Ring-Current Properties of Bispentalenes and Related Structures — Comparison of Ab Initio and Hückel-London-Pople-McWeeny (HLPM) ‘Topological’ Calculations

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INTRODUCTION

Within the last few years, the present authors have been taking opportunities, whenever they have arisen, to compare predictions of ab initio calculations of the magnetic properties of conjugated systems with those based on the traditional, recently formalised,[1,2] model of Hückel–London–Pople–McWeeny (HLPM) ‘topological’ ring-currents. Exhaustive details of the history and concept of topological ring-currents are available in two recent reviews,[3,4] and in some older ones.[5,6] The predictions of topological ring-current calculations have generally been compared with two particular ab initio approaches:

(a) what has become known as the ipso-centric approach, the method of Continuous Transformation of the Origin of Current Density (CTOC); this was originally
devised by Keith & Bader[7] and the Lazzeretti group[8,9] and has been much applied, over the years, by Fowler and others (e.g., Refs. [10–12]) and by Monaco & Zanasi and co-workers (e.g., Refs. [13–15]), and (b) the approach called Gauge Including Magnetically Induced Current (GIMIC) proposed, somewhat later, by the Sundholm group.[16–19] The GIMIC formulation makes use of the traditional[20–25] GIAO (Gauge Including[26] — formerly[20–25] ‘Gauge Invariant’ — Atomic Orbitals).

Our previous work[6,27–33] has shown encouraging qualitative, and sometimes even quantitative, agreement between the predictions of the graph-theoretical (‘topological’) HLPM formalism[1–6] and the ab initio theories.[7–19] We say ‘graph-theoretical’ because that is the sense in which, here and elsewhere,[1–6] we are using this somewhat unfortunate adjective ‘topological’. As was pointed out on Page 298 of Ref. [4], the term ‘topological’ is, in the present context, effectively being used as a synonym for ‘graph-theoretical’ and it carries none of the connotations usually associated with algebraic topology per se — e.g., as in Ref. [34]. In particular, we are not here talking about ‘topological ring currents’ in the sense meant in (for example) the classic work of Gomes[35,36] and, more topically, in the very recent paper by Lazzeretti,[37] which even makes direct reference in its title to a ‘topological definition of ring currents’.

Cao et al.[38] recently reported experimental and theoretical work on the magnetic properties of some derivatives of \([4n+2]\)-\(n\)-electron conjugated systems (called ‘bispentalenes’) formed by annelating two pentalene groups with a benzene or a naphthalene moiety. The molecular graphs of naphthalene (1) and pentalene (2) and those of the structures (3–5) studied by Cao et al.[38] are illustrated in Figure 1.

This motivated Sundholm, Berger & Fliegl[39] to study the same systems by means of their GIMIC \(ab\) \(initio\) formalism.[16–19] The computational approach adopted by Sundholm et al. is fully described in the section labelled ‘2. Computational Methods’ on p. 15935 of Ref. [39]. As will be seen there, the process of calculation is by no means simple: it is a multi-step one, with specified procedures and parametrisations being adopted at every stage. This therefore gives us the opportunity to consider further what Coulson called ‘primitive patterns of understanding’,[40] this itself is very much in the spirit of Dirac’s remark,[41] some thirty years earlier, that it would be ‘... desirable that approximate methods of applying quantum mechanics should be developed that can lead to an explanation of the main features of complex atomic systems without too much computation’. We do this by subjecting the same structures as were studied in Refs. [38,39] to calculations based on the simple, pseudo graph-theoretical HLPM ‘topological’ ring-current approach.[1–4] We also include qualitative and quantitative comparison of our results with those of Sundholm et al.,[39] mentioned above, and of Cao et al.,[38] the latter of whom made predictions about magnetic properties of these same structures based on Nuclear Magnetic Resonance measurements and application of von Schleyer’s idea of Nucleus Independent Chemical Shift (NICS).[42,43] Later, we shall present HLPM calculations[1–4] on some structures with \([4n]\)-perimeters that were also studied by Cao et al.,[38] as well as on some related and specially ‘designed’ \([4n]\)- and \([4n+2]\)-perimeter structures of our own choosing. Structures of this sort have long been a subject of speculation and discussion — e.g., Ref. [44].

Once again, our aim in doing this is to see whether there is qualitative, or even semi-quantitative, agreement

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**Figure 1.** The molecular graphs of naphthalene (1), pentalene (2) and the three \([4n+2]\)-\(n\)-electron ‘bispentalenes’ ((3)–(5)) studied by Cao et al.[38] and by Sundholm et al.[39]
between a (presumably) numerically accurate but necessarily complex \( \text{ab initio} \)\textsuperscript{45} calculation\textsuperscript{38,39} (as well as other approaches\textsuperscript{38}) and a conceptually simple, quasi graph-theoretical one, whose predictions depend only on the carbon-carbon connectivity of the structure being investigated, and on the (geometrical) areas of its individual constituent rings.\textsuperscript{1–4}

**CALCULATIONS**

The topological bond-currents and ring-currents reported here were calculated by a strict application of the HLPM method, as described in exhaustive detail in Refs. [1–6] — that is, with the assumptions of (a) a (geometrically) planar carbon-atom skeleton, and (b) the areas of five-membered and six-membered rings being taken to be in the ratio\textsuperscript{[1–6,46]}

\[
5 \cot \left( \frac{\pi}{5} \right) : 6 \cot \left( \frac{\pi}{6} \right).
\]

Furthermore,\textsuperscript{[4,5]} for a conjugated system comprising \( r \) rings, if \( X_{\text{L}} \) (structure) stands for the London\textsuperscript{[20,21,46,47]} \( \pi \)-electron contribution to the structure’s magnetic susceptibility, perpendicular to an assumed molecular plane, and \( X_{\text{L}} \) (benzene) stands for the similarly calculated ‘London’ contribution\textsuperscript{[20,21,47,48]} to the (diamagnetic) susceptibility of benzene, perpendicular to its own molecular plane, then, for a conjugated system comprising \( r \) rings, we define the ‘susceptibility ratio’\textsuperscript{[4,5]}

\[
\frac{X_{\text{L}} \text{(structure)}}{X_{\text{L}} \text{(benzene)}} = \sum_{i=1}^{r} \left( \frac{S_i}{S_{\text{benzene}}} \right) \left( \frac{J_i}{I_{\text{benzene}}} \right),
\]

where \( S_i \) is the area of the \( i \)th ring of the conjugated system, which bears a topological ring-current of intensity \( J_i \) (calculated, for example, from equation (15) of Ref. [4]), whilst \( S_{\text{benzene}} \) represents the area of a standard benzene hexagon and \( I_{\text{benzene}} \) is the ring-current intensity calculated — by the same (HLPM) method — for benzene. An entirely equivalent expression (equation (2) of Ref. [49]) is derivable from Aihara’s circuit-theory approach.\textsuperscript{[50]}

What we shall subsequently call the ‘susceptibility ratio’ — the quantity defined in equation (1) — is thus seen to be a convenient, single, quasi-topological index\textsuperscript{[4,5,47,48]} associated with a given conjugated system, which has been suggested\textsuperscript{[47]} to have potential significance regarding that system’s overall diamagnetic/paramagnetic nature, according to whether the susceptibility ratio is positive/negative, (respectively). This is especially the case when, as here, some rings in a given structure bear diamagnetic ring-currents and other rings are calculated to support paramagnetic ring-currents — a difficulty that was pointed out almost fifty years ago in a much-neglected paper by Jung.\textsuperscript{[51]} We have exploited this concept of ‘susceptibility ratio’ for that very purpose on several previous occasions\textsuperscript{[4,28,32,47]} and, as we wish to do so again here, the susceptibility ratios calculated from equation (1) are listed in the right-hand columns of Tables 1–4 (for structures (1)–(21)).

**NUMERICAL RESULTS**

Ring currents (in black) and bond currents (in red) are shown in Figure 2 for the structures whose molecular graphs are presented in Figure 1. It should be noted that the HLPM bond-currents rigorously obey Kirchhoff’s law of current conservation at junctions\textsuperscript{[4,5,27,52]} — an attribute not, in general, shared by the corresponding quantities (such as integrated current-strengths (susceptibilities)\textsuperscript{[27–29]} arising from the \( ab initio \) approaches\textsuperscript{[17–19]} except in the limit of an infinite basis set.\textsuperscript{[34,18,28]} The bond currents are thus the microscopic analog of the currents in the wires in a macroscopic electrical network and the ring currents are analogous to loop currents flowing around the several irreducible\textsuperscript{[4,5,27]} cycles of the network. Both the bond currents and the ring currents are expressed as a ratio to the corresponding quantities calculated, by the same (HLPM)\textsuperscript{[1–6]} method, for benzene. Accordingly, the bond currents and ring currents depicted in Figure 2 (and in the subsequent Figures and Tables in this paper) are all pure numbers — dimensionless quantities, devoid of any physical units. Furthermore, contrary to the scheme adopted by Sundholm et al.,\textsuperscript{[39]} we here use the convention — necessary when dealing with topological ring-currents as defined, for example, in Refs. [1–6] — that diamagnetic ring-currents are considered to be positive and to circulate in the anti-clockwise sense around the rings that are their domain, whilst paramagnetic ring-currents are negative and circulate in the clockwise direction around the ring in question. Bond currents flow in the directions indicated by the individual arrows on the respective bonds. On these conventions it is seen from Figure 2 that (as was originally shown by McWeeny\textsuperscript{[51]} the current in naphthalene (\( J_1 \)) is a diamagnetic one flowing entirely around the perimeter in the anti-clockwise direction and of size about 9% greater than the benzene ring- (bond-) current.\textsuperscript{[51,52]} Further, as McWeeny himself observed,\textsuperscript{[52]} his calculated ring-current intensities of 1.093 in the individual rings of naphthalene are entirely in accord with London’s\textsuperscript{[20,21]} ‘susceptibility ratio’ for naphthalene of 2.186 (= 2 × 1.093). The paramagnetic current around the perimeter of pentalene (2), by contrast, flows\textsuperscript{[54,55]} in the clockwise sense and the magnitude of this current slightly exceeds twice the benzene value. (The currents reported for (2) in Figure 2 are consistent with the susceptibility ratios reported long ago by Berthier et al.\textsuperscript{[54]} and Salem\textsuperscript{[57]} We note in passing, in the light of previous accurate \( ab initio \) results, that Ref. [56] reports that ‘... the modulus of this paramagnetic \( \pi \) current density is comparable with that evaluated for benzene’; the GIMIC value\textsuperscript{[39]}
Figure 2. Map for the HLPM topological ring-currents (in black) and the associated topological bond-currents (in red) for structures (1)–(5), whose molecular graphs are shown in Figure 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. (It should be noted that this is the opposite of the convention adopted by Sundholm et al. in, for example, Ref. [39].) The various bond-currents run in the direction indicated by the arrow pointing along each bond. The pentalene moieties in (2)–(5) are outlined in blue, for later convenience of emphasis in the section headed ‘Discussion’.

Figure 3. HLPM topological ring-current and bond-current maps for four [4n]-π-electron systems discussed in Ref. [38]. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2. The pentalene moieties in (6) and (7) are outlined in blue, for later convenience of emphasis in the section headed ‘Discussion’.
The data in Figure 2 are evaluated in the section headed 'Discussion'.

In Figure 3, we depict the results of HLPM calculations on four \([4n\pi]-\pi\)-electron systems that arise in Ref. [38], which are further evaluated in the section headed 'Discussion'.

Finally, Figures 4–6 present HLPM calculations on structures (10)–(15) with five or six rings. Each contains two pentalene moieties (outlined in blue, for emphasis).

Figure 5 shows HLPM current-maps for four designed \([4n\pi]-\pi\)-electron systems (16)–(19), each with ten rings and four pentalene moieties (likewise outlined in blue, for emphasis).

Finally, Figure 6 presents HLPM calculations on two designed seven-ring systems (20 & 21) with \([4n\pi]-\pi\)-electron peripheries. Each contains three pentalene moieties (outlined in blue).

The ring-current and bond-current maps for structures (1)–(21) are discussed in the next section.

**DISCUSSION**

**Qualitative Comparisons with \textit{Ab Initio} Calculations**

**STRUCTURES (3)–(5)**

One of the first aspects of their \textit{ab initio} calculations and experimental observations that Cao et al. [38] and Sundholm \textit{et al.} [39] both drew attention to was that, despite the fact that structures (3)–(5) all possessed \([4n\pi]+2\)-\pi\)-electron perimeters, the net currents around these perimeters are in the clockwise (paramagnetic) direction. This observation is fully confirmed by the HLPM topological calculations being reported here, as can be seen from the bond-current maps shown in Figure 2 and from the third column of Table 1; the fourth column of that Table displays the ranges of currents within the perimeter of each of (3)–(5). The averages are ca. 0.6, 1.3 and 1.4, respectively, in the paramagnetic (clockwise) direction. As observed by Cao \textit{et al.} [38] and by Sundholm \textit{et al.} [39] this observation ostensibly appears to defy [38,39] the traditional \([4n\pi]/[4n\pi]+2\) 'rules' about paramagnetic/diamagnetic ring-currents; however, it should be recalled and emphasised that these rules apply only to monocycles [37]. In this strict sense, therefore, neither our own
Figure 5. The HLPM topological current-maps for four more \([4n+2]\)-\(\pi\)-electron structures (comprising ten rings) specially designed for the present study. Each contains four pentalene (2) moieties (outlined in blue, for emphasis) and a single naphthalene (1) moiety. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2.

Figure 6. The HLPM topological current-maps for two seven-ring \([4n]\)-\(\pi\)-electron structures specially designed for the present study. Each contains three pentalene (2) moieties (outlined in blue, for emphasis) and a single benzene moiety. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2.
calculations, nor those reported in Refs. [38] and [39], ‘violate the Hückel rule for aromaticity’. On the other hand, the basis of the calculations, structures (3)–(5) are evidently not what Trost et al., in Ref. [58], called ‘perturbed annulenes’; see also Ref. [59].

A second feature emphasised by Cao et al. and Sundholm et al. is that the pentalene moieties appear to undergo incorporation into these bispentalene structures with — to greater or lesser extents — their characteristic perimeter circulations in the paramagnetic sense surviving intact, as what they call ‘semi-local currents’. As Cao et al. put it: ‘The obtained data are indicative of the aromatic nature of the bispentalene core, despite the [4n+2] perimeter of the molecules.’

The clockwise perimeter-current in pentalene (2) itself — shown in Figure 2 — is approximately of magnitude 2.1 times the diamagnetic benzene current; the average perimeter currents (in the paramagnetic direction) around the pentalene moieties in (3), (4) and (5) (shown in the fifth column of Table 1) are approximately 0.7, 1.4 and 2.1, respectively — the latter approaching within 4% of the perimeter current in isolated pentalene (2) itself; see Figure 2. We draw attention here to the observation that the ‘London’ contributions5,20,21,47 (equation (1)) to the overall magnetic susceptibilities of (3), (4) and (5), at right angles to an assumed molecular plane — what we are here calling the ‘susceptibility ratios’15,47 — have approximate values of –2.1, –4.5 and –5.8, respectively, as can be seen from the right-hand column of Table 1.

We thus note that all three of the quantities (a) average perimeter current, (b) average current around the perimeters of the pentalene moieties, and (c) paramagnetic ‘London’12,20,21 contribution to magnetic susceptibility (‘susceptibility ratios’15,47) are all predicted by the HLPM calculations to be in the order (5) > (4) > (3). These are qualitatively in accord with previous findings in Refs. [38, 39].

We finally observe from Figure 2 that the ring-current intensities in the two symmetrically non-equivalent benzene moieties in [4n+2]-peripheral (3)–(5) in (3) & (4) — see Figure 2 — are both paramagnetic (approximately –0.24 and –0.59) — agreed38 to be very different from the benzene value of +1.00. The ring-current in the one naphthalene moiety in these structures (in (5)) is likewise paramagnetic (–0.17, when expressed as a ratio to the benzene value) and also very different from the naphthalene (1) current of +1.093 (see Table 1 and Refs. [31,53]).

<table>
<thead>
<tr>
<th>Structure</th>
<th>Size of Perimeter</th>
<th>Average Perimeter Current(a)</th>
<th>Range of Perimeter Currents(b)</th>
<th>Average Current on Perimeter(s) of Pentalene Moiety or Moieties(c)</th>
<th>Range of Perimeter Currents(d)</th>
<th>( \chi_{\pi}^{\text{per}} ) (structure)</th>
<th>( \chi_{\pi}^{\text{per}} ) (benzene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) [4n+2], with n = 2</td>
<td>+1.09</td>
<td>1.09 to 1.09</td>
<td>–0.14 to –2.14</td>
<td>–2.14</td>
<td>–2.14 to –2.14</td>
<td>–2.05</td>
<td>–2.12 to –2.11</td>
</tr>
<tr>
<td>(2) [4n+2], with n = 4</td>
<td>–2.14</td>
<td>–2.14 to –2.14</td>
<td>–0.59 to –0.87</td>
<td>–0.68</td>
<td>–0.56 to –0.87</td>
<td>–2.13</td>
<td></td>
</tr>
<tr>
<td>(3) [4n+2], with n = 5</td>
<td>–1.29</td>
<td>–0.58 to –1.51</td>
<td>–1.42</td>
<td>–0.88 to –1.51</td>
<td>–4.53</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(4) [4n+2], with n = 5</td>
<td>–1.39</td>
<td>–0.17 to –2.11</td>
<td>–2.05</td>
<td>–1.87 to –2.11</td>
<td>–5.84</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(a) All currents are dimensionless, and are expressed as ratio to the corresponding current calculated, by the same method, for benzene. All data are presented correct to two decimal places.
(b) ‘+’ indicates diamagnetic (anti-clockwise) circulations; ‘−’ indicates paramagnetic (clockwise) circulations.
(c) ‘Susceptibilities are expressed as ‘susceptibility ratios’ — that is, they are expressed as a ratio to the ‘London’ contribution to the diamagnetic susceptibility of benzene;15,47 ‘+’ indicates an overall net diamagnetic susceptibility; ‘–’ indicates an overall net paramagnetic susceptibility.
(d) There are no pentalene moieties in (1).
hand column of Table 2 also indicate that (6) is by far the most paramagnetic, overall, of the structures (6) – (9) — structure (9) being, in fact, very marginally diamagnetic, overall, according to the HLPM calculations presented in Table 2.

We finally observe from Figure 3 that the ring-current intensities in half of the six symmetrically distinct benzene moieties in [4n]-peripheral (6)–(9) are paramagnetic (ranging from −0.02 to −0.43), while the ring-currents in the other three symmetrically non-equivalent benzene moieties in these structures are, by contrast, diamagnetic (ranging from +0.27 to +0.48). All are very different from isolated benzene itself, with a value of +1.00.

Table 2. HLPM calculations on structures (6)–(9), considered in Figure 1 of Ref. [38]

<table>
<thead>
<tr>
<th>Structure Number</th>
<th>Size of Perimeter</th>
<th>Average Perimeter Current(±)[b]</th>
<th>Range of Perimeter Currents(±)[b]</th>
<th>Average Current on Perimeter(s) of Pentalene Moiety or Moieties[6][d]</th>
<th>Range of Pentalene Perimeter Currents[6][d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(6)</td>
<td>[4n], with n = 3</td>
<td>−0.97</td>
<td>−0.02 to −1.66</td>
<td>−1.64</td>
<td>−1.63 to −1.66</td>
</tr>
<tr>
<td>(7)</td>
<td>[4n], with n = 4</td>
<td>−0.56</td>
<td>−0.24 to −0.91</td>
<td>−0.65</td>
<td>−0.54 to −0.91</td>
</tr>
<tr>
<td>(8)</td>
<td>[4n], with n = 5</td>
<td>−0.98</td>
<td>−0.06 to −1.60</td>
<td>−1.38</td>
<td>−1.43 to −1.51</td>
</tr>
<tr>
<td>(9)</td>
<td>[4n], with n = 5</td>
<td>−0.86</td>
<td>−0.05 to −1.43</td>
<td>−1.33</td>
<td>−1.24 to −1.43</td>
</tr>
</tbody>
</table>

(a) All currents are dimensionless, and are expressed as ratio to the corresponding current calculated, by the same method, for benzene. All data are presented correct to two decimal places.
(b) + indicates diamagnetic (anti-clockwise) circulations; − indicates paramagnetic (clockwise) circulations.
(c) Susceptibilities[5,47] are expressed as a ratio to the ‘London’ contribution to the diamagnetic susceptibility of benzene; + indicates an overall net diamagnetic susceptibility; − indicates an overall net paramagnetic susceptibility.
(d) The predicted current flow around the perimeter is not uni-directional in (7)–(9); hence, no average flow is quoted for these structures.

Table 3. HLPM calculations on [4n+2]-Perimeter structures (10)–(19)

<table>
<thead>
<tr>
<th>Structure Number</th>
<th>Size of Perimeter</th>
<th>Average Perimeter Current(±)[b]</th>
<th>Range of Perimeter Currents(±)[b]</th>
<th>Average Current on Perimeter(s) of Pentalene Moiety or Moieties[6][d]</th>
<th>Range of Pentalene Perimeter Currents[6][d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(10)</td>
<td>[4n+2], with n = 4</td>
<td>−0.99</td>
<td>−0.52 to −1.16</td>
<td>−1.07</td>
<td>−0.62 to −1.16</td>
</tr>
<tr>
<td>(11)</td>
<td>[4n+2], with n = 4</td>
<td>−0.56</td>
<td>−0.24 to −0.91</td>
<td>−0.65</td>
<td>−0.54 to −0.91</td>
</tr>
<tr>
<td>(12)</td>
<td>[4n+2], with n = 4</td>
<td>−1.31</td>
<td>−0.59 to −1.51</td>
<td>−1.43</td>
<td>−0.91 to −1.51</td>
</tr>
<tr>
<td>(13)</td>
<td>[4n+2], with n = 5</td>
<td>−0.98</td>
<td>−0.06 to −1.60</td>
<td>−1.51</td>
<td>−1.43 to −1.60</td>
</tr>
<tr>
<td>(14)</td>
<td>[4n+2], with n = 5</td>
<td>−0.86</td>
<td>−0.05 to −1.43</td>
<td>−1.33</td>
<td>−1.24 to −1.43</td>
</tr>
<tr>
<td>(15)</td>
<td>[4n+2], with n = 5</td>
<td>−1.31</td>
<td>−0.12 to −2.05</td>
<td>−1.95</td>
<td>−1.79 to −2.05</td>
</tr>
<tr>
<td>(16)</td>
<td>[4n+2], with n = 8</td>
<td>−0.79</td>
<td>−0.29 to −1.12</td>
<td>−0.87</td>
<td>−0.65 to −1.12</td>
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<tr>
<td>(17)</td>
<td>[4n+2], with n = 8</td>
<td>−1.28</td>
<td>−0.50 to −1.56</td>
<td>−1.40</td>
<td>−1.05 to −1.56</td>
</tr>
<tr>
<td>(18)</td>
<td>[4n+2], with n = 8</td>
<td>−0.98</td>
<td>−0.42 to −1.11</td>
<td>−1.05</td>
<td>−0.67 to −1.11</td>
</tr>
<tr>
<td>(19)</td>
<td>[4n+2], with n = 8</td>
<td>−0.61</td>
<td>−0.11 to −0.92</td>
<td>−0.72</td>
<td>−0.55 to −0.92</td>
</tr>
</tbody>
</table>

(a) All currents are dimensionless, and are expressed as ratio to the corresponding current calculated, by the same method, for benzene. All data are presented correct to two decimal places.
(b) + indicates diamagnetic (anti-clockwise) circulations; − indicates paramagnetic (clockwise) circulations.
(c) Susceptibilities[5,47] are expressed as a ratio to the ‘London’ contribution to the diamagnetic susceptibility of benzene; + indicates an overall net diamagnetic susceptibility; − indicates an overall net paramagnetic susceptibility.
(d) This figure (in the cases of structures (11) & (15)–(19)) is the average of the bond currents in the bonds around the perimeters of a single pair of symmetrically non-equivalent pentalene moieties.
(e) This figure (in the cases of structures (16)–(19)) is the average of the bond currents in the bonds around the perimeters of two pairs of symmetrically non-equivalent pentalene moieties.

In Figures 4 and 5, and in Table 3, we present topological (HLPM) ring-current and bond-current maps and other quantities relating to the π-electron magnetic properties of ten [4n+2]-π-electron structures which comprise five rings (structures (10)–(12)), six rings (structures (13)–(15)), and ten rings (structures (16)–(19)). All of these have been specially ‘designed’ for the present study. Each of (10)–(15) contains two pentalene moieties (outlined in blue, for emphasis, in Figure 4), whilst (16)–(19) each contain four pentalene units (as shown in Figure 5). The third column of Table 3 shows the average perimeter current in all cases to be in the paramagnetic sense, with values ranging from
about 0.6 to 1.3 times the magnitude of the benzene ring-current.

As with structures (3)–(6), the pentalen moieties again survive incorporation into larger systems with their perimeter circulations in the paramagnetic sense essentially intact; from column 5 of Table 3 it is seen that average magnitudes of these circulations around the pentalene perimeters range from about 0.7 (for (11) and (19)) to almost twice the benzene value (structure (15)) (compared with the perimeter current in pentalene itself ((2)), of about 2.1 (Figure 2 and Table 1)). This mirrors the qualitative findings of Cao et al. and Sundholm et al. in their \textit{ab initio} and experimental studies of structures (3)–(5). With regard to the susceptibility ratios, displayed in the right-hand column of Table 3, all of (10)–(19) are seen to be unambiguously paramagnetic, overall, with (17) being the largest (at just less than 9 times the magnitude of the (diamagnetic) susceptibility-ratio for benzene).

We finally observe from Figures 4 & 5 that the ring-current intensities in the three benzene moieties in [4n+2]-peripheral (10)–(19) are paramagnetic, having values of ~0.24 to ~0.60 — very different from the current in isolated benzene itself — while the ring-currents in all eight of the symmetrically non-equivalent naphthalene moieties in these structures are also paramagnetic (ranging from ~0.06 to ~0.51, when expressed as a ratio to the benzene value of +1.00); as was the case with the naphthalenic unit in (5), these are all very different from the diamagnetic perimeter-current (of 1.093) in the parent structure, naphthalene itself (displayed in Figure 2). This qualitative observation is a point that was also noted and commented upon in the context of the \textit{ab initio} calculations on structures (3)–(5).

**STRUCTURES (20) & (21)**

In Figure 6, and in Table 4, we present topological (HLPM) ring-current and bond-current maps, and other quantities relating to the \(\pi\)-electron magnetic properties, of two seven-ring structures ((20) & (21)) with [4n]-\(\pi\)-electron perimeters, which have been specially ‘designed’ for the present study. Each contains three pentalen moieties (again, outlined in blue, for emphasis, in Figure 6). As with the [4n+2]-\(\pi\)-electron structures considered here, the peripheral circulations are all in the paramagnetic (clockwise) direction, though with small averages (as shown in column 3 of Table 4). Of the two, only (20) displays a unique (clockwise) direction of flow around all bonds in the perimeters of the pentalen moieties, and even that is with a low average magnitude of about half that of the benzene (diamagnetic) value. ‘Susceptibility ratios’ are both paramagnetic and of moderate size (2 or 3 times the benzene value), as shown in the right-hand column of Table 4.

We finally note from Figure 6 that the ring-current intensities in the two benzene moieties in [4n]-peripheral (20) & (21) are paramagnetic, having values of approximately ~0.16 and ~0.49, respectively; as with other benzenoid moieties in structures (3)–(21), the ring-current values in such rings are thus very different from the value in isolated benzene itself (+1.00).

### Quantitative Comparisons with \textit{Ab Initio} Calculations

One of the most significant advances in this field in recent years has been the ability of the \textit{ab initio} methods (e.g., Refs. [7–19]) to compute not just pictorial, semi-quantitative current-density maps, as heretofore, but also to calculate numerical quantities (variously called bond-current susceptibilities or bond-current strengths \[13,14\] or integrated current-strengths \[18,19\] or current-strength susceptibilities \[199\]) which are the equivalent of bond currents \[24,27\] in the HLPM approach. This gives the opportunity directly to compare the quantitative predictions of \textit{ab initio} methods with those of the HLPM formalism when quantities calculated from both approaches are expressed as a (dimensionless) ratio to the corresponding quantity computed, by the same respective method, for benzene. We have done this in the past, both with some (non-alternant) ‘altan’ systems \[13,30\] and (with

<table>
<thead>
<tr>
<th>Structure Number</th>
<th>Size of Perimeter</th>
<th>Average Perimeter Currents [^{\text{(26)}}]</th>
<th>Range of Perimeter Currents [^{\text{(26)}}]</th>
<th>Average Current on Perimeter(s) of Pentalen Moeity or Moieties [^{\text{(26)}}]</th>
<th>Range of Pentalen Perimeter Currents [^{\text{(26)}}]</th>
<th>(\chi_{\perp}^{\text{SDM}}) (structure)</th>
<th>(\chi_{\perp}^{\text{SDM}}) (benzene)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(20)</td>
<td>[4n], with (n = 6)</td>
<td>-0.45</td>
<td>-0.15 to -0.68</td>
<td>-0.50</td>
<td>-0.35 to -0.68</td>
<td>-2.20</td>
<td>-3.42</td>
</tr>
<tr>
<td>(21)</td>
<td>[4n], with (n = 6)</td>
<td>-0.70</td>
<td>-0.09 to -1.61</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

\[\text{Table 4. HLPM calculations on the [4n]-Perimeter Structures (20) & (21)}\]

[^26]: All currents are dimensionless, and are expressed as ratio to the corresponding current calculated, by the same method, for benzene. All data are presented correct to two decimal places.

[^27]: ‘+’ indicates diamagnetic (anti-clockwise) circulations; ‘–’ indicates paramagnetic (clockwise) circulations.

[^28]: Susceptibilities are expressed as a ratio \[^{\text{(18)}}\] to the ‘London’ contribution to the diamagnetic susceptibility of benzene; ‘+’ indicates an overall net diamagnetic susceptibility; ‘–’ indicates an overall net paramagnetic susceptibility.

[^29]: This figure is the average of the bond currents in the bonds around the peripheries of the three pairs of symmetrically non-equivalent pentalen moieties in structure (20).

[^30]: No unidirectional current flow is predicted around the peripheries of the pentalene moieties in (21); hence, no average flow is indicated, in this Table.
particular success\(^{(1)}\) in the context of a large sample of bonds (66) in several (10) altrant condensed, benzenoid hydrocarbons\(^{(1,18)}\). These comparisons have been presented in tabular form, and as ‘best-fit’ regression-lines, and also in so-called ‘comparator’ diagrams. Please see (a) presented in tabular form, and as ‘best-fit’ regression-lines, integrated current-strengths calculated for some currents\(^{(1)}\) with integrated current-strengths computed by Ref. \(^{[4]}\) for analogous comparisons of HLPM bond-currents and GIMIC integrated current-strengths reported in Ref. \(^{[39]}\) and the corresponding HLPM quantities, for a line that passed through the origin. The information presented in Table 5 is now displayed visually in two different ways:

(a) Best-fit regression-lines, shown in Figure 7. Two such lines are depicted: the top plot (with correlation coefficient 0.94) is for an unrestricted regression, and the lower plot (also with a correlation coefficient of 0.94) is for a regression in which the best-fit line is additionally constrained to pass through the origin. The slope of the constrained line indicates that, on average, the HLPM ‘topological’ bond-currents are some 25% greater than the corresponding GIMIC integrated current-strengths in structures (1)–(5), when both are expressed as a ratio to the corresponding quantities calculated, by the same method, for benzene.

(b) A ‘Comparator’ diagram, shown in Figure 8. Implicitly listed along the horizontal axis are the 11 bonds under

### Table 5. Comparison of GIMIC Current-Strengths and HLPM Bond-Currents for certain Bonds in Structures (1)–(5) that are situated in only one Ring

<table>
<thead>
<tr>
<th>Structure (as in Figure 1)</th>
<th>Bond-Plane Labelling used by Sundholm et al. in Figure 1 of Ref. (^{[39]})</th>
<th>Net GIMIC Current-Strength (from Table 1 of Ref. (^{[39]})) Expressed as a Ratio to the Net GIMIC Current-Strength in Benzene (11.8 nAT(^{-1}))(^{(a)})</th>
<th>HLPM Topological Bond-Current (Expressed Relative to the HLPM Bond-Current in Benzene)(^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>(b)</td>
<td>+1.10</td>
<td>+1.09</td>
</tr>
<tr>
<td>(2)</td>
<td>(b)</td>
<td>−1.69</td>
<td>−2.14</td>
</tr>
<tr>
<td>(3)</td>
<td>(d)</td>
<td>−1.04</td>
<td>−0.86</td>
</tr>
<tr>
<td>(3)</td>
<td>(f)</td>
<td>−0.97</td>
<td>−0.57</td>
</tr>
<tr>
<td>(3)</td>
<td>(g)</td>
<td>−0.28</td>
<td>−0.24</td>
</tr>
<tr>
<td>(4)</td>
<td>(d)</td>
<td>−1.01</td>
<td>−1.47</td>
</tr>
<tr>
<td>(4)</td>
<td>(f)</td>
<td>−0.97</td>
<td>−1.51</td>
</tr>
<tr>
<td>(4)</td>
<td>(g)</td>
<td>−0.24</td>
<td>−0.59</td>
</tr>
<tr>
<td>(5)</td>
<td>(b)</td>
<td>−0.29</td>
<td>−0.17</td>
</tr>
<tr>
<td>(5)</td>
<td>(e)</td>
<td>−1.43</td>
<td>−2.05</td>
</tr>
<tr>
<td>(5)</td>
<td>(g)</td>
<td>−1.37</td>
<td>−2.11</td>
</tr>
</tbody>
</table>

\(^{(a)}\) This net value of 11.8 nAT\(^{-1}\) for the GIMIC current-strength in benzene arises from the algebraical sum of a diatropic contribution of 16.7 nAT\(^{-1}\) and a paratropic contribution of −4.9 nAT\(^{-1}\). (Personal communication to RBM from Professor Dage Sundholm, March 15th, 2017).

\(^{(b)}\) Taken from Figure 2 and (as with the GIMIC current-strengths in the preceding column) presented correct to two decimal-places.
Figure 7. Least-squares regression-lines between HLPN topological bond-currents (from Figure 2) — plotted along the vertical axis — and (plotted along the horizontal axis) the integrated bond-current strengths/susceptibilities calculated by the GIMIC ab initio formalism for 11 of the symmetrically non-equivalent bonds in structures (1)–(5). In each case, the currents plotted along both axes are dimensionless, being expressed as a ratio to the bond current/integrated current strength (as the case may be) calculated by the corresponding method, for benzene. The top plot is for an unrestricted regression, and the lower plot is for a regression in which the best-fit line is additionally constrained to pass through the origin.

Figure 8. ‘Comparator’ diagram between relative integrated current-strengths from the GIMIC data reported in Table 5 and Ref. [39] for eleven symmetrically non-equivalent bonds in structures (1)–(5) (the red curve) and the corresponding HLPM topological bond-currents taken from Figure 2 and Table 5 (the black curve). In each case, the currents (along the two axes) are dimensionless, being expressed as a ratio to the bond current/integrated current-strength (as the case may be) calculated, by the corresponding method, for benzene. Implicitly listed along the horizontal axis are the eleven bonds under study. These are also explicitly labelled in blue at the peaks and the troughs of the curves. These labellings combine our own structure numbers (1)–(5), as displayed in Figure 1) with the bond-labelling letters depicted and defined in Figure 1 of Ref. [39] for eleven symmetrically non-equivalent bonds in 10 structures (Figure 21 on pp. 339–340 of Ref. [4]). Nevertheless, it can be seen by inspection of Figure 8 that there is a degree of correspondence in the patterns embodied in the red curve and the black curve, in that Figure.
CONCLUSIONS

The HLPM calculations\(^{1-6}\) of topological bond-currents reported in this paper for structures (1)–(21) enable the following conclusions to be drawn:

(a) The HLPM calculations reported confirm the earlier suggestions,\(^{38,39}\) based on experimental evidence and \textit{ab initio} calculations, that the current flow around the perimeters of structures (3)–(5) is in the clockwise (paramagnetic) sense, despite the fact that the lengths of these perimeters are \(4n+2\). This is perhaps hardly surprising when it is recalled that the structures being dealt with here are not monocyclic annulenes and thus the rules of Pople and Untch\(^{57}\) do not necessarily apply; (the situation is somewhat reminiscent of the analogous failure generally observed in the context of the so-called the ‘annulene-within-an-annulene model’ — see, for example, Refs. [3,29,32]).

(b) The HLPM calculations reported also reflect the view\(^{38,39}\) that the current flow around the perimeters of the several pentalene moieties in (3)–(5) shows that the pattern observed in pentalene ([2]) itself — namely, that of a strong current in the clockwise (paramagnetic) sense — essentially survives intact, to a greater-or-lesser extent, when pentalene becomes incorporated into structures of this sort, as one or more pentalene moieties.

(c) The net flow around in the perimeter of the \([4n]-\pi\)-electron structure (6) considered by Cao \textit{et al.}\(^{38}\) is also confirmed to be in the clockwise (paramagnetic) direction. No unique direction of flow was found around the perimeters of structures (7)–(9), however, though the pentalene moieties in (7) and (8) did display the pentalene patterns described in (b), above.

(d) In all the \([4n+2]-\pi\)-perimeter structures (10)–(19) that were especially ‘designed’ for this study, the consistent direction of flow around those perimeters is — as was found to be the case with (3)–(5), likewise with perimeters of size \(4n+2\) — in the clockwise (paramagnetic) direction, despite the \([4n+2]-\pi\)-perimeter which, naively, might suggest otherwise. Furthermore, all pentalene moieties in (10)–(19) preserve the pattern of paramagnetic circulations around their perimeters, as is predicted by the HLPM method for isolated pentalene itself, and described in (b), above.

(e) In the two \([4n]-\pi\)-perimeter structures ([20] & [21]) that were ‘designed’ for this study, the direction of flow around their perimeters is — as with (3)–(19), all with \([4n+2]-\pi\) perimeters — in the clockwise (paramagnetic) sense. Furthermore, all pentalene moieties in [20] & [21] once again preserve the same pattern of paramagnetic circulations around their perimeters as is predicted for isolated pentalene itself.

(f) The HLPM calculations show that benzene and naphthalene moieties that arise in structures (3)–(21) support ring currents that are qualitatively very different from the diamagnetic currents of +1.00 and +1.093, respectively, predicted for isolated benzene and naphthalene. This observation is also in qualitative agreement with the \textit{ab initio} computations documented in Refs. [38,39].

(g) Finally, where it was possible to make \textit{quantitative} comparisons (in Table 5 and in Figures 7 and 8) of individual HLPM bond-currents and the analogous quantities predicted by \textit{ab initio} calculations, agreement was moderately satisfactory — a correlation coefficient of 0.94 — though, as might be expected, the agreement was not as good as had previously been obtained\(^{4}\) (correlation coefficient 0.98) with a much bigger sample of bond-currents in a large number of (mainly geometrically planar) \textit{alternant}, benzenoid hydrocarbons.

These investigations again emphasise the important condition laid down in Pople and Untch’s classic paper of fifty years ago\(^{57}\) that the rule about \([4n+2]-\pi\)-annulenes being diamagnetic and \([4n]-\pi\)-ones being paramagnetic — like the famous Hückel Rule itself\(^{59}\) — rigorously applies only to monocytes. As Pople and Untch\(^{57}\) further observed, even when only monocyclic conjugated systems are considered, for the larger annulenes ‘... the paramagnetic currents will be partly quenched by alternation of bond-lengths and molecular non-planarity’. It should also be noted that those versions of the so-called ‘tight-binding’\(^{60}\) HLPM calculations that do not iterate resonance integrals with respect to bond orders, nor Coulomb integrals with respect to charges on the carbon atoms,\(^{48,61-65}\) ‘... can yield unsafe predictions when the geometrical distortion is important’\(^{47}\) Indeed, from much earlier investigations,\(^{47,48,61-65}\) one of us (RBM) has vigorously emphasised\(^{47}\) that such self-consistency is virtually vital in order to be sure of even qualitatively reliable ring-currents in the case of very paramagnetic conjugated species. As noted by Wilcox and Farley many years ago,\(^{48}\) one of the present authors (RBM) even concluded\(^{47}\) that this sensitivity to the sophistication of the computational method employed — especially for paramagnetic species — is a major drawback to the potential utility of adopting calculated London susceptibility ratios (equation (1)) as a criterion for defining ‘aromaticity’.\(^{6,47}\) Furthermore, in the same vein, a referee has pointed out that, although generally the ring currents depend very strongly on the ‘connection topology’, the two structures in Figure 6, for example, despite being similar...
chemical structures, show almost no similarity in the computed currents. Accordingly, this reviewer has speculated whether these quantities are similarly sensitive to molecular geometry. If this were the case, a small change in the pattern of bond lengths and bond angles (but not in the topology of the connections) would potentially induce large changes in the pattern of ring currents and our simple graph-theoretical treatment would not detect such a change. This is indeed a very pertinent point that is discussed in detail in Refs. [47, 48 and 61–65], aspects of which are alluded to above, and the consequences of which are documented below.

Now that ab initio methods (e.g., Refs. [7–19]) are routinely available, however, this consideration is, of course, no longer so relevant. That is why, in the current work, and earlier but recent ones,\textsuperscript{[27–31]} the above reservation about non-iterative calculations expressed in Refs. [47,61–65] have been temporarily set aside in order to test how well the predictions of the ab initio methods compare with even the most basic, non-iterative pseudo-graph-theoretical version of the Hückel–London–Pople–McWeeny approach;\textsuperscript{[1–6]} in this formalism, the calculated quantities (ring currents and bond currents) are effectively regarded — despite the cautions and caveats considered by one of us (RBM) in Ref. [66] — as effectively mathematical, pseudo graph-theoretical indices, rather than as quantum-mechanically calculated physical quantities per se.\textsuperscript{[1–6]} (We say ‘pseudo graph-theoretical’ for the quantities calculated by the HLPM approach do involve ring areas, which are a geometrical, rather than graph-theoretical, property of the particular conjugated system under study.) How this comparison fared in the case of structures (1)–(21), studied here, is summarised in points (a) – (g), above.

**Acknowledgments.** We are very grateful to Professor Dage Sundholm (University of Helsinki) for very kindly supplying the information that the GIMIC net integrated current-strength for benzene — when calculated on the same assumptions as were made in the computations presented by Professor Sundholm and his co-workers in Ref. [39] — is $+11.8 \text{nAT}^{-1} = (+16.7 \text{nAT}^{-1} + (-4.9 \text{nAT}^{-1})$. This information was used to translate the absolute integrated bond-current strengths reported in Ref. [39] into the ones, expressed as a ratio to this benzene value, listed in Table 5. We are also grateful to the three referees for some very astute and insightful comments on this manuscript.

We are both honoured to make this tribute to Professor Ivan Gutman on the occasion of his 70th Birthday; RBM, especially, thanks Ivan Gutman for nearly forty years of friendship and for most enjoyable (and invariably entertaining) scientific and mathematical collaboration.

**REFERENCES**


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