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A QUASI-TOPOLOGICAL METHOD FOR THE CALCULATION OF RELATIVE «RING-CURRENT» INTENSITIES IN POLYCYCLIC, CONJUGATED HYDROCARBONS

This paper investigates the possibility of estimating relative «ring-current» intensities in polycyclic, conjugated hydrocarbons from some simple topological features of these molecules. Such topological analyses have in the past mainly been used to correlate resonance energies and reactivities of this class of compounds. A very simple prescription is here proposed for estimating relative «ring-current» intensities and it is then successfully applied to a wide range of conjugated hydrocarbons — alternant and non-alternant, benzenoid and non-benzenoid. In the application of this prescription it is assumed that the so-called «conjugation circuits» in all Kekulé structures which may be devised for any given molecule make contributions which are additive, the size of such individual contributions being estimated from the «ring-current» effects calculated to be associated with the corresponding model-annulenes. The concept of «conjugated circuits» and the search for them are both purely topological in nature; the contribution to the various «ring-current» intensities made by each such circuit must however depend also on the area of that circuit, and on the «ring-current» intensity and ring area assumed for the related model-annulene — hence the description of this method as «quasi-topological». It is concluded that this novel method for «ring-current» estimation should be adequate, numerically, for most routine-applications of the concept and it is therefore hoped that this new approach, whilst admittedly naïve, will prove a considerable convenience when more-sophisticated, quantum-mechanical calculations are not available.

1 — INTRODUCTION

Ideas about the circulation of π -electronic currents in (poly)cyclic, conjugated hydrocarbons, originally invoked in order to explain the large anisotropies of magnetic susceptibility observed in this class of compounds, have a long history in the Literature. PAULING [1], and the late Dame KATHLEEN LONSDALE [2] proposed a free-electron model for benzene, while LONDON [3] gave the first quantum-mechanical account of these properties, using an LCAO-MO theory which incorporated what have since been called «gauge-invariant» atomic-orbitals. With the development of ^1H -NMR in the mid-1950's, interest in what were by then being called «ring-currents» was revived, once it was realised [4] that these same «ring currents» could account quite naturally for the low-field chemical-shifts of the protons in planar, condensed, benzenoid hydrocarbons [5], without any essential change in the models employed. Simple extensions of the London theory, by POPE [6], McWELLYN [7] and one of the present authors [8], give a good account [8, 9] of the experimental proton-chemical-shifts in these molecules [10], when the calculations are appropriately parametrised [11].

More-recent theories of the «ring-current» effect have been cast in terms of (coupled or uncoupled) SCF wave-functions (for bibliography, see refs. [12, 13]) and when the predictions of *these* theories have been confronted with experimental ^1H -NMR data [10] they have in general also met with gratifying, albeit qualified, success. Furthermore, although the concept of «ring-currents» has in the past been controversial [14-16], recent work by one of us [17, 18] has given strong justification for their use as an intermediate in the calculation of molecular properties (such as magnetic susceptibilities and NMR-shieldings) that depend on the current-density field. We therefore start from the proposition that the «ring-current» idea gives a satisfactory account of the way in which the π -electron system of a polycyclic, conjugated hydrocarbon reacts to an external magnetic-field.

In this paper we present a prescription for estimating the relative «ring-current» intensities in polycyclic, conjugated hydrocarbons, a prescription which

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is based on the topological (*) features of these molecules; we shall then test this formulation by applying it to a large number of conjugated hydrocarbons — alternant and non-alternant, benzenoid and non-benzenoid, diamagnetic and paramagnetic — and by comparing the results obtained with those of more-traditional methods of estimating «ring-current» intensities, numerical values of which are available in the literature.

The graph-theoretical aspects of simple «ring-current» calculations on conjugated systems have been discussed in detail by one of us [19] and these ideas are here extended by incorporating the concept of «conjugation circuits», recently introduced by RANDIC [20], and independently arrived at by one of the present authors [17].

2 — THE RELEVANCE OF «CONJUGATION CIRCUITS»

The classical approach [1, 2] to the problem of calculating the currents induced in a general, conjugated hydrocarbon by an external magnetic-field is a typical application of electrical-network theory (*e.g.* refs. [25, 26]); even the simple MO-formalisms based on HMO-theory, such as that of McWEENY [7], are also amenable to an interpretation in such language, for the fundamental system of circuits and the spanning-trees of the graph representing the carbon-carbon σ -bond connectivity of the conjugated system under investigation are also of relevance in this method, as was much discussed in ref. [19] (to which the reader is referred for an explanation of the graph-theoretical terms used here).

In McWEENY'S method [7], each «circuit» [7] within an M -cyclic molecule is formed by taking an arbitrary spanning-tree [27, 19] of the molecular graph and adding to it one (and *only* one) of the M edges of the original molecular-graph that does *not* appear in the particular spanning-tree on which the calculation is being based [19]; a circuit constructed in this way is unique and, for an M -cyclic molecule, there are M such distinct circuits [19]. The effect of the magnetic field should therefore properly be considered as acting separately on M independent cir-

cuits to be found within the molecular graph. This is a direct translation into classical language of the interpretation of McWEENY'S method discussed in ref. [19].

Thus, once the *actual magnitudes* of the «ring-currents» have been estimated quantum-mechanically, a network-theoretical analysis would be useful in the calculation of any property derived from them, since the currents *per se*, of whatever magnitude, may be assumed to behave truly classically. (This point is considered in detail in the footnote on page 1421 of ref. [8]). As is well known, however, the «ring-current» intensities themselves cannot be successfully estimated classically [1, 28]. Consider, for example, the case of perylene (molecule (VII) of Figure 1); quantum-mechanical estimates of the «ring-current» intensity in the central ring predict a value [29-31, 9] of *ca.* $\frac{1}{4}$ of the benzene «ring-current», while classically one might expect [1] an intensity in this ring more nearly equal to the benzene one. The contrast between classical and quantum-mechanical behaviour is more dramatically emphasised by the fact that, classically, *no paramagnetic currents can be predicted*. It is evident, therefore, that classical laws of independent behaviour of individual circuits, and consequent additivity of the magnetic induction arising from composite circuits, cannot be translated into a quantum-mechanical formalism, as far as the calculation of «ring-current» *magnitudes* is concerned. This conclusion is strengthened by the work of MADDON and McWEENY [28] and BAER *et al.* [32]; the latter workers showed by means of a one-dimensional electron-gas model in a periodic potential that the induced current in monocyclic annulenes depends not only on (of course) the ring area but also on whether the number of maxima possessed by the periodic potential around the ring is a multiple of 4, or 2 plus a multiple of 4.

Other workers [33-36] simultaneously discovered the dramatically contrasting magnetic-properties of $[4n]$ - and $[4n+2]$ -annulenes, and the relative stabilities of these two types of systems have also been investigated [35, 37, 38]. There have since been attempts to regard pyracylene (XV) and some of its isomers as «perturbed» $[12]$ -annulenes [39, 40]; this model remains, however, controversial [41, 42].

Now RANDIC [20] has recently correlated the resonance energy of benzenoid hydrocarbons with the

(*) We use the term «topological» in this paper to describe any property that may be derived from the graph which represents the carbon-atom, σ -bond connectivity of the planar, conjugated hydrocarbon in question. For further discussion on the use of this adjective in a chemical context, see refs. [21-24].

number of circuits, in the various Kekulé-structures that may be devised for such molecules, that consist entirely of alternating single- and double bonds — circuits which Randić refers to as «conjugated circuits». This dissection appears to allow a localisation of the resonance energy — *i.e.* a decomposition of the resonance energy into individual contributions from the various rings which constitute the molecule. In RANDIĆ'S analysis [20], the contribution from each «conjugated circuit» was obtained by fitting the circuit-count to calculated resonance-energies for a number of reference compounds. In view of the network-theoretical analysis outlined above, it is possible that Randić's concept of «conjugation circuits» might be a factor determining the magnetic properties of a molecule, as well as its ground-state energy. Now a property which is «local» in character («local», that is, to each *ring*) and from which other magnetic properties may be calculated [18], is the very «ring current» which we have been discussing. Hence, we now attempt to correlate «ring-current» intensities in polycyclic, conjugated hydrocarbons with the «conjugation circuits» extant in their various Kekulé-structures. In order to minimise the number of arbitrary assumptions involved in estimating the contribution to the various «ring-current» intensities arising from each «conjugated circuit», and to avoid having to fit our circuit-count expressions to other computed quantities, we make use of the systematic calculations of BAER *et al.* [32] concerning the «ring-currents» in $[4n]$ - and $[4n+2]$ -annulenes. These calculations, which are based on a free-electron, one-dimensional model involving a periodic potential, are the only systematic ones available for the whole series of the annulenes, there being difficulties with the use of more-realistic quantum-mechanical methods for $[4n]$ -annulenes [32, 17]. We also make a correction for the fact that the actual area enclosed by a particular «conjugation circuit» comprising a given number (N) of carbon atoms will in general be different from that of the regular polygon of N sides assumed for the corresponding model-anulene; the magnetic effect is taken to be proportional to the true area of the circuit — as indeed it is, both classically [1, 2] and in simple quantum-mechanical calculations [3, 6-9, 19, 34, 43-47].

3 — PRESCRIPTION FOR CALCULATING «RING-CURRENTS»

By virtue of the discussion in § 2, 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 the 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 for the harmonic potential that occurs in their calculations [17].
- (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 [20].
- (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».
- (iv) The «ring-current» intensity in any particular ring of such a polycyclic hydrocarbon receives a non-zero 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) This non-zero contribution to the «ring-current» intensity in a given ring from an indivi-

dual «conjugation circuit» comprising N bonds is equal to the «ring-current» intensity calculated (via (i), above) to be associated with a 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 «ring-currents» are proportional to 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 n th conjugated circuit, of N sides and area $A^{(n)}$, is taken to be proportional to the quantity $J^{(n)}$, where

$$J^{(n)} = J_N \times \frac{A^{(n)}}{A_N} \quad (1)$$

in which J_N and A_N are, respectively, the «ring-current» intensity and the ring area associated with an idealised, regular, planar $[N]$ -annulene (see Table 1). By rules (iv) and (vi), the relative «ring-current» intensity, J_r , in a given ring r , is then

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

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.

4 — ILLUSTRATION, TESTING, AND EVALUATION OF THE NEW «RING-CURRENT» PRESCRIPTION

As an example, we apply this prescription to naphthalene. The first step is to draw all possible Kekulé-structures and find the «conjugation circuits» in each of them. By equation (2), the «ring-current»

Table 1

Ring Areas^a and «Ring-Current» Intensities^b for Regular Annulenes, Calculated by the Method of Baer et al. [32]^c.

Number of Bonds (N)	Ring Area ^a (A_N)	«Ring Current» ^b (J_N)
4	0.385	− 2.189
5	0.662	—
6	1	1
7	1.339	—
8	1.858	− 1.273
10	2.962	+ 0.721
12	4.309	− 0.691
14	5.902	+ 0.375
16	7.740	− 0.375
18	9.823	+ 0.165
20	12.151	− 0.1 ^d

a) Expressed as a ratio to the area of a standard benzene-hexagon.

b) Expressed as a ratio to the benzene «ring-current» intensity calculated, by the same method [32], for benzene.

c) With the parametrisation described in § 3.

d) (Extrapolated).

intensity in a particular ring of the molecule is then obtained by adding the contributions $J^{(n)}$ (equation (1)) from all the «conjugation circuits» in which that ring participates. For naphthalene, $K = 3$ and the «conjugation circuits» are shown in fig. 1. It is clear that, by symmetry, the «ring-current» intensi-

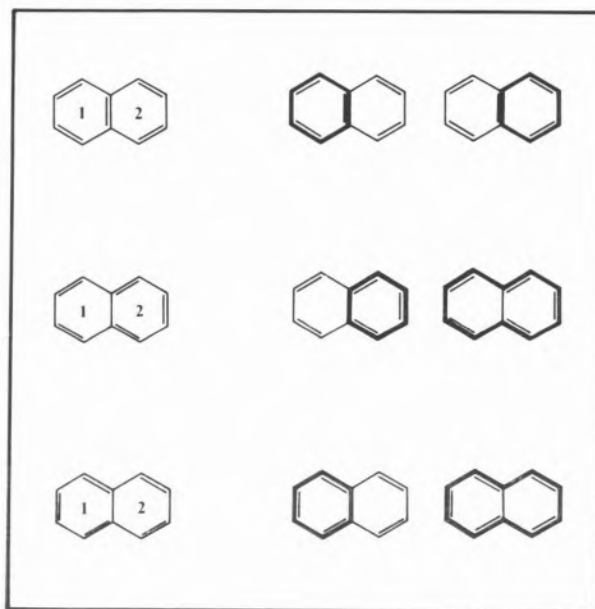


FIG. 1

Table 2
«Ring Currents», and Related Quantities, Estimated by Various Methods

Molecule	Ring	London-Pople-McWeeny «Ring-Current» Intensity ^a	«Integrated π -Electron Current» Intensity ^b	«Ring Current» Estimated by Present Prescription ^c
Benzene (I)		1	1	1
Naphthalene (II)	A	1.09 ^d	1.07	0.99
Anthracene (III)	A	1.08 ^e	1.05 (0.96)	0.84
	B	1.28	1.28 (1.32)	1.08
Phenanthrene (IV)	A	1.13 ^e	1.13	1.07
	B	0.97	0.95	0.86
Pyrene (V)	A	0.96 ^f	0.94	0.80
	B	1.33	1.34	1.20
3,4 Benzopyrene (VI)	A	1.21 ^g	—	1.01
	B	1.29	—	1.15
	C	0.85	—	0.61
	D	1.30	—	1.18
	E	1.08	—	0.94
Perylene (VII)	A	0.97 ^h	1.03	0.99
	B	0.24	0.22	0
Zethrene (VIII)	A	0.37 ⁱ	—	0
	B	0.87	—	0.99
	C	0.92	—	0.99
Peropyrene (IX)	A	1.03 ^j	—	0.80
	B	1.45	—	1.34
	C	1.33	—	1.18
Diphenyl (X)	A	0.94 ^k	0.96	1
Biphenylene (XI)	A	0.25 ^k	0.40	0.27
	B	-1.81	-1.76	-1.79
Azulene (XII)	A	1.07 ^l	1.03	0.49
	B	1.15	1.28	0.49
Acenaphthylene (XIII)	A	0.93 ^k	0.94	0.99
	B	0.11	-0.14	0
Fluoranthene (XIV)	A	0.99 ^m	1.00 (1.02)	0.99
	B	0.05	-0.04 (- 0.02)	0
	C	0.86	0.89 (0.97)	1.00
Pyracylene (XV)	A	-0.39 (+ 0.31) ⁿ	-0.20 (+ 0.56)	0.29
	B	-2.32 (- 1.01)	-2.16 (- 0.74)	-0.64

^a) «Ring-Current» intensities (expressed as a ratio to the «ring-current» intensity calculated, by the same method, for benzene) by the London-Pople-McWeeny method [6-8], taken from a variety of literature sources. Figures in parentheses are from the iterative calculation described in ref. [41]. A positive entry indicates a diamagnetic current; a negative entry signifies a paramagnetic current.

^b) «Integrated π -electron current-densities» by the method of COULSON *et al.* [12]. For easy comparison with the other two columns of this Table the values here (which, except for those in parentheses, are taken from ref. [12]) are given as ratios to the «integrated π -electron current-density» calculated, by the same method, for benzene ($e^2 B/2m_e \times 0,946$ A nm) [17]. The results in parentheses are from an unpublished, iterative calculation by the present authors, in which resonance integrals between pairs of σ -bonded carbon-atoms have been made self-consistent with the corresponding bond-orders. (A positive entry indicates a diamagnetic current; a negative entry denotes a paramagnetic current.)

^c) «Ring-Current» estimates obtained *via* equations (1) and (2) and the data of Table 1. A positive entry indicates a diamagnetic current; a negative entry signifies a paramagnetic current.

^d) Refs. [7, 29, 19]. ^e) Ref. [29]. ^f) Refs. [29, 30, 9]. ^g) Refs. [30, 44]. ^h) Refs. [30, 9]. ⁱ) Refs. [19, 47]. ^j) Ref. [31]. ^k) Ref. [12].

^l) Ref. [6]. ^m) Ref. [45]. ⁿ) Refs. [41, 12].

ties in the two rings, 1 and 2, of naphthalene will be equal and, by equations (1) and (2), they are:

$$J_{1,2} = \frac{1}{3} \left\{ \frac{(2 \times 1 \times \frac{1}{1})}{1} + (2 \times 0.721 \times \frac{(1+1)}{2.962}) \right\} = 0.99$$

(to 2 significant figures)

— *i.e.*, each ring receives a «[6]-annulene» contribution (twice) and a «[10]-annulene» contribution (twice). This result is to be compared with the 1.09 obtained *via* the Hückel-London-Pople-McWeeny approaches [3, 7, 29, 19, 34] and the value of 1.07 which COULSON *et al.* [12] reported for their so-called «integrated π -electron current». Equations (1) and (2) and postulates (i)-(vi) were applied to the 15 conjugated hydrocarbons shown in fig. 2; the results are shown in Table 2 where the corresponding «ring-current» intensities calculated by more-conventional methods are also reproduced, for comparison.

By and large, a very reasonable qualitative agreement is observed with the results of conventional methods of calculation, particularly as far as the condensed, benzenoid hydrocarbons are concerned, and several important details of «ring-current» distribution in these molecules displayed in the more-traditional «ring-current» calculations are properly reproduced by the present prescription. For example:

- (i) The relative order of «ring-current» intensities within a given molecule is correctly predicted for all the condensed, benzenoid hydrocarbons treated. This is true even of the carcinogen 3,4-benzopyrene (VI) with five symmetrically-non-equivalent rings, where the smallest current is correctly predicted to be in the «K-region» ring, ring C.
- (ii) Full quantum-mechanical «ring-current» calculations predict [31] that the central ring (B) in peropyrene (IX) bears a much larger «ring-current» than does the (formally) analogous central ring (B) in perylene (VII), which is similarly condensed, with four surrounding rings. One of us [31] has intuitively and heuristically rationalised this observation by invoking the well known fact that the central bonds in perylene, connecting the two naphthalenic units,

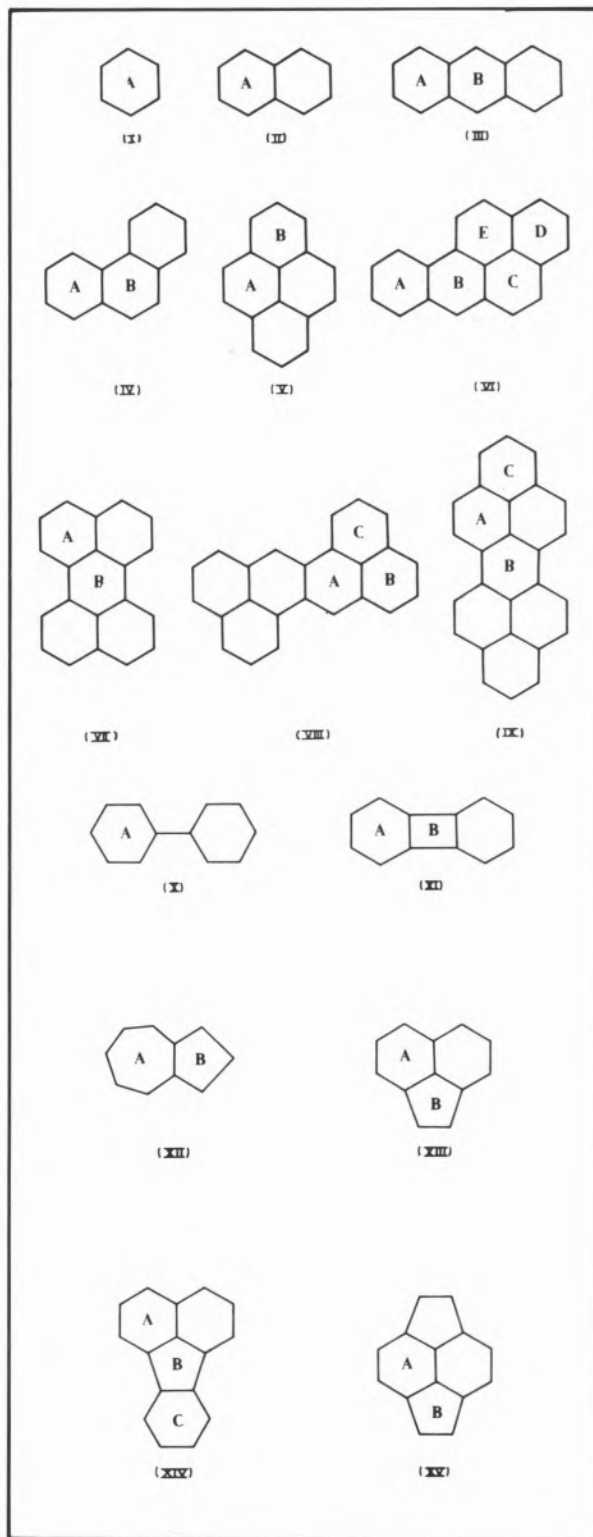


FIG. 2

never appear other than as single bonds in any of the several Kekulé-structures which can be devised for the molecule as a whole; in pero-

pyrene, however, there is no such «bond fixation» and hence, in this molecule, *all* bonds in the central ring necessarily participate fully in the conjugation between the upper and lower halves of the molecule. This interpretation is fully supported by the prescription we are proposing in this paper (*).

- (iii) Zethrene (VIII), in which there is also such «bond fixation» [19, 46] in the central rings (A), is predicted to bear «ring-currents» which are *all* smaller in intensity than the benzene value, that in the central ring being the smallest.

Those molecules considered that are alternant, but not condensed, benzenoid hydrocarbons ((X) and (XI)) are predicted to bear «ring currents» which are nicely in accord with the corresponding values calculated by quantum-mechanical methods. It should, in all fairness, be pointed out, however, that, in view of what we shall say below concerning strongly paramagnetic molecules, it is very likely that the extremely good agreement amongst the variously calculated «ring-current» intensities for biphenylene (XI), whilst gratifying, is probably fortuitous. As for the non-alternant hydrocarbons considered ((XII)-(XV)), the agreement is disappointing for azulene (XII) (particularly as the molecule is unambiguously diamagnetic in both rings) but encouraging for acenaphthylene (XIII) and fluoranthene (XIV) in which, for the latter two hydrocarbons, the quantum-mechanical predictions of a very low «ring-current» intensity in the five-membered rings, B, are confirmed. The two quantum-mechanical calculations quoted in Table 2 differ on whether this small «ring-current» is diamagnetic or paramagnetic, while the present prescription does not entertain the notion of a «ring-current» of *any* type in these rings, for the rings in question never participate in any conjugated circuits. In the case of the one non-alternant molecule studied that has paramagnetic [13] regions (pyracylene (XV)), the «ring-current» estimates obtained on the basis of the present prescription correlate better with the results of iterative quantum-mechanical calculations (in which resonance integrals between σ -bonded car-

bon-atoms have been made iteratively self-consistent with respect to the corresponding, calculated π -bond-orders) than with the predictions of quantum-mechanical calculations in which this refinement has not been made. This is mildly surprising since, as we [41, 17, 42] and others [13, 48, 49] have previously pointed out and rationalised [41, 42] (and as is well illustrated by the figures for pyracylene quoted in Table 2), quantum-mechanically predicted «ring-current» intensities for strongly paramagnetic systems are extremely sensitive to whether or not the wave-function used to calculate them has been made iteratively self-consistent with respect to resonance integrals and calculated bond-orders.

5 — CONCLUSION

On the strength of the above tests, it seems fair to conclude that when no elaborate quantum-mechanical calculations are available for a particular conjugated, polycyclic hydrocarbon, the procedure described in § 3 and illustrated and evaluated in § 4 represents a rapid method of obtaining estimates of «ring-current» intensities reliable enough to be used in the qualitative or semi-quantitative prediction of π -electron magnetic-susceptibilities and ^1H -NMR chemical-shifts.

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(*) The strikingly different «ring-current» intensities in the central rings (B) of perylene (VII) and peropyrene (IX) have also been explained, *via* a superficially very different approach, by one of the present authors and HAIGH [46] who make appeal to a molecular-orbital argument based on perturbation theory.

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RESUMO

Neste artigo são exploradas as possibilidades de estimar as intensidades relativas das «correntes de anel» em hidrocarbonetos conjugados policíclicos, a partir da simples caracterização topológica das moléculas. Análises topológicas deste tipo têm, no passado, sido usadas principalmente para correlacionar energias de ressonância e reactividades desta classe de compostos. Propõe-se agora uma prescrição muito simples para estimar intensidades relativas de «correntes de anel» e faz-se aqui a sua aplicação a um apreciável número de hidrocarbonetos de vários tipos — alternantes ou não, benzenóides ou não.

Consideram-se as contribuições, supostas aditivas, de todos os chamados «circuitos conjugados» em todas as estruturas de Kekulé que podem ser escritas para a molécula; a grandeza destas contribuições é estimada directamente das «correntes de anel» calculadas para os anulenos modelo associados aos «circuitos conjugados». O conceito de «circuito conjugado» e o processo de os encontrar são de natureza puramente topológica; a contribuição para as várias «correntes de anel» que é proveniente de cada circuito deve contudo depender também da área desse circuito e da intensidade da «corrente de anel» e área de anel consideradas para o anuleno — daí a descrição deste método como quase topológico.

Conclui-se que o método aqui proposto para a estimativa de «correntes de anel» deve ser apropriada para a grande maioria das aplicações de rotina; ainda que se admita o seu simplismo, espera-se que este novo método se mostre muito conveniente quando não se disponha de resultados de cálculos por processos mais sofisticados de mecânica quântica.