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A diatropic ring current in a fluorofullerene trannulene

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Ipsocentric current-density maps for a fluorofullerene derivative, $C_{60}F_{15}H_3$, modelling the addition pattern of the experimentally characterised $C_{60}F_{15}[CBr(CO_2Et)_2]_3$ which contains an [18]*trans*-annulene system, reveal a diamagnetic ring current dominated by the contribution of the four HOMO electrons, as in a classical ($4n + 2$) aromatic annulene.

The first all-*trans*-annulene[1] was derived from reaction of $C_{60}F_{18}$ with diethyl bromomalonate in the presence of DBU. The expected cyclopropanation[2] is diverted: the three most accessible fluorine atoms are replaced, substitution taking place δ to the leaving group. The C_{3v} product, $C_{60}F_{15}[CBr(CO_2Et)_2]_3$, has an intense emerald-green colour, presumably arising from electron delocalisation in the equatorial [18]annulene belt.[1] The belt bonds have a length variation of only 0.018 Å (in [60]fullerene[3] the bond lengths are 1.388 and 1.432 Å). In terms of raw counting, the 18 π electrons *of the belt* obey the Hückel ($4n + 2$) rule, but the constituent p-orbitals point radially outwards, whereas a planar aromatic has parallel π p-orbitals, and here the belt is part of a larger 36-atom conjugated system. Previous studies[4,5] on hypothetical *trans*-annulenes suggested realising these in-plane analogues of conventional aromatics *via* functionalised fullerenes. Should the first experimental instance of a trannulene structure then be considered to be *aromatic*?

One criterion of aromaticity is the ability of a system to support an induced diatropic ring current.[6] If the annulene/trannulene analogy is correct, the implication is that such a current exists and[7] originates with the HOMO electrons. We investigate this question using an extension of an approach of proven value in the visualisation and interpretation of ring currents, the ipsocentric method.[7,8] For computational reasons we replace the bromomalonato groups with hydrogens, retaining the pattern of sp^2 and sp^3 cage carbons, but economising on addend basis functions. The cage contains two separate π systems: one is an isolated hexagonal ring, the other is a helmet-like structure with an 18-carbon rim linked to a triphenylene-like bowl by pentagon edges (Fig. 1). The geometry was optimised at the RHF/6-31G** level, reproducing two key features of $C_{60}F_{15}[CBr(CO_2Et)_2]_3$: uniformly short bonds (X-ray, (RHF/6-31G**) h: 1.410 (1.400), i: 1.392 (1.387), j: 1.397 (1.389), all in Å) in the cycle, and long bonds (k: 1.468 Å (1.470 Å)) linking it to the triphenylene unit.[1] These geometric features are consistent with separation of the π system into [18]trannulene and a remainder, implicit in the Hückel model of the 36-centre unsaturated system, where the k bonds have low π bond order (0.407) compared with those of the 18 cycle (h: 0.600; i: 0.575; j: 0.652). Hückel theory also gives the frontier electronic structure. In C_{3v}, the basis of 36 radial π orbitals spans the permutation representation $7A_1 + 5A_2 + 12E$, with $4A_1 + 2A_2 + 6E$ occupied. As a separate unit, an [18]annulene/trannulene has a basis spanning $3A_1 + 3A_2 + 6E$ ($2A_1 + A_2 + 3E$ occupied). Nodal structures show the E HOMO/LUMO of the 36 system to be locally unperturbed [18]annulene HOMO/LUMO orbitals, compressed by the doubling up of symmetries: a gap of 0.6946 $|\beta|$ becoming 0.4360 $|\beta|$. These orbitals will be the major contributors to the HOMO and LUMO of $C_{60}F_{15}H_3$; as symmetry and nodal character of frontier orbitals are key to the existence and sense of circulation of ring current,[7] this gives grounds for expecting annulene-like currents in the fullerene derivative.

Our next step is generation of the ring current map using a new version of the ipsocentric formulation previously applied to many (poly)cyclic systems[7] and hypothetical trannulenes.[5] For a large system, full *ab initio* calculations are expensive and interpretation of results for cage structures is complicated by loss of strict σ/π separation. We therefore first examine the trannulene π system with the 'pseudo-π' method,[9] which uses only a single orbital per centre but reproduces the sense, magnitude and geometry dependence of *ab initio* currents. It relies on symmetry matching of σ- and π-orbitals, to make formal replacement of π p by hydrogenic s orbitals. In a planar system, the relation involves a multiplication of each σ symmetry by that of an out-of-plane vector, but for trannulenes the σ- and π-like symmetries are identical.

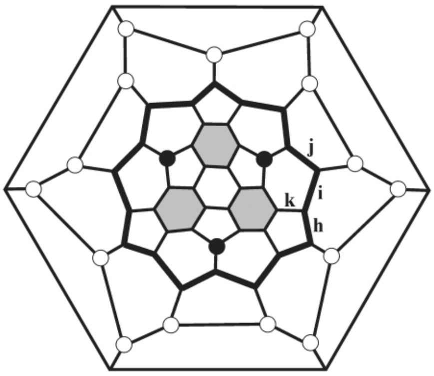

Fig. 1 Schlegel diagram of addition pattern in $C_{60}F_{15}X_3$. White = F, black = X = H, bond labels as in Ref. 1. The diagram is inverted with respect to the usual convention[1] and places the 36-atom π system (trannulene bold, triphenylene Clar hexagons shaded) within the F_{15} perimeter.

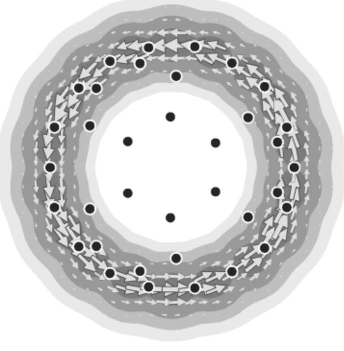

Fig. 2 Ipsocentric pseudo-π ring-current maps[7] in the median plane of the [18]-trannulene system of $C_{60}F_{15}H_3$. Anticlockwise flow is diamagnetic, arrows (shading) represent in-plane projections (modulus) of current density. Filled circles are projected C positions.

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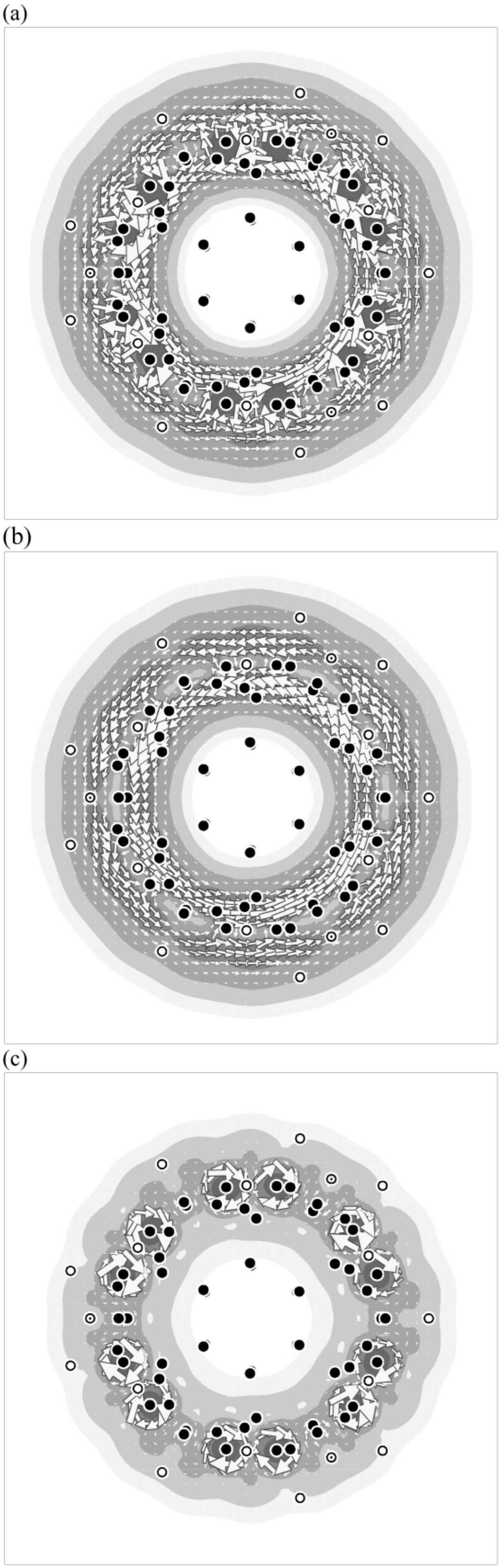

Fig. 3 Current-density maps computed for $C_{60}F_{15}H_3$ *via* the full coupled-Hartree–Fock ipsocentric method in a 6-31G** basis (a) total current density; (b) contribution of the 8 HOMO + HOMO-1 electrons; (c) contribution of the 490 remaining electrons. Filled, open and dotted circles are projected C, F and H positions.

Following Ref. 9, therefore, we attach a single 1s orbital to each position of the 18-carbon annulenic system in the optimised structure, and then calculate self-consistent 18-electron wave-functions by the ipsocentric method. Fig. 2 shows the total pseudo-π current density plotted in the median plane of the 18-cycle. This exhibits a large diamagnetic circulation – a ring current – with a maximum value of 0.151 a.u., significantly larger than the benzene value of 0.079 a.u., as could be expected from the larger radius and smaller gap of the trannulene. Moreover, this ring current is dominated entirely by the contribution of the four *E* HOMO electrons; total and orbital currents maps being visually indistinguishable. Benzene-like ring currents are seen in the outer rings of the triphenylene substructure of the 'helmet', but not in its central hexagon.[10] Restriction to the 18-centre trannulene system gives essentially the same picture (maximum 0.173 a.u., HOMO dominated).

To check that the conclusions from this first application of the pseudo-π model to a 'real' system survive an all-electron treatment, current density maps were re-computed at the *ab initio* RHF/6-31G** level. Fig. 3 shows the total current density in the median plane. The map now has more structure. Separation of orbital contributions reveals the total current in the median plane to consist of a global ring current, now stronger on the cage interior, *plus* localised paratropic circulations where the plotting plane cuts C–C bonds. The global current is dominated by the four HOMO electrons, with some contributions from the four HOMO-1 electrons. This is the classic pattern of a (4*n* + 2) aromatic cycle: diatropic global current, with main contributions from the translationally allowed, node-count increasing, HOMO–LUMO transition.[7] The local paratropic circulations originate in rotationally allowed transitions between occupied σ edge-bonding orbitals and empty π* trannulene orbitals.[5] Ring-current calculations at pseudo-π and *ab initio* levels on a D_{6h}[11] [18]annulene show currents with the same sense, orbital decomposition and similar magnitude (0.181 a.u., pseudo π).

We have shown that a close model of trisbromomalonato-pentadecafluoro-[60]fullerene contains a trannulene structure with its own conjugated, delocalised pathway supporting a ring current that has exactly the same orbital symmetry explanation as in an aromatic annulene. The answer to our opening question is therefore: Yes, $C_{60}F_{15}X_3$ is aromatic in the magnetic sense.

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