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COMMUNICATION

Topological Ring-Currents and Bond-Currents in the *Altan*-[*r, s*]-Coronenes

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π -Electron ring-currents for the *altans* of the four regular [*r, s*]-coronenes are calculated by the topological HLP approach. The bond-current pattern of the parent structure is generally preserved in the core of the corresponding *altan*. *Altan*-[10,5]-coronene appears to support an anomalous diamagnetic current in its [4*n*]-periphery. This invites further investigation.

The parts of Figure 1 coloured in blue show the molecular graphs¹ of the four regular [*r, s*]-coronenes — [3,12]-coronene (1), [4,8]-coronene (2), [6,6]-coronene (3) (better known simply as coronene itself) and [10,5]-coronene (4) — which were first discussed, by Bochvar *et al.*,² more than forty years ago. The present authors³ have recently used these classic structures as vehicles for testing the applicability of the so-called ‘Annulene-Within-an-Annulene’ (AWA) rule.⁴ This test was effected by determining Hückel–London–Pople–McWeeny (HLP)⁵ ‘topological’^{6,7} π -electron ring-currents and bond-currents in the conjugated systems (some extant and some hypothetical) represented by these regular [*r, s*]-coronenes. The AWA ‘rule’⁴ — now largely discredited^{7–10,3} — requires that conjugated cycles of carbon atoms within conjugated systems whose lengths are [4*n*] (where *n* is an integer) bear *paramagnetic* π -electron currents whereas cycles of length [4*n*+2] should support *diamagnetic* π -electron currents. The conclusion³ was that the only one of structures 1–4 that appeared to respect the AWA rule was [10,5]-coronene (4) in which the central ([10]-membered) cycle and the [20]-membered cycle that constitutes the perimeter of 4 are ‘decoupled’ (in the sense in which this adjective is used in, for example, refs. 3, 7 and 10).

Monaco, Memeli and Zanasi^{11–13} have very recently proposed and applied the process of ‘*altanisation*’, in which an arbitrary conjugated system is surrounded by a [4*n*]-annulene and metamorphosed, in a precisely prescribed way, to the corresponding ‘*altan*’ structure (as described in detail in refs 11–16). The four complete structures shown in Figure 1 represent the molecular

graphs of the *altan* structures (5–8), each consisting of one of the four regular [*r, s*]-coronenes (1–4) considered in refs 2 and 3 (whose edges are depicted in blue), together with the additional edges (shown in black) that are needed^{11–16} to form the corresponding *altan*-[*r, s*]-coronene.

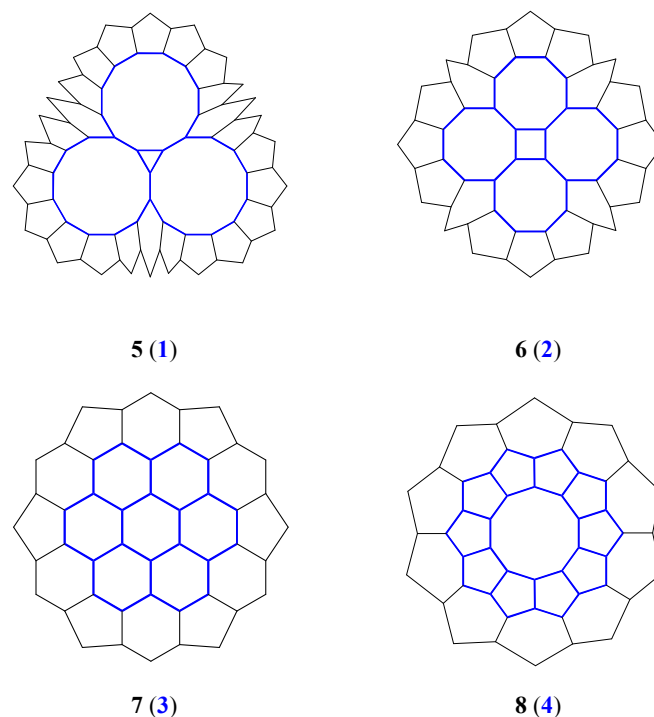


Fig. 1 Molecular graphs¹ of the respective *altans*^{11–16} (5–8) of the regular [*r, s*]-coronenes (1–4). The blue parts of the structures represent the ‘parent’ [*r, s*]-coronenes (1–4), and each of the four composite structures (5–8) — comprising the union of the part denoted in blue and that depicted in black — represent the corresponding *altan*-[*r, s*]-coronene.

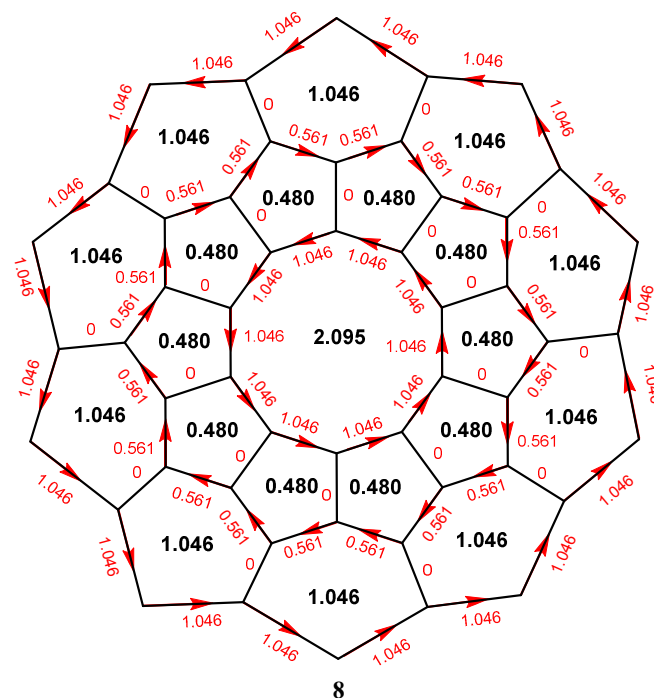
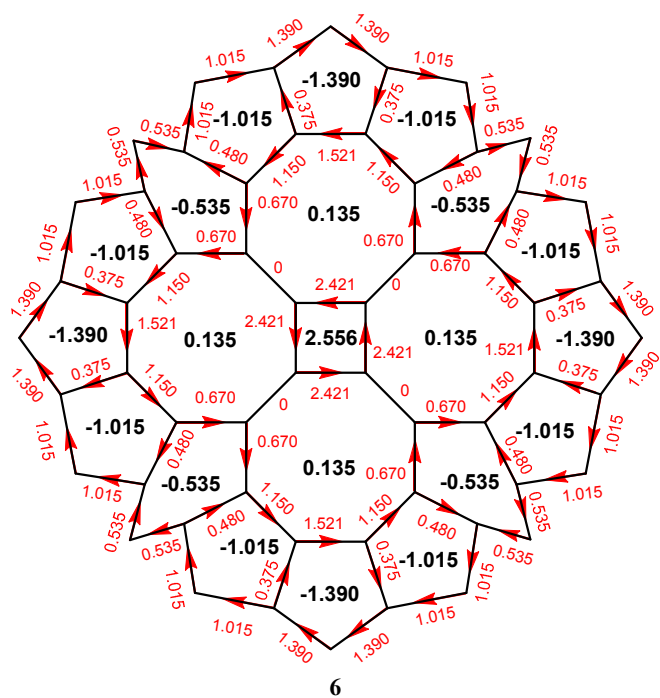


Fig. 2 Topological ring-current intensities (depicted in black, in the centre of each ring) and topological bond-currents (in red, along each bond) for [4,8]-coronene (**2**)³ (bottom of Figure) and altan-[4,8]-coronene (**6**) (top). Positive ring-currents indicate circulation in the diamagnetic (anti-clockwise) direction around the ring in question and a negative ring-current denotes a circulation in the clockwise (paramagnetic) sense. Bond currents flow in the direction indicated by the arrow on each bond.

Fig. 3 Topological ring-current intensities (depicted in black, in the centre of each ring) and topological bond-currents (in red, along each bond) for [10,5]-coronene (**4**)^{3,10} (bottom of Figure) and altan-[10,5]-coronene (**8**) (top). (For the conventions on the depiction of ring currents and bond currents, please see the caption to Figure 2.)

HLP⁵ topological⁶ π -electron ring-currents⁷ were calculated as described in refs. 6,7,9,10 and 17, by application of the equation

$$\left(\frac{J_i}{J_{\text{benzene}}}\right) = 9 \left\{ \sum_{(\mu)} [P_{(\mu)} + \beta \bar{\pi}_{(\mu)(\mu)}] S_{(\mu)} C_{(\mu)}^i + \sum_{(\mu < \nu)} \sum_{(\nu)} \beta \bar{\pi}_{(\mu)(\nu)} [S_{(\mu)} C_{(\nu)}^i + C_{(\mu)}^i S_{(\nu)}] \right\}$$

where J_i is the ring-current intensity in the i^{th} ring of the conjugated system and J_{benzene} is the corresponding ring-current intensity calculated, by the same method, for benzene (which has a numerical value,⁷ in these units, of (1/9)). The quantities $P_{(\mu)}$, $\beta \bar{\pi}_{(\mu)(\mu)}$, and $\beta \bar{\pi}_{(\mu)(\nu)}$ — the latter two being dimensionally independent of β , despite explicitly mentioning this parameter because $\bar{\pi}_{(\mu)(\mu)}$ and $\bar{\pi}_{(\mu)(\nu)}$ are in units of $1/\beta$ — are all calculable from the field-free Hückel-matrix (that is, the vertex-adjacency matrix of the associated molecular-graph¹),

the $C_{(\mu)}^i$ and $C_{(v)}^i$ are also entirely *topological* quantities;^{6,7,17} the $S_{(\mu)}$ and the $S_{(v)}$ are, however, *geometrical*, as they depend on the conjugated system's ring areas.^{6,7,17,18} These ring areas, in their turn, are estimated by means of the standard procedure adopted when calculating HLPMP topological ring-currents and bond-currents^{6,7,9,10,14,15} — namely, polygonal rings in an assumed planar network are taken to have the area of a regular polygon (with sides equal in length to the carbon–carbon bond in benzene) with the appropriate number of sides. Topological ring-currents and bond-currents — presented for **6** and **8** and their parent structures (**2** and **4**, respectively) in Figures 2 and 3 — are expressed as a ratio to the analogous quantity calculated, by the same method, for benzene; they are, accordingly, dimensionless.

The problems arising from the occurrence of a triplet ground-state in [3,12]-coronene (**1**), described in ref 3, were also encountered with *altan*-[3,12]-coronene (**5**) and, accordingly, no results for **5** are presented here; furthermore, topological current-maps for coronene itself (technically considered here as '[6,6]-coronene' (**3**)) have been given earlier,^{3,7,9,10,14,19} and the corresponding HLPMP-maps for its *altan* (*altan*-coronene (**7**)) were recently fully reported.¹⁴ Topological current-maps for [4,8]-coronene (**2**)³ and its *altan* (**6**), and for [10,5]-coronene (**4**)^{3,10} and its *altan* (**8**) — the maps for **6** and **8** being novel ones — are presented here in Figures 2 and 3, respectively.

If *altan*-[4,8]-coronene (**6**) (Figure 2) were regarded as a three-layered 'annulene-within-an-annulene-within-an annulene' it would be described as a [4]-membered-within-[20]-membered-within-[32]-membered system. As such, one might naïvely expect the pattern of current flow around its innermost/middle/outer cycles¹⁴ to be (respectively) **paramagnetic / paramagnetic / paramagnetic**, as all three cycles are of the '[4n]' type. In fact, as can be seen from Figure 2, the calculated pattern of topological bond-currents indicates **diamagnetic / diamagnetic / paramagnetic**. Like the parent structure (**2**), *altan*-[4,8]-coronene (**6**) thus violates the AWA 'rule' by virtue of diamagnetic current-flow predicted for the first two layers. Two points should, however, be noted, from Figure 2: (i) the bonds in the [4n]-membered cycle on the perimeter do, as expected, bear avowedly paramagnetic currents, ranging in value from about 0.5 to about 1.4; (ii) as was observed for other *altan*-structures — originally by Monaco *et al.* from *ab-initio* calculations^{12,13} and subsequently confirmed by the present authors^{14,15} by means of the much more rudimentary HLPMP topological approach⁵⁻⁷ — the pattern of *bond*-current flow in the parent structure is generally preserved in the inner core of the corresponding *altan*, even though the individual *ring*-current intensities themselves might in fact be quite different. In [4,8]-coronene (**2**), for example, the strong diamagnetic flow (*ca.* 3.2) around the central [4]-membered ring is qualitatively preserved in the *altan* (**6**) by the presence of a diamagnetic flow in these bonds of intensity of about 2.4; furthermore, the peripheral diamagnetic flow in **2** of size *ca.* 1.1 is matched by a variable diamagnetic current-flow around the middle cycle of **6** which, nevertheless, averages to an almost identical value (*ca.* 1.0).

Much more remarkable, however, is *altan*-[10,5]-coronene (**8**) (Figure 3). Considered as a three-layered annulene, this is a [10]-membered-within-[20]-membered-within-[20]-membered system. A naïve AWA approach would thus expect the pattern **diamagnetic / paramagnetic / paramagnetic** (for the innermost, middle and outer cycles, respectively). As with [10,5]-coronene itself^{3,10} (**4**), the first two layers from the centre in **8** do obey the AWA 'rule', for the observed bond-current pattern in the three layers is **diamagnetic / paramagnetic / diamagnetic**. A very important anomaly, however,

is that, although the perimeter of **8** is [4n]-membered ($n = 5$), its bonds bear a substantial current (*ca.* 1.0) in the anti-clockwise (diamagnetic) sense. Now, in their *ab-initio* study of several *altan*-systems (all necessarily with [4n]-peripheries^{11,16}) Monaco, Memeli and Zanasi¹³ found paramagnetic circulations in the [4n]-peripheries of all the *altan*-structures that they studied, with the one exception of *altan*-Kekulene (structure 4 of ref 13 and structure 6 of ref 15). Precisely the same exception was found by the present authors¹⁵ when basing calculations on the much more rudimentary topological HLPMP method.⁵⁻⁷

Inspection of Figure 3, shows that, overall, the current flow around the *bonds* in [10,5]-coronene (**4**) is once again¹⁵ in qualitative/semi-quantitative agreement with the currents borne by the analogous bonds in the *altan* version of the same structure (**8**). This is remarkable when it is considered that *all* rings in [10,5]-coronene (**4**) are associated with *paramagnetic* ring-currents and yet *all* rings in the corresponding *altan* (**8**) support *diamagnetic* ring-currents. This observation again emphasises the conceptual insight gained by thinking in terms of individual *bond*-currents rather than overall *ring*-currents.

Conclusions

The preceding paragraph indicates how important it is to consider net *bond*-currents when interpreting calculations like these, rather than merely assessing *ring*-currents *per se* — despite the fact that knowing a set of ring-currents for any given structure is tantamount to knowing all the bond currents of that structure, as the two collections of quantities are simply related to each other by Kirchhoff's Laws.²⁰ It is thus quite possible for structures to have very different *ring*-currents, and yet — because the bond currents in bonds shared by two rings are the result of algebraic summation of the currents in those adjacent rings — for them still to exhibit corresponding bonds that bear semi-quantitatively comparable *bond*-currents. Structures **4** and **8**, compared in Figure 3, constitute the most extreme example of this phenomenon that we have come across up till now.

It would be of considerable interest if colleagues who are engaged in *ab-initio* approaches to the magnetic properties of these structures could study *altan*-[10,5]-coronene (structure **8** of Figure 3) and thus establish whether such calculations could confirm the anomalous presence, according to our HLPMP topological calculations,⁵⁻⁷ of a *diamagnetic* circulation in the [4n]-periphery of *altan*-[10,5]-coronene (**8**). In a reversal of what we are suggesting here, a similar anomalous finding of *ab-initio* calculations¹³ — in the case of *altan*-kekulene — was later confirmed by our own graph-theoretical HLPMP computations.¹⁵ It may be noted in passing that an anonymous referee has commented that, according to the conjugated-circuits approach,^{20,21} the currents in the [10] – [20] – [20] cycles of (**8**) should be **diamagnetic / paramagnetic / paramagnetic**.

We emphasise that our philosophy here is to test to what extent chemically intuitive insight into the magnetic properties of π -electron systems may be obtained from a rudimentary, *parameter-free*²² approach that depends solely on carbon-carbon connectivity and ring area, without recourse to

sophisticated *ab-initio* formalisms. We appropriately follow Kutzelnigg²² in use of the term ‘parameter-free’ because the ‘topological’ bond-currents and ring-currents are conventionally expressed as ratios to the corresponding quantities calculated, by the same method, for benzene, thereby freeing the calculations from any necessity to specify the numerical values of any of the standard Hückel parameters. For any given particular molecule, *ab-initio* methods may well give rise to more-accurate numerical predictions that might more closely mirror observed experimental data, but they do not so readily afford more-basic patterns of understanding that are appreciated by the wider community of practical chemists. The HLP approach⁵⁻⁷ being applied here, by contrast, provides just such a tool for investigating the electronic π -systems of polycyclic conjugated molecules and thus for deducing trends in chemical behaviour. This is what we attempt to achieve here, in the context of these novel *altan*-systems.

Notes and references

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