

Evidence from current-density mapping for σ -delocalisation in the aromatic hexaiodobenzene cation

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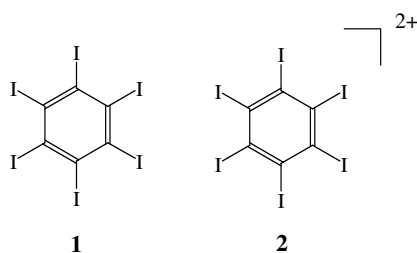
Abstract

Calculation of high σ -delocalisation in the iodine periphery of the hexaiodobenzene cation, accompanied by a four-electron through-space σ ring current, provides direct computational evidence for the attribution to this ion of σ -aromaticity co-existing with the conventional π -aromaticity that it shares with its neutral parent.

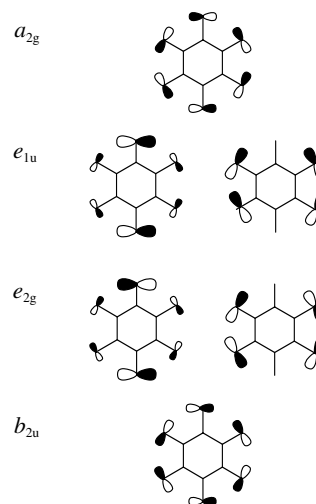
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Notions of π -delocalisation and π -aromaticity are well established in the organic chemistry of planar unsaturated molecules, although the underlying σ bonding in these molecules is almost always described in terms of localised orbitals.^{1,2} It has been suggested, however, that a delocalised picture of the σ electronic structure will give a better account of the properties of species containing cyclic arrays of hypervalent main-group atoms.^{3,4} The particular example cited is the dication $C_6I_6^{2+}$ (**2**) formed by the oxidation of hexaiodobenzene, C_6I_6 (**1**).



Overlap of in-plane iodine 5p orbitals gives rise to six molecular orbitals (see Scheme below), all occupied in the neutral C_6I_6 (**1**), of which the least bonding combination, corresponding to head-to-tail anti-bonding overlap between tangential p orbitals on all I neighbours, is the calculated^{3–5} HOMO.



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On the magnetic criterion of aromaticity, and using the experimental evidence available from NMR spectroscopy, Sagl and Martin⁴ argued that an upfield shift of 42.6 ppm in the position of the ¹³C NMR singlet on the oxidation of hexaiodobenzene to the dication indicates the presence of an extra ring current in the charged species, and they attributed this to σ -delocalisation within the array of iodine atoms. The carbon nuclei would then lie *inside* a diatropic circulation, and hence would be shifted upfield.

Recent ab initio calculations by Ciofini *et al.*⁵ yielded a value of 37.2 ppm at the GIAO/PBE0/6-311G(d,p)//PBE0/LANL2-DZ level for the upfield shift, in good agreement with the experimental value. In the same study, as evidence for the ring-current explanation of this shift, the authors computed a height profile of the difference in NICS (nucleus-independent chemical shift) values⁶ between neutral and cationic species, and deduced an increase in aromaticity in the dication (The fact that the height profile has a maximum in the molecular plane also points to an origin within the σ distribution for the additional ring current.).

In the present work, we used two complementary theoretical techniques to study σ -delocalisation and σ -aromaticity. The first is capable of displaying ring current directly and also of disentangling σ and π contributions to it. Current-density maps and the orbital contributions to them, as computed in the ipsocentric approach,^{7–10} show that there is indeed a separately identifiable σ ring current in the iodine array of the cation (**2**), in addition to the benzenoid π current sustained by the central ring in both neutral and cationic species. We provide an orbital model for the sense of the current, and couple these calculations with a second quantitative measure, the multi-centre index,^{11–13} which characterises the underlying cyclic electron delocalisation in both carbon and iodine circuits. Both criteria support the attribution of σ -aromaticity to the iodine array in $C_6I_6^{2+}$.

Geometries of neutral **1** and cationic **2** were optimised at the RHF level in the 6-311G* basis. The D_{6h} -symmetric optimum geometry of **1** lies in a local minimum at this level of theory ($R_{CC}(\mathbf{1}) = 1.401 \text{ \AA}$, $R_{CI}(\mathbf{1}) = 2.131 \text{ \AA}$), albeit with some low vibrational frequencies (9 cm^{-1} (e_{2u}), 18 cm^{-1} (b_{2g})). However, at the RHF level, the D_{6h} geometry of **2** is a higher-order stationary point, with a doubly degenerate imaginary frequency ($R_{CC}(\mathbf{2}) = 1.383 \text{ \AA}$, $R_{CI}(\mathbf{2}) = 2.086 \text{ \AA}$; $57i \text{ cm}^{-1}$ (e_{1u})). At the DFT level, both are local minima, with bond lengths little changed from the RHF values ($R_{CC}(\mathbf{1}) = 1.410 \text{ \AA}$, $R_{CI}(\mathbf{1}) = 2.138 \text{ \AA}$, $R_{CC}(\mathbf{2}) = 1.395 \text{ \AA}$, $R_{CI}(\mathbf{2}) = 2.106 \text{ \AA}$). Soft modes for out-of-plane distortion are to be expected for C_6I_6 . In the crystal structure,^{14,15} this molecule adopts a crown-like structure with a small (0.04 \AA) difference between the planes defined by triplets of iodine atoms.

Current-density maps were calculated for **1** and **2** in the ipsocentric approach, at the RHF geometries in the same 6-311G* basis, using the sysmo program.¹⁶ This involves calculation of the coupled Hartree–Fock response of the

system to an external magnetic field, under the imposition of a special choice of origin for current density, where each point is its own origin. The ipsocentric approach leads to the partition of total current density into physically non-redundant occupied-orbital contributions, and also has advantages of economy and accuracy of the computed results.⁹ The calculated currents can be rationalised using symmetry and node-counting selection rules.^{9,10} Plotting conventions are that the current density is determined in a plotting plane at a fixed height from the molecular plane (either $1a_0$ or zero). Contours represent the magnitude, and arrows the 2D-projection, of the current density per unit inducing magnetic field. Anticlockwise circulation represents diatropic current, and clockwise circulation represents paratropic current.

Multi-centre indices are calculated in the Mulliken approach from the charge and bond-order matrix, and the basis function overlap matrix.^{11–13} In these calculations, carried out at the RHF/6-311G* geometries and using the same 6-311G* basis, separate indices are calculated for the C_6 and I_6 cycles, and separate σ and π contributions are obtained for each.

The calculated multi-centre delocalisation indices at the RHF/6-311G* level are shown in Table 1. In the neutral system, π -delocalisation is significant for the carbon cycle, whereas σ -delocalisation is small, and for the set of iodine atoms, both σ - and π -delocalisation measures are small. In the dication, the indices for the carbon cycle remain more or less unchanged, but for the set of iodine atoms the σ -delocalisation becomes significant. These trends are compatible with expectations from the normal aromaticity properties of the central benzene ring (large C–C π -delocalisation) and the proposed σ -aromaticity of the iodine array (large I–I σ -delocalisation, but in the cation only).

Within the ipsocentric framework for magnetic response, delocalisation plays an interesting role. It is to be expected that an aromatic system (in the sense of one supporting a ring current) will be delocalised, but the existence of ring current requires more than delocalisation, in that there must be available virtual transitions of appropriate symmetry (translational in the case of diatropic, aromatic current).

Delocalisation therefore emerges as a necessary rather than a sufficient condition for magnetic aromaticity.

Direct insight into the induced currents is provided by the computed maps (Figs. 1 and 2). Both molecules show

Table 1
Multi-centre delocalisation indices calculated at the RHF/6-311G* level, each quoted as a percentage of the ‘reference’ $\sigma + \pi$ benzene value calculated in the same approach

		C_6I_6 1	$C_6I_6^{2+}$ 2	C_6H_6
C	σ	0.9	1.0	2.0
	π	76.0	72.1	98.0
I	σ	0.0	50.8	—
	π	0.0	0.0	—

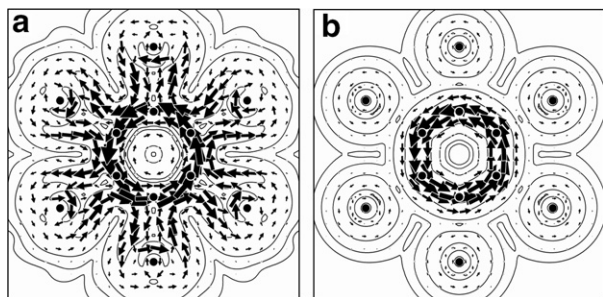


Fig. 1. Map of the current density induced in C_6I_6 (**1**) by a perpendicular magnetic field, as calculated at the ipsocentric CT OCD-DZ/6-311G**/RHF/6-311G* level. Contributions of (a) all ($\sigma + \pi$) electrons and (b) the four electrons of the π HOMO are shown, plotted at a height of 1 bohr from the molecular plane. Arrows indicate the projection of current density in the plotting plane, and anticlockwise circulation corresponds to a diatropic current.

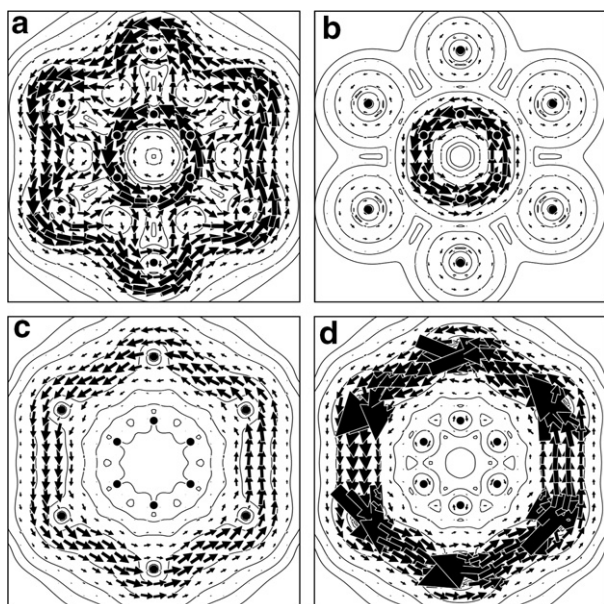


Fig. 2. Map of the current density induced in $C_6I_6^{2+}$ (**2**) by a perpendicular magnetic field, as calculated at the ipsocentric CT OCD-DZ/6-311G**/RHF/6-311G* level. Contributions of (a) all ($\sigma + \pi$) electrons, (b) the four electrons of the highest-lying π orbital, and (c) the four electrons of the σ HOMO ($21e_{1u}$) are shown, plotted at a height of one Bohr from the molecular plane. Panel (d) again shows the contribution from the four electrons of the σ HOMO ($21e_{1u}$), but plotted in the molecular plane itself. Arrows indicate the projection of current density in the plotting plane, and anticlockwise circulation corresponds to a diatropic current.

a global diatropic response (Figs. 1a and 2a). Neutral C_6I_6 supports a diatropic π ring current (Fig. 1b). As in benzene itself, this current is dominated by the contribution of the top occupied π orbital, an orbital which has one angular node and hence has a translationally allowed transition to the lowest unoccupied π orbital, which has two angular nodes. Thus, C_6I_6 is a conventional 4π aromatic.^{9,10} The σ response of C_6I_6 consists only of localised bond currents and so, on the magnetic criterion, does not constitute an indication of aromaticity.

Dicationic $C_6I_6^{2+}$ shows a similar central 4π ring current (Fig. 2b), but also a pronounced current associated with the iodine perimeter. This current is significant in the $1a_0$ plotting plane (Fig. 2c), but stronger in the plane of the molecule (Fig. 2d), indicating its σ character. This too is a 4-electron current, arising in this case from the contribution of the e_{1u} HOMO of $C_6I_6^{2+}$.

This evidence for the σ -aromaticity of **2** is readily understood within the ipsocentric approach. The ipsocentric formulation is a frontier-orbital, ‘spectroscopic’ account of ring current, in that contributions to induced current density arise from virtual excitations governed by symmetry selection rules, and moderated by energy denominators that depend on differences between orbital energies.⁹

The symmetry selection rule for diatropic ring current is that a virtual excitation from an occupied orbital ψ_1 to an empty orbital ψ_2 will contribute a diatropic current if there is a totally symmetric component in the product of representations $\Gamma(\psi_1) \times \Gamma(T_{x,y}) \times \Gamma(\psi_2)$, where $T_{x,y}$ is the pair of translations in the molecular plane. For the π system of a monocyclic molecule, this rule reduces to an angular-momentum requirement: a transition is translationally allowed if and only if ψ_1 and ψ_2 differ by one unit of angular momentum. For the σ system formed by tangential in-plane p orbitals, the orbital symmetries are in one-to-one correspondence with those of the conventional π system, each being multiplied by a one-dimensional irreducible representation (Γ_{σ} , the representation of a concerted rotation at all sites). Significantly, therefore, the symmetry products of π orbitals ψ_1 and ψ_2 and their σ counterparts are equal, and the selection rules are preserved: in both out-of-plane- π and tangential- σ ladders of energy levels, diatropic currents arise from one-step transitions from occupied to empty orbitals.

This formal analogy allows a precise prediction about the perimeter aromaticity of **1** and **2**. In neutral **1**, the whole set of six tangential-p orbitals is occupied, leaving no occupied-to-unoccupied excitations to give rise to a perimeter ring current. In cationic **2**, however, the most anti-bonding tangential-p orbital is empty, allowing a transition from e_{1u} HOMO to a_{2g} LUMO to give rise to a diatropic σ current on the iodine perimeter, an exact analogue of the HOMO–LUMO transition that would be expected to give rise to a conventional π current in a planar 6-centre, 10-electron π system. Therefore, **2** should support a perimeter ring current, whereas **1** should not. As the current-density maps show, this extra σ ring current predicted by basic symmetry arguments is exactly what is found in the computations.

The existence of current is also compatible with the interpretation of reported experimental ^{13}C chemical shifts. In principle, calculations that predict induced current density also predict nuclear magnetic shieldings, and the ipsocentric method and its variants have been tested in this respect for many small molecules.¹⁷ However, quantitative calculation of the ^{13}C nuclear shieldings and chemical shifts in these heavy halocarbons is known to be a difficult

problem, requiring explicit consideration of spin–orbit effects.¹⁸ Conventional calculations that neglect such extra terms reproduce the sign and order of magnitude of the difference in chemical shift between **2** and **1**, but give poor and highly method-dependent values for the individual shifts. With the present basis set, the difference chemical shift (experimental value 42.6 ppm⁴) is variously predicted as: 54.8 ppm (coupled Hartree–Fock (CHF) calculation with the DZ2 variant¹⁷ of the ipsocentric approach); 63.1 ppm (CHF calculation with the PZ2 variant,¹⁷ normally more reliable for the calculation of shieldings); 53.8 ppm (CHF calculation employing gauge-including atomic orbitals (GIAO)); 38.1 ppm (GIAO/PBE0/6-311 G*/RHF/6-311G* calculation); and 39.2 ppm (GIAO/PBE0/6-311G(d,p)//PBE0/LANL2-DZ calculation⁵). In all cases, even those of the density-functional calculations where the difference shift is close to the measured value, the individual ¹³C chemical shifts are in poor agreement with experiment, apparently overestimating the shift for **1** (experiment: 121.7 ppm⁴) by 30–40 ppm and for **2** (experiment: 79.1 ppm⁴) by 15–40 ppm. Inclusion of spin–orbit effects has been predicted to cause increases of ~30 ppm in calculated ¹³C shieldings for centres bonded directly to iodine.¹⁸ Interestingly, these results underline for this difficult case the delicate nature of the deduction of ring current from chemical shift; ring currents are predicted to be present, and the direction of the shift is compatible with their presence, but other effects apparently also make a large contribution both to the separate shieldings and their difference. Quantitative calculation of shieldings is difficult in this case, though the detection of substantial ring current in the calculations has proved to be more straightforward.

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