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# On the diatropic perimeter of iterated *altan*-molecules†

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**Ab initio calculations of the current density induced by an external magnetic field in *altan*-[10,5]coronene 3 (or *altan*$^2$-[10]annulene) indicate the onset of a diatropic current on the outer loop (the "perimeter"), thus in contrast with the intentional design of *altan*-molecules. Spectral decomposition of the current shows that the failure of the altanisation design can be expected whenever the perimeter of the *altan*-molecule is of nearly the same size of that of the parent molecule. Equal lengths of these two perimeters always occur in iterated *altan*-molecules, which contain a cycloacenic fragment. Like longer polyacenes and cycloacenes, *altan*$^2$-[10]annulene 3 and *altan*-kekulene 2 are predicted to have an open-shell singlet ground state.**

Soon after the discovery of their curved structures, fullerenes and nanotubes have given two major challenges to chemistry: their rational chemical synthesis, and the synthesis of novel molecules suggested by fragments of their unusual skeletons.[1] A good example of the second challenge is offered by trannulenes, all-trans annulenes initially envisaged as fragments of small fullerenes and studied computationally,[2] and then effectively synthesized.[3] A similar candidate for a new synthesis is *altan*-corannulene hexaanion **1**$^{6-}$, which forms half-cage of many $C_{80}{}^{6-}$ fullerenes, and is predicted to be an aromatic molecule.[4] The structure of **1** has been actually proposed as a member of the family of *altan*-molecules, which are formed from parent conjugated molecules with outgoing C–H bonds, upon substitution of the C–H bonds with C–C bonds to *alt*ernating carbon atoms only of an *an*nulene.[5,6] As a result of this "altanisation",[7] the parent molecule is surrounded by a [4$n$]annulene; this property, already demonstrated for benzenoid hydrocarbons,[8] holds for any totally fused polycyclic hydrocarbon with an even number of C atoms.[9] Therefore, in the limit of weak coupling with the inner molecule, the outer annulene of *altan*-molecules is predicted to host a paratropic current in presence of a magnetic field perpendicular to the (average) annulenic plane. It is this peculiar feature which has allowed the in silico design of paramagnetic closed-shell molecules,[10] and aromatic closed-shell anions.[4]

The expectation of a paratropic circulation on the outermost loop (the "perimeter") of *altan*-molecules has been verified in several molecules by ab initio computations;[6,10,11] the only exception is presently the rather large molecule *altan*-kekulene **2**.[6] The paratropic perimeter of *altan*-molecules has been also found[12–15] in those and other molecules by the much simpler tight-binding Hückel-London-Pople-McWeeny (HLPM) approach, which, when results are expressed with reference to benzene, only depends upon connectivity and size of the rings.[16] Interestingly, the HLPM method also reproduces the anomalous ab initio current density pattern of **2**.[14] Using that simple method it has been recently reported that *altan*-[10,5]coronene **3** also has a diatropic perimeter, in contrast with the behaviour expected for an *altan*-molecule.[7] The persistence of this second exception at the ab initio level is not granted, considering that qualitative changes in the current density patterns between the two methods can occur.[17] Here we will disclose ab initio calculations of the current density pattern in **3**, and we will then consider limitations in the design of large paratropic loops by the altanisation process, as already apparent from the current density pattern of **2**.[6,14]

Electronic energies and chemical shieldings have been computed using Gaussian 09.[18] At the B3LYP/6-31G* level bowl-shaped minimum energy structures of $C_6$ and $C_{10v}$ symmetry have been obtained for **2** and **3**, respectively. Current densities at the restricted Hartree-Fock or B97-2[19] density functional[20,21] level have been computed by the SYSMO package,[22] using the ipsocentric choice for the gauge.[23–25] The small 6-31G** basis set is able to produce good current density maps within the ipsocentric approach,[26] and ring current strengths are consistently expected to undergo a small change upon use of larger basis sets (a few percent points in the case of benzene[27,28]). Ring current strengths[28,29] have been computed using the improved integration method first used in ref.[30]. Computed current strengths are compared in Table 1 with those of the HLPM method reported in Ref.[7] As can be seen, the three methods agree almost quantitatively in predicting for the innermost loop a diatropic current of a strength

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† Electronic Supplementary Information (ESI) available: Diagram of orbital energy levels close to the Fermi level, Full ref. 18, Sketches of HOMOs and LUMOs for the UB3LYP calculations on **2** and **3**, Absolute values of the energies and NOONs, Details of fits of $\sigma_{zz}$ scans, Optimized Cartesian coordinates. See DOI: 10.1039/b000000x/

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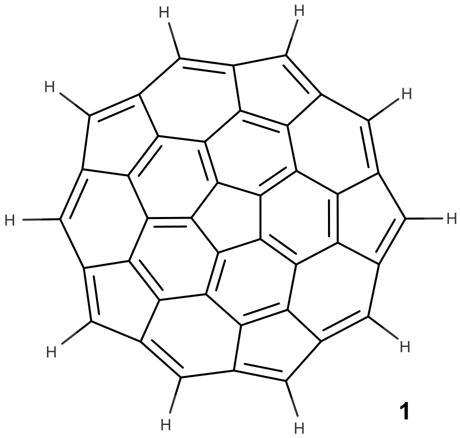
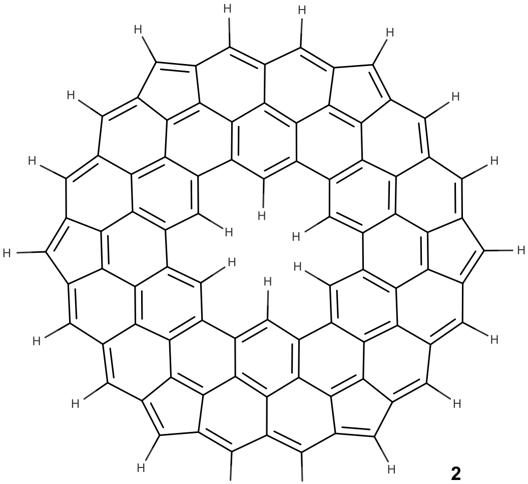
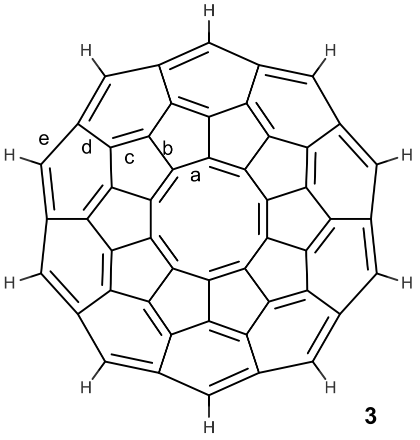


**1**



**2**



**3**

**Table 1** Symmetry-unique bond lengths (Å) of the B3LYP/6-31G* minimum energy structure of **3** and current strengths flowing in the a→b→c→d→e direction for a magnetic field directed outwards, computed with three different methods. Current strengths are in relative units with respect to the all-electrons ring current strength of benzene ($-12.48$ nA T$^{-1}$ and $-11.64$ nA T$^{-1}$, at the HF and B97-2 level, respectively).

| bond | length | HLPM[7] | HF/6-31G** | B97-2/6-31G** |
|---|---|---|---|---|
| a | 1.445 | 1.615 | 1.419 | 1.531 |
| b | 1.510 | 0 | 0.000 | 0.000 |
| c | 1.380 | −0.566 | 0.749 | 1.979 |
| d | 1.454 | 0 | 0.000 | 0.000 |
| e | 1.434 | 1.046 | 1.050 | 2.159 |

roughly one-and-a-half times that of benzene, and they all predict a diatropic current for the perimeter, thus confirming the second exception within *altan*-molecules. However, the tight binding approach predicts a paratropic middle loop, while the other two methods predict all diatropic currents, and, although the tropicities are the same in HF and the DFT calculations, the DFT current strengths on the middle and outer loop are more than twice the HF ones.

For the interpretation of the failure of the altanisation method, we recur to the spectral decomposition of the current density within the ipsocentric approach.[31–33] This method highly benefits from molecular symmetry. When applied to structures with a $C_n$ symmetry axis (like regular $[n]$annulenes), the components of the current density decompositions can be well described if orbitals are labelled by half of the azimuthal node count (HANC[5]): transitions with $\Delta(\mathrm{HANC}) = 0$ and $\Delta(\mathrm{HANC}) = \pm 1$ give paratropic and diatropic contributions to the current, respectively.[5,31] Moreover, the transitions of the orbitals close to the Fermi level matter the most.[25,31] In polycyclic systems the transitions can be tentatively interpreted in terms of the HANCs of the circuits with the larger coefficients. This seemed pretty easy in *altan*-annulenes, where, within the tight-binding approach, upon altanisation the pair of frontier orbitals of the outer $[4n]$annulene with HANC$= n$ were so split that an orbital remained strictly localized on the annulene (becoming the LUMO of the *altan*-molecule), while the other orbital got slightly lowered in energy by combination with the orbitals of the inner parent annulene, becoming one of the highest occupied orbitals.[10,11] What the altanisation assumes is that no molecular orbital with HANC$= n \pm 1$ on the perimeter gives a larger contribution to the current density. This, according to the higher relevance of orbitals close to the Fermi level, requires that orbitals with HANC$= n \pm 1$ have either lower or higher energy than the splitted pair with HANC$= n$. A part from *altan*-annulenes,[10,11] this ordering occurs for *altan*-coronene and **1**,[5] but not for **2** and **3**. In addition to the usual Mulliken symbols $M$, the orbitals for these and other *altan*-corannulenes[34] can be conveniently labelled using the HANC values of innermost, middle and outermost annulenes, as $M(\mathrm{HANC_iHANC_mHANC_o})$. As can be seen form the diagram of orbital energies reported in the

ESI (Figures ESI1-ESI2), a part from minor shifts of orbitals and an expected shrinkage of the HOMO-LUMO gap in the DFT calculation, the three methods used for the computation of current strengths agree in giving a higher energy (and thus a higher contribution to the current) to the occupied pair $e_4(444)$ which gives a diatropic contribution stronger than the lower energy $b_2(055)$ orbital which comes from the splitting of the outermost $[4n]$annulene pair with HANC$= 5$. This intrusion of orbitals with a HANC$\neq n$ occurs also in **2**, where the two [36]annulene orbitals with HANC label (009) split in order that the LUMO of **2** is a b(009) orbital, as expected, but one has to go down in the orbital list till the HOMO$-5$, b(399), to have the same HANC$_o$ of the LUMO; moreover the HOMO$-2$/HOMO$-3$ $e_2(478)$ pair has HANC$_o = 8$ on the outermost annulene (thus giving a diatropic contribution to the current). The origin of the different orbital schemes for **2** and **3**, as compared with the other *altan*-molecules like **1**, can be traced back to a stronger interaction of the outer $[n_o]$annulene and the middle $[n_m]$annulene. These two annulenes will interact more strongly as their energy levels are closer. Notably, whenever the altanisation is iterated as in **3**, which is probably better called *altan*$^2$-[10]annulene,[35] the middle and outermost annulene have the same size and then the same eigenvalues, and are thus expected to couple strongly. According to a perturbation argument, a similar behaviour can be expected for middle and outermost annulenes of close size, like in **2**, where their size is 30 and 36.

All *altan*$^2$-molecules have a cycloacenic fragment; in the case of **3**, the fragment is [10]cycloacene. All the many attempts to synthesize cycloacenes have failed. The elusive character of these molecules can be ascribed to a very small HOMO-LUMO gap. According to the scheme proposed for the frontier orbitals by Houk et al.,[36] $[2n]$cycloacenes, like long linear acenes, can be described as two weakly coupled trannulenes.[37] The 2+2 non-bonding orbitals of the trannulenes couple in such a manner to have a bonding and an anti-bonding orbital with respect to the C–C bonds connecting the trannulenes, and two orbitals of intermediate energy, both close to zero, with in-phase and out-of-phase combinations of orbitals mainly localized on the remaining C atoms which do not form the bonds between the two trannulenes. The small HOMO-LUMO gap is then the cause of the high reactivity, and complicates the computational study of the ground state. Indeed, after the report of a triplet ground state for long polyacenes and cycloacenes,[36] it has been shown that, upon refining the theoretical models with an unrestricted formalism, open-shell singlet states are more stable than either closed-shell singlet states or triplets for $[n]$cycloacenes with $n > 5$.[38–40]

The presence of a cycloacenic fragment in **3** and of annulenes of similar size in **1**, and even more in **2**, has prompted us to consider the stability[41,42] of the restricted Hartree-Fock singlet solution for these systems. The wavefunction turned out to be stable only for **1**. By further geometry optimization at the UB3LYP/6-31G* level, the $C_{10v}$ symmetry of **3** was preserved, while that of **2** lowered to $C_2$. The UB3LYP wavefunctions have significant fractional occupation numbers: the natural orbital occupation numbers (NOONs) of frontier orbitals are 1.37/0.63 and 1.29/0.71 in **2**$-C_2$ and **3**, respectively, and have a poor spatial overlap (Fig. ESI3-ESI4), as expected for open-shell singlets. In order to get rid of the spin contamination characteristic of unrestricted calculations, we have also accomplished CASSCF(10,10)/STO-3G calculations for singlets and triplets. The singlets are always preferred and they have a significant open-shell diradical character, which persists with the larger 6-31G* basis; NOONs of frontier orbitals with the smaller (larger) basis set are 1.79/0.25 (1.87/0.16) and 1.02/0.98 (1.36/0.64) for **2**-$C_6$ and **3**, respectively (Table ESI1).

Coming now back to the onset of a diatropic perimeter in **2** and **3**, the current density should best be recomputed at the multi-configurational level, which has recently become possible.[43] However, preliminary information on the influence of the open-shell character on the current density can already be obtained by the long used investigation of the magnetic properties, i.e. integrated values of the current density.[44,45] As shown in Fig. 1, at odds with the $\sigma_{zz} = -\text{NICS}_{zz}$ scans of **2** (Fig. ESI5), those of **3** do not show qualitative changes upon consideration of correlation and of the unrestricted character of the wavefunction, and are all consistent with a fully diatropic molecule. The scans can be modelled in terms of 3 Infinitely-thin Circular Loops Of Currents (ICLOCs)[45] displaced from the symmetry axis by the average displacements of the C atoms of the concentric loops, leading to a semiquan-

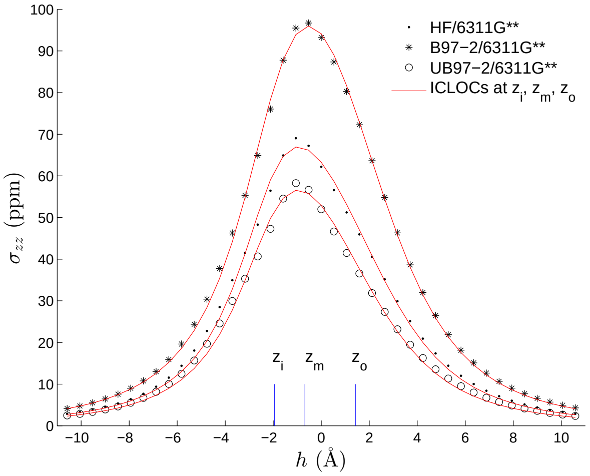


**Fig. 1** Scans of $\sigma_{zz}$ along the symmetry axis of **3**. The lines are from fits with three ICLOCs. See the Table ESI3 for fit details.

titative agreement with the ring current strengths computed at the restricted level, and a diatropic perimeter is retrieved by the ICLOC fitting of all the scans of **3** (Table ESI3).

The present investigation has shown that the altanisation approach, which has already allowed to design molecules satisfying the otherwise unsatisfactory[13,34,46] annulene-within-an-annulene ansatz[10,11] as well as a molecule-within-an-annulene ansatz,[6] breaks down for systems like *altan*-kekulene **2** and *altan*$^2$-[10]annulene **3**, due to the intrusion of orbitals with a different nodal structure with respect to that of the pair of orbitals localized on the outermost annulene. This event can be expected whenever the outermost and the middle annulene of the *altan*-molecule have close sizes. Equal size of these two annulenes occurs in all *altan*$^2$-molecules, which actually contain a cycloacenic fragment, and, according to the computation reported above, are expected to have open-shell singlet ground states. Therefore, while *altan*-corannulene hexaanion $\mathbf{1}^{6-}$ is expected to be a stable aromatic molecule,[4] *altan*-molecules like **2** and **3** are low gap molecules with an open-shell singlet ground state, and they could be reasonably added to the gamut of molecules which is nowadays under intense experimental and computational scrutiny for the development of novel systems with improved optical and conductive properties.[47,48]

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