Some Comments on Topological Approaches to the π-Electron Currents in Conjugated Systems

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ABSTRACT: Within the past two years, three sets of independent authors (Mandado, Ciesielski et al., and Randić) have proposed methods in which π-electron currents in conjugated systems are estimated by invoking the concept of circuits of conjugation. These methods are here compared with ostensibly similar approaches published more than 30 years ago by two of the present authors (Gomes and Mallion) and (likewise independently) by Gayoso. Patterns of bond currents and ring currents computed by these methods for the nonalternant isomer of coronene that was studied by Randić are also systematically compared with those calculated by the Hückel−London−Pople−McWeeny (HLPM) "topological" approach and with the *ab initio*, "ipso-centric" current-density maps of Balaban et al. These all agree that a substantial diamagnetic π-electron current flows around the periphery of the selected structure (which could be thought of as a "perturbed" [18]-annulene), and consideration is given to the differing trends predicted by these several methods for the π-electron currents around its central six-membered ring and in its internal bonds. It is observed that, for any method in which calculated π-electron currents respect Kirchhoff's Laws of current conservation at a junction, consideration of *bond* currents—as an alternative to the more-traditional *ring* currents—can give a different insight into the magnetic properties of conjugated systems. However, provided that charge/current conservation is guaranteed—or Kirchhoff's First Law holds for bond currents instead of the more-general current-densities—then ring currents represent a more efficient way of describing the molecular reaction to the external magnetic field: ring currents are independent quantities, while bond currents are not.

1. INTRODUCTION

Thirty-five years ago, Randić proposed[1] the approach for calculating resonance energies of conjugated systems that has become known as the method of conjugated circuits. Very recently, the same author[2] and—independently and almost simultaneously—Mandado[3] and Ciesielski et al.[4] have adapted this formalism in order to estimate the relative intensities of the π-electron currents that (classically) are considered to flow along the individual bonds of such conjugated systems when excited to do so by the presence of an external magnetic field; this magnetic field may be assumed, without a loss of generality, to be oriented in a direction at right angles to the molecular plane of the conjugated system in question (taken to be geometrically planar). This phenomenon is generally known as the "ring-current effect" (see refs 5−7 for reviews)—but Randić specifically, in his recent note,[2] has been especially careful not to invoke any explicit assumptions about "rings" *per se*.

Randić's work,[2] which follows from his earlier, preliminary thoughts on the matter,[8] has developed from Balaban et al.'s recently published[9] maps pictorially indicating the patterns of π-electron current densities in 18 isomers that include, and are all related to, coronene. Ciesielski et al.[4] have also compared predictions (on the carcinogen 3,4-benzopyrene) arising from their own method[4] with a current-density map provided by Fowler.[10] The computations that give rise to Fowler's maps[9,10]—like the calculations of Randić[2]—also make no presuppositions about the existence of rings. The so-called "ipso-centric" method that the Fowler school routinely adopts[9,10] invokes *ab initio* Gaussian computations in order to produce what Randić[2] describes as "well converged current maps with rather modest basis-sets." The origin of the contributions to the overall π-electron current density is also closely tracked and traced by this approach:[9] diamagnetic contributions come from [4n + 2] cycles and paramagnetic ones from [4n] cycles. For the purpose of comparing the predictions of Balaban et al.[9] with the results of his own calculations based on the method described in ref 2, Randić[2] singled out a particular one of the 18 isomers studied by Balaban et al.[9] (though he has since extended his investigation to include all of them[11]); this was the conjugated system that Balaban et al. labeled[9] "13" and called—on a systematic notation that they introduced and defined[9]—"[567567]". It has 180° rotational symmetry about a perpendicular axis through the center of the middle six-membered ring; if the structure is planar, its symmetry is C_{2h}. The carbon-atom skeleton of this system is shown in Figure 1. Randić[2] obtained encouraging agreement between his results and the pictorial, qualitative current-density map of Balaban et al.[9] and thereby drew some conclusions of a philosophical nature about the virtues of quantum mechanical vs graph-theoretical approaches to conjugated systems of this type—conclusions that were somewhat akin to those that had been expressed by Gayoso, in a similar context, in the 1979 *Comptes Rendus*.[12,13]

As is to be expected of a theory that is concerned with the microscopic equivalent of classical electrical networks,[6] many previous treatments[14] of the "ring-current" effect—for example, those due to London, Coulson, Pople, McWeeny (as generalized by Veillard and by Gayoso and Boucekkine), Aihara, and
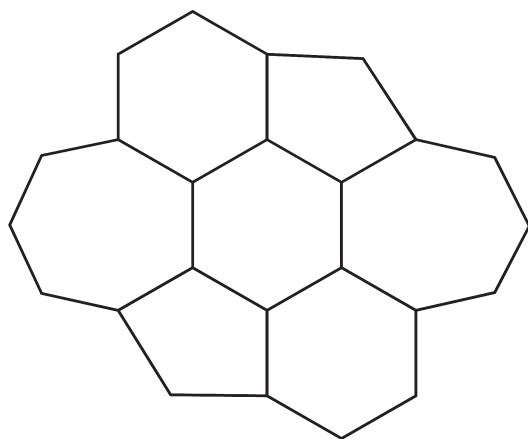
Figure 1. The carbon-atom skeleton of the conjugated system named "[567567]" by Balaban et al.[9] It is an isomer of coronene and, on the assumption that it is planar, it is of symmetry C_{2h}, having 2-fold rotational symmetry about an axis through the center of the middle six-membered ring, at right angles to the plane of the paper.

Mizoguchi[14]—have naturally invoked the concept of *circuits*,[14] *per se*, but these have not, in general, been circuits, specifically, *of conjugation*. The sudden and (to us) unexpected recent resurgence of interest[2−4,8] in approaches to magnetic properties that involve, specifically, *circuits of conjugation*—a topic that was originally studied independently some 30 years ago by two of us (Gomes and Mallion)[15−19] and by Gayoso[12]—has therefore motivated us to draw attention to three areas, developed in this paper:

(a) *Previous Similar Work.* We point out that, in the latter part of the 1970s, Gomes and Mallion,[15−19] and (independently) Gayoso,[12] applied what the former authors called "conjugation circuits"[20] when calculating the magnetic properties of conjugated systems. We point out that the approaches of Gomes and Mallion,[15−19] and that of Gayoso,[12] have many similarities to those recently proposed by Randić,[2,8,11,21] by Mandado,[3] and by Ciesielski et al.,[4] and we apply these (and other) methods to the particular conjugated system [567567] (Figure 1) that was selected for study by Randić in ref 2.

(b) *Bond Currents.* We draw attention to the fact that when what have been called "topological ring currents"[22−25]— computed for [567567] (Figure 1) by the recently defined Hückel−London−Pople−McWeeny (hereafter HLPM) approach[23,24]—are expressed (entirely equivalently) as *bond* currents, qualitative and even semiquantitative agreement is frequently seen between these "topological" bond currents, Randić's bond currents,[2] the bond currents calculated by the methods of Mandado[3] and of Ciesielski et al.,[4] and the qualitative π-electron current-density maps of Balaban et al.[9]

(c) *Kirchhoff's Law of Current Conservation.* We observe that, in the context of any method in which calculated currents strictly obey Kirchhoff's Law on conservation of current at a junction,[26−29] consideration of *bond* currents—as distinct from (entirely equivalent, but more traditional) *ring* currents—can give a different conceptual insight into the reaction of the molecule to the external magnetic field in the case of conjugated systems like [567567] (Figure 1).

2. THE "CONJUGATION CIRCUITS" METHOD OF GOMES AND MALLION[15,16] (1976 AND 1979)

Details of the Method. In order clearly to recount the method that two of us (Gomes and Mallion) proposed in the second half of the 1970s,[15,16] we here quote *verbatim* what we at the time described as our "prescription"—directly and *in extenso*—from the 1979 *Revista Portuguesa de Química*.[16] This paper was itself a distillation of the method first proposed by one of us (Gomes) in a thesis,[15] written three years earlier; some theoretical justification for the "prescription" in terms of valence-bond theory was attempted in the early 1980s.[17−19] We adopt this procedure because, although the details of the method were openly published more than 30 years ago,[16] the Gomes−Mallion formalism is evidently *not* well-known—two of the sets of very recent authors,[2,4] for example, were, it seems, not aware of it, and the third[3] cited it only in passing, as being a general reference relating merely to the concept of conjugation circuits and not, specifically, to the calculation of magnetic properties *per se*.[30] We therefore quote from ref 16, as follows:[31]

It is assumed in this prescription that the effect of the magnetic field on a molecule is felt independently by every one of the various "conjugation circuits" which are extant in each Kekulé-structure; as far as magnetic properties are concerned, an individual Kekulé-structure may be regarded as a superposition of its constituent "conjugation circuits", the effects of which are simply additive. The system of "ring currents" in the actual molecule is then obtained by finally averaging the contributions from individual Kekulé-structures over all possible Kekulé-structures which can be devised for the molecule as a whole. Accordingly, the method proposed here for estimating the relative "ring-current" intensities in a given molecule is based on the following postulates:

(i) The method of Baer et al.[32] gives reliable estimates of the relative "ring-current" intensities in regular annulenes, when an amplitude of 3.60 eV (*ca.* 348 kJ mol^{-1}) is taken[33] for the harmonic potential that occurs in their calculations.[15−19,34]

(ii) A "conjugation circuit" within a given Kekulé-structure of an arbitrary, planar, polycyclic, conjugated hydrocarbon is a circuit that consists entirely of alternating single- and double bonds.[1,15,16,35]

(iii) *If a particular ring lies entirely within a given "conjugation circuit" − even if no bond of that ring actually lies on the "conjugation circuit" itself − this ring shall be said to "participate" in that "conjugation circuit".*[36]

(iv) The "ring-current" intensity in any particular ring of such a polycyclic hydrocarbon receives a nonzero contribution from each "conjugation circuit" that occurs in all the various Kekulé-structures that can be devised for the molecule as a whole, *provided that* the ring in question *participates* in that "conjugation circuit". These contributions are strictly additive. If the ring in question *does not participate* in a specific "conjugation circuit", that particular "conjugation circuit" makes no contribution to the "ring-current" intensity in the ring under discussion.

(v) The nonzero contribution to the "ring-current" intensity in a given ring from an individual "conjugation circuit" comprising N bonds is equal to the "ring-current" intensity calculated (*via* (i), above) to be associated with a

Table 1. Data Needed for a Series of Idealized Annulenes (With Ring Sizes from [4] up to [22]) When Applying the Method Described in Refs 15 and 16 (Adapted with permission from ref 16. Copyright 1979 by The Portuguese Chemical Society.)

number of bonds (N)	ring area^a (A_N)	ring-current intensity^{b,c} (J_N)
4	0.385	−2.19
5	0.662	
6	1	1
7	1.399^d	
8	1.858	−1.27
10	2.962	+0.72
12	4.309	−0.69
14	5.902	+0.38
16	7.740	−0.38
18	9.823	+0.17
20	12.151	−0.2^{e,f}
22	14.724	+0.0^{e,g}

^{a} Expressed (to three decimal places) as a ratio to the area of a standard benzene hexagon. For idealized regular [N]-gons, all of uniform side length, it can be shown by elementary trigonometry that:

$$\left(\frac{\text{area of regular } [N]\text{-gon}}{\text{area of regular hexagon}} \right) = \left(\frac{N \cot(\pi/N)}{6 \cot(\pi/6)} \right)$$

This formula is the source of the figures listed in the middle column, above. ^{b} Expressed (to two decimal places) as a ratio to the benzene ring-current intensity calculated, by the same method,[32] for benzene. Extrapolated values (see footnotes e, f, and g to this table) are given to fewer decimal places. ^{c} Calculated by the free-electron, one-dimensional model of Baer et al.[32,34] with a periodic potential as described in rule (i) of the method of Gomes and Mallion,[15,16] presented in the text. ^{d} The value of 1.339 given in ref 16 is a misprint. ^{e} (Extrapolated) Baer et al.[32] did not report ring currents for [20]- and [22]-annulenes; because the present calculations require ring-current data for the [22]-annulene, the (virtually zero) value for it was estimated[15,16] by extrapolation. ^{f} In ref 16, this extrapolation was estimated to be −0.1, rather than the −0.2 estimated here. Such small differences are insignificant[34] as far as the ring-current estimates reported here are concerned because of the rare occurrence—indeed, nonoccurrence, in the present case—of circuits of size 20, and the relatively large number of Kekulé structures (9) and sets of conjugation circuits ($9(9 − 1) = 72$) that are extant in the conjugated system under study ([567567]—see Figure 1). ^{g} This estimated, extrapolated ring-current contribution is virtually zero.[34] Again, our final results will not be sensitive to any errors that there might be in this extrapolation because only four of the 72 conjugation circuits that arise among the relatively large number (9) of Kekulé structures involved in the present calculation involve annulenic circuits of length [22].

model [N]-annulene, except for a correction which takes into account the difference between the area of the model [N]-annulene and the actual area of the "conjugation circuit" in question; in applying this correction it is assumed that the "ring currents" are proportional to the ring areas. Any one, specified, "conjugation circuit" contributes equally in this manner to the intensities of the "ring currents" in *all* the rings that participate in it.

(vi) The relative "ring-current" intensity in a given ring may finally be obtained by averaging all such contributions (including the zero ones) over the total number of Kekulé-structures possessed by the complete molecule.

Consistent with the rule (v), the "ring-current" contribution due to the nth conjugated circuit, of N sides and area $A^{(n)}$, is taken

to be proportional to the quantity $J^{(n)}$, where

$$J^{(n)} = J_N \left(\frac{A^{(n)}}{A_N} \right) \tag{1}$$

in which J_N and A_N are, respectively, the "ring-current" intensity and the ring area associated with an idealized, regular, planar [N]-annulene [*given in a table, reproduced, and slightly modified, in Table 1*]. By rules (iv) and (vi), the relative "ring-current" intensity, J_r, in a given ring, r, is then

$$J_r = \frac{1}{K} \sum_{\substack{\text{All "conjugation circuits"} \\ \text{in which ring participates}}} J^{(n)} \tag{2}$$

where K is the total number of Kekulé structures that may be devised for the molecule as a whole; the summation runs over all "conjugation circuits", n, in which the ring r participates and all Kekulé structures are to be considered, one at a time.

Discussion of the Gomes–Mallion Formalism and the More Recent Approaches. Gomes and Mallion[16] concluded by giving a worked example of their "prescription" (to calculate the ring currents in naphthalene), and they then proceeded to apply it to a total of 15 structures and to compare the ring currents so calculated with those evaluated by what we nowadays refer to as the HLPM[23,24] "topological" approach—with, overall, encouraging results.[15,16] If the above, 30-year-old description[16] is compared with the formulations recently presented by Randić,[2] by Mandado,[3] and by Ciesielski et al.,[4] it will be seen that the older theory ostensibly has the following features:

(a) The method presented in ref 16 does make some attempt to take into account (by its rule (v) and its eq 1, above) the effect of differing *ring areas*—as, also, do the methods of Mandado[3] and Ciesielski et al.,[4] but the formalism of ref 2 does not. In the Mandado method,[3] the proper dependence of the current (as well as that of the resonance energy) on the size of the circuit is obtained by numerical fitting (to arrive at the parameter $b = 2$), while Gomes and Mallion[15,16] separately use the circuit area (as it defines the magnetic flux) and the number of alternating single and double bonds (as this defines the quantum mechanical response of the electronic system).

(b) As Gomes and Mallion stated:[16] "*...the magnetic effect is taken to be proportional to the true area of the circuit — as indeed it is, both classically and in simple quantum-mechanical calculations.*"[5−7,14,22−25] Since the external magnetic-field manifests itself in this phenomenon by means of magnetic fluxes through *rings*,[5−7,14,22−25,29] it is clear that any satisfactory account of it must recognize the influence of the *areas* of the different rings. For example, in structure 13 of ref 9 ([567567], shown in our Figure 1), five-membered, six-membered, and seven-membered rings lie side-by-side in the same molecule, and if they were isolated regular polygons of the same side length, their areas would vary[24] between about 66% (in the case of the five-membered rings) and about 140% (for the seven-membered rings) of the area of a standard benzene hexagon (see footnote a of Table 1). It should, however, be emphasized that, especially for the larger conjugation circuits, the actual areas are always smaller than the areas of the idealized, regular annulenes of the same perimeter.[16]

(c) The method proposed in refs 15 and 16 attempts to differentiate contributions not just from $[4n]$ and $[4n + 2]$ circuits *per se*, but also for $[4n]$ circuits with different values of n and for $[4n + 2]$ circuits with different values of n. It does this partly by acknowledging the effect of differing ring areas *and* partly by incorporating into its founding tenants—by means of rule (i) of ref 16—the numerical values of annulenic ring-current intensities reported by Baer et al.[32] The methods described in refs 3 and 4 take the size of the conjugation circuit into account by recognizing the effect of the different *areas* of the several conjugation circuits, but the method of ref 2 does not.

(d) By virtue of its rule (vi) and its eq 2, above, the method of Gomes and Mallion[16] effectively "normalizes" the final ring-current intensity by a division, at the very end of the arithmetical process of calculation, by the total number of Kekulé structures—as was also done by Gayoso[12] who, like Gomes and Mallion,[16] published independently on this subject in 1979; consequently, the resulting ring currents can easily be compared between one molecule and another—as, indeed, was done in refs 16−19, over a wide range of different conjugated systems. Furthermore —as is conventional and usually convenient, and also as in ref 16—ring currents so-calculated can easily be presented as *dimensionless quantities* (and hence as *pure numbers*) by the simple device of expressing them as a *ratio* to the ring-current intensity calculated, by the same method, for benzene (the ring-current intensity in which is, therefore, by definition, precisely 1). This conventional procedure[5−7] of expressing quantities as a ratio to benzene is also adopted by Gayoso[12] and by Mandado[3] but not by Randić in ref 2 nor—at least in the case of the bond currents—by Ciesielski et al.[4] (even though certain "local" and "global" quantities immediately calculated by Ciesielski et al.,[4] once they have obtained the computed bond currents, *are* themselves "normalized" by an appropriate division (in this case, $(1/2)K(K − 1)$, the number[37] of sets of distinct conjugation circuits[38]). In the approach of ref 2, however—and in the case of the bond currents calculated by the algorithm presented in ref 4— there appears to be no such averaging over all Kekulé structures or sets of conjugation circuits, and so not only are the units of measurement of the calculated π-electron currents not obvious but comparisons from one molecule to another would appear to be difficult.[39] We believe that this "averaging factor" is very important because of the physics that it conveys. In the old work of Gomes,[17,19] and in the recent work of Mandado,[3] it is not an averaging but a quantum-mechanical normalization factor; in our original work in ref 16, it was essentially an averaging factor. Accordingly, although it would be possible to compare a series of similar molecules without such "averaging" or "normalization"—for example,[11] the family of coronene and its 17 isomers that were studied by Balaban et al.[9]—it is not clear how a comparison would be made between the π-electron currents outside such a closely related series without doing so. As an illustration of this claim, we note that the method described in ref 2 would appear to give a π-electron current of size 2 for benzene, whereas, in ref 2, π-electron currents as high as 36, in these units, are reported for structure [567567] (Figure 1). Likewise, if

no "normalization" is done on the bond currents, the numbers presented by Ciesielski et al. in Figure 6 of ref 4 would seem to imply that a bond current more than 20 times the benzene ring current is extant in 3,4-benzopyrene.[4] It is appropriate at this stage to note that both Gomes and Mallion[16] (1979) and Gayoso[12] (also 1979) independently chose to divide, at the end of the calculation, by the number (K) of *Kekulé structures*—this procedure later being justified by an application of valence-bond theory.[17−19] An essentially similar procedure was invoked by Mandado,[3] while Ciesielski et al.,[4] in their approach, have (as stated) opted (like Randić[2]) *not* to normalize their bond currents at all—though, as mentioned, they do immediately divide some "local" and "global" quantities calculated from the bond currents by the number[37] $((1/2)K(K − 1))$ of sets of distinct *conjugation circuits*.[38] Finally, it should be noted that, in subsequent versions[11,21] of his basic method,[2] Randić and his collaborators *have* invoked "normalizations"—by dividing by K (for example, in ref 21), as did Gomes and Mallion, Gayoso,[11] and Mandado,[3] or by dividing by $K(K − 1)$ (as, for example, in ref 11). For more, very recent, discussions on normalizing bond currents in molecules of different sizes, see refs 11, 21, and 40.

The recent methods of Randić[2] and of Ciesielski et al.[4] do have the aesthetic virtue of being entirely graph-theoretical in nature,[41] while the Mandado approach,[3] relying, as it does, on some parametrization, may be considered to be not purely graph-theoretical. By virtue of its rule (i), above, the approach of Gomes and Mallion[16] is likewise not purely graph-theoretical, either, for it borrows from quantum mechanics,[32] and, because of its rule (v) and its eq 1, above, it invokes what, on the face of it, is a non-graph-theoretical procedure[29] in an attempt to take ring areas[41] into account (but see ref 24 for an argument that ring areas should be treated as "topological"). This is why, at the time, the method presented in ref 16 was described as a "*quasi*-topological" one. Randić's method[2] and that of Ciesielski et al.[4] do, though, stop at the graph-theoretical analysis; Gomes and Mallion[16] go further:

(i)   to use estimates of the conjugation increment that depend on its area—as also do the recent approaches of Mandado[3] and Ciesielski et al.[4]—as well as on a simple quantum-mechanical model calculation for the ring current in an annulene of appropriate size[32] (a feature that is not explicitly adopted by any of the modern authors[2−4] but the parametrization applied by Mandado[3] effectively serves the same purpose[42]) and

(ii) to average over all Kekulé structures

The prescription described in refs 15 and 16 was later given a theoretical foundation by one of us (Gomes);[17−19] this was based on a simple valence-bond formalism with a nonempirical parametrization that was valid for resonance energies and magnetic ring currents. The same author has suggested[43] that this approach may be generalized in order to provide a more realistic description of currents outside the conventional "bond lines". Mandado's approach[3] is based on first-order response theory and, at the level of the formalism, is essentially equivalent to that of Gomes.[19] To ensure that the method was theoretically well grounded, Gomes[19] avoided parametrizations by fitting and using a simple quatum-mechanical model
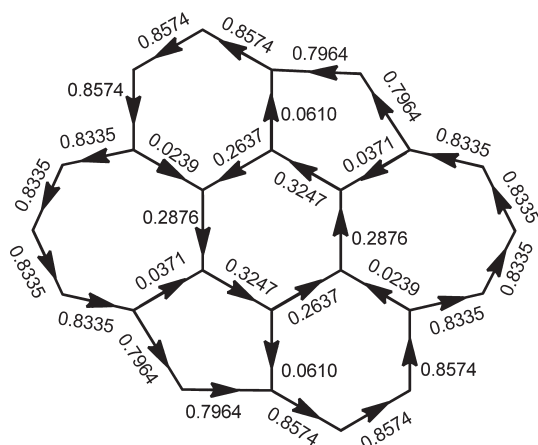
Figure 2. Ring currents in the conjugated system [567567], calculated by the method of Gomes and Mallion.[15,16]

Figure 3. Bond currents in the conjugated system [567567], calculated by the method of Gomes and Mallion.[15,16] These bond currents—which are entirely consistent with the ring currents presented in Figure 2—obey Kirchhoff's Law[26−29] of conservation of currents at a junction.

calculation of the energies and magnetically induced currents of the annulenes.

Application of the Gomes−Mallion Method[16] to [567567]. Ring currents calculated for the structure [567567] (Figure 1) by an application of the method of Gomes and Mallion[16] (in conjunction with the data given in Table 1, which is modified from refs 15 and 16) are presented in Figure 2. These diamagnetic currents are, by convention, considered to circulate in an anticlockwise sense around their respective rings (as indicated by the arrows in Figure 2). Because the annulene ring-current intensities of Baer et al.[32] are available to only two decimal places (Figure 1, right-hand column), ring-current (and, later, bond-current) intensities calculated using the Gomes−Mallion method[16] are quoted only to that accuracy, whereas such currents predicted by all the other methods dealt with in this study are quoted to three or more places of decimals. (Reporting data to apparently higher accuracy is in any case perhaps not entirely justified as we are here dealing with rather crude approaches to experimental observables.)

3. RING CURRENTS AND BOND CURRENTS

General Considerations. Randić's recent calculation[2] has presented π-electron currents not as ring currents but as bond currents. Likewise, the method of Ciesielski et al.,[4] for example, is also initially aimed at calculating bond currents (from which other quantities—both "local" and "global"—are subsequently computed). Therefore, in order conveniently to compare the π-electron currents calculated by these methods with the predictions of other approaches, we shall deal here with bond currents, as well as ring currents. In the literature, over the course of many years, consideration has been given overwhelmingly to ring currents rather than bond currents.[5−7,14,22−25] It does not, however, seem to be widely emphasized that, for any method of calculation that guarantees the applicability of Kirchhoff's Law[26−29] for conservation of currents at a junction (in a classical, macroscopic electrical network), *the two representations are entirely equivalent.*[6] By analogy with the theory of such macroscopic classical networks, the "ring current" in a conjugated molecule is the microscopic analog of the "loop current" (e.g., refs 6, 27, and 28) in a macroscopic "Kirchhoff" network,[26] while the "bond current", considered as a "line current"[43] along the bond, is the microscopic analog of the current in a wire that constitutes a single branch of the (macroscopic) Kirchhoff network[26] in question.[29] This idea has been evaluated by two of us (Gomes and Mallion) in a review.[6] However, in a molecular context, it was originally discussed—with bond currents being regarded classically as "line currents"—by Longuet-Higgins and

Salem,[44] some 50 years ago, and since then, it has been capitalized upon from time to time by several authors (e.g., refs 45−47). Adopting ring currents may be said to have the advantage of allowing a description by means of a set of independent numbers (or variables), while bond currents are related among themselves by Kirchhoff's Law.[26−29] The sum of currents coming out of a given junction is the (algebraical) sum of all those going into it; one of the currents involved in that junction is, therefore, not independent of the others. However, if—as here and in refs 2, 4, and 9—there is interest in the currents flowing in a particular bond, or around a certain region of the molecule, then bond currents may be more informative; in order to obtain the bond currents for shared bonds, ring currents in adjacent rings have (algebraically) to be added.

By no means do all theories of the ring-current effect, however, give rise to calculated bond currents that respect Kirchhoff's Law for conservation of currents at a junction; this law is violated, for example, in some quantum-mechanical approaches such as the "uncoupled Hartree−Fock" SCF one of Amos and Roberts[48,49] where, unlike in, for example, the HLPM method[23,24] (in which "Hückel"-type assumptions[50] are made about neglect of non-neighboring interactions in the Hamiltonian), matrix elements between non-neighboring centers are, in general, nonzero.[51]

Bond Currents by the Method of Gomes and Mallion[16] in the Structure [567567] (Figure 1). Accordingly, as a result of our discussion above, the ring-current data presented in Figure 2 are shown in Figure 3—entirely equivalently—as bond currents. These will be discussed later (in section 4).

"Topological" Ring Currents and (Entirely Equivalent) "Topological" Bond Currents in the Structure [567567] (Figure 1). The idea of what one of us (Mallion[23]) has called "topological" ring currents (originally discussed informally, 35 years ago[22]) was only recently well-defined, initially for benzenoid hydrocarbons,[23] and, later, its definition was formally extended[24] to encompass conjugated systems containing rings of more than one size. We believe that the HLPM method[23,24] is self-evidently the most appealing of the so-called "topological" approaches to the calculation of π-electron currents in conjugated systems because

(a) it is based on the well-established Hückel−London−Pople−McWeeny formalism,[14,23,24] and it is, thereby, legitimately founded on sound physics and quantum mechanics, and yet

Figure 4. "Topological" ring currents in the conjugated system [567567], calculated by the HLPM method.[23,24]

Figure 5. "Topological" bond currents in the conjugated system [567567], calculated by the HLPM method.[23,24] These currents—which are entirely consistent with the ring currents presented in Figure 4—obey Kirchhoff's Law[26−29] of conservation of currents at a junction.

(b) it has all the advantages of a graph-theoretical approach because, once the carbon—carbon connectivity of the conjugated system under study has been written down, and values are agreed for its ring areas, then ring-current and bond-current intensities calculated by the HLPM method[23,24] *do not depend on any empirical* (or, indeed, on any other) *parameters*, provided (as their definition requires[23,24]) that such ring- and bond-current intensities are expressed as a ratio to the corresponding quantity, calculated by the same method, for benzene.

The isomer of coronene that is under study, the structure [567567] illustrated in Figure 1, is a system of the appropriate type containing, as it does, five-, six-, and seven-membered rings. In Figure 4, therefore, we present topological ring currents ("loop currents"[27,28] on the macroscopic classical-network analogy described earlier) for [567567]. As is conventional (and as was done in Figure 2), the (diamagnetic) ring currents are presented as circulating anticlockwise around the rings that are their respective domains. Their relative intensities have been calculated by the HLPM method on the detailed assumptions carefully specified in refs 23 and 24; the same assumptions were also recently adopted for calculations on a family of benzo-annelated perylenes.[25] In accordance with the required definition of what constitutes "topological" ring currents,[23,24] ring areas were calculated according to the formula given in footnote *a* of Table 1.

Figure 6. "Normalized" π-electron bond currents in the structure [567567], calculated using the method of Randić.[2] These currents obey Kirchhoff's Law[26−29] of conservation of currents at a junction.

Figure 7. "Normalized" π-electron ring currents in the structure [567567], deduced from the normalized bond currents shown in Figure 6, calculated using the method of Randić.[2] These currents, which are conventionally defined in the anticlockwise direction around each ring, obey Kirchhoff's Law[26−29] of conservation of currents at a junction.

In Figure 5, we present these same "topological" ring-current data but, this time, broken down into individual bond currents, as previously described.

These "topological" bond currents will be discussed later (in section 4).

Randić's Bond Currents and Ring Currents in Structure [567567] (Figure 1). In Figure 6, we display Randić's bond currents[2] for later discussion and comparison with the bond currents already encountered and with those calculated by the methods of Mandado[3] and of Ciesielski et al.,[4] to be reported later in the paper. In order to facilitate such comparisons, we have taken the liberty of "normalizing" the "raw" (integral) bond currents depicted by Randić in Figure 5 of ref 2 by dividing them by $K(K − 1)$ (= 72, in this case, as, here, $K = 9$)—as Randić and co-workers[11] themselves did in later work—and rounding the results to four decimal places.

Figure 7 shows Randić's data equivalently presented as ring currents.

Bond Currents and Ring Currents in Structure [567567] (Figure 1) by the Method of Mandado[3]. In the initially submitted version of this paper, we did not report a calculation using Mandado's method[3] and an anonymous reviewer very kindly supplied us with one for the structure [567567]. In order to have an independent check on the data that the reviewer had provided, we asked Professor P. W. Fowler and his colleagues

Figure 8. π-electron bond currents in the structure [567567], calculated using the method of Mandado[3] (reproduced here by the kind permission of Professor P. W. Fowler[52]). These currents obey Kirchhoff's Law[26−29] of conservation of currents at a junction.

Figure 9. π-electron ring currents in the structure [567567], deduced from the bond currents shown in Figure 8, calculated using the method of Mandado[3] (reproduced here by the kind permission of Professor P. W. Fowler[52]). These currents, which are conventionally defined in the anticlockwise direction around each ring, obey Kirchhoff's Law[26−29] of conservation of currents at a junction.

W. Myrvold, W. Bird, and S. Cotton at the Universities of Sheffield (England) and Victoria (Alberta) to perform a calculation on [567567] using the Mandado[3] method. The results that they obtained are somewhat different from the bond currents provided by the reviewer. What we present in Figure 8 are the results of Professor Fowler et al. (used with his kind permission[52])— effected by Mandado's model[3] (with Mandado's parameter "a" = 1, as is appropriate for this structure—see ref 3) rather than the reviewer's data. We adopt this policy because we are sure of the provenance of Professor Fowler's calculations (which, furthermore, we know have been effected automatically, by application of a computer algorithm, rather than by hand). It should be pointed out that Mandado's parametrization, designed for benzenoid structures,[3] might not be entirely appropriate for structures (like [567567]—Figure 1) that contain rings of other sizes. (We may observe in passing here that, although he does not stress it in ref 3, we feel that one of the strengths of Mandado's approach[3] is that magnetic susceptibilities and currents are produced in parallel, without the need for independent parametrizations.) The calculations presented in Figures 8 and 9 were effected adopting ring areas calculated according to the formula quoted in footnote a of Table 1. Bond currents (relative to benzene) are presented in Figure 8, and the ring currents that have been
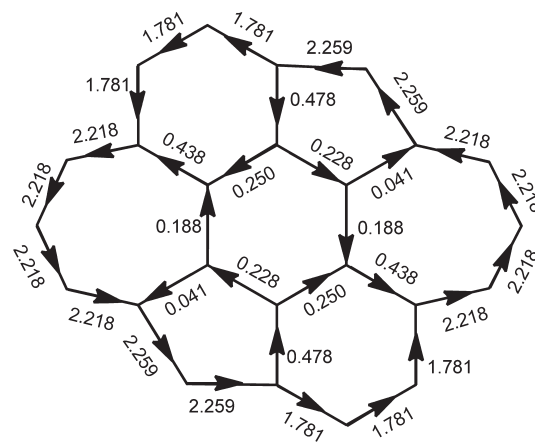
Figure 10. Bond currents (additionally—and against the prescription proposed in ref 4—divided by $K(K - 1)$) in the conjugated system [567567], computed from the "raw" (unnormalized) bond currents calculated using the method of Ciesielski et al.[4] These currents—which are entirely consistent with the ring currents presented in Figure 11— obey Kirchhoff's Law[26−29] of conservation of currents at a junction.
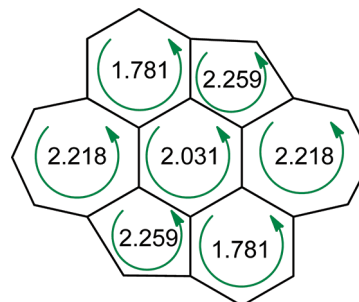
Figure 11. "Normalized" π-electron ring currents in [567567], using the method of Ciesielski et al.[4] These ring currents, which are conventionally defined in the anticlockwise direction around each ring, have been deduced from the calculated bond currents depicted in Figure 10; they obey Kirchhoff's Law[26−29] of conservation of currents at a junction (within the round-off error displayed).

deduced from them are depicted in Figure 9. The numerical values quoted in these Figures differ only slightly—and, for the purposes of our discussion in this paper, not significantly—from the computations offered by the anonymous reviewer. The data in Figures 8 and 9 will be discussed later (in section 4).

Bond Currents and Ring Currents in Structure [567567] (Figure 1) Using the Method of Ciesielski et al.[4] We have also applied the third of the recent methods, that of Ciesielski et al.,[4] to the structure [567567]. Bond currents are presented in Figure 10, and the ring currents that have been deduced from them are depicted in Figure 11. It should be noted that these bond currents have here been "normalized" by division by $K(K - 1)$ (= 72, in this case, as $K = 9$) and—as a reviewer has pointed out —should not, therefore, strictly be called "Ciesielski et al." currents at all; however, we take this small liberty for reasons of comparability between different molecules and different methods of calculation, as explained elsewhere in this paper. We emphasize that each bond current was separately and independently calculated by application of the formalism of Ciesielski et al.,[4] thereby enabling many independent checks to be made on the computations and verifying, in actual practice, that Kirchhoff's
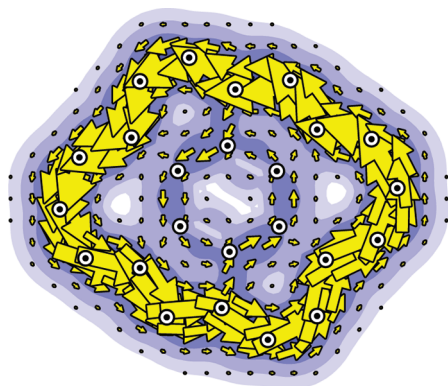
Figure 12. Pseudo-π current-density map for [567567], calculated by use of the maximum-symmetry B3LYP/6-31G** geometry,[9] reported in ref 9 (and reproduced here by the kind permission of Professor P. W. Fowler and the Slovenian Chemical Society). Maps of this kind show the current densities $1a_0$ above the molecular plane after they have been projected *into* the molecular plane; as such, the projected current densities do not necessarily respect Kirchhoff's Law[26−29] of conservation of currents at a junction[54] because they are just one component of the real current. Therefore, although they are visually appealing, these current-density maps are not directly comparable with the "bond currents"—which are regarded strictly as classical "line-currents"[26−29,44−47]—that are being considered elsewhere in this paper.

First Law[26−29] does indeed hold within the context of Ciesielski et al.'s method.[4,53] The required ring areas were again calculated by means of the expression in footnote *a* of Table 1. The data in Figures 10 and 11 will be discussed later (in section 4).

4. COMPARISON OF Π-ELECTRON CURRENTS FROM THE FIVE METHODS STUDIED WITH THE CURRENT DENSITY MAP OF BALABAN ET AL.[9]

Overall Approach. In this section, we compare the calculated current densities in the *ab initio* ("ipso-centric"[9]) pictorial current-density map for the structure [567567] (Figure 1), due to Balaban et al.[9] (Figure 12), with the following five sets of quantities calculated for the same structure:

(a) Ring currents (Figure 2), and bond currents deduced from them (Figure 3), computed using the 1976/1979 "quasi-topological" method of Gomes and Mallion,[15,16] which invokes the concept of "conjugation circuits"[1,15−19]

(b) "Topological" ring currents (Figure 4) evaluated by the HLPM approach[23,24] and the bond currents that have been deduced from them (Figure 5)

(c) Bond currents (Figure 6) and the ring currents (Figure 7) that are consistent with them, calculated using Randić's recent, purely graph-theoretical, method[2]—which, like the methods of Gomes and Mallion,[16] Gayoso,[12] Mandado,[3] and Ciesielski et al.,[4] is also based on the idea of "conjugated circuits"[1,8,11,15−19,21]

(d) Bond currents calculated (Figure 8) using the method of Mandado[3] and ring currents deduced from them (Figure 9), on the assumption of Kirchhoff's Laws of current conservation at a junction[26−29]

(e) Bond currents calculated (Figure 10) using the method of Ciesielski et al.[4] and ring currents deduced from them (Figure 11), on the assumption of Kirchhoff's Laws. The method of Ciesielski et al.[4] is also based on conjugation
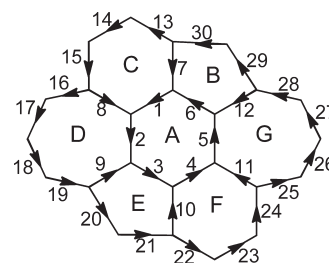
Figure 13. Labeling of rings (A–G), labeling of bonds (1−30), and (arbitrary) definition of bond directions (indicated by the direction of the arrow on each bond) in the structure [567567].

circuits, and may likewise be considered to be graph-theoretical even though (unlike in the method of Randić,[2] but as in the HLPM "topological" approach and that of Mandado[3]) it does take into account the effect of ring areas.[41,42]

Qualitatively, the current-density map of Balaban et al.[9] (Figure 12) indicates a strong diamagnetic current around the periphery, with minimal activity, so far as currents are concerned, in the region of the central six-membered ring, A (which is completely surrounded by the six other rings—two five-membered (B and E), two six-membered (C and F), and two seven-membered (D and G)—see Figure 13). Very weak currents are also predicted in what Balaban et al.[9] refer to as the "spokes" bonds, connecting the central six-membered ring to the periphery of the structure (these are the bonds labeled 7, 8, 9, 10, 11, and 12 in Figure 13). It should be emphasized that the current-density maps under discussion[9] do not directly allow a quantitative estimate of the relative size of the bond currents in the molecule. In fact, Balaban et al. calculate[9] a current-density field—as described in the caption to Figure 12—and do not purport to be evaluating a bond current. The latter could in principle be effected by, for example, use of the integration technique of Atkins and Gomes[55]—though, to do this, knowledge would be needed of the current field (vector) over the surface that was used for the integration.

The current-density pattern of Figure 12 is well reproduced by the π-electron bond currents (Figure 6) that Randić[2] has calculated for this structure. It is also faithfully reflected in the patterns of the HLPM "topological" bond currents displayed in Figure 5. Comparison of Figures 5, 6, and 12 shows that all three of these models predict that, within the central six-membered ring (A) itself, although the overall circulation around this ring is weak, a (relatively) stronger (diamagnetic) current is apparent in the bonds to the "northwest" (bond 1 of Figure 13) and to the "southeast" (bond 4 of Figure 13) in that ring (when the structure is depicted in the orientation shown in Figures 1−13) than in the other four bonds (2, 3, 5, and 6) in the central six-membered ring (ring A of Figure 13). The methods of Ciesielski et al.[4] (Figure 10) and of Gomes and Mallion[4] (Figure 3) likewise concur—though much less markedly—about the "northwest" and "southeast" bonds in the central ring, while, by contrast, the Mandado[3] approach suggests that the "northeast" (bond 6 in Figure 13) and the "southwest" bonds (bond 3) have the largest bond currents in the central ring (A).

Overall, the Gomes−Mallion approach[15,16] and that of Mandado[3]—contradicting the other methods[2,4,23,24]—predict a ring-current intensity in the central ring, A (Figure 13), that is considerably stronger than that in the rings around the perimeter.

Because of this, only partial cancellation takes place in the bonds that are shared by the central six-membered ring (A) and the outer rings (B−G). As a result, reasonably substantial diamagnetic π-electron currents are still predicted, by these methods, to be extant in all of the bonds of that central six-membered ring (Figures 3 and 8). In the case of the Gomes−Mallion method,[15,16] this observation is undoubtedly explained almost entirely by the fact that this latter method incorporates into its foundations the quantum-mechanically calculated annulene ring currents of Baer et al.[32] Inevitably, therefore, this method, as it stands at the moment, does intrinsically have built into it the phenomenon that contributions from both [4n] and [4n + 2] circuits *decrease rapidly* as n becomes larger—to the extent that, by the time circuits of size [20] and [22] are encountered, the ring-current contribution, according to the calculations of Baer et al.,[32] is virtually zero (see Table 1). The *ring areas*, of course, become larger as the conjugation circuits increase in length—it is the quantum-mechanically estimated *ring current* in the [4n] or [4n + 2] conjugation circuit that, according to Baer et al.,[32] shrinks rapidly as n becomes larger (see Table 1, right-hand column). Furthermore, the conjugation circuits with the longer lengths (lengths of [16], [18], [20], and [22]) that arise in the course of a calculation on [567567] invariably "contain" (that is, enclose within them —in the sense of rule (iii) of the Gomes−Mallion method described in section 2—and thus make contributions to the ring currents in) some or all of the peripheral rings (rings B−G in Figure 13). Inevitably, therefore, those rings eventually accumulate smaller calculated ring-current intensities than they would if the larger circuits all contributed equally (as they do in Randić's method[2]) or if the contributions from conjugation circuits increased solely in proportion to their area (as they do, for example, in the method of Ciesielski et al.[4]). Although the central ring (A) is also "contained within" (see rule (iii) of section 2) these larger conjugation circuits—and thus, in the Gomes−Mallion approach, this ring A likewise receives diminished contributions from these larger circuits—actually carrying out such a calculation by hand (as we have)[56] shows that by far the greatest effect on the ring current in the central ring, A, arises from many conjugation circuits *that include that ring as a circuit of length* [6]. In fact, eight of the 72 sets of conjugation circuits (including the disjoint ones[2,4]) for [567567] involve a contribution to that central ring from a [6]-membered circuit; each of these (as can be seen from Table 1) makes a relatively large contribution (of 1, in these units) to the calculated ring current in ring A. Hence, this rapid diminution of annulenic ring current for the conjugation circuits of larger size would *exaggerate* the ring current associated with the central ring (A) and *underestimate* the ring currents for the peripheral rings (B−G). This would give rise to the prediction of a substantially greater current circulation in the six bonds of ring A, as a result of only partial cancellation of the (smaller) ring currents in adjacent rings. This finding could thus possibly be merely an artifact of the Gomes−Mallion method, as originally formulated.[15,16] To investigate this point, we have carried out some simple "topological" calculations, using the HLPM method,[23,24] on the ring currents in the family of [4n+2]-annulenes and have found—to our surprise— that, far from decreasing with annulene size, they actually increased quite dramatically. This matter will be the subject of future study. Meanwhile, it should be observed in passing that the Mandado approach also predicts a relatively large ring-current intensity in the central ring. We have not investigated why this should be so, but we speculate that it might be connected (a) with the fact that the Mandado method[3] does not take into account contributions from disjoint conjugation circuits and (b) by virtue of its initially assigning
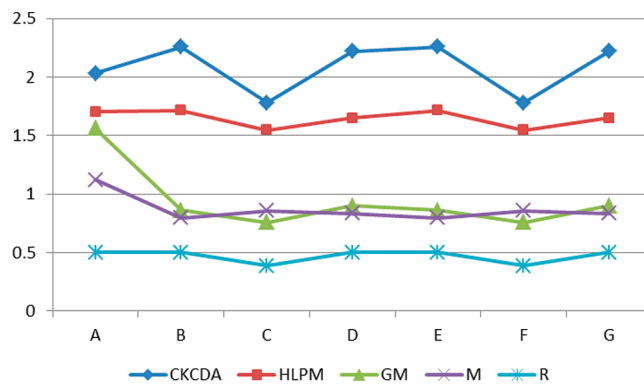
Figure 14. Comparator diagram for ring currents. Key to methods of calculation: CKCDA = Ciesielski et al.[4] (but "normalized", contrary to the prescription of Ciesielski et al.,[4] by division by $(1/2)(K(K − 1))$); HLPM = Hückel−London−Pople−McWeeny ("topological");[23,24] GM = Gomes−Mallion;[16] M = Mandado;[3] R = Randić[2] (but "normalized" by division[55] by $K(K − 1)$). The horizontal axis refers to the seven rings, A−G, labeled as in Figure 13. The vertical axis gives ring-current intensities expressed, effectively, as a ratio to the benzene ring current, calculated by the corresponding method; the ring currents may thus be regarded as dimensionless quantities.

a weighting to conjugation-circuit contributions that varies as the reciprocal of the ring area (rather than being proportional to conjugation-circuit ring areas, as in the formalisms of Gomes and Mallion[15,16] and of Ciesielski et al.[4]); the consequence might be that the Mandado method[3] likewise contrives to minimize the importance of the contributions from the larger conjugation circuits.[42] Mandado[3] takes $H_{LL} = H_0/(af_L)^b$. For b = 2, the energy becomes independent of the area (f), and the current becomes proportional to $1/f$. In the Gomes−Mallion method, the dependence is different, but the current also decreases when the area increases.

Analysis of "Comparator" Diagrams for Ring Currents and Bond Currents Calculated by the Five Methods Studied. In this section, we use "comparator diagrams" in order visually to compare trends in ring currents and in bond currents using the five methods that we have studied. We first define (by means of Figure 13) the ring labelings, the bond labelings, and the bond directions adopted in the comparator diagrams themselves (Figures 14 and 15). The seven rings of the structure [567567] are labeled A−G, and the 30 bonds are labeled 1−30 (as in Figure 13). Diamagnetic (that is, on our conventions, *positive*) ring currents are defined as running anticlockwise around the ring in question; bonds are defined in the directions of the arrows depicted in Figure 13. These directions are arbitrary. If the net current calculated for a given bond, by any of the five methods applied, is in the direction of the arrow shown in Figure 13, it is counted positive; if against the direction of the arrow, it is negative. With these conventions, we present the comparator diagrams for the ring currents (Figure 14) and the bond currents (Figure 15) calculated for the structure [567567] using the five methods[2−4,16,23,24] that we have studied. The reader is directed to the captions of Figures 14 and 15 for explanations about the axes, scales, and units that feature in these comparator diagrams, and for the key to the five methods of calculation that have been considered.

The feature discussed in the last paragraph of the previous subsection is immediately and strikingly illustrated by the green curve in the ring-current comparator diagram (Figure 12), which
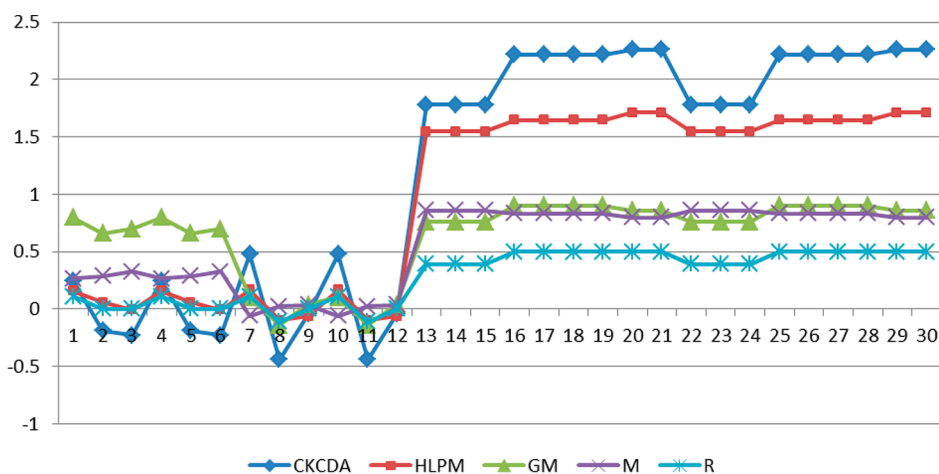
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dx.doi.org/10.1021/ct2002539 |*J. Chem. Theory Comput.* 2011, 7, 3661–3674

Figure 15. Comparator diagram for bond currents. Key to methods of calculation: CKCDA = Ciesielski et al.[4] (but "normalized", contrary to the prescription of Ciesielski et al.,[4] by division by $(1/2)(K(K-1))$; HLPM = Hückel−London−Pople−McWeeny ("topological");[23,24] GM = Gomes−Mallion;[16] M = Mandado;[3] R = Randić[2] (but "normalized" by division[55] by $K(K-1)$).The horizontal axis refers to the 30 bonds, labeled 1−30 as in Figure 13, with their directions defined as in that figure. The vertical axis gives bond-current intensities, as dimensionless quantities, effectively expressed as a ratio to the bond-current intensity calculated, by the corresponding method, for benzene.

concerns the Gomes−Mallion (GM) method, and by the purple curve representing the Mandado[3] (M) method. The central ring, A, bears a ring-current intensity materially greater than those in the peripheral rings, B−G, whose ring currents are themselves noticeably smaller in size than the corresponding ones calculated either by the HLPM "topological" method[23,24] (the brown curve) or by the method of Ciesielski et al.[4] (CKCDA, the dark-blue curve). The (light-blue) curve from the Randić[2] method is more attenuated and less variable, but it generally follows the pattern of the HLPM and CKCDA curves. However, with the exception of that central ring, A, the relative pattern of variation of (smaller) ring currents in the peripheral rings (B−G) that is observed along the green (GM) curve in Figure 14 does follow quite closely those of at least three of the other methods studied (HLPM, R, and CKCDA).

In turning to a consideration of the comparator diagram for bond currents (Figure 15), we recall (Figure 13) that the bonds labeled 1−6 are those comprising the central six-membered ring, A; those labeled 7−12 are what Balaban et al.[9] call the "spoke" bonds, connecting the perimeter to the entirely internal, central ring, A (Figure 13); and the bonds labeled 13−30 are those that lie around the periphery of the structure [567567]. When assessing the bond currents in the bonds (1−6) situated in the central ring (A) and those in the so-called[9] "spoke" bonds (7−12), it should be borne in mind that these bond currents (a) are small and (b) are the result of "cancellation" (by subtraction) of two much larger, but approximately equal, quantities—the ring currents in the two adjacent rings that flank any of these bonds that are labeled 1−12. Sometimes this process of cancellation results in a small positive current in the (arbitrary) direction in which the bond in question has been defined in Figure 13; sometimes it results in a small negative one—and, furthermore, this is the situation for *each* of these 12 bonds *and* for *each* of the five methods (HLPM, GM, R, M, and CKDA) that we have applied. Any correspondences among the five methods in these regions (i.e., those involving bonds 1−12) of the bond-current comparator diagram (Figure 15) are, therefore, difficult to discern visually—though it can be seen that the correspondence in variation between curve R (light blue) and curve CKCDA (dark blue)

is in fact close, even in this region. However, we arbitrarily chose to define all of the (unshared) peripheral bonds, 13−30 (Figure 13), in the *same* direction as the diamagnetic (*i. e.*, anticlockwise) ring currents in the rings of which these bonds form a part. Examination of *this* area of the bond-currents comparator diagram (Figure 15)—that for bonds 13−30— reveals an entirely consistent pattern of trends among the five methods. (Recall that, in comparator diagrams, the *pattern* of variation is what counts.) Once again, for the reasons discussed in the last paragraph of the previous subsection, the GM method and method M (as well as method R) predict much lower bond-current intensities in these peripheral rings than do the HLPM and CKCDA approaches.

5. UNITS IN BOND-CURRENT AND RING-CURRENT CALCULATIONS: "NORMALIZATION"

Before concluding, we draw attention to the *units* to be adopted when various types of π-electron currents are presented. The bond currents evident in Figures 3, 5, 6, 8, and 10 and the ring currents depicted in Figures 2, 4, 7, 9, and 11 are, effectively, all expressed as a *ratio* to the ring-current/bond-current intensity calculated, by the corresponding method, for benzene; accordingly, currents calculated in this way are, as already noted, *dimensionless* quantities, with the benzene value being identically 1, by definition. This conventional approach was followed by Gomes and Mallion,[14] Gayoso,[12] and Mandado[3] and was followed in the definition of "topological ring current" in the context of the HLPM formalism.[22−25] This, however, does not appear to be the case with Randić's π-electron bond currents presented in Figure 5 of ref 2. These are not expressed as a ratio to the corresponding value for benzene, and neither are they (unlike in the Gomes−Mallion "conjugation-circuit" method[16] and in that of Gayoso[11]) "normalized" by averaging the contributions to each π-electron bond-current over all Kekulé structures (K) that can be devised for the conjugated system as a whole. Because of this, it is not clear in what *units* such π-electron bond currents are actually expressed. The same criticism could strictly be leveled at the "raw" bond currents calculated by

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dx.doi.org/10.1021/ct2002539 |*J. Chem. Theory Comput.* 2011, 7, 3661–3674

the method of Ciesielski et al.[4] and displayed, for example, in Figure 6 of ref 4. In their calculation, although they do at a later stage "normalize" by dividing by $(1/2)(K(K - 1))$, this (as a reviewer pointed out to us) is *not* in fact done at the stage of the calculation when the actual *bond currents* themselves are calculated. Consequently, if the method of Ciesielski et al. were taken at its face value, as presented in ref 4., the initial, "raw" bond currents (like those arising from Randić's initial formulation[2]) would likewise be difficult to interpret. Another consequence of this lack of division by the number of Kekulé structures (or, if preferred, the number of sets of conjugation circuits) is that it would appear, as a general rule, that the greater the number of Kekulé structures a system has, the larger its calculated π-electron bond currents are likely to be—by a process of sheer accumulation—when estimated by the methods described in refs 2 and 4. Because of this, it is not obvious how diverse types of conjugated systems (such as, for example, the range of structures treated in ref 16) can be compared, one with the other, on this model. For example, in [567567], a π-electron bond current of "36" is encountered (Figure 6). Now, as already noted, if the approach of ref 2 were applied to benzene, the π-electron current would be calculated to be "2", on these units. It would clearly be unreasonable to deduce from this—and, indeed, we emphasize that Randić[2] does not claim to do so—that there is, in some of the peripheral bonds in [567567], a π-electron current that is *18 times* the size of the π-electron current in benzene (which, of the face of it, seems unlikely). An analogous comment could be made about the "raw" bond currents in 3,4-benzopyrene reported in Figure 6 of ref 4. Nevertheless, these examples do illustrate the difficulties, in the context of the method described in refs 2 and 4, that can arise when comparisons between different types of conjugated structures are sought.

In any case, these problems may easily be averted, in the case of the methods of refs 2 and 4, if bond currents are simply "normalized", by a suitable division. This is why we have taken the liberty of normalizing our bond currents and ring currents calculated by the methods of Randić[2] (in Figures 6 and 7) and of Ciesielski et al.[4] (in Figures 10 and 11). In fairness, it ought to be noted that, in subsequent versions of his method,[11,21,40] Randić (and his co-workers) *have* performed a "normalization" process, either by dividing[21] by the number (K) of Kekulé structures (as Gomes and Mallion,[15,16] Gayoso,[12] and Mandado[3] do) or by dividing,[11] not by K, but by $K(K-1)$, the total number[37] of sets of conjugation circuits—or, if preferred $(1/2)(K(K - 1))$, the number of *distinct* sets of conjugation-circuits.[40]

6. CONCLUSIONS

(a)   We have personally repeated (and successfully reproduced) the calculations on [567567] presented by Randić[2,58] and the calculations on 3,4-benzopyrene reported by Ciesielski et al.[4] and can thereby verify that these methods do have considerable elegance and aesthetic appeal. As Randić points out,[2] and as we have noted previously, his approach has the philosophical virtue of being entirely graph-theoretical in nature. The method of Ciesielski et al.[4] is also purely graph-theoretical —if it is accepted (as, indeed, we do propose[24]) that ring areas can legitimately be considered as part of a graph-theoretical "prescription".[22−24,41,42] We suggest, however, that, for maximum efficacy in practical applications, the conjugated-circuit approach outlined in ref 2—and, to a lesser extent, that presented in ref 4—would benefit from

(i)   Averaging the final computed π-electron currents by dividing at the end by the total number of Kekulé structures (as was done in refs 16, 12, and 21) or by the number of conjugation circuits (as was done in ref 11). This would aid comparability between diverse molecules (such as, for example, [567567]—Figure 1—and benzene), and it would go some way toward solving the vexed problem of *units*, discussed earlier in the context of Randić's method[2] and that of Ciesielski et al.[4] Randić has dealt now with this point.[11,21,40]

(ii)   Weighting the contributions of individual conjugation circuits according to the actual (or, failing this, the idealized[22−25,41]) areas of the rings that lie within them

(iii)   Taking account of the fact that, quite apart from the area factor,[41,42] just referred to in (ii), above, not all conjugated circuits should be considered to contribute to bond currents to an equal extent. Randić's approach does allow distinction between the diamagnetic contributions from $[4n + 2]$ circuits and the paramagnetic ones arising from $[4n]$ circuits; however, there would appear to be no provision in the method of ref 2 for specifying that, for example, a $[4n + 2]$ circuit with, say, $n = 3$, should contribute differently from one with, say, $n = 4$. Likewise, the (paramagnetic) contribution appropriate for a $[4n]$ circuit with (say) $n = 2$ is different from that properly due to a $[4n]$ circuit with (say) $n = 4$—but there is no mechanism for taking this into account in the method described in ref 2. This problem is partially considered in ref 4 by a consideration of ring areas,[41] but in the recent methods,[2−4] no further account is taken of the variation in annulenic ring currents[32] for annulenes of different sizes[32]— though, in ref 3 this effect does seem successfully to be mimicked by an appropriate parametrization.

(b)   If the provisions suggested in (a), above, were to be adjoined to the methods of Randić[2] and of Ciesielski et al.,[4] the end result would be something very similar to the old prescription of Gomes and Mallion.[13,14] Furthermore, the method of ref 2 is equivalent to that proposed in ref 16 if we

(i)   assume that the contributions from all conjugation circuits are equal and

(ii)   omit the last stage of averaging (or normalizing) over all Kekulé structures.

The elegance of purely topological methods[2,4] and the simplicity of their calculation should thus be evaluated against the advantages of bringing in physical considerations through

(i)   the dependence of a magnetic effect on the circuit area

(ii)   the dependence—much discussed in the classical literature[59]—of the *size* (and not just the *sign*) of the annulenic ring current on the number of carbon atoms forming the ring.

The method of Ciesielski et al.[4] does the former (i) but not the latter (ii).

(c)   Randić[2] pointed out that his π-electron (bond) currents for [567567] (Figure 1) compare favorably with the qualitative current-density maps presented by Balaban et al.[9] The same can be said for the HLPM "topological" bond currents that we have illustrated in Figure 5. The calculations (presented in Figure 3) that were obtained *via* Gomes and Mallion's 1979 method[16] based on "conjugation circuits" do,

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dx.doi.org/10.1021/ct2002539 |*J. Chem. Theory Comput.* 2011, 7, 3661–3674

however, only partially support this view, though they do concur with the other approaches—HLPM bond currents[23,24] (Figure 5), Randić bond currents[2] (Figure 6), Mandado's bond currents[3] (Figure 8), Ciesielski et al.'s bond currents[4] (Figure 10) and the current-density map of Balaban et al.[9] (Figure 12)—that, in the case of the structure [567567] (Figure 1) which could, perhaps, be thought of as a "perturbed [18]-annulene"),[60,22] the strongest current does flow around its perimeter (see also Figure 15).

(d) Regarding the methods of Randić,[2] Mandado,[3] Ciesielski et al.,[4] and Gomes and Mallion,[16] we note the following similarities, differences, and comparisons:

(i) All four methods rely on knowledge of the conjugation circuits[1,12,15,16,20,35] in the structure under study.

(ii) The approaches of Gomes and Mallion,[16] Randić,[2] and Ciesielski et al.[4] explicitly consider *disjoint* conjugation circuits (as illustrated, for example in Figure 2 of ref 2 and Figure 4 of ref 4), and the method of Mandado[3] excludes[35] them (see, for example, ref 3 and the Supporting Information of that reference).

(iii) The methods of Mandado,[3] Ciesielski et al.,[4] and Gomes and Mallion[16] rely on knowledge of the various *ring areas* of the structure—but Randić's method[2] does not. Refs 4 and 16 do, however, incorporate consideration of the areas of conjugation circuits very differently from ref 3—see, for example, ref 42.

(iv) The method of Gomes and Mallion[16] requires "external" knowledge of the ring-current intensities in the family of [N]-annulenes, calculated using a quantum-mechanical method,[32] based on a one-dimensional cyclic model with a periodic potential, in order to mimic the nuclear positions by the troughs of the potential; Mandado's approach[3] requires a suitable parametrization.[42]

(It should be noted the HLPM formalism[23,24]—the approach that we favor as being the least subjective of all of the methods considered here—requires for its application knowledge only of the carbon−carbon connectivity of the structure in question *and* the areas of its constituent rings.)

(e) Finally, we remark that this study has demonstrated that consideration of bond currents, as distinct from the more traditional ring currents, can give an extra conceptual insight into the magnetic properties of conjugated systems like [567567] (Figure 1). This is evident from the detailed, semiquantitative deductions that we have been able to make from these computations when the information about the calculated π-electron currents is displayed in the form of individual bond currents, as it is in Figures 3, 5, 6, 8, and 10, rather than as ring currents (as in Figures 2, 4, 7, 9, and 11). As is self-evident—though the point is not often emphasized—both are rigorously equivalent representations in the case of any method that respects Kirchhoff's Law of current conservation at a junction.[26−29] Nevertheless, provided that charge/current conservation is guaranteed—or Kirchhoff's Law is valid for bond currents instead of the more-general current densities—ring currents do represent a more efficient way of describing the molecular reaction to the external magnetic field: ring currents are independent, while bond currents are not.[61]

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(9) Balaban, A. T.; Bean, D. E.; Fowler, P. W. *Acta Chim. Slov.* **2010**, *57*, 507–512.

(10) See Figure 7 of Ciesielski et al.,[4] which depicts a π-electron current-density map of 3,4-benzopyrene that had been provided by Professor Fowler.

(11) Randić, M.; Nović, M.; Vračko, M; Vukičević, D.; Plavšić, D. *Int. J. Quantum Chem.* In press. DOI: 10.1002/qua.23081.

(12) Gayoso, J. *C. R. Hebd. Séances Acad. Sci.* **1979**, *C 288*, 327–330.

(13) A reviewer has suggested that we should explicitly quote Gayoso's "philosophical" conclusion in his 1979 paper.[12] Gayoso wrote:[12] *En relevant, sans passer la mécanique quantique, toute la richesse descriptive de la formule développé, la théorie chimique des graphes est selon nous à revivifier l'activité théorique en chimie.* After translation into English, this reads approximately as follows: *Observing the wealth of descriptive formulation developed without quantum mechanics, we think that chemical graph theory is set to revive activity in theoretical chemistry.*

(14) (a) Pople, J. A. *Mol. Phys.* **1958**, *1*, 175–180. (b) McWeeny, R. *Mol. Phys.* **1958**, *1*, 311–321. (c) Veillard, A. *J. Chim. Phys. Phys. Chim.—Biol.* **1962**, *59*, 1056–1066. (d) Gayoso, J.; Boucekkine, A. *C. R. Hebd. Séances Acad. Sci.* **1971**, *C272*, 184–187. (e) Aihara, J.-I. *J. Am. Chem. Soc.* **1979**, *101*, 558–560. (f) Mizoguchi, N. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 2005–2010. (g) O'Leary, B.; Mallion, R. B. *J. Math. Chem.* **1989**, *3*, 323–342. (h) It should be noted that, despite its authorship, ref 14g is actually a historical paper reporting previously unpublished work (dating from 1953) by the late Professor C. A. Coulson, F.R.S., in which the London theory[14i] of diamagnetic susceptibility in conjugated systems is couched in terms of Coulson's own contour-integral formalism.[14j] (i) London, F. *J. Phys. Radium (7e Sér.)* **1937**, *8*, 397–409. (j) Coulson, C. A. *Proc. Cambridge Philos. Soc.* **1940**, *36*, 201–203.

(15) Gomes, J. A. N. F. *Some Magnetic Effects in Molecules*. D. Phil. Thesis, University of Oxford (Linacre College): England, United Kingdom, 1976; pp 69–73.

(16) Gomes, J. A. N. F.; Mallion, R. B. *Rev. Port. Quìm.* **1979**, *21*, 82–89.

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(18) Gomes, J. A. N. F. *Croat. Chem. Acta* **1980**, *53*, 561–569.

(19) Gomes, J. A. N. F. *Theoret. Chim. Acta* **1981**, *59*, 333–356.

(20) The term "conjugation circuit" was adopted[15,16] in order to emphasize the implication that the said circuits are considered as agents for the "transmission of conjugation", rather than the fact that the circuits themselves are actually "conjugated", as such—as is implied by the name ("conjugated circuit") that Randić (independently) coined[1] for the same idea.

(21) Randić, M.; Plavšić, D; Vukičević, D. *J. Indian Chem. Soc.* **2011**, *88*, 13–23.

(22) Coulson, C. A.; Mallion, R. B. *J. Am. Chem. Soc.* **1976**, *98*, 592–598.

(23) Mallion, R. B. *Croat. Chem. Acta* **2008**, *81*, 227–246.

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(25) Dickens, T. K.; Mallion, R. B. *J. Phys. Chem. A* **2011**, *115*, 351–356.

(26) Kirchhoff, G. *Anal. Phys. Chem.* **1845**, *64*, 497–514.

(27) Cundy, H. M. *S.M.P. Advanced Mathematics Book 3 [Metric]*; Cambridge University Press: London, 1970; p 911.

(28) Smart, D. *Linear Algebra & Geometry*; Cambridge University Press: Cambridge, England, United Kingdom, 1988; S. M. P. Further Mathematics Series, pp 307–308.

(29) Mallion, R. B. *Proc. R. Soc. London, Ser. A* **1974/1975**, *341*, 429–449.

(30) Even more neglected is the pioneering work of Gayoso[12]—published in 1979, independently of the paper by Gomes and Mallion[16] (also 1979). In an attempt to apply Randić's theory of conjugation-circuit increments[1] to estimate magnetic-susceptibility exaltations in conjugated hydrocarbons, Gayoso[12] used eight fitted parameters and applied his formalism to 19 test molecules; he obtained semiquantitative agreement with the experimental data. Gayoso's contribution[12] has, however, been overlooked entirely by all three schools[2–4] reporting recent work on the relevance of conjugation circuits to the magnetic properties of conjugated systems.

(31) Note that the wording of rule (iii)—here printed in italics—has been modified; please see also ref 36.

(32) Baer, F.; Kuhn, H.; Regel, W. *Z. Naturforsch. A* **1967**, *22*, 103–112.

(33) The reasons for adopting this approach are explained in the Introduction to ref 16.

(34) We have frequently emphasized in the text that, as part of its intrinsic canon, the method of Gomes and Mallion[15,16] adopts the relative ring-current intensities calculated by Baer et al.[32] for the [N]-annulenes of a size up to [18] (and extrapolations of them beyond that size—please see footnotes e and f to Table 1). The magnitudes of these decrease very rapidly to zero as ring size increases (Table 1, right-hand column). The idea that contributions should decrease with the size of the conjugation circuit was also evident in Randić's original study[1] on

resonance energies. Such a decline of contributions with the size of the conjugation circuit is also a feature of Mandado's method[3] because, in that approach, contributions from conjugation circuits are initially weighted according to the reciprocals of their areas. Gayoso's parametrization[12] in the context of magnetic susceptibilities did not, however, support a monotonic decrease with the size of the conjugation circuit. Furthermore, we have carried out some simple "topological" calculations, using the HLPM method,[23,24] on the ring currents in the family of $[4n+2]$ annulenes and have found that, far from decreasing with annulene size, they actually *increased*—and quite dramatically. This aspect will be the subject of future investigation.

(35) As Randić[2] and Ciesielski et al.[4] explicitly point out—and as follows directly from the theory proposed by one of us (Gomes)[17–19]—full account should be taken of any *disjoint* conjugation circuits that are extant within the Kekulé structures that are under consideration—see, for example, Figure 2 of ref 2 and Figure 4 of ref 4. According to ref 3, and the Supporting Information to it, such disjoint conjugation circuits appear to be omitted from consideration in the method of Mandado.[3] Furthermore, the inclusion of disjoint conjugation circuits was neither explicitly prescribed nor yet expressly proscribed in the initial formulation of Gomes and Mallion's 1979 approach[16] (this did not, in any case, affect the final numerical results for the majority of the structures initially studied in ref 16, in which no such disjoint conjugation circuits actually arise). For small molecules, simple inspection of the set of Kekulé structures ("perfect matchings") allows identification of all of the required conjugated circuits.[16] In general, however, we recommend examining all of the overlaps between all pairs of Kekulé structures;[19] application of this algorithm will guarantee that sets of disjoint conjugation circuits are automatically identified and retained for consideration in the bond-current/ring-current calculations.

(36) (a) In view of the theoretical formulation of the method proposed by Gomes,[17–19] this rule—printed in the text in *italics*—is here given a wording that is more general than that adopted for the corresponding rule (iii) in ref 16. (The original wording in ref 16 was "(iii) If at least one bond of a particular ring forms a part of a given "conjugation circuit", this ring shall be said to "participate" in that "conjugation circuit".") Professor P. W. Fowler[36b,c] has recently proposed an equivalent version of rule (iii) that is couched entirely in terms of *bond* currents, rather than *ring* currents: (b) Fowler, P. W. Personal Communication, June 19th, 2011. (c) Fowler, P. W.; Myrvold, W. *J. Phys. Chem.* DOI: jp-2011-06548t.R1.

(37) Gutman, I.; Randić, M. *Chem. Phys.* **1979**, *41*, 265–270.

(38) (a) An anonymous reviewer has pointed out that a coefficient, c_L, is defined in Mandado's approach[3] as the ratio of the number of conjugated circuits of a certain type, L, and the number of Kekulé structures (n_K in Mandado's paper)—please see ref 3 for a definition of these quantities. This ratio emerges from the valence-bond treatment of the resonance energy proposed in ref 3, which starts with the valence-bond wave function proposed by Herndon,[38b] in which the root of the number of Kekulé structures is introduced in order to normalize the wavefunction (equation 1 in Mandado's paper—see also ref 19). It seems that Mandado effectively "normalizes" by dividing by $K/2$ (2 being the number of Kekulé structures in benzene). Regarding the approach of Ciesielski et al.,[4] we are unclear why the so-called "local" and "global" quantities calculated from the bond currents are normalized (by division by $(1/2)K(K - 1)$, the number of sets of distinct conjugation circuits) but *not* the actual bond currents themselves—which, of course, are what we ourselves are primarily interested in in this paper: (b) Herndon, W. C. *J. Am. Chem. Soc.* **1973**, *95*, 2404–2406.

(39) If, in the context of ref 3, one were to parametrize or simulate a quantum-mechanical method, one would more naturally fit the quantity H_{LL} to the number of bonds in the circuit, rather than to the number of rings.

(40) (a) Even more elaborate "normalizations" have been discussed and argued for by Randić[40b] in the context, specifically, of structures related to perylene: (b) Randić, M. Personal communication to R.B.M., May 3, 2011.

(41) The method of Ciesielski et al.[4] does involve ring *areas*, but it has been claimed[22] that consideration of such areas, if properly effected

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dx.doi.org/10.1021/ct2002539 |*J. Chem. Theory Comput.* 2011, 7, 3661–3674

according to certain well-defined rules[24] (as specified in footnote *a* of Table 1), need not necessarily deprive an approach of being aptly described as "topological" or "graph-theoretical".[22−25]

(42) (a) The method of Gomes and Mallion[16] takes into account the effect of the number of centers on the ring-current intensity by incorporating the numerical values of the annulenic ring-current intensities reported by Baer et al.[32] An anonymous reviewer has pointed out that this is also taken into consideration, in an equivalent way, in Mandado's method.[3] In fact, Mandado introduces a variable f_L defined as the number of benzene rings enclosed by the circuit, in order to represent the size of the circuit. In the method of Gomes and Mallion,[15−19] the size of the circuits is measured in idealized molecular geometries with equal bond lengths; the energy and the current associated with a annulene are assumed to depend on the number of centers of that annulene. These energy terms depend mainly on the number of alternating double and single bonds, which, in turn, depend on the number of centers. Gomes and Mallion[15,16] adopted the annulenic ring currents of Baer et al.[32] as an alternative to a possibly arbitrary parametrization. Mandado[3] has instead opted for a parametrization. The following is a summary[42b] of how all four "conjugation circuits" approaches[15,16,2−4] count the contributions of conjugation circuits as they increase in size. In both the Gomes−Mallion[15,16] and Mandado[3] models, contributions taper off[42b] with ring size—they start off large for small conjugation circuits, settle down, and then virtually disappear altogether at $[N] = 22$. In the Randić[2] model, all conjugation circuits, of whatever size, give an equal contribution per occurrence. In the approach of Ciesielski et al.,[4] larger conjugation circuits contribute more per occurrence, as they have larger area. In Mandado's model,[3] the larger conjugation circuits contribute less per occurrence, because, in this formulation, the area is in the denominator. In the approach of Gomes and Mallion,[15,16] although circuit area is in the numerator, contributions from the larger conjugation circuits fall off rapidly with the size of the conjugation circuit because of the fact that the Baer et al.[32] "annulenic" currents decrease virtually to zero at annulene size [22]). This phenomenon of the decrease in importance of the contributions from the larger conjugation circuits is thus essentially the same in both the Mandado[3] and Gomes−Mallion[15,16] formalisms: (b) Fowler, P. W. Personal communication, July 3, 2011.

(43) Gomes, J. A. N. F. *THEOCHEM* 1990, *210*, 111–119.

(44) (a) Longuet-Higgins, H. C.; Salem, L. *Proc. R. Soc. London, Ser. A* 1960, *257*, 445–456. (b) Salem, L. *The Molecular Orbital Theory of Conjugated Systems*; W. A. Benjamin: Reading, MA, 1966; Chapter 4.

(45) (a) Haddon, R. C. *Tetrahedron* 1972, *28*, 3613–3633. (b) *idem ibid.* 3635−3655.

(46) Mallion, R. B. *Mol. Phys.* 1973, *25*, 1415–1432.

(47) (a) Mallion, R. B. *Empirical Appraisal and Graph Theoretical Aspects of Simple Theories of the "Ring-Current" Effect in Conjugated Systems*. D. Phil. Thesis: University of Oxford (Christ Church): England, United Kingdom, 1979; pp 124−131. (b) Haigh, C. W.; Mallion, R. B. *Croat. Chim. Acta* 1989, *62*, 1–26.

(48) Amos, A. T.; Roberts, H. G. Ff. *Mol. Phys.* 1971, *20*, 1073–1080.

(49) (a) Kirchhoff's Law of current conservation[26−29] is, by contrast, *not* violated in, for example, the "coupled Hartree−Fock" procedure described in: (b) Coulson, C. A.; Gomes, J. A. N. F.; Mallion, R. B. *Mol. Phys.* 1975, *30*, 713−732.

(50) (a) Coulson, C. A.; O'Leary, B.; Mallion, R. B. *Hückel Theory for Organic Chemists*; Academic Press: London, 1978. (b) Yates, K. *Hückel Molecular Orbital Theory*; Academic Press: New York, 1978.

(51) The reasons why such methods lose current conservation at junctions are gone into in some detail by one of the present authors (R.B.M.) in a long footnote on page 1420 of ref 46.

(52) Fowler, P. W. Personal communication to R. B. M., June 8, 2011.

(53) An anonymous reviewer has, very conscientiously, repeated our calculations using the method of Ciesielski et al.[4] and claimed that some of our bond currents reported in Figure 10 are incorrect. We therefore invoked the help of Professor P. W. Fowler and his colleagues W. Myrvold, W. Bird, and S. Cotton at the Universities of Sheffield (England) and Victoria (Alberta), in order to effect an independent check.[51] When

"normalized" by division by the factor $K(K − 1)$—against, however, the recommendations of Ciesielski et al.,[4] at *this* stage of the calculation—the bond currents in [567567] calculated by Fowler et al. using the method of Ciesielski et al.[4] agreed entirely with ours (displayed in Figure 10) to *four* significant figures and disagreed with those that had been provided by the reviewer. We therefore persist with our original data, confident that they have been independently confirmed by Professor Fowler and his above-named colleagues.

(54) Fowler, P. W.; Bean, D. E. Personal Communication to R. B. M. at the Fifth Conference on Computers in Scientific Discovery, Sheffield, England, United Kingdom, July 2010.

(55) Atkins, P. W.; Gomes, J. A. N. F. *Mol. Phys.* 1976, *32*, 1063–1074.

(56) Although our calculations using the Gomes−Mallion method[15,16] were effected by hand, they were independently checked by means a computer algorithm written and run by Professor P. W. Fowler and his colleagues W. Myrvold, W. Bird, and S. Cotton at the Universities of Sheffield (England) and Victoria (Alberta). Complete agreement was found (to the number of decimal places quoted in Figures 2 and 3).

(57) Ring currents by method R are determined by the count of conjugation circuits contributing to them, arising from the K perfect matchings/Kekulé structures and, in Randić's later work, are "normalized" by dividing either[11] (i) by the total number,[37] $K(K − 1)$, of pairwize overlaps or[21] (ii) merely by K itself. In more recent work, on perylenes, even more delicate and elaborate "normalizations" have been argued for.[40]

(58) It should be noted that, in Figure 1 of ref 2, the Kekulé structure labeled "E" is in fact—in error—merely a repetition of the one labeled "B". Kekulé structure "E" should actually have been the one that is displayed there *but* with the single/double bonds in the *central* ring running in the alternative way (the patterns in the other six rings remaining undisturbed). Professor Randić has evidently used the *correct* Kekulé structure "E" in his calculations, for, on repetition of them, we independently agree with his final "bond currents", displayed in Figure 5 of ref 2. (and—after "normalization"[11] by division by 72—in our Figure 6).

(59) (a) Pople, J. A.; Untch, K. G. *J. Am. Chem. Soc.* 1966, *88*, 4811–4815. (b) Haddon, R. C.; Haddon, V. R.; Jackman, L. M. *Top. Curr. Chem.* 1971, *16*, 103–220. (c) Sondheimer, F. *Acc. Chem. Res.* 1972, *5*, 81–91.

(60) Trost, B. M.; Bright, G. M.; Frihart, C.; Brittelli, D. *J. Am. Chem. Soc.* 1971, *93*, 737–745.

(61) (a) This observation is re-enforced by Figure 3 of ref 61b, in which the bond currents in the 60 bonds of kekulene are expressed in terms of just three independent parameters, A, B, and δ. These are not actually the ring currents in the three symmetrically non-equivalent rings of kekulene, but they are related to them in the following way: the ring current in the six-membered ring that Steiner et al.[61b] label "I" is equal to $(A + \delta)$; the ring current in ring II is $(A − \delta)$, and that in the internal, 18-membered, ring III is $(A − B)$. Once again, therefore, in this example, a bond-current description is entirely equivalent to a ring-current one, with as many independent variables being needed to specify the several bond currents as there are symmetrically non-equivalent rings (and, hence, distinct ring currents) in the structure under consideration: (b) Steiner, E.; Fowler, P. W.; Jenneskens, L. W.; Acocella, A. *Chem. Commun.* 2001, 659–660.