Comparisons of π-Electron Ring-Current and Bond-Current Patterns Calculated by Topological ('HLPM') and *Ab Initio* ('*Ipso*-Centric') Formalisms for Two Isomeric Conjugated Hydrocarbons, Corazulene and Cornaphthalene

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Abstract: The π-electron ring-currents and bond-currents associated with the isomeric structures corazulene (**1**) and cornaphthalene (**2**) are calculated by means of the rudimentary topological Hückel–London–Pople–McWeeny (HLPM) method (which is entirely equivalent to the recently named 'graph-theoretical CD–HL' approach).These currents are compared with analogous quantities computed by Lillington *et al*. by use of the more-sophisticated *ipso*–centric *ab initio* approach. The simple HLPM method is seen to exhibit a remarkable ability to reproduce complex patterns of current in large polycyclic hydrocarbons — the successful prediction of which, ostensibly, might naïvely be expected to be the preserve only of more sophisticated, and much less intuitive, *ab initio* calculations. This conclusion is entirely consistent with findings from contemporary work on other structures by the present, and other, authors.

Keywords: HLPM ring-currents & bond-currents, *ipso*-centric *ab initio* calculations, graph theory, conjugated hydrocarbons.

INTRODUCTION

IN THIS PAPER, we take the opportunity afforded by the availability of certain *ab initio* calculations[1] to assess how well predictions of π-electron ring-current and bond-current intensities calculated for conjugated systems by the rudimentary Hückel[2]–London[3]–Pople[4]–McWeeny[5] ('HLPM') formalism[6] mimic those of more-sophisticated approaches, notably the *ab initio* '*ipso*-centric'[7] and 'pseudo-π'[8] methods. *Ab initio* procedures frequently depend first on the application of elaborate software, such as the Gaussian program,[9] in order to optimise starting geometries, and then on the choice of wave-function basis-set employed (see, for example, 'Computational Details' [p. 848] of Ref 10, '*Ab Initio* Calculations' [p. 7448] of Ref. 11 and 'Method' [p. 655] of Ref. 1.) Application of the HLPM formalism,[2–6] on the other hand, depends only on

knowledge of how the carbon atoms forming the conjugated system in question are joined to each other in the σ-bonded network, and on the areas of its constituent rings.[6] Once the matter of ring areas has been decided, topological π-electron bond-currents and ring-currents in such systems are thus effectively latent in the molecular graph of the hydrocarbon under study and, accordingly — even though their actual computation may still have to be effected — these currents are at least implicitly and immediately predetermined as soon as the structure's molecular graph[12] has been written down.[6]

In isolated cases (for example, that of 7-coronene[13–15]) there have been discrepancies; however, in the large majority of the structures examined so far — such as coronene and many of its 17 non-alternant isomers,[16,17] [10,5]-coronene,[11,13,14] and especially the novel series of '*altan*' structures,[18–24] recently defined and introduced by
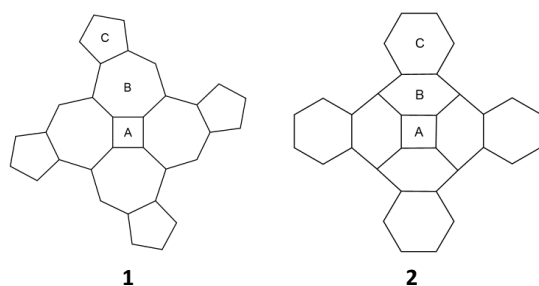
Figure 1. Molecular graphs[12] of non-alternant[2] corazulene (**1**) and its alternant isomer cornaphthalene (**2**), showing their carbon-carbon connectivities and the labellings, in each, of the three symmetrically distinct rings.

Monaco and Zanasi[18–20] and studied mathematically by those authors and (exhaustively) by Gutman[23,24] — the HLPM formulation has manifested a remarkable ability to reproduce complex patterns of current in large polycyclic hydrocarbons.[6,17,21,22] Many of these systems have been specially 'designed'[11,13,14,18–20,25,26] to illustrate particular aspects of expected bond-current and ring-current behaviour.

We here effect comparison between the topological HLPM and the *ab initio* philosophies by comparing predictions from the two approaches relating to a pair of isomeric structures: namely, the non-alternant[2] corazulene (**1**) and its alternant isomer cornaphthalene (**2**) (Figure 1). These were studied by Lillington *et al.*[1] by means of the *ipso*-centric method.[7] (These structures were considered of interest because it has been suggested that **1** and **2** could act as building blocks for carbon nano-structures.[27]) Lillington *et al.*[1] have observed that if a 'circulene' (also known[6] as a 'super-ring' system) can be visualised as 'a wheel with spokes',[11,16] **1** and **2** can be thought of as a wheel with the addition of what they[1] call 'crossing chords'. Both **1** and **2** may thus be regarded as arrangements of [4]-membered central-rings inside a [28]-membered perimeter, '...with four spokes and four chords cross-linking the outer cycle.'[1]

CALCULATIONS

The computations were carried out by the HLPM method[2–5] as described in step-by-step detail in Ref. 6, the main crux of which is equation (14) of that reference. As is a requirement of the 'topological' version[6,28,29] of the HLPM approach,[2–5] adopted here, both **1** and **2** are assumed to be planar structures whose ring areas are those of regular polygons[4,29] of the appropriate number of sides, each of which is of uniform length (and equal to the carbon–carbon bond-length in benzene) — please see equation (16) of Ref. 6. In the present calculations, this implies adoption of the following ratios for the ring areas in **1** and **2**:[4] if A_n is the area of a regular polygon of n sides, then,
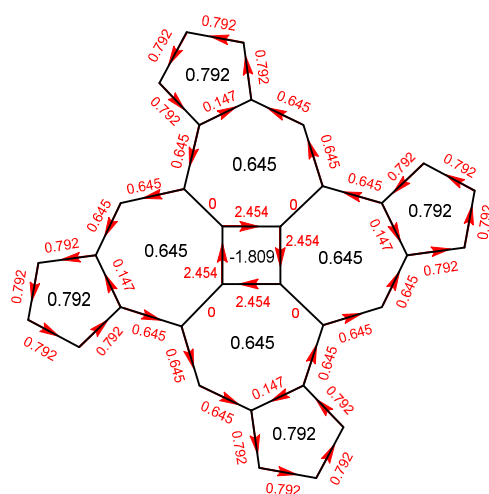

Figure 2. Maps for the topological[6,28,29] ring-currents (in black) and the associated topological[6,28,29] bond-currents (in red) for (non-alternant[2]) corazulene (**1**). The topological ring-currents and bond-currents are dimensionless quantities. Positive (diamagnetic) ring-currents are considered to circulate anti-clockwise around their respective rings whilst negative (paramagnetic) ring-currents flow in the clockwise sense around those rings. The various bond-currents flow in the direction indicated by the arrow pointing along each bond.

$$A_4 : A_5 : A_6 : A_7 = 4\cot\frac{\pi}{4} : 5\cot\frac{\pi}{5} : 6\cot\frac{\pi}{6} : 7\cot\frac{\pi}{7}. \qquad (1)$$

(The only circumstances in recent work where a different assumption about ring areas needs to be made are in the case of structures with 'holes', such as kekulene[6,22,30–33] and the *p*-coronenes.[13,14])

Lillington *et al.*[1] have pointed out that **1** is indeed planar (with C_{4h} symmetry) and so also is **2**, in a transitional form (with D_{4h} symmetry); in reality, however, **2** is bowl-shaped in its equilibrium conformation, with symmetry C_{4v}. In the present calculations we adopt C_{4h} symmetry for corazulene (**1**) and D_{4h} symmetry for cornaphthalene (**2**). The topological[6,28,29] HLPM ring-current and bond-current maps of **1** and **2**, calculated as just described, are illustrated in Figures 2 and 3. As is conventional,[6] the ring currents and bond currents are presented as dimensionless numbers, expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene.

It is perhaps material to point out at this stage that what we have for some time been calling[6,13,14,17,21,22,26,28–31] 'topological HLPM calculations' are precisely what Fowler *et al.* have very recently[34–37] given the appellation 'graph-theoretical Current-Density Hückel–London (CD-HL) calculations'. Given the same geometrical assumptions, the two

methods (HLPM[6,28,29] and CD–HL [34–37]) should yield identical numerical ring-currents and bond-currents (within machine error of the computation), which, as already claimed, are themselves instantly *latent* in the molecular graph, once the latter has been specified.

RESULTS AND DISCUSSION

(i) Comparson of Overall Patterns Observed in the Topological HLPM Ring-Currents in Structures 1 and 2

Structures **1** and **2** both contain a central four-membered ring (labelled A, in Figure 1) in which the topological HLPM paramagnetic ring-currents are similar (*ca*. −1.81 and −1.65, respectively). In **1**, each edge of the central square (A) is shared with a seven-membered ring (B) (with diamagnetic ring-current *ca*. 0.65) and in **2** each bond of the central four-membered ring (A) is shared with a six-membered ring (B) bearing very nearly the same diamagnetic ring-current (0.63) as the corresponding (seven-membered) ring (B) in **1**, just described. Each of the seven-membered rings (B) in **1** shares a bond with an outer five-membered ring (C) that bears a diamagnetic ring-current of *ca*. 0.79, whilst the six-membered rings (B) in **2** that share an edge with the central four-membered ring (A) also share a bond with an outer six-membered ring (C) bearing a qualitatively similar, but quantitatively larger, diamagnetic ring-current (*ca*. 1.02).

The ring-current pattern for both **1** and **2** is, therefore, summarised as follows:
(a) Central four-membered rings (A): paramagnetic (−1.81 and −1.65, in **1** and **2**, respectively).
(b) Rings (B) sharing a bond with the central square: diamagnetic (0.65 and 0.63).
(c) Peripheral rings (C): diamagnetic (0.79 and 1.02).

(ii) Comparison of *Ab Initio* and HLPM Topological Currents in Corazulene (1)

Lillington *et al*.[1] reported a strong paramagnetic circulation around the central four-membered ring with a somewhat weaker diamagnetic current around the perimeter. Qualitatively, this pattern is confirmed by the topological HLPM calculations displayed in Figure 2. Quantitatively, the comparison is less impressive: Lillington *et al*.[1] find that what they call j_{max}, the largest value in their 'plotting plane'[1] of the current density per unit inducing field, is (when expressed as a ratio to the benzene value) about −0.91 for the central ring, whereas for the diamagnetic circulation on the perimeter it is *ca*. 0.65. These are to be compared with HLPM values (from Figure 2, likewise expressed as a ratio to the HLPM bond-current in benzene) of about −2.45 and 0.73, respectively — thereby emphasising, once

again, the previously observed phenomenon[38–44] that calculated paramagnetic currents, which are especially sensitive to HOMO–LUMO separations, tend to be overestimated by methods (such as our topological, non-iterative[38–44] version of the HLPM[2–6] approach, being applied here) which do not make Hückel resonance-integrals iteratively self-consistent with respect to the corresponding calculated Coulson bond-orders.[2,38–44] We have, however, resisted applying this refinement here because, as we are testing a method that claims to depend on no empirical or subjective parameters whatsoever, we wish to maintain the description of the resulting π-electron currents as 'topological'.[6,28,29]

Lillington *et al*.[1] further observe that the 'chord bonds' completing the four pentagonal rings (C) in **1** also support current that closes a ring-current loop in which the circulation is in the diamagnetic direction, '…but this is much smaller than the main perimeter current.'[1] This finding is also supported by the topological HLPM calculations presented in Figure 2: the 'chord bonds' carry a current of about 0.15, whereas the main perimeter current varies between approximately 0.65 and *ca*. 0.79. Consistent with what Lillington *et al*.[1] called the 'circulene analogy', the current in the 'spokes' bonds was said[1] to be 'negligible', even though, with the symmetry that Lillington *et al*. assumed in Ref. 1, it was not forced to be zero by symmetry (as was the case in D_{5h} planar corannulene and D_{6h} coronene.[7,16,17,30]) In the course of carrying out the HLPM calculations displayed in Figure 2, however, C_{4h} symmetry was assumed (as described under the heading 'Calculations') and, hence, in the case of our own computations being presented here, bond currents in the spokes bonds are indeed constrained to be zero by *symmetry*.

Overall, Lillington *et al*.[1] concluded, on the basis of their *ipso*-centric *ab inito* calculations,[7] that corazulene (**1**) '…is predicted to have the magnetic properties of a circulene, with paired counter-rotating paratropic-hub and diatropic-rim currents.' The HLPM topological bond-currents depicted in Figure 2 agree entirely with this.

(iii) Comparison of *Ab Initio* and HLPM Topological Currents in Cornaphthalene (2)

Lillington *et al*.[1] observed that, among the induced currents that they calculated for the planar transition-state of structure **2**, there is again a strong paramagnetic circulation around the central four-membered ring (A) (with a j_{max} value — relative to benzene — of −1.0) but with stronger local diamagnetic currents (j_{max} = 1.05) on the periphery of the four outer hexagons (C), and with weak currents linking them on the perimeter. Once again, the topological HLPM bond-currents for cornaphthalene (**2**) shown in Figure 3
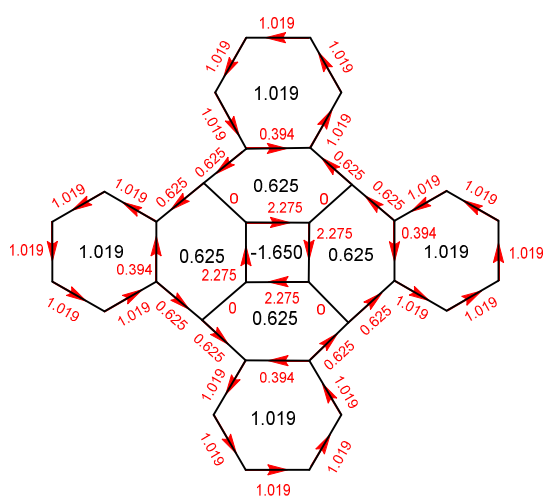
Figure 3. Maps for the topological[6,28,29] ring-currents (in black) and the associated topological[6,28,29] bond-currents (in red) for (alternant[2]) cornaphthalene (**2**). For the conventions on displaying topological ring-currents and bond-currents please see the caption to Figure 2.

qualitatively confirm this view. Quantitatively, the position is as follows: (a) the current in the bonds of the central four-membered ring (A) is *ca.* −2.28 (again an overestimate compared with the *ab initio* values, an observation which is rationalised by the same explanation[39–44] as was offered in the previous section for a similar phenomenon encountered in corazulene (**1**)); (b) the peripheral bonds in the four outer hexagons (C) bear a diamagnetic bond-current of about 1.02 (very close to the *ab initio* estimate of 1.05); and (c) the currents in the bonds linking those outer hexagons to the rest of the structure are likewise weaker, at *ca.* 0.39. Lillington *et al.*[1] remark that when they relax their assumption of a planar (D_{4h}) geometry for **2**, assuming instead a 'bowl-shaped' structure with C_{4v} symmetry, the features observed are reduced in intensity compared with the planar form, but these authors do retain in their conclusions the identification of (a) a paramagnetic π-electron circulation around the bonds of the four-membered central-ring (A), and (b) a diamagnetic circulation, of magnitude equal to that of the ring-current in benzene, in the peripheral bonds of the four outer hexagonal rings (C). These claims are again qualitatively — and, in the case of the four outer hexagonal rings, even quantitatively — consistent with the topological HLPM currents presented in Figure 3.

CONCLUSIONS

Comparison of predictions from the *ipso*-centric *ab initio* calculations of Ref. 1, and those from the topological[6,28,29] HLPM computations[2–6,28,29] displayed in Figures 2 and 3, confirm the following conclusions of Lillington *et al.*:[1]

(a) Both corazulene (**1**) and cornaphthalene (**2**) show a strong paramagnetic current around the bonds of their central squares.

(b) Corazulene (**1**) presents '... concentric counter-rotating rim-and-hub currents'.

(c) The bond currents in the 'chord' bonds linking the outer six-membered rings (C) of cornaphthalene (**2**) are in such a direction that they complete diamagnetic current-loops around each of those hexagons (as seen in Figure 3). This is in agreement with the claim of Lillington *et al.*[1] that **2** exhibits a 'Clar-like' structure[45] with diamagnetic currents circulating around the four outer hexagonal rings (C).

(d) Corazulene (**1**) has a single global diamagnetic circulation on its perimeter whilst cornaphthalene (**2**) has strong local diamagnetic circulations in separated parts of the perimeter.[1]

Once again, therefore, the simple topological HLPM approach[2–6,28,29] — which depends on knowledge only of the molecular graph[12] of the conjugated system in question (in the form of a vertex-adjacency matrix describing it),[46] and the areas of its constituent rings — has been seen to demonstrate a possibly unexpected ability to reproduce complex patterns of current in large polycyclic hydrocarbons. According to common belief, such predictive success should ostensibly be the preserve only of sophisticated, and much less intuitive,[47,48] *ab initio* calculations. This conclusion is entirely consistent with our own previous findings[21,22] and with the view expressed in the recent, independent and simultaneous work of Gershoni-Poranne *et al.* on phenylenes,[34] that the relative currents calculated by the (equivalent of the) HLPM topological approach '...are remarkably similar to those extracted from the pseudo-π maps,[8] which themselves mirror the full *ab initio* maps[7,11,15,19,20,49]'...and that, in general, the HLPM topological method '...has a remarkable ability…to capture essential features of delocalised systems including patterns of current…' There is therefore now a growing body of evidence[17,21,22,32–37] that this is the case.

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