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Sigma-delocalized aromatic species formed from cyclic arrays of hypervalent main-group element species

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Abstract - Evidence suggests that the dication formed by oxidation of hexaiodobenzene may reasonably be called a sigma-delocalized aromatic species. A variety of experimental results supports the suggestion that two electrons are removed from the sigma-delocalized HOMO of hexaiodobenzene to form the 10-electron (4n+2) aromatic dication. The higher field chemical shift observed for the ^{13}C NMR singlet upon conversion of hexaiodobenzene to the dication, an upfield shift of 42.6 ppm, is best described by the proposed sigma-delocalized ring-current of the circular array of six iodines, calculation of the graph-theoretical resonance energy for the hexaiodobenzene dication, 0.013 β_{CC} per delocalized sigma electron, provides evidence for sigma-delocalized aromatic stabilization for the cyclic array of coplanar overlapped p-orbitals of the six iodines of the dication. The sigma-aromaticity of the dication is similar to the pi-aromaticity of the 10-pi-electron species, azulene (0.015 β_{CC} per electron). The six sigma-delocalized orbitals of the six iodines of the dication are arranged similarly to the pi-delocalized orbitals of benzene but are not as widely separated as are those of benzene. This provides lower frequency absorptions of the dark blue solution of the dication ditriflate with two peaks in the near infrared region (985 nm and 1155 nm). Current evidence supports the suggested 10-electron sigma-delocalized aromatic species, the hexaiodobenzene dication, 1.

INTRODUCTION

Common species, such as alkanes, may be described as involving sigma-delocalized bonding along chains of carbon atoms (ref. 1). Most chemists prefer the other way to view the bonding of saturated alkanes, as localized two-center bonding. The sigma-delocalized bonding is more widely accepted for polysilanes with Si-Si bonding (ref. 2) along chains of 8-Si-4 silicon atoms. It is even more common to consider the three-center, four-electron (3c,4e) colinear apical bonding of hypervalent species (ref. 3) in pseudo-trigonalbipyramidal geometry as sigma-delocalized bonding (ref. 3). Examples of linear 5c-6e bonded species are also well known (ref. 4). A cyclic array of main group element atoms, bonded together in a similar sigma-delocalized manner, becomes relevant to the ideas that have been used to consider the cyclic pi-delocalized aromatic species.

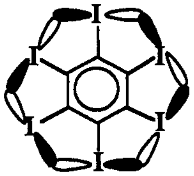


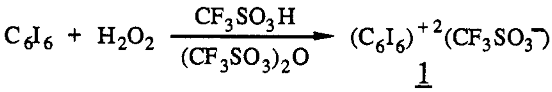
Fig. 1. The HOMO of C_6I_6, as calculated by extended Hückel.

Hexaiodobenzene, C_6I_6, has six coplanar, large diameter main group atoms constrained into a geometry providing strong repulsive interaction between adjacent iodines. This makes the pictured sigma-delocalized MO high in energy (ref. 5). Calculations by the extended Hückel method designate the pictured molecular orbital as the HOMO of C_6I_6. Our evidence (ref. 5) for easy oxidation of hexaiodobenzene to form a stable dication $(C_6I_6)^{++}$ is compatible with removal of two electrons from this HOMO to give a singlet dication with 6c-10e cyclic sigma-delocalized bonding. The upfield shift of the ^{13}C NMR singlet of C_6I_6, 121.7 ppm, to the upfield singlet at 79.1 ppm for $(C_6I_6)^{++}$, supports this conclusion. Is a 6c-10e sigma-delocalized bonded species a sigma-delocalized aromatic species? This will be discussed.

Replacements of iodine atoms of C_6I_6 by other large atoms (such as Te, Se, etc.) (ref. 6) provide compounds which can be oxidized to species related to $(C_6I_6)^{++}$. Using geometric centers other than the benzene ring of C_6I_6 allows the constraint of a number of atoms other than six into a cyclic array analogous to that of C_6I_6. This makes it possible to consider other types of sigma-delocalized aromatic species, such as Möbius sigma aromatic species (ref. 7), etc.

A SINGLET GROUND-STATE HEXAIODOBENZENE DICATION

The dication made by photochemical oxidation of hexachlorobenzene at low temperature was found by Wasserman, *et al.* (ref. 8) to exist as a triplet ground state. This was suggested as a removal of two electrons from two HOMO pi-orbitals of equal energy in the benzene pi system to make the ground state a triplet state. The analogous hexaiodobenzene dication was found (ref. 5) to exist as a singlet ground state, determined by measuring magnetic susceptibility to establish its diamagnetic nature.



$$C_6I_6 + H_2O_2 \xrightarrow[(CF_3SO_3)_2O]{CF_3SO_3H} \underset{\underline{1}}{(C_6I_6)^{+2}(CF_3SO_3^-)_2}$$

Oxidation of hexaiodobenzene to the dication is rapidly accomplished (ref. 5) by the addition of chlorine, hydrogen peroxide, or the persulfate anion to a suspension of insoluble C_6I_6 in a solvent of triflic (trifluoromethanesulfonic) acid containing triflic anhydride or trifluoroacetyl triflate. The dication salt is very soluble in each medium, while the neutral species is not. It is interesting that the presence of suspended neutral C_6I_6 in the triflic acid solution of the dication does not provide a soluble radical cation ($C_6I_6^{\bullet+}$) by electron transfer from C_6I_6 to the dication. We suggest that the great insolubility of C_6I_6 in triflic or sulfuric acid provides a force for the disproportionation of the radical cation producing the stable crystals of C_6I_6 and a solution of the dications.

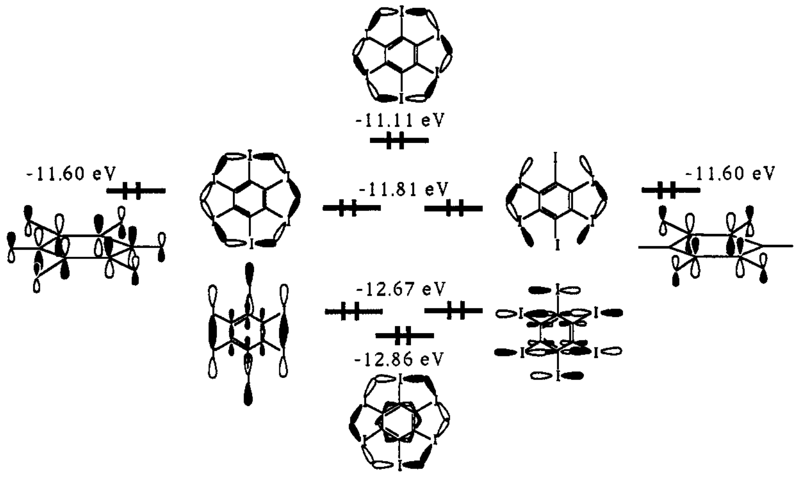
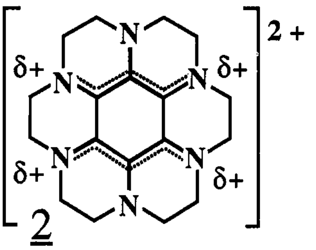


Fig. 2. Highest occupied extended Hückel molecular orbitals for C_6I_6.

The pictured molecular orbitals show the HOMO of C_6I_6 to be a sigma-delocalized orbital (ref. 5). It is possible that removal of two electrons from the HOMO, rather than from the pi-orbitals that are lower in energy by this sort of calculation could provide the singlet ground state. Similar results were obtained by MNDO (ref. 9) and AM1 (ref. 10) calculations for C_6I_6.

Another way to provide a singlet ground state aryl dication is to provide the Jahn-Teller distortion determined (ref. 11) by X-ray crystallography for the hexaazaoctadecahydrocoronene dication 2. The dication of this hexaamino substituted benzene is distorted to provide two allylic cations by removing two electrons from the pi-orbitals with elongation of two of the C-C bonds of the central hexagon, as shown in 2.



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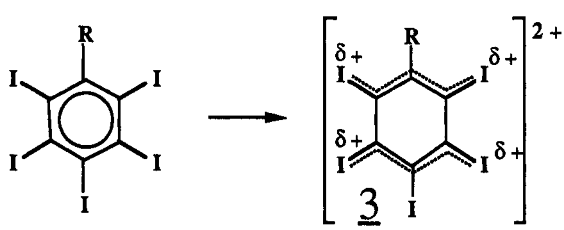
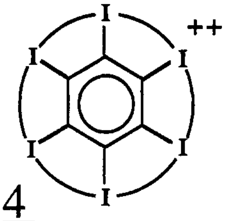
The two allylic cations are expected to be stabilized by the pi-donor nitrogens of 2. If the dication of $C_6I_6^{++}$ had a similar geometry (3) the pi-donor stabilization of the dication by the iodine substituents would be expected to be less than that of the nitrogen of 3. The sigma$^+$ constant (ref. 12) for p-NMe$_2$ is -1.7 while that for p-I is +0.13, making it clear that it would provide less pi-donor stabilization for an allylic cation. An X-ray structure for 1 is being attempted to show a structure more symmetrical than that of 2, as would be required for the sigma-delocalized dication. It is also interesting to note that substitution of one of the iodine atoms of C_6I_6 with a smaller atom (O, F or H) makes it impossible to oxidize it to the dication. If the structure (3) were analogous to 2 it is not clear how a structure (R = H) should be less stable.



The much smaller energy difference between the sigma-delocalized orbitals, compared to the larger energy differences between the pi-delocalized aromatic orbitals, is consistent with the observed spectra for the dark blue solution of $C_6I_6^{++}$ in triflic acid or sulfuric acid. The two peaks observed in the near infrared region (985 and 1155 nm) are compatible with the suggested electronic structure for $C_6I_6^{++}$.

The formation of the dication, by oxidation of the neutral C_6I_6 molecule, results in an upfield shift of the ^{13}C NMR singlet from 121.7 ppm to 79.1 ppm. An upfield shift of 42.6 ppm would not be expected if the dication were a distorted hexagonal species providing two allylic cations by removal of two electrons from the pi-system of C_6I_6. The decrease in electron density at the carbons would probably result in a downfield shift of the ^{13}C NMR peak. If one accepts the suggested 10-electron sigma-delocalized system, involving the six iodine atoms, the central carbons are inside the 10-electron ring-current system of the six iodines as pictured in 4. The two central carbons of 5 were found (ref. 13) to have upfield shifts in their ^{13}C NMR spectrum, interpreted as a ~30 ppm upfield shift for the 14-electron pi-aromatic ring current of the external pi-delocalized cycle. The carbons of benzene are, however, not in the inside region of the pi ring-current, and therefore do not show an upfield shift in the ^{13}C NMR spectrum.



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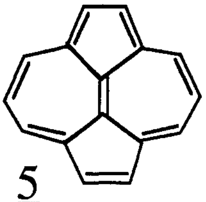

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GRAPH-THEORETICAL RESONANCE ENERGY OF $C_6I_6^{++}$

The interaction of the 5pσ iodine orbitals that are in the molecular plane and are perpendicular to the C-I bonds (Fig. 2) can easily be treated by the Hückel method. Let these orbitals be arranged so that an arrow from the negative to the positive lobe points alternately clockwise and counterclockwise as one moves around the ring of the six iodine atoms. Then all neighboring interactions are bonding and the Hückel determinant is identical to that of the six pπ carbon orbitals in benzene. Hence the secular equation is

$$x^6 - 6x^4 + 9x^2 - 4 = 0 \tag{1}$$

as in benzene except that x depends on the 5pσ-5pσ resonance integral of iodine instead of the carbon 2pπ-2pπ integral. The roots of equation 1 are, as in benzene, $x_i = \pm 2, \pm 1, \pm 1$, and the orbital energies are

$$E_i = \alpha_I - x_i\beta_{II} \tag{2}$$

where α_I and β_{II} are the Coulomb and resonance integrals for the iodine 5pσ orbitals.
The graph theoretical resonance energy (ref. 14) is gotten by first constructing a reference polynomial by dropping all cyclic contributions in the graph theoretical expression for the coefficients in equation 1. This gives

$$x^6 - 6x^4 + 9x^2 - 2 = 0 \tag{3}$$

with roots $x = \pm 1.9319, \pm 1.4142, \pm 0.5176$. The ten iodine σ electrons are put into the five lowest orbitals of equation 1 and of the reference equation 3. The energy difference of $2(2 - 1.9319)\beta_{II} = 0.136\,\beta_{II}$ is the computed graph theoretical resonance energy of the ring of ten sigma electrons in the six iodine atoms.To put this result in terms of the more familiar resonance integral between 2pπ orbitals for carbon, we can make use of the Wolfsberg-Helmholz formula (ref. 15)

$$\beta_{ij} = \frac{k}{2}(\alpha_I + \alpha_j)\, S_{ij} \tag{4}$$

where S_{ij} is the overlap integral between orbitals i and j. Then assuming k to be constant gives

$$\frac{\beta_{II}}{\beta_{CC}} = \frac{\alpha_I\, S_{II}}{\alpha_C\, S_{CC}} \tag{5}$$

The Coulomb integral α_C is minus the valence state ionization potential for the pi-electron in carbon, given as 11.16 eV by Hinze and Jaffé (ref. 16). They do not list the valence state ionization potential for I, but a plot of those given for F and Cl together with the ground state ionization potentials of the halogens (ref. 17) suggests a value of between 10.5 and 12.25 eV with a best guess of about 11.25 eV. An early paper by Mulliken (ref. 18) gives a higher value of 12.93 eV. The overlap integral between $2p\pi$ orbitals on carbon is given by Roothaan's (ref. 19) formula (25a). With an orbital exponent of 1.625 as given by Slater's rules this gives $S_{CC} = 0.244$ at an internuclear distance of 1.40 Å. Roothaan does not list overlap integrals above principal quantum number 2, but the required iodine overlap integrals may be worked out following his methods to give

$$\begin{aligned} S_{II}^{\sigma} = {} & [-3.628\,880 \times 10^{6} - 3.628\,880 \times 10^{6}\,\rho - 1.596\,672 \times 10^{6}\,\rho^{2} \\ & - 3.870\,720 \times 10^{5}\,\rho^{3} - 4.706\,743 \times 10^{4}\,\rho^{4} + 1.316\,571 \times 10^{3}\,\rho^{5} \\ & + 1.784\,686 \times 10^{3}\,\rho^{6} + 4.242\,286 \times 10^{2}\,\rho^{7} + 7.048\,312 \times 10^{1}\,\rho^{8} \\ & + 9.530\,736\,\rho^{9} + 1.108\,225\,\rho^{10}]\, e^{-\rho}/10! \end{aligned} \tag{6}$$

$$\begin{aligned} S_{II}^{\pi} = {} & [3.628\,880 \times 10^{6} + 3.628\,880 \times 10^{6}\,\rho + 1.741\,824 \times 10^{6}\,\rho^{2} \\ & + 5.322\,240 \times 10^{5}\,\rho^{3} + 1.158\,583 \times 10^{5}\,\rho^{4} + 1.909\,029 \times 10^{4}\,\rho^{5} \\ & + 2.472\,229 \times 10^{3}\,\rho^{6} + 256\,\rho^{7} + 2.061\,299 \times 10^{1}\,\rho^{8} \\ & + 1.108\,225\,\rho^{9}]\, e^{-\rho}/10! \end{aligned} \tag{7}$$

where ρ is defined as in Roothaan's paper. Both these are needed since the iodine orbitals used here, although in the ring plane, are a mixture of σ and π components as defined by Roothaan. Then using an iodine Slater exponent of 1.9 and the C_6I_6 inter-iodine distance of 3.507 Å gives 0.194 for the S_{II} in equation 5, and then with Mulliken's value for α_{II} one gets

$$\beta_{II} = 0.921\,\beta_{CC} \tag{8}$$

so that the resonance energy of these ten iodine sigma electrons is computed to be 0.13 β_{CC} or 0.013 β_{CC} per electron. This may be compared with graph theoretical resonance energies per pi electron of 0.046 β_{CC} for benzene and 0.015 β_{CC} for azulene (ref. 20). Hence the computed aromaticity of these ten sigma electrons in $C_6I_6^{++}$ is roughly like that of the pi system in azulene.

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