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IMPLICATIONS FOR THE DESIGN OF ORGANIC FERROMAGNETS BASED UPON HEXAAZAOCTADECAHYDROCORONENE

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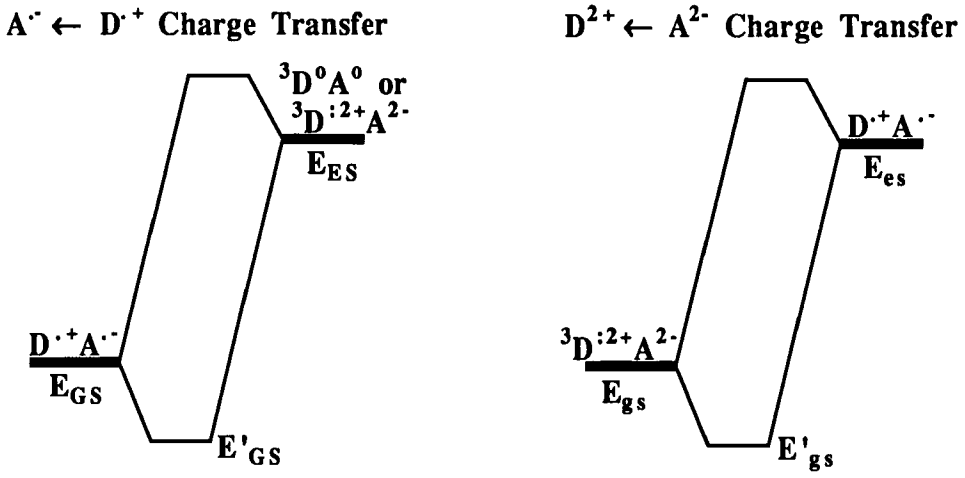
Abstract The molecular and electronic structures of $[HOC]^n$, n = 0 - 4+, have been studied by a variety of experimental and theoretical techniques. The ground state structures for n = 0 and 4+ are closed shell systems. The structures for n = 1+ and 3+ are doublets and show Jahn-Teller distortions. The structure for n = 2+ in the solid is a Jahn-Teller distorted closed shell singlet. The Jahn-Teller distorted structures all resemble two cyanine dyes coupled by single C-C bonds. The 1:1 complex of $[HOC]^{\cdot+}[TCNE]^{\cdot-}$ was synthesized following McConnell's model for ferromagnetism but the complex was found to be antiferromagnetic. A number of suggestions for designing triplet dications and dianions with degenerate orbitals based on benzene derivatives are presented following our experience with $[HOC]^n$.

INTRODUCTION

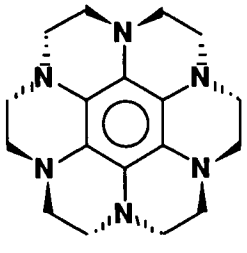
The design and synthesis of molecular ferromagnets is an area of increasing interest among inorganic, organic and physical chemists. A variety of mechanisms for how ferromagnetism in molecular systems can be achieved have been developed.[1] The best example of ferromagnetic behavior in a molecular solid is the electron transfer salt of decamethylferrocene, $Fe(C_5Me_5)_2$, and tetracyanoethylene, TCNE.[1,2] The model used to explain this behavior derives from a short proposal by McConnell[1-4] and the basis of this model is illustrated in Scheme I. The ground state is the $D^{\cdot+}A^{\cdot-}$ radical pair generated by electron transfer from a donor D, $Fe(C_5Me_5)_2$, to an acceptor, A, TCNE. Ferromagnetism requires spin alignment throughout the bulk and thus the radical pair must be high spin, e. g., a triplet. McConnell originally proposed that mixing of an $^3D^oA^o$ excited state with the $D^{\cdot+}A^{\cdot-}$ excited state will stabilize the triplet ground state for the repeat unit.[1,3,4] Breslow extended this idea in his quest to prepare a bulk molecular

ferromagnet, but based it upon forward, not retro, charge transfer, Scheme I, and made the triplet the ground state. He has thus focused research activities

Scheme I



in the area toward the design of stable triplet dications.[5] One feature of the McConnell model is that there be an orbital degeneracy (intrinsic or accidental) in the excited state triplet.[1,3,4] Thus, in the Breslow modification, the triplet, dication ground state should have a degenerate orbital. With his long interest in antiaromatic systems, Breslow proposed the use of $4n$ π systems with $C_{>2}$ symmetry as the source of the ground state triplet. A logical starting place are hexasubstituted benzenes for which triplet dications had been identified. For example, Wasserman and co-workers have shown that $[C_6Cl_6]^{2+}$ is a ground state triplet in the matrix.[6] However, this system is not chemically stable and the search for chemically stable dications derived from C_6R_6 evolved. The search lead to the synthesis of hexaazaoctadecahydrocoronene, HOC, **1**, and its dication, $[HOC]^{2+}$ was reported to be a ground state triplet.[7]



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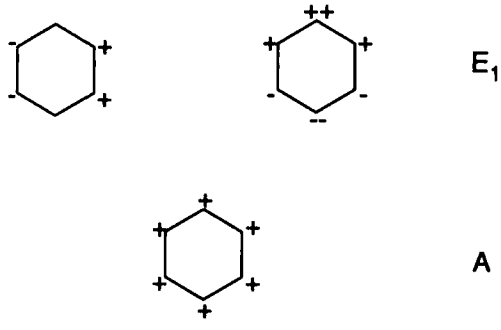
Based on the discovery of the bulk ferromagnetism in $[Fe(C_5Me_5)_2]^{\cdot+}$-$[TCNE]^{\cdot-}$,[2] we were interested in designing a completely organic ferromagnet. Specifically, we sought an $S = 1/2$ $D^{\cdot+}$ as a $[D]^{\cdot+}[TCNE]^{\cdot-}$ salt with an $S = 1$ charge transfer excited state, and identified the HOC donor.[7,8] In our model we are using a dication excited state. Thus, HOC was synthesized and studied electrochemically.[9] We prepared several $[HOC]^n$ salts where n = +1 - +5 and showed that with appropriate care we could structurally characterize all of these charged ions except for n = 5+ using x-ray crystallography.[9a,b,d] The 1:1 electron transfer complex between TCNE and HOC, $[HOC]^{\cdot+}[TCNE]^{\cdot-}$, was indeed synthesized. The solid is comprised of segregated $\cdots D^{\cdot+}D^{\cdot+}D^{\cdot+}\cdots$ and $\cdots A^{\cdot-}A^{\cdot-}A^{\cdot-}\cdots$ chains and it exhibits strong antiferromagnetic behavior, *not* ferromagnetic behavior. From the magnetic susceptibility measurements, the high temperature data can be fit by the Curie Weiss expression, $\chi = C/(T - \theta)$, with $\theta = -50$ K. Thus, [HOC][TCNE] has strong antiferromagnetic coupling[9b] and our original motivation for studying this system was not successful. Subsequently, we embarked on an extensive study of the electronic, structural, and spectroscopic behavior of $[HOC]^n$ as a function of n in order to better understand this novel molecule and the mechanism of antiferromagnetic coupling.

THEORETICAL MODEL

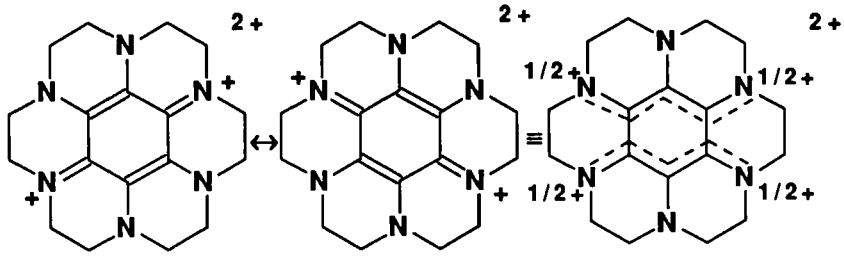
Before discussing our experimental and theoretical results, it is appropriate to review the basic electronic structure of hexasubstituted benzenes. We focus initially on the benzene π orbitals, Scheme II, presuming no mixing with the substituent orbitals. Of course such an argument is simplistic as there must

Scheme II



be mixing of the substituent orbitals with the benzene π orbitals if the molecule is to be easily oxidized. Furthermore, removal of more than 4 π electrons may be significantly different because of the sigma orbitals that interleave between the π HOMO and the doubly occupied π orbital.[10] Neutral HOC should be aromatic with a ^1A ground state. The n = 1+ ion has an a^2e^3 orbital occupancy leading to a ^2E electronic state. This state must exhibit a Jahn-Teller distortion in order to remove the orbital degeneracy. The n = 2+ ion has an a^2e^2 orbital occupancy which leads to a number of possible electronic states. The triplet state is a ^3A state which is not electronically degenerate; this is the reason for the interest in $[HOC]^{2+}$. However, there are two possible singlet states, ^1E and ^1A, that can be derived from the above occupancy. The ^1A state is also nondegenerate and is expected to be very high in energy. The ^1E state must of course undergo a Jahn-Teller distortion to break the degeneracy. One desires that such a distortion will not lead to an energy below that of the ^3A state, but there is no guarantee that this will be fulfilled. The n = 3+ ion has an a^2e electron configuration resulting in a ^2E electronic state as in the n = 1+ ion and, just like the n = 1+ ion, $[HOC]^{3+}$ must also undergo a Jahn-Teller distortion. The n = 4+ ion has an a^2 occupancy and has a totally symmetric ^1A state.

We now discuss possible Jahn-Teller distortions that could be present in the n = 1+, 2+ and 3+ ions. Because of the presence of the nitrogens, which can stabilize the excess charge, there are two likely C_{2v} distortions as illustrated for HOC^{2+}. The first distortion leads to a structure **2** which is best described as two cyanine dyes each with three carbons and two nitrogens and the dye fragments are connected by C-C single bonds. For this structure, the two positive charges are nominally assigned to the four equivalent nitrogens. The remaining two nitrogens, which are connected to the central



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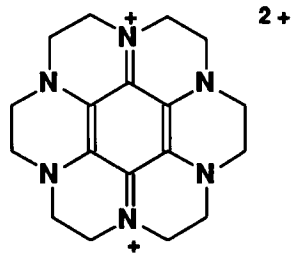

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carbon of the cyanine fragment, do not change in length and can be considered as spectator groups. The other alternative is the formation of the *p*-phenylendiiminium dication **3** which places two short double bonds in the C_6-ring with four longer C-C bonds and two short C=N+ bonds with four longer spectator bonds.[9a,b] It is important to note that a significant amount of the positive charge is expected to be on the nitrogens in contrast to the simple benzene orbital-based model described above where the charge would be localized on the C_6-ring. A schematic of the region of the conical intersection for the ^1E state of $[HOC]^{2+}$ is shown in Figure 1. There are three equivalent ways to perform each of the two C_{2v} distortions, thus, six curves are illustrated. As discussed below, the distortion to **2** is of lower energy than the distortion to **3** so the two sets of curves are shown with unequal energies. By making the ^1E conical intersection a ^2E similar sets of curves will be found for $[HOC]^{\cdot+}$ and $[HOC]^{\cdot 3+}$.

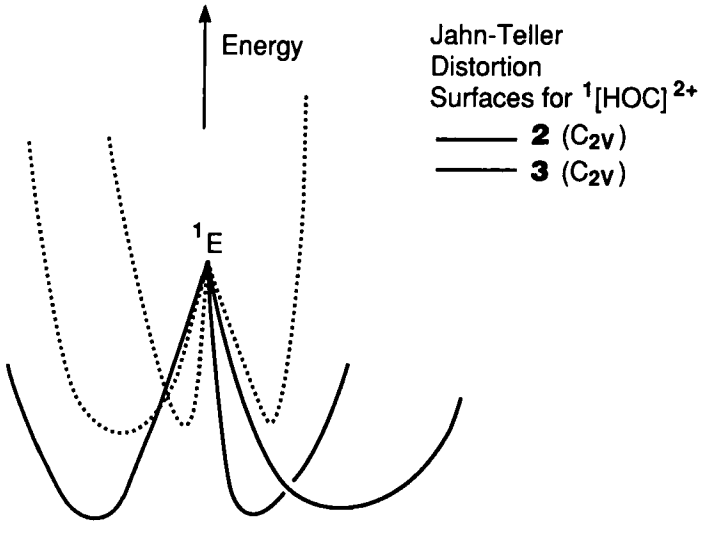
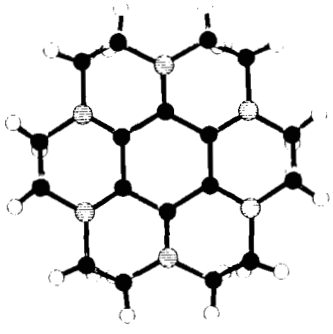


FIGURE 1 Conical intersection showing Jahn-Teller distortions for $[HOC]^{2+}$ ^1E state.

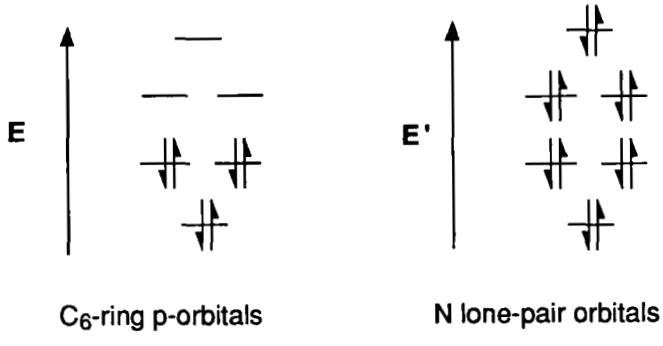
MOLECULAR STRUCTURES FOR $[HOC]^n$

The structure of HOC, **1**, was determined and as shown below the molecule is not planar. With monatomic substituent groups C_6R_6 is planar with D_{6h} symmetry. For most polyatomic R, the molecular symmetry will be lower[11] because the substituents do not lie in the molecular plane as observed for HOC where the symmetry is D_{3d}. HOC is best described as a C_6 benzene core with six pyramidal $N(CH_2)$ groups bonded to it. The CH_2 groups alternate above and below the molecular plane. In this arrangement, the lone



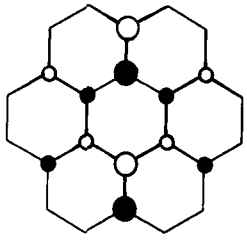
pairs on the nitrogens are parallel to the benzene π orbitals and there are three with larger lobes above the C_6 plane and three with larger lobes below this plane. The three benzene occupied π orbitals mix with the six occupied nitrogen π lone-pair orbitals, Scheme III. (Note that the energy scales are different.) This results in a HOMO with significant electron density on the nitrogens as shown in Scheme IV. These molecular orbitals were obtained at

Scheme III

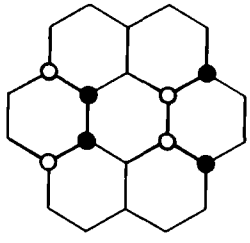


the optimized geometry from an ab initio calculation[12] with the STO-3G basis set.[13] Not only do the orbitals show mixing of the C and N orbitals, but there is more electron density on the N than on the C. This leads to profound consequences on ionization as we shall show below.

Scheme IV



HOMO



LUMO

The variation in the C_6 ring C-C bond lengths and in the distance between the N and the C_6 ring carbons is shown in Figure 2. For HOC all of the C-C and all of the C-N bond distances are equal within experimental error. Generation of the n = 1+ ion as the $[HOC][BF_4]$ salt shows that the C-C and C-N bond distances are no longer equivalent in the crystal.[9b] Thus $[HOC]^{\cdot+}$ is undergoing one of the expected Jahn-Teller distortions which leads to a C_{2v} symmetry structure. The ion has two long C-C bond distances and four shorter C-C bond distances. The shorter C-C distances are like those found for HOC^0. For the C-N bond distances, the two longer bond distances are like those in HOC^0 and the shorter ones are now shorter than the C-C bond distances. The distortion is the one leading to two cyanine dye moieties coupled by single bonds, i. e., **2**. Since only one positive charge is present, the structure cannot completely form two coupled cyanine dye fragments.[9b] The ionic forces in the crystal place the ion in a lower symmetry environment and we thus observe a static Jahn-Teller distortion.[21]

$[HOC]^{\cdot+}$ is paramagnetic and exhibits complicated temperature dependent ESR spectra.[9b] As expected from other work,[14] the carbons and the nitrogens are all equivalent in solution or in a glass. The path to interconvert the lower symmetry C_{2v} structures about the conical intersection at the D_{3d} structure is of very low energy, Figure 1, and thus we cannot observe a dynamic Jahn-Teller distortion. It is important to note that there is a

low energy path involving asymmetric vibrations that connects the six distorted structures without the need for accessing the conical intersection. We cannot yet determine whether both sets of C_{2v} distortions yield minima on

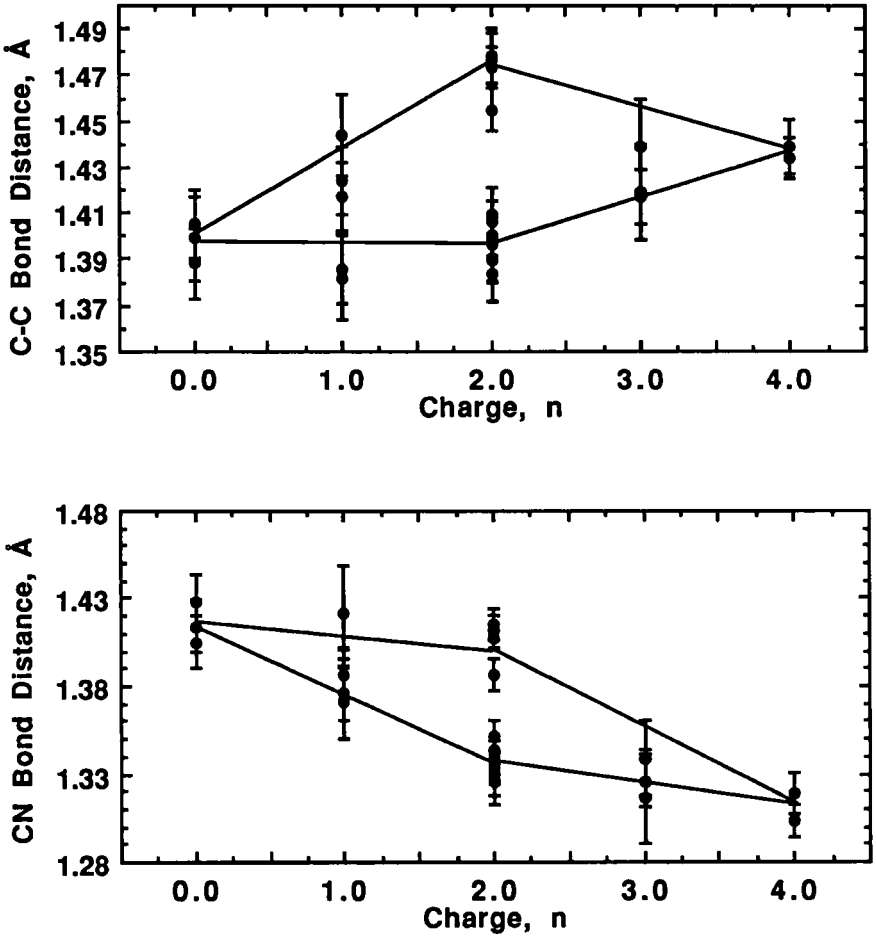


FIGURE 2 C_6-ring CC bond distance (•) as a function of n (top). C_6-ring C-N bond distance (•) as a function of n (bottom). The brackets are 3 esd's for each distance. The solid lines are a guide for the eye.

the potential energy surface or whether only the distortions leading to **2** yield minima and those leading to **3** yield transition states on the path interconnecting the three equivalent structures of **2**. Such low energy paths have also been seen in M_3 systems where M is a Group IA or IB metal.[15] At higher temperatures the protons are all equivalent, but at lower temperatures

the axial and equatorial protons on the CH_2 groups can be distinguished. The barrier to making the protons all equivalent is 5.6 kcal/mol. This higher energy process is different from the process which makes all of the carbons and nitrogens equivalent and can be considered as coupled inversions of the pyramidal nitrogens. The calculated spin populations show that there are approximately equal spin populations on the C_6-ring carbons and on the nitrogens[9b] after accounting for the spin polarization. The observed distortion shows that the electron is removed from the HOMO, **B**, and thus the excess spin reflects the nature of this orbital.

Magnetic susceptibility experiments on the $[HOC]^{2+}$ ion prepared as the 1:2 $[BF_4]^-$, $[PF_6]^-$, $[SbF_6]^-$, $[C(CN)_3]^-$, and $[F_3CSO_3]^-$ salts show that $[HOC]^{2+}$ is diamagnetic and thus has a closed shell ground state.[9b] The observed upturn at higher temperatures shows that there is a thermally accessible excited triplet state. The crystal structures of five different salts were determined. As shown in Figure 1, the C_6 ring C-C bond distances and the C-N bond distances are clearly inequivalent. Thus the structure does not have the D_{3d} symmetry expected for the symmetric triplet, but has a C_{2v} structure consistent with a distorted singlet. The distortion shows two long C-C bond distances (1.471 Å) and four short ones (1.395 Å). The C-N bond distances show a similar distortion with four short distances (1.337 Å) and two longer ones (1.405 Å). Clearly the distortion is the one yielding the coupled cyanine dyes **2** just as observed for the n = 1+ ion. The static Jahn-Teller distortion observed for the dication is larger than the static distortions observed for either the n = 1+ or 3+ ions. Ab initio calculations on $[HOC]^{2+}$ are consistent with the cyanine dye distortion being more stable than the phenylenediiminium distortion. At the MP2 level,[16] **2**, is more stable than **3** by 5.4 kcal/mol.[9a,b] This ~5 kcal/mol energy difference between **2** and **3** is consistent with the value of 5.6 kcal/mol found in $[HOC]^{\cdot+}$ for making all of the protons equivalent. The barrier to making the carbons and nitrogens equivalent in $[HOC]^{\cdot+}$ is significantly lower than 5.6 kcal/mol as the distorted structures were never observed by ESR in solution for $[HOC]^{\cdot+}$. The barrier for motion about the conical intersection, however, could be larger for $[HOC]^{2+}$ because the distortions are greater due to the need to pair the spins and break the orbital degeneracy. Single crystal ESR measurements give a singlet-triplet splitting of 3.4 kcal/mol with the singlet being the ground state for the $[C(CN)_3]^-$ salt.[17] The structures of the dications of 1,2,4,5-

tetrakis(dimethylamino)benzene[18a] and hexakis-(dimethylamino)benzene[18b] have also been determined. These structures do not have the external ring framework but they show the static Jahn-Teller distortion **2** that we observed for $[HOC]^{2+}$. Because they lack the rigidity of $[HOC]^{2+}$, these dications show a very nonplanar benzene ring with twisting about the two C-C single bonds. These results are all consistent with $[HOC]^{2+}$ being a ground state singlet in the crystal.

The above results do not identify the ground state of $[HOC]^{2+}$. Since by necessity there are anions present for any practical material that will be synthesized, our results show that the dication in the solid is unlikely to be a good candidate for a molecular ferromagnet based on a triplet dication ground state. Further evidence that determining the actual ground state of the isolated dication is difficult comes from ESR measurements of $[HOC]^{2+}$ in glasses.[9c] At least three different sites have been identified. Site A has a population of 0.1 - 5% and is a ground state triplet. It is only observed below 40 K and the population is dependent on the thermal history of how the sample was prepared. Site B is a ground state singlet with an excited state triplet with a singlet-triplet energy splitting of 0.5 kcal/mol. It is this triplet signal that swamps the signal from site A at higher temperatures. At even higher temperatures, another triplet signal can be observed. We designate this as site Γ and note that the singlet-triplet energy splitting is >0.5 kcal/mol.

As would be expected from the above results, $[HOC]^{\cdot 3+}$ also has a static Jahn-Teller distorted structure. The distortion (**2**) is the same as observed for the n = 1+ and 2+ ions. The ion is paramagnetic as expected and has a different ESR behavior than the n = 1+ ion. We were unable to freeze out either the motion about the conical intersection or the motion leading to inequivalent axial and equatorial protons. This is in accord with a more flexible structure for n = 3+ than for n = 1+. The ab initio calculations on the n = 3+ ion were difficult to converge, but do show that the excess α spin population will be found largely on the nitrogens. Since there is only one α electron to be placed in the original degenerate HOMO, the electron goes into HOMO (Å) and thus the spin populations reflect the nature of the orbital.

The n = 4+ ion is diamagnetic without a thermally accessible open-shell excited states detectable from magnetic susceptibility measurements below 320 K. The structure of the salt $[HOC][SbF_6]_4 \cdot MeCN$ shows that the C_6

ring C-C bond distances are equivalent to each other and the C-N bond distances are equivalent to each other.[9b]

The average C_6 ring C-C bond distances increase whereas the C-N bond distances decrease with increasing positive charge, Figure 2. Thus, there is more C-C single bond character in the benzene ring and more iminium double bond character in the C-N bonds. This can be quantified by determining the APS bond order[19] at the PRDDO level[20] for the three totally symmetric structures, HOC, $^3[HOC]^{2+}$, and $[HOC]^{4+}$, Figure 3. The bond orders for the C_6-ring C-C bonds decrease from 1.40 to 1.11 Å whereas the C-N bond orders increase from 1.02 to 1.52 Å. Another feature is the increased deviation of the C_6 ring carbons and the nitrogens from the plane defined by these atoms as charge is increased, Figure 4. Clearly, increasing the single bond character in the C_6 ring leads to larger deviations from planarity and a more flexible ring.[9b]

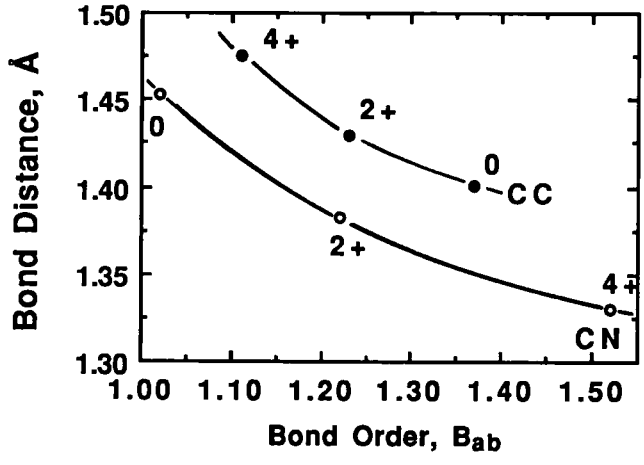


FIGURE 3. Bond distance as a function of APS bond order, B_{ab}.

A simple valence bond summary of the structures is given in Figure 5. The n = 0 and n = 4+ structures are closed shells and are formally aromatic based on the benzene orbitals; for a 4m+2 Huckel system, HOC^0 has m = 1 and $[HOC]^{4+}$ has m = 0. The other three charged species all show Jahn-Teller distorted structures with the largest distortion found for the n = 2+ ion. This ion has two degenerate electrons that must be spin paired in order to form the distorted structure by breaking the orbital symmetry. Since they are

doublets, the other two structures (n = 1+, 3+) must break only the orbital degeneracy and the effect can be smaller.

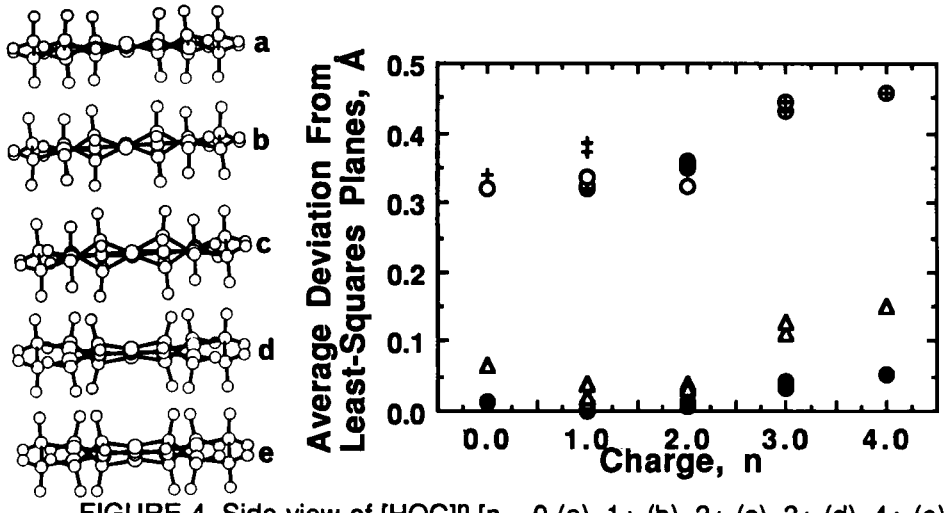


FIGURE 4. Side view of $[HOC]^n$ [n = 0 (a), 1+ (b), 2+ (c), 3+ (d), 4+ (e)] (left) and the average ring-C and CH_2 deviations from C_6-ring (• and Δ, respectively) and C_6N_6 (o and +, respectively) least-squares planes as a function of n. distance as a function of n (right). The solid and dashed lines are a guide for the eye.

IMPLICATIONS FOR THE DESIGN OF A MOLECULAR FERROMAGNET

Although we were unsuccessful in preparing a bulk ferromagnet from $[HOC]^{\cdot+}$ as various radical anion salts, we did gain a significant amount of understanding about the behavior of substituted benzenes with high symmetry. It is clear that one must be careful in designing not only the donor but also the structure of its radical cation and dication. A dication that can have a large stabilizing Jahn-Teller distortion that lowers the singlet state below the ^3A state should be avoided. A key feature is the ease of oxidation of the benzene ring. Substituents that stabilize positively charged structures and have the appropriate oxidation potentials must interact with the benzene π orbitals. If the mixing is too great, then the electrons may be removed from the wrong fragment of the molecule stabilizing the Jahn-Teller singlet state of the dication. This is especially true with hexasubstituted benzenes for which the dications can be stabilized by the same resonance structures that stabilize $[HOC]^{2+}$. For example, the following two molecules have been reported to have ground state triplet dications and we suggest that they be re-examined

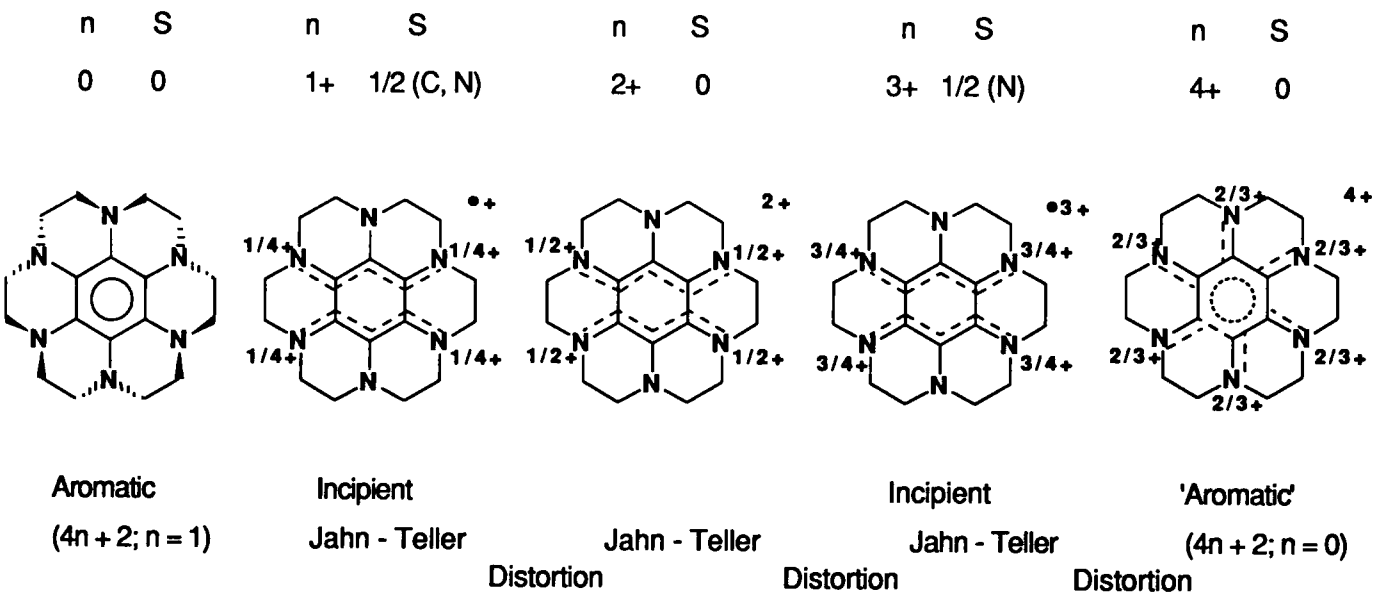
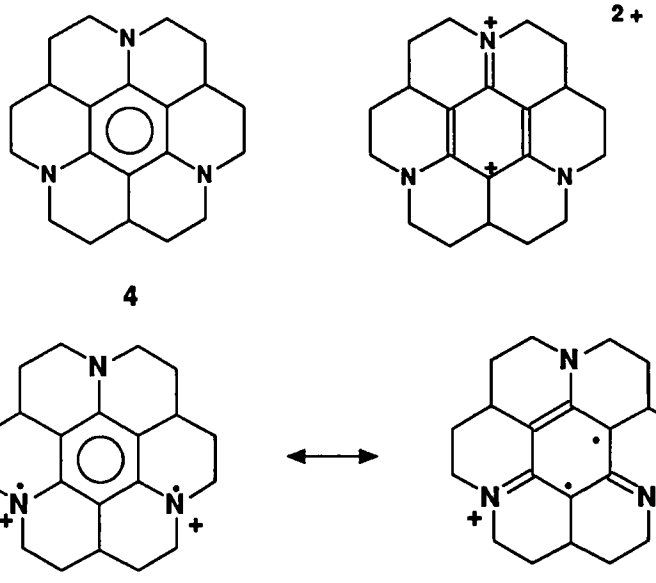


FIGURE 4. Summary of the $[HOC]^n$ structures as a function of n.

in light of our study: 2,3,6,7,10,11-tris(*N*,*N*'-diethyldiamino)triphenylene and hexamethoxytriphenylene. As discussed above, practical materials will have counterions which due to their interactions can lead to lower symmetry environments which enhance the static Jahn-Teller distortions. One should try to design materials that even in such lower symmetry environments will not undergo a large enough static Jahn-Teller distortion to lower the singlet below the triplet.

One reason that such structures may be ground state singlet dications is that there are two fragments that can stabilize the singlet by delocalizing the positive charge over several atoms. This can be avoided by formation of two stabilizing fragments by lowering the symmetry. Rather than having the six equivalent substituents in HOC (due to the presence of the S_6 axis), the symmetry can be lowered from D_{3d} to a structure where the highest symmetry axis is only 3-fold. A simple modification of HOC leads to **4** which now has only three symmetrically placed substituents. This reduction in symmetry



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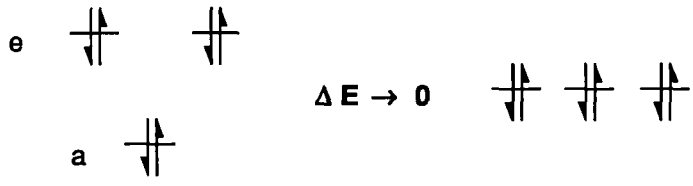
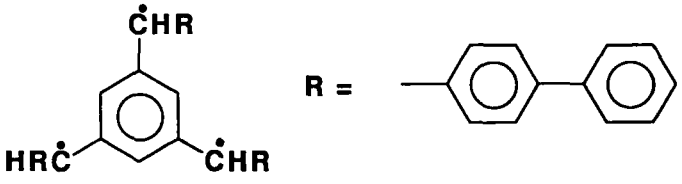
leads to a different set of orbital interactions than found for the hexasubstituted benzenes. Although the benzene orbitals remain the same, there are only three orbitals for the substituents, an a and an e, Scheme V. The lower energy a orbital mixes with the benzene orbital of the same symmetry and the e orbital mixes with the benzene orbital of e symmetry so

Scheme V

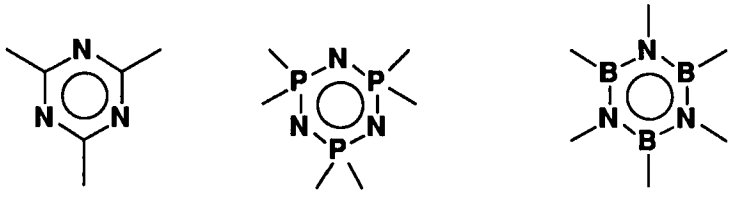


there are no obvious electronic consequences. However, the substituents are not adjacent to each other and the energy splitting between the a and e substituent orbitals will be very small. In fact, to first order the substituent orbitals are degenerate. Thus, removal of two electrons from these orbitals could lead directly to a triplet depending on the energy of these orbitals in comparison to the benzene orbitals. In the hydrocarbon system **5** the molecule is in the high spin quartet state.[21] (This would be isoelectronic to the trication of our proposed molecule.) Thus, we would expect that the monoanion which is isoelectronic to the dication of our proposed structure would be a triplet. Of course, charge separation may also play a role in determining the singlet-triplet splitting.

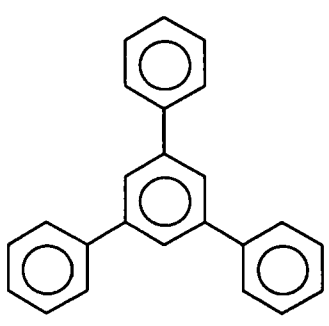


5

The dication cannot undergo distortion to a C_{2v} structure, but must undergo distortion to a C_s structure. The consequences of this are shown above. The available distortion leads to only one cyanine dye fragment which has one positive charge and the other positive charge is an allyl cation. However, the positive charges are not as well separated as in $[HOC]^{2+}$ and the energy of the distorted singlet structure may not fall below that of the triplet which may have better charge separation. Furthermore, the triplet may be stabilized because the spin and charge can be highly delocalized. Other similarly substituted S and O tri-substituted benzenes may also have ground state triplet dications. It is also possible that the dications derived from triazines, **6**, cyclophosphazenes, **7**, and borazenes, **8**, may also be ground state triplets.

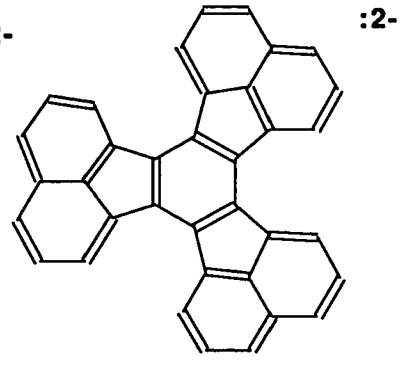


6 7 8



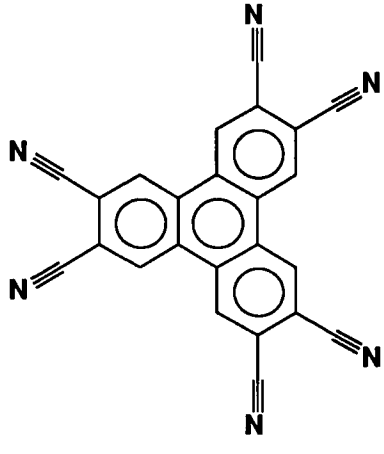
S = 1

9

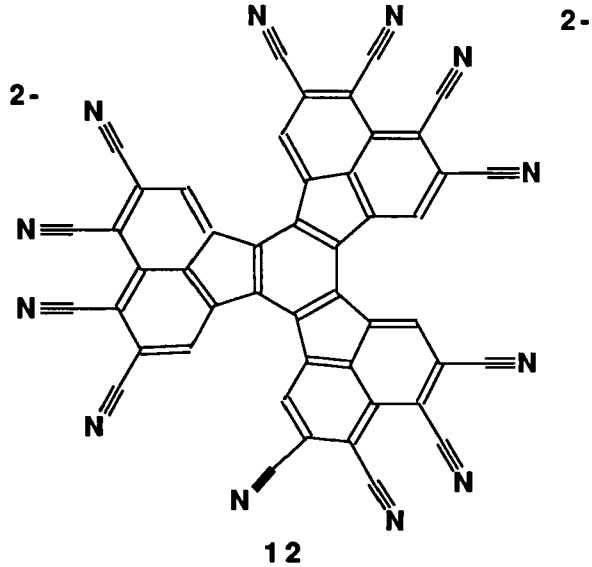


S = 1

10



11



12

There is no physical reason in the McConnell model that specifies that the triplet must be in the dication. If one considers appropriately substituted benzene dianions as the source of the triplet, it may be possible to synthesize

such species. The benzene dianion also has a $[]e^2$ electron configuration as does the dication. Although the dianion of coronene is reported to be a singlet, the dianions of **9** and **10** are reported to be triplets. One might use such dianions to form the following types of ferromagnetic chains: $D^{\cdot}+A^{\cdot-}D^{\cdot}+A^{\cdot-}$ or $D^{2+}A^{:2-}D^{2+}A^{:2-}$. Thus, stable mono- and dianions, for example, **11** and **12**, should be designed.

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REFERENCES

1. J. S. Miller and A. J. Epstein, *NATO Adv. Study Ser. 168B*, 159 (1987). J. S. Miller, A. J. Epstein, and W. M. Reiff, *Chem. Rev. 88*, 201 (1988). J. S. Miller, A. J. Epstein, and W. M. Reiff, *Acc. Chem. Res. 23*, 114 (1988). J. S. Miller and A. J. Epstein, *Adv. Org. Chem. XX*, 000 (1989).
2. J. S. Miller, J. C. Calabrese, H. Rommelmann, S. Chittapeddi, J. H. Zhang, W. M. Reiff, and A. J. Epstein *J. Am. Chem. Soc. 109*, 769 (1987). S. Chittapeddi, K. R. Cromack, J. S. Miller, and A. J. Epstein *Phys. Rev. Lett. 58*, 2695 (1987).
3. H. M. McConnell, *Proc. R. A. Welch Found. Chem. Res. 11*, 144 (1967).
4. J. S. Miller and A. J. Epstein, *J. Amer. Chem. Soc., 109*, 3850 (1987).
5. R. Breslow, *Mol. Cryst. Liq. Cryst, 125*, 261 (1985). R. Breslow, *Pure Appl. Chem., 54*, 927 (1982). R. Breslow, B. Jaun, R. Q. Klutz, and C-Z. Xia,*Tetrahedron, 38*, 863 (1982).
6. E. Wasserman, R. S. Hutton, V. J. Kuck, and E. A. Chandross, *J. Am. Chem. Soc. 95*, 1965 (1974).
7. (a) R. Breslow, P. Maslak, and J. S. Thomaides, *J. Am. Chem. Soc. 106*, 6453 (1984). (b) J. S. Thomaides, P. Maslak,and R. Breslow, *J. Am.Chem. Soc. 110*, 3970 (1988). (c) T. J. LePage and R. Breslow,*J. Am. Chem. Soc. 109*, 6412 (1987).
8. B. Kohne, K. Praefcke, and A. Reichmann, *Chem-Ztg. 109*, 17 (1985).
9. (a) J. S. Miller, D. A. Dixon, Calabrese, J. C. *Science 240*, 1185 (1988). (b) J. S. Miller, D. A. Dixon, J. C. Calabrese, C. Vazquez, P. J. Krusic, M. D. Ward, R. L. Harlow, submitted. (c) P. J. Krusic, E. Wasserman, R. Breslow; J. S. Miller, in preparation. (d) D. A. Dixon, J. C. Calabrese, R. L. Harlow, and J. S. Miller, *Angew. Chem. 101*, 81 (1989); *Angew. Chem. Int. Ed. Engl. 28*, 92 (1989).

10. D. A. Dixon, D. A. Kleier, and W. N Lipscomb, *J. Am. Chem. Soc.100*, 5691 (1988).
11. D. A. Dixon, J. C. Calabrese, and J. S. Miller, *Angew. Chem. 101*, 79 (1987); *Angew. Chem. Int. Ed. Engl. 28*, 90 (1989).
12. All calculations were done with the program GRADSCF which is an ab initio gradient program system designed and written by A. Komornicki at Polyatomics Research Mountain View, CA.
13. W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys. 51*, 2657 (1969).
14. (a) G. R. Liebling and H. M. McConnell *J. Chem. Phys. 42*, 3931 (1965). (b) M. K. Carter and G. Vincow *J. Chem. Phys. 47*, 292 (1967). (c) T. R. Tuttle and S. I. Weissman, *J. Am. Chem. Soc. 80*, 5342 (1958). (d) R. W. Fessenden and S. Ogawa, *J. Am. Chem. Soc. 86*, 3591 (1964). (e) J. R. Bolton and A. Carrington, A. *Mol. Phys. 4*, 271 (1961). (f) M. G. Townsend, and S. I. Weissman *J. Chem. Phys. 32*, 309 (1960).
15. S. C. Richtsmeier, R. A. Eades, D. A. Dixon, and J. L. Gole, in *Metal Bonding and Interactions in High Temperature Systems,* ed. J. L. Gole and W. C. Stwalley, *A. C. S. Symposium Series 179*, 177 (1982) and references therein. C. A. Mead, *J. Chem. Phys.78*, 807 (1983). T. C. Thompson, D. G. Truhlar, and C. A. Mead, *J. Chem. Phys. 82*, 2392 (1985). D. G. Truhlar, T. C. Thompson, and C. A. Mead, *Chem. Phys. Lett. 127*, 287 (1986).
16. (a) C. Moller and M. S. Plesset, *Phys. Rev. 46*, 618 (1934). (b) J. A. Pople, J. S. Binkley, and R. Seeger, *Int. J. Quantum Chem. Symps. 10*, 1 (1976).
17. E. J. Gabe, J. R. Morton, K. F. Preston, D. A. Dixon, P. J. Krusic, E. Wasserman, and J. S. Miller, *J. Phys. Chem. XX*, 0000 (1989).
18. (a) K. Elbl, C. Krieger, and H. A. Staab, H. A. *Angew. Chem. Int. Ed. Engl. 25*, 102 (1986); *Angew. Chem. 98,* 1024 (1986). (b) J. M. Chance, B. Kahr, A. B. Buda, J. P. Toscano, and K. Mislow, K. *J. Org. Chem. 53*, 3226 (1988). J. Siegal, J. C. Calabrese, and J. S. Miller, unpublished.
19. D. R. Armstrong, P. G. Perkins, and J. P. Stewart, *J. Chem. Soc. Dalton Trans.* 838 (1973).
20. (a) T. A. Halgren and W. N. Lipscomb, *Proc. Nat'l Acad. Sci. USA 69*, 652 (1972). (b) T. A. Halgren and W. N. Lipscomb, *J. Chem. Phys. 58*, 1569 (1973). (c) D. S. Marynick and W. N. Lipscomb, *Proc. Nat'l Acad. Sci., USA, 79*, 1341 (1982).
20. J. Brickmann and G. Kothe, *J. Chem. Phys. 59*, 2807 (1973).G. Kothe, E. Ohmes, J. Brickmann, and H. Zimmerman, *Angew. Chem. 83*, 1015 (1971); *Angew. Chem. Int. Ed. Engl. 10*, 938 (1971). G. Schmauss, H. Baumgartel, and H. Zimmerman, *Angew. Chem. 77*, 619 (1965). *Angew. Chem. Int. Ed. Engl. 4*, 596 (1965). See also K. Itoh, *Pure and Appl. Chem. 50*, 1251 (1978).
21. I. Hargitaiand I. Hargitai *Symmetry Through the Eyes if a Chemist*, VCH Publishers, New York, NY, 1987, p273-277.