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GROUND STATE Pi-ELECTRON TRIPLET MOLECULES OF POTENTIAL USE IN THE SYNTHESIS OF ORGANIC FERROMAGNETS

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Abstract—2,3,6,7,10,11-Tris(N,N'-diethylethylenediamino)triphenylene (HET) has been synthesized by a route involving hexabromination of triphenylene, reaction with ethylenediamine, hexa-acetylation, and reduction with diborane. Cyclic voltammetry shows that HET can be reversibly oxidized to a mono-cation HET^+, a dication HET^{2+}, a trication HET^{3+}, and a tetraction HET^{4+}. Beyond that the oxidation is irreversible. The dication HET^{2+} is a ground-state triplet species. This fact, and the low oxidation potential required to produce it, make it of interest in testing a proposed mechanism for preparing organic ferromagnetic materials.

Cyclic conjugated systems with 4n pi electrons (n = integer) are unusual for at least three reasons. First of all, they are not strongly stabilized by conjugation, in contrast to the aromatic 4n + 2 systems. In some cases they may indeed be destabilized by conjugation, leading to the phenomenon we have called "antiaromaticity".[1] Secondly, they may exhibit paratropic ring currents, in contrast to the normal diatropic ring currents of aromatic systems. This can be detected in the NMR by a shielding, rather than deshielding, of protons outside the ring.[2] Finally, 4n pi electron molecules can sometimes exist as ground-state triplet molecules, with less than the full spin-pairing needed to maximize the number of pi bonds in the molecule.

The simplest 4n pi electron molecule which has been shown[3,4] to exist as a ground state triplet is cyclopentadienyl cation, $C_5H_5^+$. A salt of this cation was prepared[3] from 5-bromocyclopentadiene and SbF_5. It showed a typical triplet ESR spectrum, with D having a value of $0.1865 \pm 0.0005\,cm^{-1}$ and E being zero ($<$ 0.001). The zero value of E is expected for a triplet of plane polygonal symmetry; the fairly large D value indicates that the two unpaired electrons are close, as expected for this small molecule.

A 4n pi electron cyclic conjugated system has the potential to have a triplet ground state if it has C_3 or greater symmetry. In simple terms, the symmetry leads to degeneracies in some orbitals, while the presence of 4n pi electrons leads to half occupancy of a degenerate orbital pair with consequent spin unpairing and single occupancy of each orbital. However, real molecules need not adopt such symmetric structures. Instead the putative degeneracy of orbitals can be split by molecular distortion. Such Jahn–Teller distortion 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 (Fig. 1).

Another consideration is important—the above is a simplified description in simple MO terms. The four pi electrons of $C_5H_5^+$ triplet in Fig. 1 have been considered in terms of a single electronic configuration $(1, \bar{1}, 2, 3)$ but a better quantum mechanical description can be obtained by *configuration interaction* (CI), in which the wave function for this molecule is a mix of the lowest energy configuration with excited state configurations such as those involving orbitals 4 and 5. In general it can be shown that CI stabilizes singlet states more than it does triplet states (i.e. the single configuration description is less adequate for singlets than for triplets). Thus even in a *symmetrical* 4n molecule it would in principle be possible that the ground state be a singlet.[5]

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 point was brought home in the first cyclopentadienyl cation actually examined, the pentaphenyl derivative.[6] The ESR spectrum of this cation showed that the triplet state was present at − 110° with $E = 0$ and $D = 0.1050\,cm^{-1}$. 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 could be seen that in pentaphenylclopentadienyl cation the ground state is a singlet, and the triplet state lies 0.35 to 1.15 kcal/mole higher in energy. With such a small energy gap there is a detectable population of triplets in thermal equilibrium at essentially all temperatures.

By contrast, the unsubstituted $C_5H_5^+$ triplet followed the Curie law down to 4°K, so it is a ground-state triplet.[3] Similarly, pentachlorocyclopentadienyl cation, $C_5Cl_5^+$, also had a triplet ESR spectrum ($E = 0$, $D = 0.1495\,cm^{-1}$) which followed the Curie law.[7] In line with the results for $C_5Ph_5^+$, cyclopentadienyl cation substituted with five *p*-anisyl groups also has a singlet ground state and a low lying triplet state.[8]

The triplet ground state species $C_5H_5^+$ and $C_5Cl_5^+$ are chemically quite unstable, and this is also true of the hexachlorobenzene dication[9] and some dianions[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 they 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[11] which might cause certain organic compounds to exhibit ferromagnetism, but of all these the most interesting is the proposal of McConnell[12] with

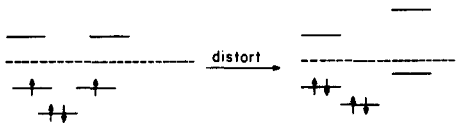


Fig. 1. Symmetrical and unsymmetrical cyclopentadienyl cation.

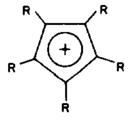
respect to ground state triplet molecules. Because the theoretical model was described only briefly, and in a relatively inaccessible source, it will be quoted here:

"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, $D^+A^-D^+A^-\cdots$. 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.† 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 of 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 free radicals in certain ionic molecular crystals is a very real possibility".

The mechanism proposed is illustrated in Fig. 3. The result of such charge transfer will be to favor a system in which the spins on two neighboring species $D^{\dagger}$ and $A^{\overline{\cdot}}$ 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 $A^{\overline{\cdot}}$ will be parallel to the spins on both neighboring $D^{\dagger}$ species, which in turn must be parallel to both other neighboring $A^{\overline{\cdot}}$ 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 Fig. 4 we show a version in which species M has fully donated an electron to species N, making the $M^{\dagger}/N^{\overline{\cdot}}$ 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 the structure. If M^{2+} has a triplet ground state this charge transfer will lead to ferromagnetic coupling; it would also work if N^{2-} were the triplet and M^{2+} the singlet.



COMPOUND	R	D(cm⁻¹)	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.

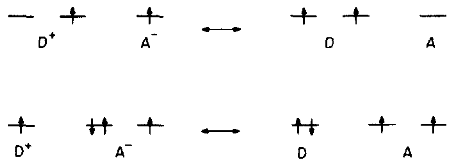


Fig. 3.

Fig. 4.

These considerations led us to note with interest the report by Parker[13] of the preparation of the hexamethoxytriphenylene dication 7. This species showed a triplet ESR with $E = 0$ and $D = 0.038\,\mathrm{cm}^{-1}$, and it was described as a "ground-state triplet". Furthermore, cyclic voltammetry showed that the cation radical **6** could be reversibly oxidized to the dication **7**, at a potential of +0.85 V vs SCE. Thus if an appropriate anion radical $N^{\overline{\cdot}}$ could be found with such a high oxidation potential, it might be possible to utilize dication **7** in the scheme of Fig. 4.

RESULTS

We have repeated the preparation of dication **7** and have confirmed the reported[13] ESR and electrochemical data. Furthermore, we have examined the triplet ESR intensity of **7** as a function of temperature and find that **7** is indeed a ground-state triplet, following the Curie 1/T law down to 10°K. As reported, **7** has no real chemical stability above −80°.

Furthermore, the very high positive potential involved in the **6** to **7** oxidation is a severe limitation on the search for anions $N^{\overline{\cdot}}$. For these reasons we set out to prepare a more stabilized triphenylene dication.

The trimerization of veratrole to hexamethoxytriphenylene had been achieved by oxidation with ferric chloride[14] or with chloranil[15] prior to the anodic[13] trimerization. Thus we have examined several o-phenylenediamine derivatives, including amides, with chemical and electrochemical oxidation methods, but could not see evidence for trimerizations.[16] Apparently the electronic requirements of this reaction are special. For this reason we adopted another approach to the synthesis of a symmetrical hexa-aminotriphenylene derivative.

Triphenylene (**8**) was allowed to react with an excess of bromine in nitrobenzene solution with iron (bromide) catalysis. A good yield (65% of recrystallized material) of 2,3,6,7,10,11-hexabromotriphenylene (**9**) was obtained, identified as this pure isomer by analytical and mass spectral data and a sharp single aromatic proton signal at δ 8.54 in the NMR. This hexabromide was then heated with ethylenediamine with copper catalysis, and the resulting hexamine **10** was directly converted to the

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†See P. L. Nordio, S. G. Soos and H. M. McConnell, *Ann. Rev. Phys. Chem.* 17, 237 (1966).

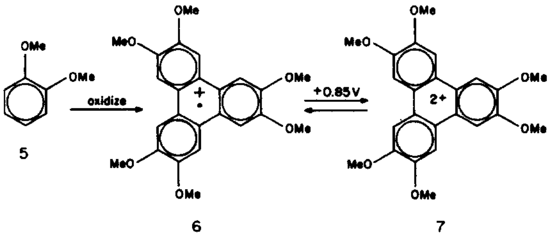


Fig. 5.

hexa-acetamide **11**. In contrast to the extremely air-sensitive aminotriphenylenes (*vide infra*) the hexa-amide **11** could be handled in the normal way and isolated as a pure crystalline solid in *ca* 20% overall yield based on **9**.

The hexa-acetyl derivative **11** was smoothly reduced with diborane to 2,3,6,7,10,11-tris(N,N'-diethylethylenediamino)triphenylene (**12**), which we refer to as HET. This neutral hexamine **12** is very easily oxidized by traces of O_2 to the green cation radical, but with care it can be obtained pure in 75–80% yield. It shows remarkable behavior on electro-chemical oxidation.

Cyclic voltammetry (Fig. 7) showed that HET (**12**) can be reversibly oxidized to a mono-cation (**13**), dication (**14**), trication (**15**), and tetra-cation (**16**). A further oxidation wave is irreversible. The oxidations occur at quite cathodic potentials (Table 1). Thus as expected the six nitrogens of HET make the oxidation to the dication ($E_{1/2} = +0.271$ V) much easier than it was ($E_{1/2} = +0.87$ V) for the hexamethoxytriphenylene system.

All the systems **12**–**16** 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 focussed on the examination of **13**, the mono-cation, 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 I_2 or Br_2. It shows a strong ESR signal with thirteen lines, as expected from splitting by

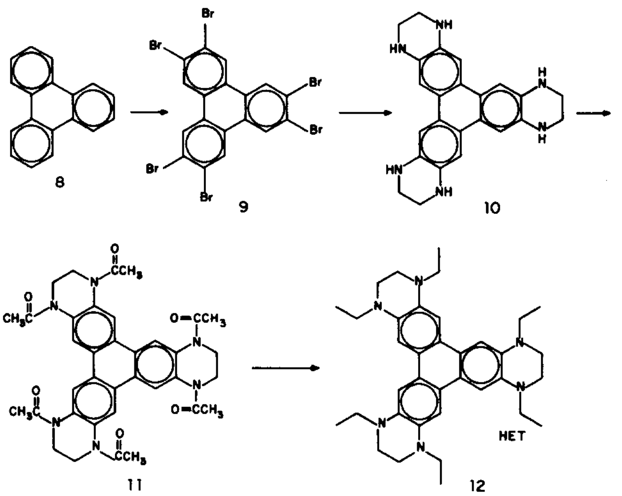


Fig. 6.

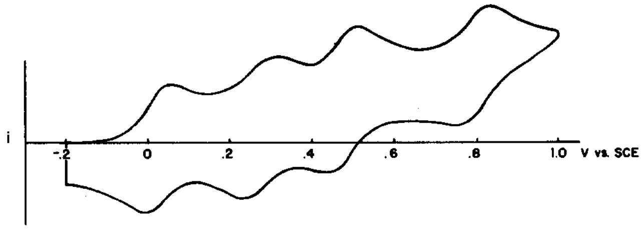


Fig. 7. Cyclic voltammogram of HET in the reversible region.

Table 1. Cyclic voltammetry on HET (12)[a]

wave	1	2	3	4	5
$E_{½}$[b]	0.022	0.271	0.475	0.790	E_p=1.46
i_c/i_a	1.01	1.02	1.02	0.91	~0

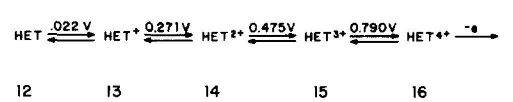
a. At 25°C with HET 2m$\underline{M}$ in CH_3CN with 0.1 $\underline{N}$ tetrabutylammonium perchlorate and a glassy carbon electrode. b. vs. SCE. Calibrated against internal ferrocene, taken as +0.419 vs SCE.

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 Br_2 was also examined in the UV spectrometer; the spectrum of **13** (Experimental) 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 Br_2. The resulting blue-green solution from either procedure, frozen to 120°K, gave a characteristic triplet ESR spectrum with satellites to the radical signal. From their positions we calculate $D = 0.022\,cm^{-1}$ 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 10 min, then frozen.

The intensity of the $\Delta m_s = 2$ line was studied over the temperature range 12°K to 150°K. The data are plotted in Fig. 9 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 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 HET^{2+} the two electrons are further apart ($D = 0.022\,cm^{-1}$) than they are in the hexamethoxy-dication **7** ($D = 0.038\,cm^{-1}$). 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 ($0.1050\,cm^{-1}$) 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 substitutent.



$$\underset{12}{HET} \underset{}{\overset{.022\,V}{\rightleftharpoons}} \underset{13}{HET^{+}} \overset{0.271\,V}{\rightleftharpoons} \underset{14}{HET^{2+}} \overset{0.475\,V}{\rightleftharpoons} \underset{15}{HET^{3+}} \overset{0.790\,V}{\rightleftharpoons} \underset{16}{HET^{4+}} \xrightarrow{-e}$$

Fig. 8.

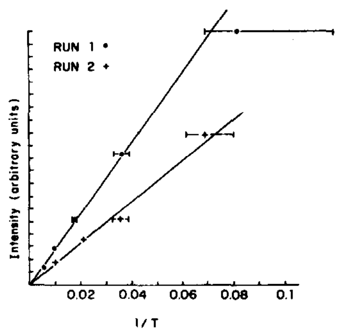


Fig. 9. Curie law plot of the $\Delta m_s = 2$ line of HET^{2+}.

The properties of HET are quite attractive for tests of the McConnell proposal for synthesis of an organic ferromagnet. The cation radical is very stable, and the potential required to convert it to the triplet dication is low enough that many anions N^- should be able to participate in the charge transfer of Fig. 4. The results of our studies of such systems will be reported elsewhere.

EXPERIMENTAL

2,3,6,7,10,11-*Hexabromotriphenylene* (**9**). To a soln of triphenylene (2.0 g) in nitrobenzene (80 ml) with Fe powder (0.18 g) was added Br_2 (4 ml) dropwise over 5 min. The soln was allowed to stand for 10 hr (solid separates), then heated under reflux at 205° for 2 hr (the solid dissolves, HBr is evolved and a new solid separates). The mixture was cooled, mixed with 200 ml ether, and filtered. The crude product, obtained in 95% yield, was recrystallized from 800 ml o-dichlorobenzene to afford pure **9**, m.p. 500–502° (sealed capillary, dec.). (Found: C, 30.52; H, 0.84; Br, 68.89. Calc. for C, 30.81; H, 0.86; Br, 68.33%.) The NMR (in $CDCl_2CDCl_2$ at 145°) showed a singlet at δ 8.74 ($CDCl_2CHCl_2$ standard at δ 5.93). The UV spectrum had λ_{max} 278 nm (210,000) while the IR and MS were as expected.

2,3,6,7,10,11 - *Tris*(N.N' - *diacetylethylenediamino*)*triphenylene* (**11**). A mixture of **9** (3.0 g), *freshly* prepared Cu_2Br_2 (0.24 g), Cu powder (0.2 g) and freshly distilled ethylenediamine (60 ml) were placed in a heavy-walled reaction tube which was carefully degassed (three freeze-thaw cycles) and sealed under vacuum (liquid N_2). The tube was then heated in an oil bath at 220–230° for 2 days. After cooling the excess diamine was removed *in vacuo* (2.5 days) without air exposure of the reaction mixture and degassed Ac_2O (90 ml) and pyridine (15 ml) was added to be brown residue. After 6 hr heating at 90–100° the volatile material was evaporated and the residue taken up in 200 ml H_2O and extracted with four 200 ml portions $CHCl_3$. Evaporation and washing with MeOH gave 840 mg (30%) crude **11**; it was recrystallized from MeOH to afford 550 mg (18%) of **11**, m.p. 380°(dec.). The NMR ($CDCl_2CDCl_2$ at 77°) showed expected singlets at δ 8.63 (6 H), 4.03 (12 H), and 2.38 (18 H). The CI/MS showed $M+1 = 649$. (Found: C, 64.22; H, 6.20; N, 12.24. Calc. for 11·2MeOH: C, 64.03; H, 6.22; N, 11.79%.)

2,3,6,7,10,11 - *Tris*(N,N' - *diethylethylenediamino*)*triphenylene* (*HET*, **12**). A suspension of **11** (65 mg) in 5 ml 1 M B_2H_6 in THF under N_2 was heated under reflux for 3 hr, producing a clear yellow soln. After cooling, 20 ml of degassed 6 N HCl was added, the solvent evaporated *in vacuo* and an additional 25 ml degassed 6 N HCl was added. The filtered soln was then neutralized with degassed 6 N NaOH under N_2 with rigorous exclusion of air, and the resulting solid **12** was collected under N_2 and washed several times with degassed water. Vacuum dried **12** was obtained in 75% yield as an air-sensitive solid. EI/MS 564 (HET^+), 282 (HET^{2+}). NMR δ 7.48 (s), 3.54 (q), 3.41 (s), 1.30 (t) in the expected ratios.

Cyclic voltammetry was performed on HET at 2 mM in acetonitrile with 0.1 N tetrabutylammonium perchlorate at a glassy carbon electrode at 25°. Calibration was against ferrocene (419 mV vs SCE). No significant difference was seen at −45°.

A soln of HET in CH_2Cl_2 at −78° was treated with one equiv Br_2, then frozen to −150°. It showed a typical triplet ESR spectrum, with xy lines at 3360 and 3130 gauss, z lines at 3470 and 3030 gauss, and a weak $\Delta m_s = 2$ line at 1606 gauss. The intensity of this line was measured over the temp region 150°K to 12°K. The results are plotted in Fig. 9.

The HET^+ ion **13** was formed when HET or its solns were exposed to air. The resulting green solns showed a strong ESR radical spectrum with 13 lines, corresponding to splitting by the six nitrogens with $a_N = 3.5$ gauss. Fine structure from coupling to protons was not observed. The radical could also be prepared by treating HET in CH_2Cl_2 with 1/2 equiv I_2, or with $AgClO_4$ aq. A soln of HET in CH_2Cl_2 (2 mM) at room temp was treated with 1/2 equiv Br_2 in a UV cell. It showed λ_{max} (log ϵ) of 1147 (3.08), 990 (3.73), 700–630 (3.73), 477 (3.08), 366 (3.68), 328 (3.72) and 290

(3.68) nm. There were isosbestic points at 344, 304, 283 and 247 nm on conversion of HET (**12**) to the HET$^+$ (**13**) by addition of portions of the Br_2. On addition of more than 1/2 equiv Br_2 the spectrum decayed. The epsilons are based on the assumption that the formation of **13** was quantitative.

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