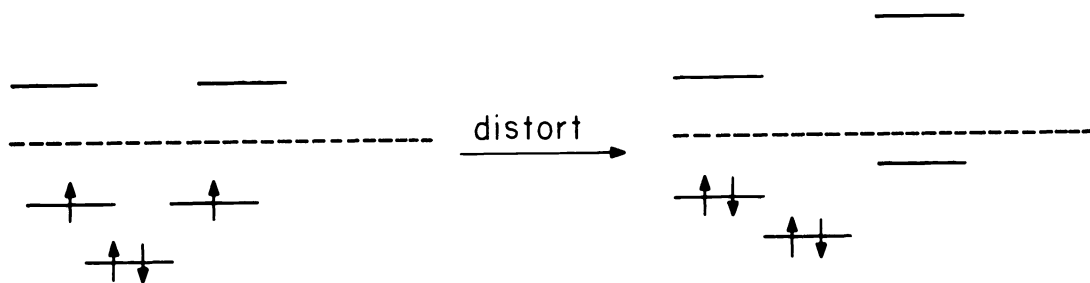


Fig. 1 Symmetrical and Unsymmetrical Cyclopentadienyl Cation

mechanical description can be obtained by configuration interaction (CI), in which the wave function for this molecule is obtained by mixing the lowest energy configuration mentioned above with various excited state configurations, including those involving orbitals 4 and 5. In general it can be shown that CI stabilizes singlet states more than it does triplet states, which is another way of saying that the simple single electron configuration description is less adequate for singlets than it is for triplets. Thus even in a symmetrical  $4n$  pi electron molecule it would in principle be possible that the ground state be a singlet, in contrast to the simple ideas about orbital degeneracy and Hund's rules.

For these reasons there is no assurance that a  $4n$  pi electron molecule with potential  $C_3$  or greater symmetry will actually have a triplet ground state.

Even when a triplet is detected at thermal equilibrium it is important to do Curie law studies to establish that the triplet is the ground state; this was brought home in the first cyclopentadienyl cation actually examined, the pentaphenyl derivative 3 (Ref. 4,5, & 6). The esr spectrum of this cation showed that the triplet state was present at  $-110^\circ\text{C}$  with  $E = 0$  and

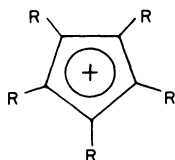
$D = 0.1050 \text{ cm}^{-1}$ . However, when the temperature was lowered the intensity of the esr signal decreased, contrary to the Curie law that  $I = C/T$ . From the temperature dependence of the signal it was seen that the ground state of pentaphenylcyclopentadienyl cation is actually a singlet, with a triplet state lying 0.35 to 1.15 kcal/mole higher in energy. With such a small energy gap there was a detectable population of triplets in thermal equilibrium with the singlet at essentially all temperatures.

By contrast, the unsubstituted cyclopentadienyl cation triplet followed the Curie law down to  $4^\circ\text{K}$ , so it is a ground state triplet. Similarly, pentachlorocyclopentadienyl cation 2 (Ref. 4,5 & 7) also had a triplet esr spectrum, with  $E = 0$  and  $D = 0.1495 \text{ cm}^{-1}$ . This one also followed the Curie law, and thus the triplet was the ground state. In line with the results for pentaphenylcyclopentadienyl cation, cyclopentadienyl cation substituted with five p-anisyl groups 4 also has a singlet ground state and a low-lying triplet state (Ref. 8). Some of the data on cyclopentadienyl cations is summarized in Fig. 2.

The triplet ground state species cyclopentadienyl cation and pentachlorocyclopentadienyl cation are chemically quite unstable. This is also true of the hexachlorobenzene dication (Ref. 9) and of some dianions (Ref. 10) which have been reported to be triplets. This was unfortunate, since there are a number of reasons to want to prepare and study stable organic triplet molecules. Of these reasons, perhaps the most interesting is the possibility that stable triplets could play the key role in the synthesis of organic ferromagnetic materials.

#### ORGANIC FERROMAGNETISM

No purely organic compound with confirmed ferromagnetic properties has yet been prepared. Several theoretical models have been suggested (Ref. 11) which might cause certain organic compounds to exhibit ferromagnetism, but of all these the most interesting is the proposal of McConnell (Ref. 12) with respect to ground state triplet molecules. Because the theoretical model was described only briefly, and in a relatively inaccessible source, it will be



COMPOUND	R	D(cm <sup>-1</sup> )	TRIPLET STATE ENERGY (kcal/mole)
1	H	0.1865	0
2	Cl	0.1495	0
3	Phenyl	0.1050	+0.35 - 1.15
4	p-Anisyl	—	+0.05

Fig. 2

quoted here:

"Consider an ionic molecular crystal, say  $D^+A^-$ , that is built up from the positive ions of the donor molecule D and the negative ions of the acceptor molecule A. In many crystals of this type, the positive and negative ion molecules

form an alternating linear sequence,  $D^+A^-D^+A^- \dots$ . To the best of my knowledge, in all such systems that have been described in the literature, the D and A molecules have diamagnetic ( $S = 0$ ) ground states, as isolated molecules. Thus, back charge transfer in the ionic crystal mixes some neutral singlet ( $S = 0$ ) character into the ground state of the ionic crystal, and this produces an effective antiferromagnetic coupling of the spins on adjacent ions. [See P. L. Nordio, S. G. Soos and H. M. McConnell, *Ann. Rev. Phys. Chem.* 17, 237 (1966)]. The elementary excitations of these antiferromagnetically coupled spin systems are known to be triplet excitons.

On the other hand, if an ionic molecular crystal  $D^+A^-$  could be formed with a donor molecule whose neutral ground state was a triplet ( $S = 1$ ), then one would expect back charge transfer of the type described above to lead to ferromagnetic coupling of the spins on adjacent ion molecules. The same effect could be achieved if instead the neutral acceptor molecule A had a triplet ( $S = 1$ ) ground state. Thus, it appears to me that ferromagnetic coupling of the spins of free radicals in certain ionic molecular crystals is a very real possibility."

The mechanism proposed is illustrated in Figure 3. The result of such charge transfer will be to favor a system in which the spins on two neighboring species  $D^+$  and  $A^-$  are parallel, so that charge transfer can lead to the favored triplet state of one of the partners (the model will not work if both D and A are triplets). Since such charge transfer can go in either direction, the spin on a given  $A^-$  will be parallel to the spins on both neighboring  $D^+$  species, which in turn must be parallel to both other neighboring  $A^-$  species, etc. Such parallel spin correlation leads to a ferromagnetic domain; if the charge transfer is not only linear there could be two-dimensional or three-dimensional domains.

The mechanism can obviously be general. In an example of particular interest to the current work, the triplet species could be a dication. In Figure 4 we show a version in which species M has fully donated an electron to species N, making the  $M^+/N^-$  pair, but the redox potentials are such that charge transfer is in the forward direction so there is some contribution of  $M^{2+}/N^{2-}$  to

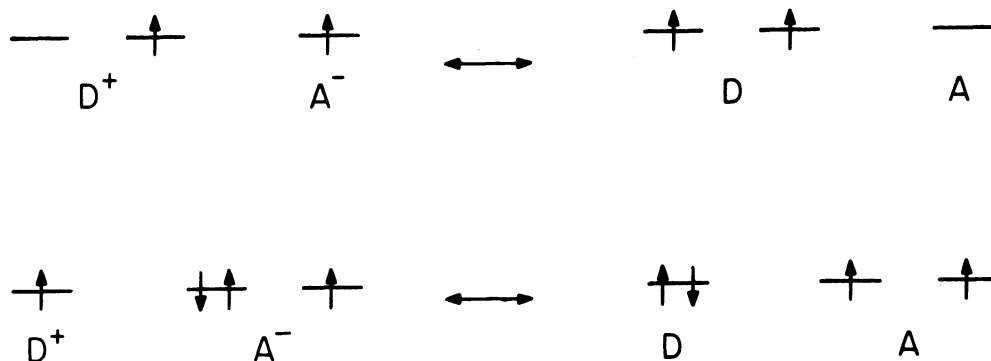


Fig. 3

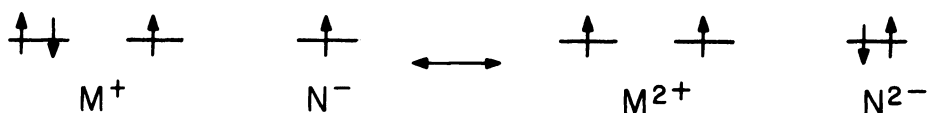


Fig. 4

the structure. If M<sup>2+</sup> has a triplet ground state this charge transfer will lead to ferromagnetic coupling; it would also work if N<sup>2-</sup> were the triplet and M<sup>2+</sup> the singlet.

Up to the current point no experimental test of these proposals has been reported in the literature. However, over the past few years we have been pursuing approaches to this interesting potential class of organic ferromagnetic materials, and wish to report our results to date. As will become apparent, full success is not yet in our grasp but very promising early results are available.

#### APPROACHES TO STABLE TRIPLETS

We have examined the possibility of generating the required stable triplet species in many of the possible 4n pi electron systems. Thus in the cyclopropenyl anion area one would expect essentially any derivative of the anion to be a ground state triplet provided it has planar trigonal symmetry. Of course if the anion is pyramidal at one of its carbons no such expectation is present. By electrochemical methods we have generated the unsubstituted cyclopropenyl anion, some trialkylcyclopropenyl anions, and the triphenylpropenyl anion (Ref. 13). All of these species in principle could meet the above requirements, but in every case the species are transient at best and are so unstable that no direct observation of them has been possible. In particular, we do not yet know whether their ground states are singlet or

triplet.

One might hope that a cyclopropenyl anion could be generated and observed if it carried three strongly stabilizing groups on it such as carbonyl groups. Some years ago we did an extensive study of the chemistry of 1-bromo-1,2,3-tribenzoylcyclopropane (Ref.14). On base treatment this molecule readily eliminated HBr to generate tribenzoylcyclopropene, but no evidence could be obtained for the formation of the anion by further base reaction. Instead under all conditions examined various side reactions occurred such as attack by the base on the double bond or ring expansion to a furan derivative. The results in this area suggested that tribenzoylcyclopropenyl anion is not a good candidate for a stable triplet species which could be used to study the possible generation of a ferromagnet.

In recent work we have also examined the possibility that we could generate tricyanocyclopropenyl anion, which if it is flat and symmetrical should also be a ground state triplet species. Tricyanocyclopropane was chlorinated with t-butyl hypochlorite, and remarkably it produced as the only product the trichlorotricyanocyclopropane. (Our other work has made it clear that when a single chlorine is added the resulting monochlorocyclopropane eliminates HCl very readily. This generates tricyanocyclopropene, which would be expected to undergo allylic halogenation followed by chlorine addition to produce the trichloro derivative.) Reduction of this compound with solvated electrons led to the formation of hexacyanobenzene. Apparently the reduction does generate the tricyanocyclopropenyl system, but probably only as the radical which then dimerizes. As will be mentioned again below, we know that such bis-cyclopropenyls readily rearrange to benzene derivatives.

As another approach to the anion, the trichlorotricyanocyclopropane was selectively reduced with tributyltin hydride. With this technique we were able to generate either the dichloro or the monochlorotricyanocyclopropane, as well as the completely unchlorinated original starting material. As expected from our observations on the chlorination process, these species undergo extremely ready elimination of HCl. When the monochloro compound is treated with a strong base such as lithium 2,2,6,6-tetramethylpiperidide the resulting cyclopropene could be trapped as an adduct with diphenylisobenzofuran. However, with an excess of the base we could obtain no evidence for the formation of a stable tricyanocyclopropenyl anion. Thus at the current time stable derivatives of the cyclopropenyl anion have not been isolated. Certainly this system does not yet seem promising in our search for organic ferromagnetism.

Some calculations had indicated that cyclobutadiene would have a triplet ground state, but the experimental evidence seems to be quite clear that in the parent compound the ground state is a singlet, not a triplet. This is undoubtedly a reflection of the kinds of factors we discussed earlier, but it does suggest that tetrasubstituted cyclobutadienes, even if they could be prepared and handled as stable substances, are not likely to have triplet ground states and are therefore not likely to be useful in the search for ferromagnetism.

Cyclopentadienyl cations are another story. As was mentioned above, both the parent cyclopentadienyl cation and the pentachlorocyclopentadienyl cation are ground state triplet species, but chemically they are so terribly unstable that there is no chance of using these particular systems in the construction of a ferromagnet. However, there seems to be a real possibility that some highly stabilized derivative of the cyclopentadienyl cation could be used in which the substituents did not perturb the symmetry of the system and in which the stabilization did not involve such a large area for electron delocalization that the energetic advantage of the triplet over the singlet was too far diminished. In general one expects that if electrons are delocalized over a very large area the special energetic advantage of the triplet state will be smaller, and then various distortions of the molecule could stabilize the singlet state to the point at which it fell below the triplet in energy. For this reason, it is particularly attractive to use five simple substituents on the cyclopentadienyl cation system.

We have been approaching this problem by attempting to synthesize cyclopentadienyl cation carrying five dialkylamino groups, such as dimethylamino, diethylamino, or pyrrolidino groups. Progress has been good, but the project is not yet complete. As we have reported elsewhere (Ref. 15), we can prepare the iron carbonyl derivative of a cyclopentadienone carrying four dialkylamino groups by the procedure shown in Figure 5. Oxidative removal of the iron

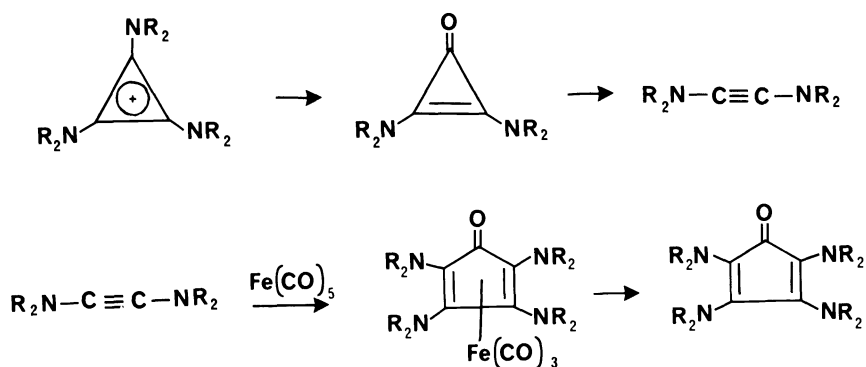


Fig. 5

carbonyl group generates the cyclopentadienone itself carrying four dialkylamino groups, but under the conditions we have been able to develop so far one of the enamine systems hydrolyzes so the product is a cyclopentenedione. However, methods for converting such a system back to the enamine, and for converting the resulting cyclopentadienone to a cyclopentadienyl cation carrying the fifth dialkylamino group, are well-precedented. Thus we hope to have this species in hand shortly.

It should be stable enough to be handled, although it will probably be hydrolytically unstable and difficult in that respect. Furthermore, it seems extremely likely that its ground state will be a triplet, and it thus might be incorporated into one of the ferromagnetic composites described earlier. However, it seems most obvious that the cation would have to be paired with an anion of an oxidation potential such that the charge transfer interaction led to a significant contribution of neutral cyclopentadienyl radical with the corresponding neutral partner radical. Thus the chemical stability of such a system is of some concern, as well as the question of whether it will have a tendency to stack with the alternating structure which is required for the production of ferromagnetism. As an alternative, one could imagine pairing the pentaaminocyclopentadienyl cations with anionic partners which are such excellent electron acceptors that the charge transfer interaction involves oxidation of the cyclopentadienyl system to a dication radical with corresponding production of a dianion radical in the partner. Until the compounds are in hand we cannot be sure of whether partners with the necessary oxidation potential will be available.

The benzene dication system is in principle an appropriate basis for ground state triplet molecules provided that whatever derivative of this system is used has at least threefold symmetry. Wasserman has described the preparation of the hexachlorobenzene dication and the observation that it is a ground state triplet species (Ref. 9), but it is chemically so unstable that it is hard to imagine how this could be incorporated into a stable ferromagnetic system. However, in the benzene dication series one might hope to be able to stabilize the system with appropriate substituents while retaining the necessary symmetry and small delocalized area so that the dication is still a ground state triplet.

As one approach to this we have examined the possibility of preparing the dication derived from hexa-aminobenzenes. A particularly amusing general synthesis of such substances is shown in Figure 6 (Ref. 16). With this

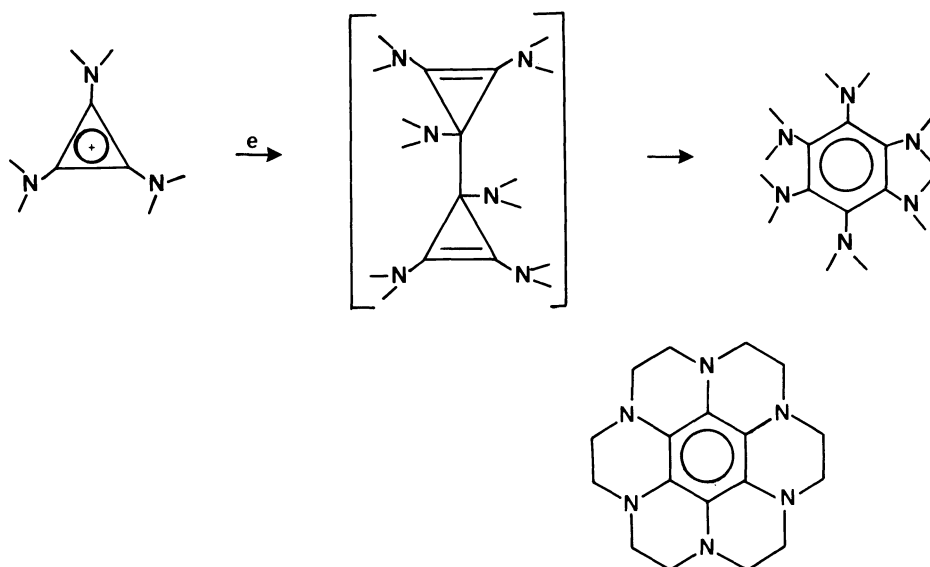


Fig. 6

reaction sequence, for instance, the hexakis-dimethylaminobenzene is readily prepared. However, we find that it cannot be reversibly oxidized under ordinary conditions to the dication, apparently because the crowding of the substituents is such that they do not fully contribute to stabilizing this high oxidation state. Thus we have not yet been able to prepare the corresponding dication as an isolable species for examination, and are not sure whether it is a ground state triplet or not. Nevertheless the attractiveness of this class of substances is great, and we are still pursuing studies in this area. Particularly attractive is a molecule (Fig. 6) we refer to as the "wheel", in which the crowding of the dialkylamino groups is no longer present. Thus one would expect to have full conjugation and stabilization. Several reasonable approaches to this system are currently underway, but the compound is not yet in our hands.

#### THE HEXAAMINOTRIPHENYLENE (HET) SYSTEM

Considering the synthetic problems we have outlined in approaching stable triplet state molecules in some of the smaller ring systems, we were particularly interested in the report by Parker (Ref. 17) that hexamethoxytriphenylene can be prepared readily by electrochemical oxidation of o-dimethoxybenzene **5** (Fig. 7). Parker furthermore reported that this material readily formed the cation radical **6** and, most important from our point of view, that it could be converted under some conditions to the dication **7** which showed a triplet esr signal. As we have outlined earlier, in an approach to an organic ferromagnet it is particularly attractive to have a system which exists as a radical ion and which by charge transfer is converted to the triplet state species. In principle such charge transfer could be such as to convert the ion back to a neutral triplet species, but for many reasons it is more attractive to have the charge transfer convert the ion to a di-ion. Thus the finding that the dication is a triplet was very promising.

In several respects, however, this still did not seem to be an ideal system. Perhaps most bothersome, oxidation of the cation radical to the dication occurs at a potential of +0.85 V. an extremely positive value. Thus to use the Parker system in the construction of a ferromagnet it would be necessary to find an anion radical which was such a strong oxidizing agent that it could at least partially accept a second electron from the cation with this very high positive oxidation potential.

The theory outlined for the production of an organic ferromagnet above is of

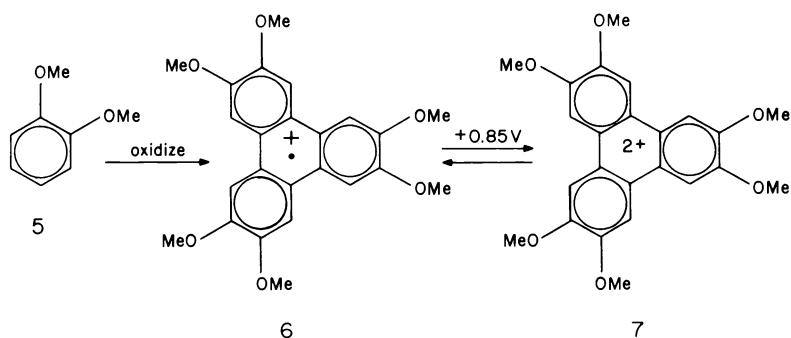


Fig. 7

course qualitative, not quantitative. It does not contain in it any indication of the extent of mixing of the charge transferred state which is required in order to achieve ferromagnetic correlation of the electron spins. Obviously in real life this extent of mixing will be one of the factors which comes into determining whether a system is ferromagnetic, along with such questions as the energies involved in disrupting the organized structure needed to permit correlation over a significant domain and also the energy advantage of the triplet state over the singlet. Thus it is perfectly possible that as little as a one percent contribution of the charge transferred state might be enough to achieve ferromagnetic correlation, but even this would require that charge transfer occur against a potential difference of only 100 mV. Thus the partner of Parker's cation need not have an oxidation potential of +0.85 V for the second electron, but the potential should at least be close to this value.

A second problem with the Parker system was the report that the dication, which was the triplet, was thermally unstable at temperatures above  $-80^{\circ}\text{C}$ . We have confirmed that this is indeed the case. The final difficulty was that no temperature studies had been done on the dication, so that it was not even established that the triplet state being observed was in fact the ground state. We have solved this last problem by doing Curie law studies on this dication, and have found that the triplet esr signal follows the  $1/T$  law down to  $10^{\circ}\text{K}$ . Thus it does seem clear that the hexamethoxytriphenylene dication is indeed a ground state triplet. However, the other difficulties still remained.

For this reason we set out to synthesize a nitrogen analog in which six amino groups stabilize the triphenylene cation systems. It was hoped that the extra stability expected from such substituents would strongly shift the oxidation potentials required to establish the mono and dications while still leaving the dication as a ground state triplet. This hope proved to be justified. We also hoped that the nitrogen stabilized dication would be thermally much more stable. While this also proved to be true, the properties of our dication are still not ideal.

The trimerization of veratrole to hexamethoxytriphenylene had been achieved previously by oxidation with ferric chloride or with chloranil, prior to the Parker electrochemical trimerization. We hoped that a suitable derivative of *o*-phenylenediamine might also undergo such oxidative trimerization to generate the desired structure. We have examined a number of derivatives of *o*-phenylenediamine, including those in which the electron donor properties of the nitrogen were temporarily strongly diminished by acylation, but in no case were we able to achieve an oxidative trimerization corresponding to that which is known for the veratrole system. Thus we went to a different synthetic approach (Fig. 8).



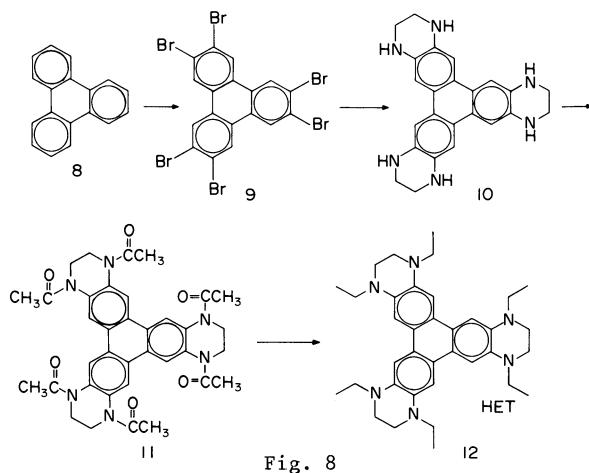


Fig. 8

Triphenylene was allowed to react with an excess of bromine in nitrobenzene solution with ion bromide catalysis. This led cleanly to the formation of a good yield of 2,3,6,7,10,11-hexabromotriphenylene 9, uncontaminated by other materials or isomers. This hexabromide was then heated with ethylenediamine with copper catalysis, and the resulting hexamine 10 was directly converted by acetylation to the hexa-acetamide 11. In contrast to the air-sensitive hexa-aminotriphenylenes (*vide infra*) this hexa-amide could be handled in the normal way and isolated as a pure crystalline solid. This was then smoothly reduced with diborane to 2,3,6,7,10,11-tris(N,N'—ethylenediamino)triphenylene (12). We refer to this neutral hexamine as HET. It is very easily oxidized by even traces of oxygen to the green cation radical, but with care can be obtained pure in good yield. It shows remarkable behavior on electrochemical oxidation.

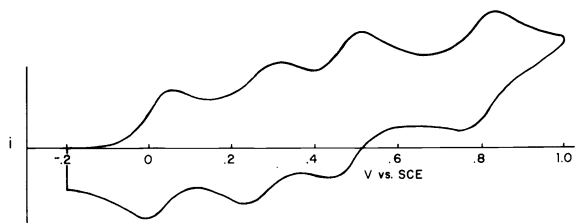


Fig. 9 - Cyclic voltammogram of HET in the reversible region.

Cyclic voltametry (Fig. 9) shows that HET can be reversibly oxidized to a monocation, a dication, a trication, and a tetracation. A further oxidation wave is irreversible. The oxidations occur at quite cathodic potentials (Fig. 10). Thus as expected the six nitrogens of HET make the oxidation to the dication ( $E_{1/2} = +0.271\text{V}$ ) much easier than it was ( $E_{1/2} = 0.87\text{V}$ ) for the

hexamethoxytriphenylene system. All of these systems are of interest. The ion 16, for instance, seems to be the first example of a fully conjugated organic tetracation. However, to date we have focused on the examination of 13, the monocation, and 14, the dication.

Cation 13 is formed spontaneously when HET is exposed to air, and it can also be produced by stoichiometric addition of  $\text{I}_2$  or  $\text{Br}_2$ . It shows a strong esr signal with thirteen lines, as expected from splitting by six equivalent nitrogens. The coupling constant  $a_N$  is 3.5 gauss, and the g-factor is very near the free electron value. The conversion of HET (12) to the cation radical 13 with  $\text{Br}_2$  was also examined in the ultraviolet spectrometer; the spectrum of 13 was the same as that observed when 13 was generated by controlled-potential electrolysis with direct ultraviolet observation of the electrolysis cell.

The dication 14 can be prepared by controlled potential electrolysis of HET, but is most conveniently made by chemical oxidation with one mole equivalent of  $\text{Br}_2$ . The resulting blue-green solution from either procedure, frozen to  $120^\circ\text{K}$ , gave a characteristic triplet esr spectrum with satellites to the

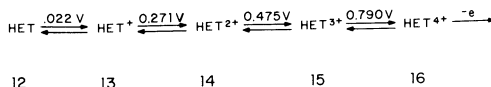


Fig. 10

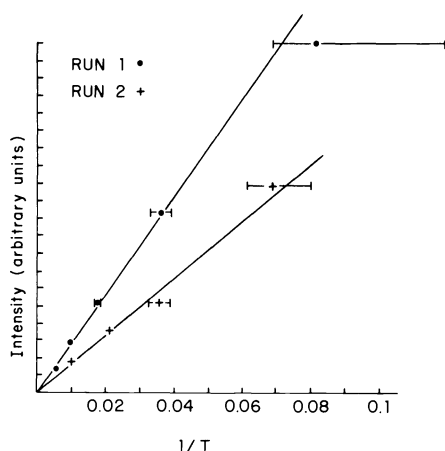


Fig.11

Curie Law plot of the  $\Delta m_s = 2$  line of  $\text{HET}^{2+}$ 

radical signal. From their positions we calculate  $D = 0.022 \text{ cm}^{-1}$  and  $E = 0$ . The  $\Delta m_s = 2$  line was rather weak. The triplet signal was lost when the solution of 14 was held at room temperature for ten minutes, then frozen.

The intensity of the  $\Delta m_s = 2$  line was studied over the temperature range  $12^\circ \text{ K}$  to  $150^\circ \text{ K}$ . The data are plotted in Figure 11 according to the Curie law, and show good linearity. Thus the HET dication 14 is apparently a ground-state triplet molecule, as was 7. From the uncertainty of the Curie law plot the triplet state of 14 can lie at most  $0.013 \text{ kcal/mole}$  above the ground state.

Since the  $D$  value in triplet EPR spectra reflects the average separation of the two unpaired electrons, comparisons among the various pi electron triplets are of interest. In  $\text{HET}^{2+}$  the two electrons are further apart ( $D = 0.022 \text{ cm}^{-1}$ ) than they are in the hexamethoxy dication 7 ( $D = 0.038 \text{ cm}^{-1}$ ). Such diminished interaction of the two unpaired electrons because of delocalization onto the heteroatoms should decrease the energy advantage of the triplet state over the singlet state, but this is clearly not the only factor which determines whether a given species with potential degeneracy is in fact a ground state triplet. In pentaphenylcyclopentadienyl cation (3) the  $D$  value of ( $0.1050 \text{ cm}^{-1}$ ) was larger, but in 3 the triplet state is not the ground state while in 7 and 14 it is. Distortion of 7 or 14 to break up the symmetry of the system is apparently not facile, while in 3 the symmetry can be easily disrupted if one of the phenyls is simply rotated so as to take it further out of conjugation relative to the other four. The smaller energy gap in the penta-anisylcyclopentadienyl cation 4 may mean that such deconjugation is less easy with a more stabilizing substituent.

#### PARTNERS FOR HET IN POSSIBLE FERROMAGNETIC SYSTEMS

In selecting a second component, several factors have to be considered. Perhaps most important is the choice of oxidation potentials. It is necessary that the partner fully accept one electron from HET, so that one has a salt consisting of the HET cation radical and the partner anion radical. A salt would be expected to have the alternating structure needed in this model for ferromagnetism. In addition to this it is necessary that the partner be able to accept a second electron with a potential close to that of the second potential for HET. Ideally this electron should be accepted to the extent of 50% or a little less, so that the second potential should be equal or a little more negative in the partner than it is in HET. This is really true for the potentials in the solid state, but these potentials are only conveniently measured in solution. Thus one must include the consideration that the solution potentials will not be a perfect guide to the extent of electron transfer in the HET-partner solid.

It seems likely that charge transfer to produce more highly charged species will be favored in the solid state by the presence of counter-ions as immediate neighbors. Thus we might expect that charge transfer in the solid will

be more extensive than would be predicted from the solution potentials. In trying to tune the potential for the second electron transfer to the partner, it thus may be desirable that this be somewhat uphill if judged from the solution values.

Although the Curie law studies seem to indicate that HET dication is a ground state triplet, the singlet state probably does not lie much higher energetically. HET is a rather large system, and the zero field splitting parameter  $D$  is quite small. Thus one must be concerned about whether the preference for a triplet state is preserved in any solid salts made between HET and the partner. For this reason it is quite desirable that the partner have a  $C_3$  rotational symmetry axis if possible, so that it does not produce local anisotropy. Even so there is an excellent possibility that the symmetry of the environment of the HET dication might be perturbed, and this could lead to a reversal in which the singlet state is lower than the triplet state. As we will describe below, this seems to have happened in at least one of the systems we have examined so far.

We have prepared one to one complexes of HET with tetrachlorobenzoquinone, tetrafluorobenzoquinone, tetracyanoquinodimethane (TCNQ) and tetracyanobenzoquinone. The reduction potentials of these compounds are listed in Table 1.

TABLE 1. Reduction potentials vs SCE

Compound	$E_1$	$E_2$
Tetrachlorobenzoquinone	-.02	-.85
Tetrafluorobenzoquinone	-.04	-.82
TCNQ	+1.19	-.36
Tetracyanobenzoquinone	+1.00	+1.17
HET oxidation	+1.02	+1.27
Hexamethoxytriphenylene oxidation	+1.55	+1.85

Judging from these reduction potentials, which are of course characteristic only of the free solution values, we can make some predictions about the extent of charge transfer expected in a one to one complex of each of these substances with HET. For instance, the transfer of the first electron to tetrafluorobenzoquinone is an uphill process by 60 mV, while the second electron transfer is uphill by 1.09 V. Thus we would expect that this pair would not meet our requirements, even on the basis of electrochemical potentials. We find that a weak esr signal in this system follows the Curie Law from room temperature down to  $-170^\circ\text{C}$ . Thus it seems that we have a hybrid structure in which a contribution from the neutral state, with no unpaired electrons, is mixed with that from a (cation radical/anion radical) state while there is no significant contribution from a (dication/dianion) state.

A similar prediction and finding concerns the complex of HET with TCNQ. Now the first electron transfer is favorable by 170 mV, but the second one is still unfavorable and by 630 mV, a lot of energy. Again a weak esr signal follows the Curie Law from room temperature to  $-170^\circ\text{C}$ . With both of these complexes the detailed structures are not yet established. It seems likely that they exist as the donor stack/acceptor stack characteristic of organic electrically conducting systems, but further work which is underway will be needed to clarify this.

With tetracyanobenzoquinone the situation is different. Now the first electron transfer is favorable by almost 1.0 V, so the complex should exist entirely as the (cation/anion) salt. This should therefore have an alternating structure, as we need for our ferromagnetic model. Furthermore, transfer of a second electron is only 100 mV unfavorable, so there should be a 2% contribution of the (dication/dianion) structure if we take these potentials as valid in the solid state. Thus this could be a good candidate for ferromagnetism if the HET dication is still a ground-state triplet in this system.

Experimentally, the one-to-one complex of HET with tetracyanobenzoquinone shows an esr signal which corresponds to ca. 15% radical at room temperature. In contrast to the Curie Law, this signal weakens on lowering the temperature. Thus the cation radical and anion radical have antiferromagnetic coupling, not ferromagnetic. The temperature dependence of the esr intensity is reversible over the region  $-170^{\circ}$  to  $+50^{\circ}\text{C}$ , and corresponds to an esr active excited state lying 0.6 kcal/mole above the inactive ground state. Thus the radical pair state is mixing with a singlet, not triplet, state to produce the esr inactive ground state.

The potentials are such that it seems unlikely the mixing is with the neutral donor and acceptor, which are of course singlets. Therefore we conclude that HET dication, in this system, is no longer a ground-state triplet species. The asymmetric environment has dropped the singlet state below the triplet, perhaps because tetracyanobenzoquinone does not have  $C_3$  symmetry. However, the triplet state must be close, and we believe that the 0.6 kcal/mole needed to produce an esr signal is the energy needed to reach the triplet state and set up ferromagnetic interactions. Thus a partner with the desirable electrical properties of tetracyanobenzoquinone but with the proper symmetry might be able to produce a ferromagnetic complex with HET. Good candidates, related to some species described by Fukunaga (Ref. 18), are currently under study.

As an alternative, new stable triplet species with a larger triplet-singlet energy gap are of interest, since they should be less sensitive to the symmetry of the environment. If any of these approaches does produce an organic ferromagnet, it will have converted the chemistry of antiaromatic species from a matter of theoretical interest to a new realm of great practical potential.

Acknowledgement - The unpublished work I have described was performed by D. Cortes, J. Demers, B. Jaun, R. Kluttz, D. Mitchell, and C. Xia. Support by the National Science Foundation is gratefully acknowledged.

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