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

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**Abstract:** Two different groups (Cao *et al*. (2015) and Sundholm *et al*. (2016)) have recently reported (a) experimental Nuclear Magnetic Resonance data and *ab initio* Nucleus Independent Chemical Shift (NICS) calculations, and (b) GIMIC (Gauge Including Magnetically Induced Currents) *ab initio* computations, on the magnetic properties of some derivatives of [4*n*+2]-π-electron conjugated systems called 'bispentalenes'. These are formed by annellating two pentalene groups with a benzene or a naphthalene moiety. The same structures are here subjected to calculations based on the simple, pseudo graph-theoretical, Hückel–London–Pople–McWeeny (HLPM) 'topological' ring-current approach. In addition, HLPM calculations are presented on some structures with [4*n*]-perimeters that were also studied by Cao *et al*., as well as some other related, specially 'designed', [4*n*]- and [4*n*+2]-perimeter structures of our own choosing. The aim is to see whether there is qualitative, or even semi-quantitative, agreement between a (presumably) numerically accurate but necessarily complex *ab initio* calculation and a conceptually simple, quasi graph-theoretical one — the HLPM approach — whose predictions depend only on the carbon-carbon connectivity of the structure being investigated, and on the (geometrical) areas of its individual constituent rings. The HLPM calculations agree with the more-sophisticated studies that all the structures examined, whether they be [4*n*]- or [4*n*+2]-perimeter systems, bear *para*magnetic π-electron currents around their perimeters. Furthermore, all the many pentalene moieties in these conjugated systems appear to undergo incorporation into these bispentalene structures with — to greater or lesser extents — their characteristic perimeter circulations in the paramagnetic sense surviving intact. Quantitative regression comparisons between GIMIC *ab initio* integrated bond-current susceptibilities and HLPM bond-current intensities in a small sample of bonds in the structures studied by Sundholm *et al.* are found to have a correlation coefficient of 0.94 — not as high as that obtained (0.98) when similar data for a larger sample of bonds in several alternant, condensed, benzenoid were previously compared. It is again emphasised that Pople and Untch's rule about [4*n*+2]-annulenes being diamagnetic and [4*n*]-ones being paramagnetic — like the famous Hückel Rule itself — rigorously applies only to *mono*cycles.

**Keywords**: topological ring-currents, bispentalenes, [4*n*]- and [4*n*+2]- π-electron systems, comparisons with *ab initio* calculations.

## INTRODUCTION

**W**ITHIN 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 (CTOCD); 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[4,27–33] 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]-π-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
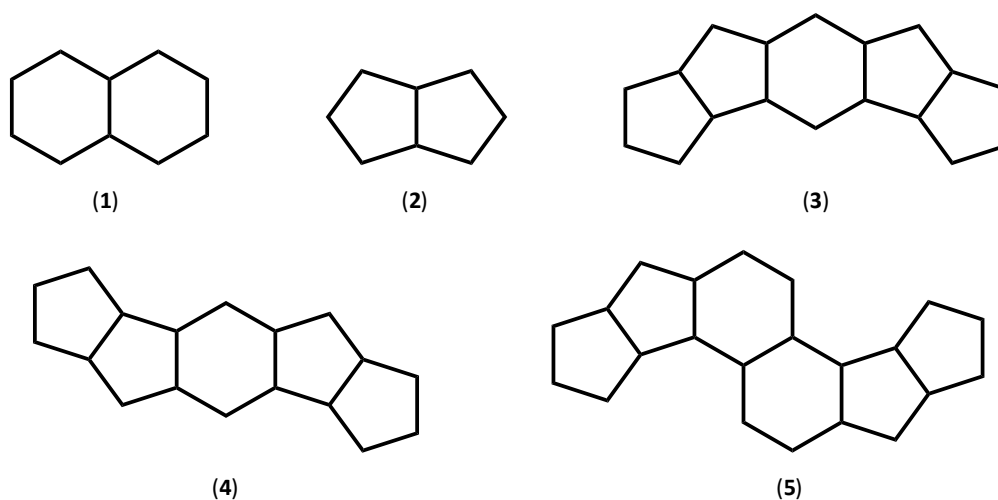


**Figure 1.** The molecular graphs of naphthalene (**1**), pentalene (**2**) and the three [4n+2]-π-electron 'bispentalenes' ((**3**)–(**5**)) studied by Cao *et al.*[38] and by Sundholm *et al.*[39]

between a (presumably) numerically accurate but necessarily complex *ab initio*[45] calculation[38,39] (as well as other approaches[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.[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[1–6,46]

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

Furthermore,[4,5] for a conjugated system comprising $r$ rings, if $\chi_{\perp}^{\pi-\text{London}}$(structure) stands for the 'London'[20,21,46,47] $\pi$-electron contribution to the structure's magnetic susceptibility, perpendicular to an assumed molecular plane, and $\chi_{\perp}^{\pi-\text{London}}$(benzene) stands for the similarly calculated 'London' contribution[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':[4,5]

$$\frac{\chi_{\perp}^{\pi-\text{London}}(\text{structure})}{\chi_{\perp}^{\pi-\text{London}}(\text{benzene})} = \sum_{\substack{(\text{rings}) \\ i=1}}^{r} \left(\frac{S_i}{S_{\text{benzene}}}\right)\left(\frac{J_i}{J_{\text{benzene}}}\right), \quad (1)$$

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 $J_{\text{benzene}}$ 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.[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,[4,5,47,48] associated with a given conjugated system, which has been suggested[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.[51] We have exploited this concept of 'susceptibility ratio' for that very purpose on several previous occasions[3,4,28,32,47] 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[4,5,27,52] — an attribute not, in general, shared by the corresponding quantities (such as integrated current-strengths (susceptibilities)[17–19]) arising from the *ab initio* approaches,[7–19] except in the limit of an infinite basis set.[14,18,23] The bond currents are thus the microscopic analogy 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[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)[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.*,[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[53]) the current in naphthalene ((**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.[31,52] Further, as McWeeny himself observed,[52] his calculated ring-current intensities of 1.093 in the individual rings of naphthalene are entirely in accord with London's[20,21] 'susceptibility ratio' for naphthalene of 2.186 (= 2 × 1.093). The paramagnetic current around the perimeter of pentalene (**2**), by contrast, flows[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.*[54] and Salem[55]) We note in passing, in the light of previous accurate *ab initio* results, that Ref. [56] reports that '... the modulus of this paramagnetic π current density is comparable with that evaluated for benzene'; the GIMIC value[39]
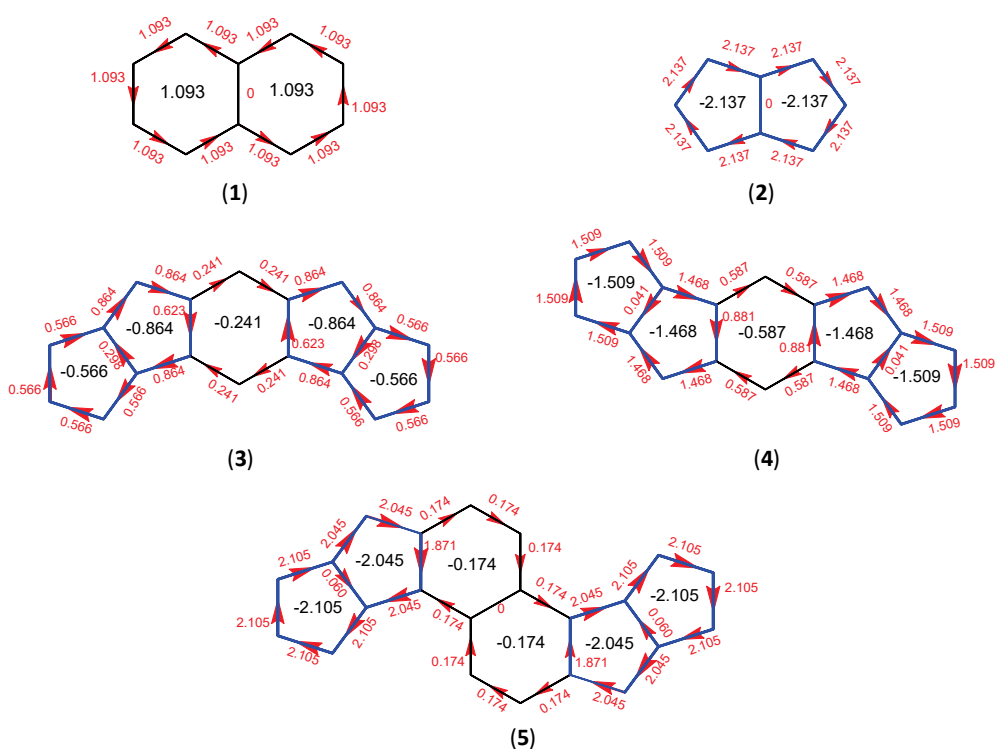
**Figure 2.** Map for the HLPM topological ring-currents (in black) and the associated topological bond-currents (in red) for structures (**1**)–(**5**), whose molecular graphs are shown in Figure 1. The topological ring-currents and bond-currents are dimensionless quantities. Positive (diamagnetic) 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'.
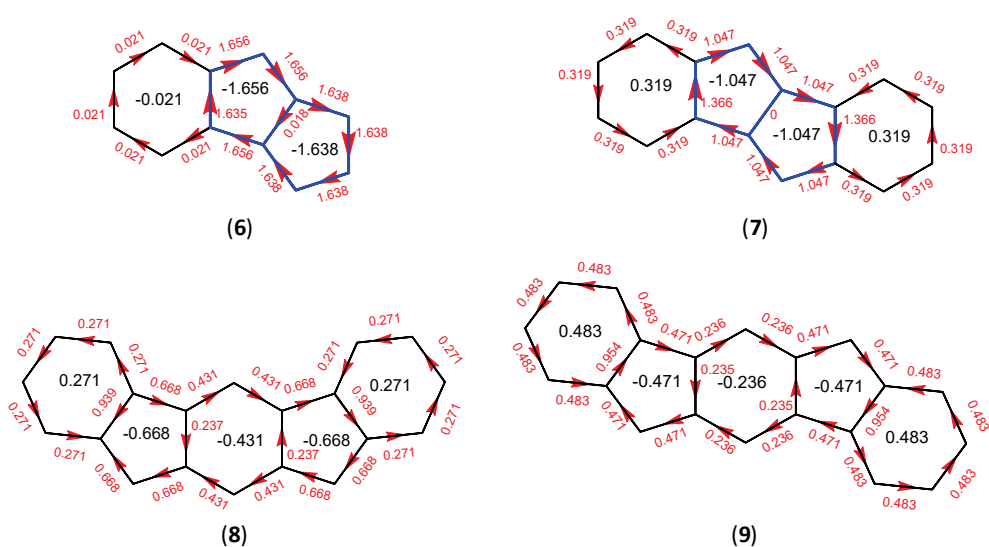


**Figure 3.** HLPM topological ring-current and bond-current maps for four [4*n*]-π-electron systems discussed in Ref. [38]. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2. The pentalene moieties in (**6**) and (**7**) are outlined in blue, for later convenience of emphasis in the section headed 'Discussion'.
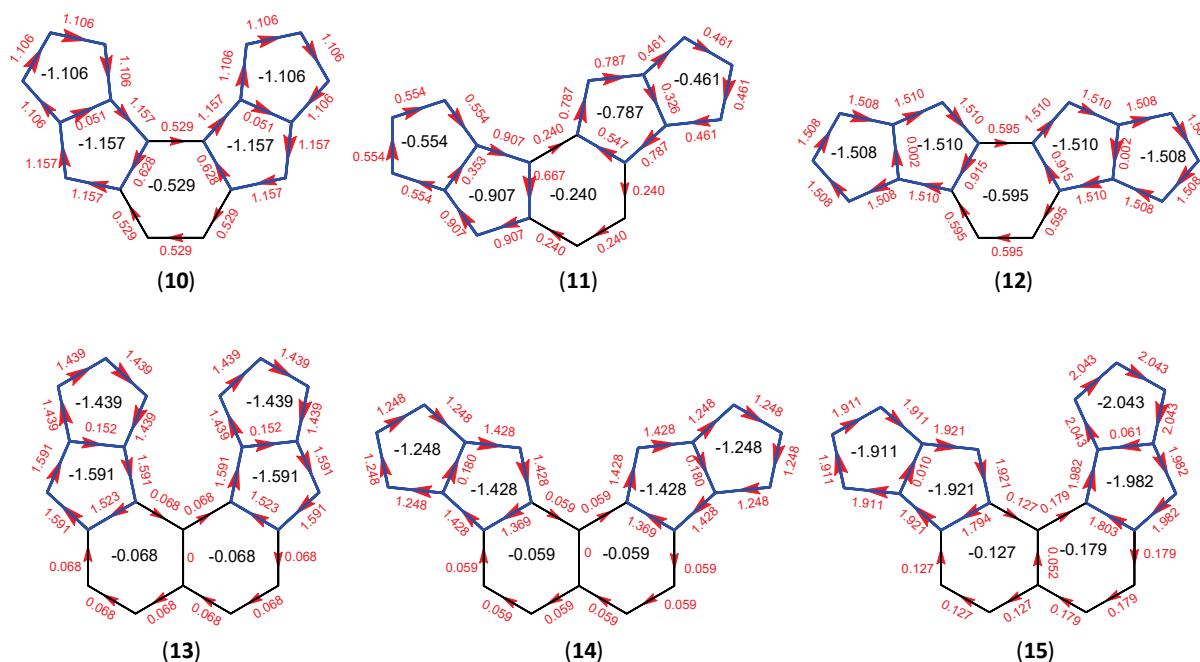
**Figure 4.** The HLPM topological current-maps for six [4*n*+2]-π-electron structures (with five or six rings) specially 'designed' for the present study. Each contains two pentalene ((**2**)) moieties (outlined in blue, for emphasis) and either a single benzene moiety or a single naphthalene ((**1**)) moiety. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2.

(of –1.69, later tabulated in Table 5) is also somewhat smaller. The data in Figure 2 are evaluated in the section headed 'Discussion'.

In Figure 3, we depict the results of HLPM calculations on four [4*n*]-π-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**)–(**21**)) that have been specially 'designed' for the present study. Figure 4 depicts six designed [4*n*+2]-π-electron 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 [4*n*+2]-π-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 [4*n*]-π-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 *Ab Initio* Calculations

### STRUCTURES (3)–(5)

One of the first aspects of their *ab initio* calculations and experimental observations that Cao *et al.*[38] and Sundholm *et al.*[39] both drew attention to was that, despite the fact that structures (**3**)–(**5**) all possessed [4*n*+2]-π-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 *et al.*[38] and by Sundholm *et al.*,[39] this observation ostensibly appears to defy[38,39] the traditional [4*n*]/[4*n*+2] 'rules' about paramagnetic/diamagnetic ring-currents; however, it should be recalled and emphasised that *these rules apply only to monocycles*.[57] In this strict sense, therefore, neither our own
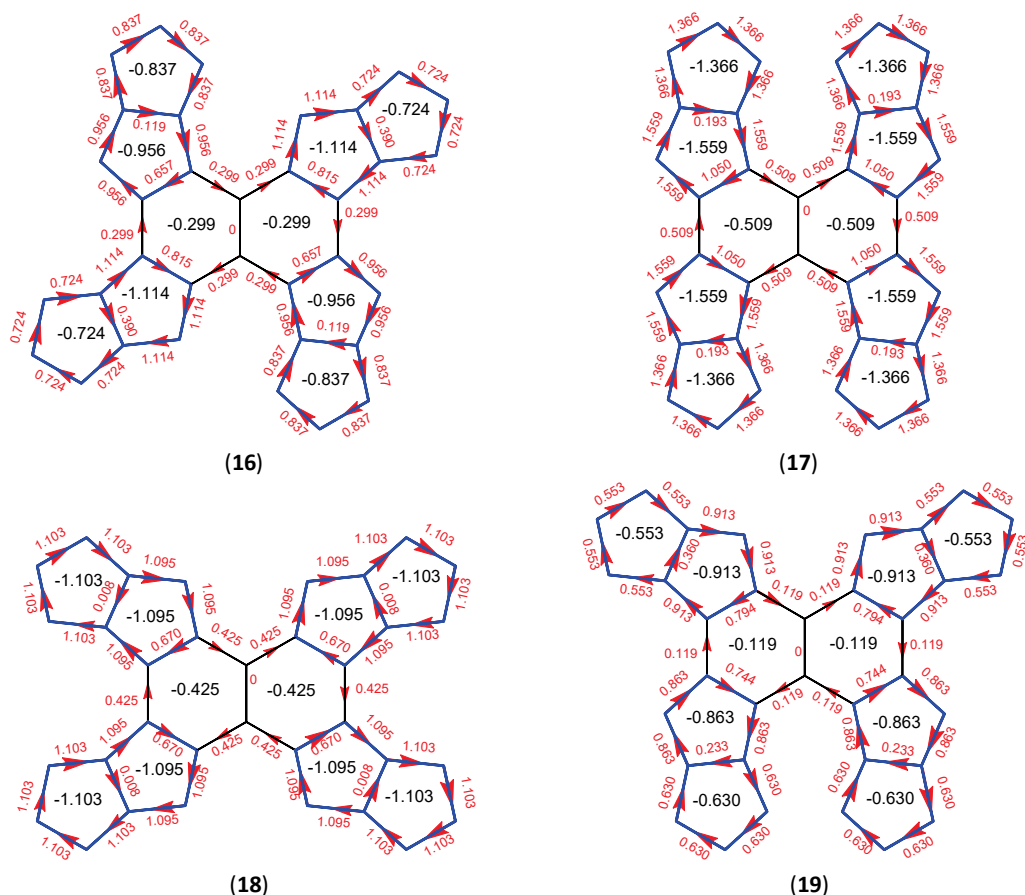
**Figure 5.** The HLPM topological current-maps for four more [4*n*+2]-π-electron structures (comprising ten rings) specially designed for the present study. Each contains four pentalene ((**2**)) moieties (outlined in blue, for emphasis) and a single naphthalene (**1**) moiety. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2.
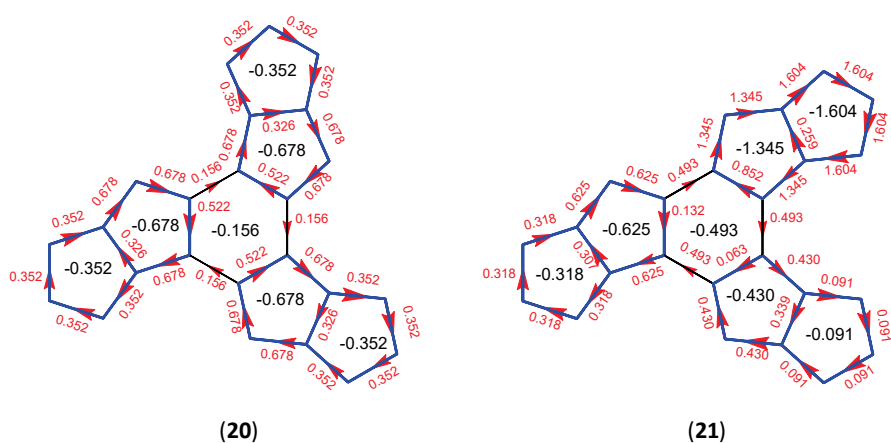


**Figure 6.** The HLPM topological current-maps for two seven-ring [4*n*]-π-electron structures specially designed for the present study. Each contains three pentalene ((**2**)) moieties (outlined in blue, for emphasis) and a single benzene moiety. For the conventions on displaying ring currents and bond currents in these maps please see the caption to Figure 2.

**Table 1.** HLPM calculations on structures (**1**)–(**5**) — Naphthalene ((**1**)), Pentalene ((**2**)) and the Structures (**3**)–(**5**) studied in Refs. [38,39]

| Structure Number | Size of Perimeter | Average Perimeter Current[(a),(b)] | Range of Perimeter Currents[(a),(b)] | Average Current on Perimeter(s) of Pentalene Moiety or Moieties[(a),(b)] | Range of Pentalene Perimeter Currents[(a),(b)] | $\left( \dfrac{\chi_\perp^{\pi-London}(\text{structure})}{\chi_\perp^{\pi-London}(\text{benzene})} \right)$ (Calculated From Equation (1))[(c)] |
|---|---|---|---|---|---|---|
| (**1**) | [4n+2], with n = 2 | +1.09 | 1.09 to 1.09 | —[(d)] | —[(d)] | +2.19 |
| (**2**) | [4n], with n = 2 | −2.14 | −2.14 to −2.14 | −2.14 | −2.14 to −2.14 | −2.83 |
| (**3**) | [4n+2], with n = 4 | −0.59 | −0.24 to −0.87 | −0.68 | −0.56 to −0.87 | −2.13 |
| (**4**) | [4n+2], with n = 4 | −1.29 | −0.58 to −1.51 | −1.42 | −0.88 to −1.51 | −4.53 |
| (**5**) | [4n+2], with n = 5 | −1.39 | −0.17 to−2.11 | −2.05 | −1.87 to −2.11 | −5.84 |

(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;[5,47] '+' indicates an overall net diamagnetic susceptibility: '−' indicates an overall net paramagnetic susceptibility.

(d) There are no pentalene moieties in (**1**).

calculations, nor those reported in Refs. [38] and [39], 'violate the Hückel rule for aromaticity'. On the other hand, on the basis of these 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.*[38] and Sundholm *et al.*[39] 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[38,39] call 'semi-local currents'. As Cao *et al.* put it:[38] 'The obtained data are indicative of the anti-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' contributions[5,20,21,47] (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'[5,47] — 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'[20,21]] contribution to magnetic susceptibility ('susceptibility ratios'[5,47]), 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) — agreed[39] 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]).

### STRUCTURES (6)–(9)

In their paper under discussion,[38] Cao *et al.* made brief allusion to a series of structures ((**6**)–(**9**), all illustrated in Figure 3) having [4n]-π-electron perimeters, two of which contain pentalene moieties. However, in three of these structures ((**7**)–(**9**)) the current flow predicted by the HLPM approach being adopted here is not uni-directional; accordingly, no average flow is quoted for these structures in Table 2. For the one structure of this quartet ((**6**)) that does display a perimeter current in a uniform sense — of magnitude about 1.0 — this sense is clockwise (paramagnetic), as anticipated by Cao *et al.*,[38] supposedly on account of the structure's [4n]-perimeter. In this respect, therefore, the [4n]-perimeter structure (**6**) does not distinguish itself from the [4n+2]-perimeter structures (**3**)–(**5**) just discussed in that, like the analogous [4n+2]-structures, it, too, supports a paramagnetic perimeter-current. Evidently, therefore, the perimeter current cannot be judged simply by inspecting the size of the carbon-atom perimeter. As indicated in the fifth column of Table 2, in the two structures of these four that contain any pentalene moieties ((**6**) and (**7**)), the flow around the perimeters of those pentalene moieties is again in the paramagnetic direction, with average magnitudes of about 1.6 and 1.1, respectively (to be compared with *ca.* 2.1 in pentalene itself: please see Figure 2 and Table 1). The susceptibility ratios[5,47] listed in the right-

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

| Structure Number | Size of Perimeter | Average Perimeter Current[a],[b] | Range of Perimeter Currents[a],[b] | Average Current on Perimeter(s) of Pentalene Moiety or Moieties[a],[b] | Range of Pentalene Perimeter Currents[a],[b] | $\left(\dfrac{\chi_\perp^{\pi-London}(\text{structure})}{\chi_\perp^{\pi-London}(\text{benzene})}\right)$ (Calculated From Equation (1))[c] |
|---|---|---|---|---|---|---|
| (**6**) | [4n], with n = 3 | −0.97 | −0.02 to −1.66 | −1.64 | −1.63 to −1.66 | −2.20 |
| (**7**) | [4n], with n = 4 | —[d] | —[d] | −1.13 | −1.04 to −1.37 | −0.75 |
| (**8**) | [4n], with n = 5 | —[d] | —[d] | —[e] | —[e] | −0.77 |
| (**9**) | [4n], with n = 5 | —[d] | —[d] | —[e] | —[e] | +0.11 |

[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.

[e] There are no pentalene moieties in (**8**) & (**9**).

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

| Structure Number | Size of Perimeter | Average Perimeter Current[a],[b] | Range of Perimeter Currents[a],[b] | Average Current on Perimeter(s) of Pentalene Moiety or Moieties[a],[b] | Range of Pentalene Perimeter Currents[a],[b] | $\left(\dfrac{\chi_\perp^{\pi-London}(\text{structure})}{\chi_\perp^{\pi-London}(\text{benzene})}\right)$ (Calculated From Equation (1))[c] |
|---|---|---|---|---|---|---|
| (**10**) | [4n+2], with n = 4 | −0.99 | −0.52 to −1.16 | −1.07 | −0.62 to −1.16 | −3.53 |
| (**11**) | [4n+2], with n = 4 | −0.56 | −0.24 to −0.91 | −0.65[d] | −0.54 to −0.91 | −2.03 |
| (**12**) | [4n+2], with n = 4 | −1.31 | −0.59 to −1.51 | −1.43 | −0.91 to −1.51 | −4.59 |
| (**13**) | [4n+2], with n = 5 | −0.98 | −0.06 to −1.60 | −1.51 | −1.43 to −1.60 | −4.15 |
| (**14**) | [4n+2], with n = 5 | −0.86 | −0.05 to −1.43 | −1.33 | −1.24 to −1.43 | −3.66 |
| (**15**) | [4n+2], with n = 5 | −1.31 | −0.12 to −2.05 | −1.95[d] | −1.79 to −2.05 | −5.51 |
| (**16**) | [4n+2], with n = 8 | −0.79 | −0.29 to −1.12 | −0.87[e] | −0.65 to −1.12 | −5.41 |
| (**17**) | [4n+2], with n =8 | −1.28 | −0.50 to −1.56 | −1.40 | −1.05 to −1.56 | −8.77 |
| (**18**) | [4n+2], with n =8 | −0.98 | −0.42 to −1.11 | −1.05 | −0.67 to −1.11 | −6.67 |
| (**19**) | [4n+2], with n =8 | −0.61 | −0.11 to −0.92 | −0.72[e] | −0.55 to −0.92 | −4.16 |

[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**)) 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.

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 para-magnetic (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.

## STRUCTURES (10)–(19)

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

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

| Structure Number | Size of Perimeter | Average Perimeter Current[a],[b] | Range of Perimeter Currents[a],[b] | Average Current on Perimeter(s) of Pentalene Moiety or Moieties[a],[b] | Range of Pentalene Perimeter Currents[a],[b] | $\left( \dfrac{\chi_{\perp}^{\pi-\text{London}}(\text{structure})}{\chi_{\perp}^{\pi-\text{London}}(\text{benzene})} \right)$ (Calculated From Equation (1))[c] |
|---|---|---|---|---|---|---|
| (20) | [4n], with n = 6 | −0.45 | −0.15 to −0.68 | −0.50[d] | −0.35 to −0.68 | −2.20 |
| (21) | [4n], with n = 6 | −0.70 | −0.09 to −1.61 | —[e] | —[e] | −3.42 |

[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 a ratio[5,47] 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 is the average of the bond currents in the bonds around the perimeters of the three pairs of symmetrically non-equivalent pentalene moieties in structure (20).

[e] No uni-directional current flow is predicted around the peripheries of the pentalene moieties in (21); hence, no average flow is indicated, in this Table.

about 0.6 to 1.3 times the magnitude of the benzene ring-current.

As with structures (3)–(6), the pentalene 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.[38] and Sundholm et al.[39]in their ab initio and experimental studies of structures (3)–(5). With regard to the susceptibility ratios,[5,47] 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[20,21,31,53] itself (displayed in Figure 2). This qualitative observation is a point that was also noted and commented upon in the context of the ab initio calculations[38,39] 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 π-electron magnetic properties, of two seven-ring structures ((20) & (21)) with [4n]-π-electron

perimeters, which have been specially 'designed' for the present study. Each contains three pentalene moieties (again, outlined in blue, for emphasis, in Figure 6). As with the [4n+2]-π-electron structures considered here, the peripheral flows 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 pentalene moieties, and even that is with a low average magnitude of about half that of the benzene (diamagnetic) value. 'Susceptibility ratios'[5,47] 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 *Ab Initio* Calculations

One of the most significant advances in this field in recent years has been the ability of the *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*[18,39] or *current-strength susceptibilities*[39]) which are the equivalent of *bond currents*[4,24,27] in the HLPM approach. This gives the opportunity directly to compare the quantitative predictions of *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

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**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

| Structure (as in Figure 1) | Bond-Plane Labelling used by Sundholm *et al.* in Figure 1 of Ref. [39] | 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] | HLPM Topological Bond-Current (Expressed Relative to the HLPM Bond-Current in Benzene)[b] |
|---|---|---|---|
| (**1**) | *b* | +1.10 | +1.09 |
| (**2**) | *b* | −1.69 | −2.14 |
| (**3**) | *d* | −1.04 | −0.86 |
| (**3**) | *f* | −0.97 | −0.57 |
| (**3**) | *g* | −0.28 | −0.24 |
| (**4**) | *d* | −1.01 | −1.47 |
| (**4**) | *f* | −0.97 | −1.51 |
| (**4**) | *g* | −0.24 | −0.59 |
| (**5**) | *b* | −0.29 | −0.17 |
| (**5**) | *e* | −1.43 | −2.05 |
| (**5**) | *g* | −1.37 | −2.11 |

[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.

particular success[4]) in the context of a large sample of bonds (66) in several (10) alternant 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) Ref. [29] for comparisons of HLPM bond-currents[30] with integrated current-strengths calculated for some *altan* structures by Monaco and Zanasi[13] (by use of the '*ipso*-centric'[7–15] *ab initio* formalism), and (b) pp. 340–342 of Ref. [4] for analogous comparisons of HLPM bond-currents[1] with integrated current-strengths computed by Kaipio *et al*.[18] (using their GIMIC approach[16–19]) on 66 bonds in 10 different (alternant) condensed, benzenoid hydrocarbons. In the latter case, a correlation coefficient of as high as 0.98 was obtained between the GIMIC *ab initio* and corresponding HLPM quantities, for a line that passed through the origin. (Please see Figures 22 and 23 on pp. 341 and 342 of Ref. [4]). The slope of the best-fit regression-line showed that HLPM bond-currents are, on average, almost the same as — to be precise, about 4% lower than — the corresponding GIMIC *ab initio* integrated current-strengths (when both are expressed as a ratio to the analogous quantity calculated, by the same method, for benzene).

We now try to perform a similar analysis for the data on HLPM bond-currents and GIMIC integrated current-strengths that are available (from Ref. [39] and Figure 2, respectively) for comparison on the structures (**1**)–(**5**), dealt with in this paper. Table 5 displays data for GIMIC current-strengths (column 3) and HLPM bond-currents (column 4) for certain bonds (11 of them) in structures (**1**)–(**5**) that are situated in only one ring. In column 3 of Table 5, the current strengths reported in Ref. [39], for bond planes labelled as in Figure 1 of that Reference, have all

been divided by 11.8 nAT$^{-1}$ before being listed in column 3 of Table 5. This figure for benzene arises from the sum of a diatropic contribution of 16.7 nAT$^{-1}$ and a paratropic contribution of −4.9 nAT$^{-1}$. (We are grateful to Professor Dage Sundholm for the kind provision of this information, in a personal communication to RBM dated March 15th, 2017). As a result of this procedure for handling the GIMIC integrated current-strengths reported in Ref. [39], and the fact that topological ring-currents and bond-currents are, in any case — by their very definition[1,2] — always[1–4] expressed as a *ratio* to the corresponding quantities calculated, by the same (HLPM) method, for benzene, it follows that both the GIMIC integrated current-strengths in column 3 of Table 5, and the HLPM topological bond-currents in column 4, are all *dimensionless* quantities.

The information presented in Table 5 is now displayed visually in two different ways:

(a) <u>Best-fit regression-lines</u>, 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 values calculated, by the same respective method, for benzene.

(b) <u>A 'Comparator' diagram</u>, shown in Figure 8. Implicitly listed along the horizontal axis are the 11 bonds under

y = 1,212x − 0,0631
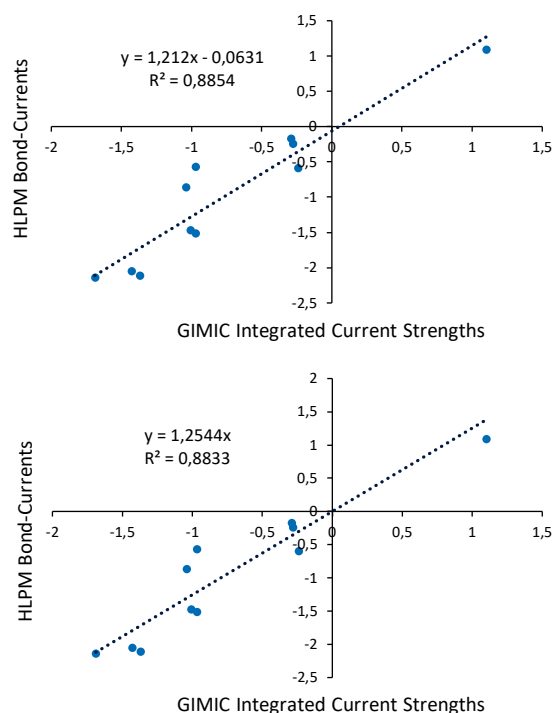R² = 0,8854



y = 1,2544x
R² = 0,8833

**Figure 7.** Least-squares regression-lines between HLPM topological bond-currents (from Figure 2) — plotted along the **vertical** axis — and (plotted along the **horizontal** axis) the integrated bond-current strengths/susceptibilities[39] 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 or the 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.



11 Unshared Bonds [See Table 5] in Structures (1)–(5) [Figure 1]

**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 structure numbers ((**1**)–(**5**), as displayed in Figure 1) with the bond-labelling letters depicted and defined in Figure 1 of p.15935 of the paper by Sundholm *et al.* (as explained in the text).[39] The order in which these labellings are listed from left to right on the diagram is thus arbitrary and hence is of no consequence: the eleven bonds considered could equally well have been listed in any desired order whatsoever and a superficially different, but entirely equivalent, comparator diagram, just as valid, would have resulted from each and every possible such permutation.

study. These are also explicitly labelled in blue at the peaks and the troughs of the two curves in Figure 8. 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 the paper by Sundholm *et al.*[39] (For example, '(**3**)*g*' means the bond-plane labelled '*g*' in Figure 1 on p. 15935 of Sundholm *et al.*[39] in the structure that we have labelled '(**3**)' in Figure 1 of the present paper.) The order in which these labellings are listed from left to right on the horizontal axis of the diagram is thus arbitrary and hence is of no consequence: the 11 bonds considered could equally well have been listed in any desired order whatsoever and an equivalent comparator diagram, just as valid though visually
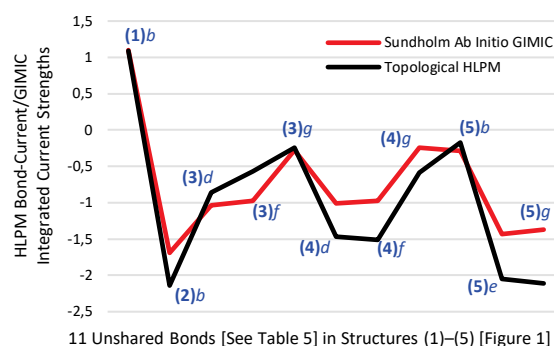
different, would have resulted from each and every possible such permutation. The red curve (*ab initio* GIMIC) and the black curve (topological HLPM) in the comparator diagram in Figure 8 do not follow each other as closely as was the case with our comparison of the (non-alternant) *altan*-structures (Figure 21 on pp. 339–340 of Ref. [4] & Figure 6 of Ref. [30]) — and certainly not nearly as closely as was observed in the case of 66 symmetrically non-equivalent bonds in 10 different (alternant) condensed, benzenoid hydrocarbons (Figure 23 on p. 342 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 *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 [4*n*+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 [4*n*]-π-electron structure (**6**) considered by Cao *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 [4*n*+2]-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 [4*n*+2] — in the *clockwise* (paramagnetic) direction, despite the [4*n*+2]-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 [4*n*]-perimeter structures ((**20**) & (**21**)) that were 'designed' for this study, the direction of flow around their perimeters is — as with (**3**)–(**19**), all with [4*n*+2]- 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 *ab initio* computations documented in Refs. [38,39].

(g) Finally, where it was possible to make *quantitative* comparisons (in Table 5 and in Figures 7 and 8) of individual HLPM bond-currents and the analogous quantities predicted by *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) *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 [4*n*+2]-annulenes being diamagnetic and [4*n*]-ones being paramagnetic — like the famous Hückel Rule itself[59] — *rigorously applies only to monocycles*. 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'[14] 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,[27–33] 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;[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*.[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.

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