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Rationalisation of Relative »Ring-Current« Sizes in Polycyclic, Conjugated Hydrocarbons

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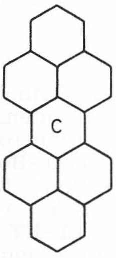
A theoretical basis is established for relating the incidence of relatively 'high' and 'low' »ring-current« intensities (as encountered, for example, in the central rings of peropyrene (*I*) and perylene (*II*), respectively) to intuitive Valence-Bond Resonance-Theory (VB-RT) ideas about 'bond fixation'. In the present treatment, this aim is not achieved by devising a »ring-current« formalism that is itself actually based on a VB-RT wave-function: the philosophy adopted here is (a) to identify, and classify, those occasions on which simple Molecular-Orbital (MO) theory predicts specific rings in conjugated hydrocarbons to have exceptionally high and low »ring-currents«, and then (b) to use topological arguments that rely simply on the carbon-atom connectivity of the conjugated system in question to show that the situations identified in (a), above, are just those in which the absence, or presence, of VB-RT 'bond-fixation' is to be expected.

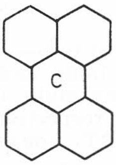
1. INTRODUCTION

Although McWeeny's approach[2,3] has been applied by a large number of authors[2-22], over the last 30 years, to calculate π-electron »ring-currents«[2] in a wide range of conjugated hydrocarbons, and the equivalent method of Pople[23] has also received some attention,[24,8] only occasional consideration appears to have been given, until recently,[25-30] to the *relative sizes* of »ring-current« intensities that arise in these calculations. If the (diamagnetic) »ring-current« in benzene is taken to be unity, the smallest »ring-current« intensity so far reported in a condensed, benzenoid hydrocarbon is 0.236 (in benzo[*b*]perylene, compound *XXI* of ref. 12), while in the 19-ring benzenoid-hydrocarbon dodecabenzocoronene Maddox and McWeeny[4] found a diamagnetic »ring-current« intensity as large as 2.44. When non-alternant (or otherwise non-benzenoid) conjugated-hydrocarbons are considered, smaller diamagnetic, or even large paramagnetic, »ring-currents« may be encountered.[31,32,7,8,16-21]

Within the domain of the condensed, benzenoid hydrocarbons, it has been observed empirically[5,13] that the more condensed a given ring is, the smaller »ring-current« it appears to bear. A dramatic exception to this rule, however, is the central ring (C) in peropyrene (*I*) which has an associated »ring-current« intensity of 1.446[13] — over six times that[5,10] (0.239) in the formally analogous central-ring (C) in perylene (*II*) which, locally is similarly condensed with four surrounding rings. The exceptionally low-field shift (δ 9.15) of the proton closest to ring C observed in the experimental ^{1}H-NMR spectrum[33] of (*I*) — more than a whole ppm to lower field than the analogous proton in perylene[24,9,10] (*II*) — is certainly consistent with the suggestion of there being a high »ring-current« intensity in ring C of (*I*). Perturbations brought about by condensation of additional rings in one region of a large, condensed, benzenoid hydrocarbon may often have only a second-order effect on the »ring-current« intensities in rings *distant* from the site of the perturbation — though, evidently, this is by no means always the case, as the above comparison between (*I*) and (*II*) indicates.



(I)



(II)

It is these sorts of observations, amongst others, that we aim to rationalise in this paper, by appeal to a well-known argument in perturbation theory,[34] and by invoking some topological considerations. We first examine some properties of imaginary bond-bond polarisabilities[3,17,29] and their relevance in »ring-current« calculations.[17,29] These ideas may be material to the recent resurgance of interest in relative »ring-current« intensities,[28–30] in 'conventional' conjugated-molecules[28,29] and in the newly diagnosed 'spheroidal' C_{50} cluster.[30]

2. PRELIMINARIES ON IMAGINARY BOND-BOND POLARISABILITIES

(i) Polarisabilities and »Bond Currents«

$\bar{\pi}_{(tu)(wv)}$, the mutual, imaginary bond-bond polarisability between two bonds $t \rightarrow u$ and $w \rightarrow v$ of the conjugated system, is defined (see equations (A1) and (A2) of ref. 17b):

$$\bar{\pi}_{(tu)(wv)} = \pi_{tu,wv} - \pi_{tu,vw} + \pi_{ut,vw} - \pi_{ut,wv} \tag{1}$$

in which, for a hydrocarbon with N carbon-atoms and M doubly-occupied orbitals,

$$\beta\, \pi_{tu,wv} = 2 \sum_{I=1}^{M} \sum_{J=M+1}^{N} \frac{c_{tI}\, c_{uJ}\, c_{wJ}\, c_{vI}}{x_I - x_J} \tag{2}$$

where $E_I = \alpha + x_I \beta$ is the energy of the I^{th} Hückel molecular-orbital, $\{c_{tI}\}$ $t = 1, 2, \ldots, N$. For even, alternant hydrocarbons, these expressions simplify, as shown in the Appendix of ref. 17b (equations (A3)—(A5)). $\bar{\pi}_{(tu)(wv)}$ is thus seen to be closely related to the real, mutual bond-bond polarisability, $\pi_{(tu)(wv)}$, earlier proposed by Coulson and Longuet-Higgins.[35] In terms of the $\pi_{tu,wv}$-quantities defined in equation (2), the latter is

$$\pi_{(tu)(wv)} = \pi_{tu,wv} + \pi_{tu,vw} + \pi_{ut,vw} + \pi_{ut,wv} \tag{3}$$

McWeeny stated[3] that there are more relations between the imaginary bond-bond polarisabilities than there are amongst the real ones. By using arguments which rely on the origin independence of bond currents, we may express these relations in general form, as follows.

The secondary field at the origin is given by equation (4.4) of ref. 3, with σ_1 and σ_2 of that equation defined by equation (4.5); (it should be noted that we are here dealing with McWeeny's formulation *before* application of his unitary transformation, much discussed in ref. 2.) By writing the sum of σ_1 and σ_2 in the form*

$$\sigma_1 + \sigma_2 = \sum_{\substack{\text{bonds}\\(tu)}} J_{tu}^{\text{bond}}\, s_{tu}\, k_{tu} \tag{4}$$

we may identify the term

$$J_{tu}^{\text{bond}} = (P_{tu} + \beta\, \bar{\pi}_{(tu)(tu)})\, s_{tu} + \sum_{\substack{(wv)\\ \neq (tu)}}{}' \beta\, \bar{\pi}_{(tu)(wv)}\, s_{wv} \tag{5}$$

as the »bond current« associated with the bond $t \rightarrow u$. (See equation (13) of ref. 17a). This quantity, made use of in ref. 17a, is analogous to the »bond-current densities« discussed in certain SCF-treatments based on the current-density operator (see ref. 36 and § 4.2.3. or ref. 2) *and it is, therefore, independent of origin.* This property is, at first sight, surprising, since J_{tu}^{bond} is seen to depend explicitly upon the area-quantities s_{wv} (the *signed* area of the triangle formed by the origin, in the plane of the molecule, and the carbon atoms w and v; $s_{vw} = -s_{wv}$.) However, it is just this origin dependence of the s_{wv}-terms which necessitates relationships amongst the polarisabilities and bond orders, P_{tu}, if J_{tu}^{bond} is finally to be invariant to a change of origin.

(ii) Monocyclic Case (Benzene)

In the monocyclic case,

$$\sum_{\substack{\text{all bonds}\\(tu)}} s_{tu} = \text{ring area (origin independent)}$$

— see § 4.1.6 of ref. 2, equation (56); this (hexagonal) ring-area is here taken to be unity. This means that the coefficient of each area-term in equation (5) must be identical, and thus, for all bonds (tu),

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* The variables s_{tu}, k_{tu} are as described by McWeeny.[3]

$$P_{tu} + \beta\,\bar{\pi}_{(tu)(tu)} = J \tag{6}$$

and, for all pairs of distinct bonds (tu) and (wv),

$$\beta\,\bar{\pi}_{(tu)(wv)} = J \qquad (7)^{37}$$

where J is now the (unique) »ring-current«. (In the monocyclic case, since no bonds are shared with other rings, the »bond current« associated with each bond is identical to the »ring current« that characterises the ring as a whole.[38])

For a six-membered ring with no symmetry, these considerations imply that 21 distinct quantities have identical values.

(iii) Bicyclic Case (Naphthalene)

Let $i \longrightarrow j$ be an *unshared* bond in ring 1. Then, from equation (5),

$$J_{ij}^{\text{bond}} = (P_{ij} + \beta\,\bar{\pi}_{(ij)(ij)})\, s_{ij} + \underset{\substack{(kl)\\ \neq (ij)\\ \text{(ring 1, unshared bonds)}}}{\Sigma'} \beta\,\bar{\pi}_{(ij)(kl)}\, s_{kl} + (\underset{\substack{(mn)\\ \text{(ring 2, unshared bonds)}}}{\Sigma} (\beta\,\bar{\pi}_{(ij)\,(mn)}\, s_{mn})) + \beta\,\bar{\pi}_{(ij)\,(vw)}\, s_{vw} \tag{8}$$

where $w \longrightarrow v$ is the bond *shared* between rings 1 and 2.
Now from the arguments given on pp. 318 and 319 of ref. 2, it is clear that

$$\underset{\substack{(kl)\\ \text{(ring 1. shared,}\\ \text{and unshared}\\ \text{bonds)}}}{\Sigma\, s_{kl}} = \underset{\substack{(mn)\\ \text{(ring 2. shared}\\ \text{and unshared}\\ \text{bonds)}}}{\Sigma\, s_{mn}} = \text{Constant } (= 1) \qquad (9).$$

For J_{ij}^{bond} to be origin independent, therefore, it follows that all coefficients of ring-1 areas must be equal, and that the coefficients of ring-2 areas are similarly all the same. Hence (remembering that $i \longrightarrow j$, is *any* unshared bond in ring 1):

$$P_{ij} + \beta\,\bar{\pi}_{(ij)(ij)} = J^{1,1} \text{ (say)} \qquad (10).$$

For all other *unshared* bonds, (kl) $(\neq (ij))$, in ring 1:

$$\beta\,\bar{\pi}_{(ij)(kl)} = J^{1,1} \qquad (11).$$

Likewise, for all unshared bonds, (mn), in ring 2:

$$\beta\,\bar{\pi}_{(ij)(mn)} = J^{1,2} \qquad (12).$$

For the sole, shared bond, (wv), since $\bar{\pi}_{(rs)(tu)} = -\bar{\pi}_{(rs)(ut)}$, we must have that

$$\beta\,\bar{\pi}_{(ij)(vw)} = J^{1,1} - J^{1,2} \qquad (13).$$

Finally, since $i \longrightarrow j$ is an *un*shared bond,

$$J_1^{\text{ring}} = J_{ij}^{\text{bond}} = J^{1,1} + J^{1,2} = \text{(say)}\,\beta\,\bar{\pi}_{(12)(23)} + \beta\,\bar{\pi}_{(12)(89)} \tag{14}$$

(on, for example, the carbon-atom numbering-scheme adopted in McWeeny's[3] Figure 2(b)), where J_1^{ring} is the »ring-current« intensity that characterises ring 1. Similar formulae define $J^{2,2}$ and J_2^{ring}. Thus, for an unsymmetrical, naphthalene-like molecule, we obtain $J^{1,1}$, $J^{1,2}$ and $J^{2,2}$; there are now no fewer than 55 distinct quantities which are equal to one of these, or are related to them by simple subtraction!

(iv) Q-Cyclic Case

As will now be shown, the above arguments may be generalised so that, for certain Q-cyclic systems composed of regular hexagons of atoms (qualified later),

$$J_1^{\text{ring}} = \sum_{r=1}^{Q} J^{1,r} \qquad (15).$$

Proof: For any *unshared* bond in ring 1:

$$\begin{aligned} J_{ij}^{\text{bond}} = {} & (P_{ij} + \beta\,\overline{\pi}_{(ij)(ij)})\,s_{ij} + \sum_{\substack{(kl)\\ \neq (ij)\\ \text{(unshared bonds in ring 1)}}}{}' \beta\,\overline{\pi}_{(ij)(kl)}\,s_{kl} \\ & + \Big(\sum_{r=2}^{Q} \sum_{\substack{\text{completely}\\ \text{unshared bonds}\\ (mn) \text{ in ring } r}} \beta\,\overline{\pi}_{(ij)(mn)}\,s_{mn}\Big) + \sum_{\substack{\text{bonds } (st)\\ \text{shared between}\\ \text{ring 1 and other}\\ \text{rings}}} \beta\,\overline{\pi}_{(ij)(st)}\,s_{st} + \sum_{\substack{\text{bonds } (uv)\\ \text{shared between certain}\\ \text{combinations of rings 2}\\ \text{to } Q}} \beta\,\overline{\pi}_{(ij)(uv)}\,s_{uv} \end{aligned} \qquad (16).$$

Again, all terms of the form $\sum s_{wv}$ taken (in the anti-clockwise sense) around a given ring are a constant (assumed here to be unity[39]). Thus, for the bond $i \longrightarrow j$:

$$P_{ij} + \beta\,\overline{\pi}_{(ij)(ij)} = J^{1,1} \qquad (17)$$

and, for (ij) and the completely unshared bonds, $(kl)\ (\neq (ij))$, in ring 1,

$$\beta\,\overline{\pi}_{(ij)(kl)} = J^{1,1} \qquad (18).$$

For the completely unshared bonds (mn) in ring r:

$$\beta\,\overline{\pi}_{(ij)(mn)} = J^{1,r} \qquad (19).$$

For the bonds, (st), shared between ring 1 and some (or, possibly, all) other rings, w,

$$\beta\,\overline{\pi}_{(ij)(st)} = J^{1,1} - J^{1,w} \qquad (20).$$

For the bonds, (uv), shared between pairs of rings, p and q $(p \neq q \neq 1)$,

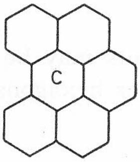
$$\beta\,\overline{\pi}_{(ij)(uv)} = J^{1,p} - J^{1,q} \qquad (21).$$

In equation (16), since the bond (ij) in ring 1 is, by hypothesis, an *unshared* bond,

$$J_{ij}^{\text{bond}} = J_1^{\text{ring}} \qquad (22).$$

Substitution of equations (17)—(21) into (16) and using the fact that $\sum_{\substack{(wv)\\ \text{around ring } r}} s_{wv} = 1$, for all rings, r, then leads to the result embodied in equation (15). □

It should be noted that this formulation applies only if the ring numbered 1 in the above proof contains at least one unshared bond — *i. e.*, it could be applied to, say, benzoperylene (*III*) central ring, C, but not (without modification) to the central ring in coronene (*IV*).



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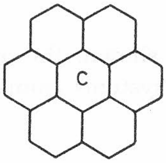
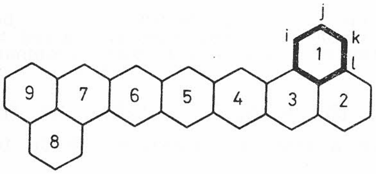


(IV)

A suitable modification is offered in § 2 (vi). In the meantime, in § 2 (v), we give a numerical example that illustrates application of the analysis presented so far.

(v) *Numerical Example*

As an example, we consider the ring indicated in nonazethrene (*V*), and focus attention on the bond (*ij*).



(V)

By computation:

$$P_{ij} + \beta\,\overline{\pi}_{(ij)(ij)} = 0.64069 - 0.56445 = 0.07624$$

and

$$\beta\,\overline{\pi}_{(ij)(kl)} = 0.07624 = J^{1,1}.$$

The other $J^{1,r}$-terms required are listed in Table I.

TABLE I

Some $J^{1,r}$-*terms for nonazethrene* (V)

r	$J^{1,r}$	r	$J^{1,r}$
2	0.01797	6	0.00017
3	0.00303	7	0.00004
4	0.00103	8	0.00001
5	0.00043	9	0.00001

$\sum_{r=1}^{9} J^{1,r}$ is thus 0.09893; since $J^{\text{ring}}_{\text{benzene}}$ in these units is[3] 1/9 (exactly), J_1^{ring} relative to benzene is 0.890 (to three significant figures). This agrees precisely (to the number of significant figures quoted) with the value calculated[40] *via* the full procedure of equation (15) of ref. 17b — an equation that arises *after* application of McWeeny's unitary transformation (see refs. 2, 3, and 17).

(vi) The »Ring-Current« Intensity in a Ring with no Unshared Bonds

We now consider the general case of a ring, such as the central ring (C) in coronene (*IV*), completely surrounded (though not necessarily — as in coronene — symmetrically) by other rings bearing »ring currents« of intensity α, β, γ, δ, ϵ, ζ (all taken to be in an anti-clockwise sense around their respective rings). The central ring bears a »ring current« of intensity J, which is to be determined; it is assumed that the α, β, γ, . . . *etc.* are known, having been calculated *via* the method of § 2 (iv) since (in coronene, at least) all rings surrounding the central one do have at least one unshared bond and hence the assumptions of § 2 (iv) do hold; (but see the end of this sub-section for the procedure to be followed if this is not so).

We focus attention on a particular bond, say BC (Figure 1), in the central ring (regarded, for this purpose, as 'ring 1'); all the previous analysis of § 2 (iv) would then still apply (with 'BC' playing the rôle of '*ij*' throughout) if (a) the word »unshared« were omitted from the opening sentence of the Proof in § 2 (iv), and (b) the term in equation (16) involving summation over »unshared bonds in ring 1«, now also inappropriate, were likewise suppressed. Furthermore, now that the bond (*ij*) in our general treatment is assumed to be shared with another ring, the statement »$J_{ij}{}^{\text{bond}} = J_1{}^{\text{ring}}$« in equation (22) is no longer true, and must be replaced by

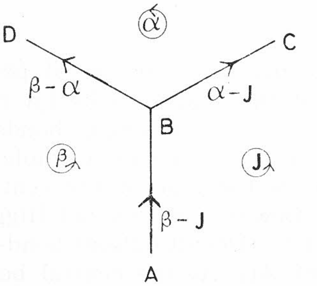


Figure 1. Ring- and bond current in rings and bonds at a junction (*B*) in the central hexagonal ring (bearing »ring current« of intensity *J*) of a general benzenoid hydrocarbon in which this central ring is completely surrounded by other rings and thus has no unshared bonds.

$$J_{ij}^{\text{bond}} = \xi - J_1^{\text{ring}} \tag{23}$$

where ξ is the intensity of the »ring current« in the ring other than the ring labelled '1' that flanks the bond *ij*, and the direction of the bond *ij* is appropriately defined.

Thus, returning to the specific example of the bond BC in coronene, we have, in the terminology of Figure 1,

$$J_{BC}^{\text{bond}} = \alpha - J \qquad (24).$$

and so

$$J = \alpha - J_{BC}^{\text{bond}}$$

In equations (24), α is assumed known and J_{BC}^{bond} is calculable by use of this modified analysis. Similarly, we also have

$$J = \beta - J_{AB}^{\text{bond}} \tag{25}$$

and four analogous expressions in terms of (separately) γ, δ, ϵ and ζ and the currents in the four other bonds in the central ring — though, clearly, only one of these six expressions is actually needed in practice.

In the most general case that could be envisaged, however, even the 'surrounding' rings may themselves be surrounded! Under these circumstances, the procedure just described would have to be applied repeatedly, starting from the 'outside' rings (to which, of course, the analysis of § 2 (iv) applies without modification, for such 'outer' rings do, *a priori,* contain unshared bonds) and working successively inwards. In such a case, we would not enthusiastically recommend this process for actual numerical evaluation of »ring-current« intensities. This is of no great concern, however, for the aim of this discussion has been not so much a computational one but rather to set up, in principle, a method that will be found conceptually convenient for the purposes of conveying our perturbation-theory ideas that are introduced in the next section.

3. HIGH AND LOW »RING-CURRENTS«: PERTURBATION THEORY ARGUMENT

(i) General Considerations

Examination of the structural formulae of perylene (*II*) and peropyrene (*I*) shows immediately that the central links (in ring C) connecting the two naphthalenic moieties are 'essentially single' bonds — *i. e.,* no Kekulé structure may be devised for the molecule as a whole in which these bonds are double — while the same is *not* true of the central links (ring C) in peropyrene. Many years ago, Dewar and Longuet-Higgins[34] showed that Pauling bond-order is proportional to HMO-(Coulson) bond-order predicted by perturbation theory (see also ref. 41). As the central bonds in ring C of perylene (*II*) have zero Pauling bond-order, their (first-order) perturbed Coulson bond-orders would also be zero — but, again, this is not true for the central links in (*I*). Thus, if one were heuristically to think of 'aromaticity' in terms of first-order stabilisation of *energy* by ring formation, ring C in peropyrene would be considered 'aromatic' while ring C in perylene would have to be regarded as 'non-aromatic'.

This is, however, not sufficient, for we are concerned here with large and small *»ring-currents«;* and it is only intuitively likely — and not in any way mathematically obvious — that the two run parallel. In view of the expression

$$J^{1,1} = P_{tu} + \beta\,\overline{\pi}_{(tu)(tu)},$$

any naive attempt to relate J^{ring} to P_{tu} is immediately frustrated by examining computed values of these quantities for a given molecule. It is found that the two terms P_{tu} and $\beta\,\overline{\pi}_{(tu)(tu)}$, making diamagnetic and paramagnetic contributions, respectively, are entirely commensurate in size, and the first decimal-place is always lost in cancellation. Therefore, although it does seem that, in general, P_{tu} and $J^{1,1}$ follow the same trends, it would be most hazardous actually to assume this without further, and less-superficial, investigation.

(ii) Perturbation-Theory Argument

We therefore invoke some previous arguments in perturbation theory[34] in order to examine the values of imaginary bond-bond polarisabilities under these circumstances. Two moieties, *A* and *B*, are imagined to be brought together, whereupon two 'new' bonds, (tu) and (wv), are formed between them, these bonds then being considered to perturb the two original moieties (see Figure 2). For example, if *A* and *B* were both 'naphthalenic' fragments, the resulting molecule could be perylene (*II*); if they were both 'phenalenyl-radical' fragments, peropyrene (*I*) could be formed. *A* and *B* need not, of course, be identical and, indeed, for the moment, we consider them (in general) to be different (but see § 4 (ii)). The individual fragments have the following MO-properties, in terms of the HMO molecular-orbitals $\{\Psi_i\}$ and the LCAO-MO atomic-orbitals $\{\Phi_i\}$:

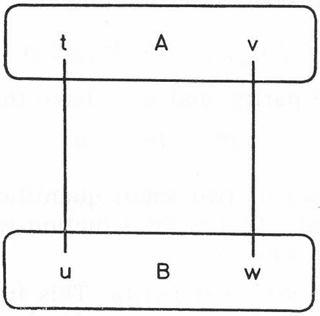


Figure 2. General scheme for bringing together two moieties, *A* and *B*, whereupon two 'new' bonds, (tu) and (wv), are formed between them.

$$\begin{aligned} &\textit{Fragment } A\text{: MO's } \Psi_\mu = \sum_r a_{r\mu}\,\Phi_r\text{: Energies } E_\mu = \alpha + x_\mu\,\beta \\ &\textit{Fragment } B\text{: MO's } \Psi_\varrho = \sum_s b_{s\varrho}\,\Phi_s\text{: Energies } E_\varrho = \alpha + x_\varrho\,\beta \end{aligned} \qquad (26)$$

With this arrangement, the perturbation process[34] leads to

$$\beta\,\overline{\pi}_{(tu)(wv)} = 2\left[\sum_{\mu\in A}^{\mathrm{occ}}\;\sum_{\varrho\in B}^{\mathrm{unocc}} - \sum_{\mu\in A}^{\mathrm{unocc}}\;\sum_{\varrho\in B}^{\mathrm{occ}}\right]\left\{\frac{a_{t\mu}\,b_{u\varrho}\,b_{w\varrho}\,a_{v\mu}}{E_\mu - E_\varrho}\right\} \qquad (27)$$

We shall now confine attention to the case in which *A* and *B* are *alternant-hydrocarbon fragments;* it then follows[34] that '$\overline{\pi}$' between any 'new' bond and any 'old' bond (*i. e.*, one already extant in either of the fragments *A* and *B*) is zero. Consequently, not only will $\beta\,\overline{\pi}_{(iu)(uv)}$ yield $J^{1,1}$, but it will also provide the complete J^{ring} (*i. e.*, »ring-current« intensity) for the newly created ring. For reasons that will become clear in § 4 (i), we further restrict ourselves for the moment to those cases in which both *A* and *B* are *even*-alternant fragments. We may then distinguish three possibilities, according to the 'starring' properties[42] of the atoms in *A* and *B*.

(a) *t, v same parity*[35]; *u, w same parity.* By appeal to the Coulson-Rushbrooke theorem[42], we may write (27) as (*cf.* equation (A3) in the Appendix of ref. 17b):

$$\beta\, \bar{\pi}_{(tu)(wv)} = 4 \sum_{\mu \in A}^{\text{occ}} \sum_{\varrho \in B}^{\text{occ}} \frac{a_{t\mu}\, b_{u\varrho}\, b_{w\varrho}\, a_{v\mu}}{x_\mu + x_\varrho} \qquad (28).$$

In order to appreciate the magnitude of this quantity, we use a mean-value approximation, $(\bar{x})$, for the energies, obtaining

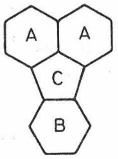
$$\beta\, \bar{\pi}_{(tu)(wv)} \approx P^0_{tv}\, P^0_{uw} / (2\, \bar{x}) \qquad (29).$$

But, as *t, v* have the same parity, and *u, w* have the same parity,

$$P^0_{tv} = P^0_{uw} = 0 \qquad (30).$$

$\beta\, \bar{\pi}_{(tu)(wv)}$ is thus the product of two small quantities, and we have therefore shown that $J^{\text{new ring}}$ *is small.* This is the situation which obtains, for example, in the central ring of perylene (*II*).

(b) *t, v same parity: u, w different parity.* This implies the formation of an *odd-membered new ring,* such as occurs, for example, (as ring C) when fluorathene (*VI*) is formally constructed form naphthalenic (*A*) and benzenoid (*B*) fragments. Immediately,



(VI)

$$\beta\, \bar{\pi}_{(tu)(wv)} = 0 \qquad (31)$$

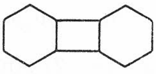
and hence

$$J^{\text{new ring}} = 0 \qquad (32).$$

$J^{\text{new ring}}$ will not, of course, be *precisely* zero, for one of our simplifying assumptions in this discussion has been that all rings have the same area as a standard benzene-hexagon, and this is clearly rather a gross approximation[39] in the case of the five-membered ring in fluoranthene which is only *ca.* 2/3 of the area of a benzene ring.[23] Nevertheless, the »ring-current« intensities in fluoranthene (*VI*) are in practice calculated[11] to be as follows: 0.987 (rings *A*), 0.860 (ring *B*), and 0.050 (ring *C*). These show that a very small »ring-current« (*ca.* one twentieth of the benzene value) is calculated for the five-membered ring.

(c) *t, v different parity; u, w different parity.* With this arrangement the exact expression for $\beta\, \bar{\pi}_{(tu)(wv)}$ is precisely *minus* the quantity on the right-hand side of equation (28); the approximate value of it is thus given by *minus* the quantity on the right-hand side of equation (29) — *i. e.*, $-P^0_{tv}\, P^0_{uv} / (2\, \bar{x})$. We here distinguish two cases:

(α) t, v bonded, u, w bonded. This implies the formation of a *four-membered ring.* In this arrangement, P^0_{tv} and P^0_{uw} are both, in general, large and positive. Therefore, $J^{\text{new ring}}$ *is large and negative* (*i. e.*, paramagnetic). This is the case, for example, with the four-membered ring of biphenylene (*VII*) which



(VII)

has[16] a »ring-current« intensity of —1.81, while the six-membered rings are calculated to bear (diamagnetic) »ring-currents« of *ca.* 0.25. (A more-sophisticated calculation, in which HMO resonance-integrals between bonded atoms are made iteratively self-consistent with corresponding Coulson bond-orders[7], gives qualitatively the same result.)

(β) t, v bonded; u, w separated by three bonds. This will occasion the formation of a *six-membered ring* (4 + 2). In this case, P^0_{tv} is > 0 and large in magnitude; P^0_{uw} is < 0 and medium. $J^{\text{new ring}}$ *is thus positive* (*i. e.*, diamagnetic) *and 'normal' in size.* This is the situation, for example, in the linear acenes (naphthalene, anthracene, *etc.*), the »ring-current« intensities in which, all positive and within 50% of the benzene value, are well documented in the literature.[3,24,5,9,22]

In general, this analysis shows that when the newly formed ring is $4n$-membered (n an integer), $J^{\text{new ring}}$ is < 0 (*i. e.*, paramagnetic), while when it is $(4n+2)$-membered, $J^{\text{new ring}}$ is > 0 (*i. e.*, diamagnetic). This is therefore an extension, to certain $4n$ and $(4n+2)$-rings in *poly*cyclic systems, of the now well-known paramagnetic/diamagnetic nature of the $4n$-/$(4n+2)$-*mono*-cyclic annulenes[31,32], and verifies, *via* different arguments, the very recent treatment and conclusions of Aihara[28] and Mizoguchi[29].

In the next section, we investigate certain circumstances under which the simple perturbation-theory rules established here may break down. Clearly, if, for example, there is any zero-order degeneracy amongst the energy levels of the two fragments A and B, appropriate linear-combinations of these must be taken.

4. SPECIAL CASES OF *A* AND *B* FRAGMENTS

We distinguish here three specific situations:

(i) A, B *both Odd-Alternant Fragments*

If A and B are both odd-alternant fragments, each will have one electron in a non-bonding MO ($E_0 = \alpha + 0\,\beta$). A degeneracy must, consequently, arise and appropriate linear-combinations must, therefore, be taken. It has been shown[31,35] that the removal of this degeneracy leads to non-zero bond-orders between A and B. We must therefore consider how $\beta\,\overline{\pi}_{(tu)(wv)}$ is affected in these cases.

(a) *t, v same parity, u, w same parity.* The formulae are essentially as before (§ 3 (ii), case (a), equations (28) and (29)), with a slight modification. In particular,

$$\beta\,\overline{\pi}_{(tu)(wv)} = 2a_{t0}b_{u0}b_{w0}a_{v0}/(2\bar{x}_0) + \text{other terms} \qquad (33)$$

(the subscript '0' stands for non-bonding MO's on both *A* and *B*). $\beta\,\pi_{(tu)(wv)}$ will be dominated by the leading term explicity written in equation (33), because $\bar{x}_0$ will, in general, be small. If *t* and *v* are separated by two bonds, and *u* and *v* are similarly segregated, a *six-membered ring* results; then:

$$a_{t0}a_{v0} < 0; \qquad b_{u0}b_{w0} < 0,$$

and hence (and, in general, for a ($4n+2$)-ring) $J^{\text{new ring}}$ *is large and positive*. This is the situation which obtains, for example, in the central ring (C) of peropyrene (*I*) and it is also the case, in general, with the ($4n+2$)-annulenes. (For a $4n$-ring, $J^{\text{new ring}}$ is, however, still large and *negative* — see (c), below.)

It will now be clear why, in § 3 (ii) (especially in case (a)), we made the stipulation that *A* and *B* shall be *even*-alternant fragments. It is the fact that the central ring of perylene (*II*) is constructed by joining two even-alternant fragments (§3 (ii), case (a)) while that of peropyrene (*I*) is the result of combining two *odd*-alternant fragments (§ 4 (i), case (a)) which is responsible for the very small »ring-current« in ring C of (*II*) and the very large one in ring C of (*I*).

$$\left.\begin{array}{l}\text{(b) } t,\ v \text{ same parity; } u,\ w \text{ different parity}\\[4pt] \text{(c) } t,\ v \text{ different parity; } u,\ w \text{ different parity}\end{array}\right\}\ \text{The non-bonding}$$

MO here has no effect and the conclusions are, therefore, the same as for the general case.

(ii) A *and* B *Identical*

If *A* and *B* are identical fragments, all zero-order levels are degenerate in (at least) pairs, and sums and differences of these levels have, therefore, to be taken in the perturbation process. Since all pairs are fully occupied, the effect on the bond orders exactly cancels; the effect on the imaginary bond-bond polarisability-formulae is thus to change the energies in the denominators. In general, however, the effect is small and the previous qualitative conclusions are valid; (see, for example, the cases of peropyrene (*I*) and perylene (*II*), above — § 4 (i), case (a), and § 3 (ii), case (a), respectively).

(iii) A *and/or* B *Large, Coloured, with Low Ionisation-Energy*

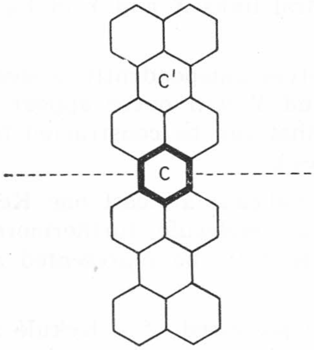
As the moieties *A* and *B* become larger, the lowest-occupied MO has an x_μ-value never exceeding 3, but the highest-occupied molecular-orbitals (HOMO's) can have steadily decreasing x_μ, and the approximation of having the $\bar{x}$-term in the denominator (as, for example, in equation (29)) becomes less valid. The case of quaterrylene (*VIII*) illustrates this.
The HOMO has

$$x' = 0.35$$

while, after degenerate perturbation-theory, the higher of the two pairs of levels has

$$x' = 0.24.$$

It is, therefore, not surprising that (although it is still fairly small) $J^{\text{new ring}}$ for ring *C* of (*VIII*) (calculated[40] to be 0.447, to three significant figures)



(VIII)

is distinctly larger than the corresponding quantity (0.239) for ring *C* of perylene (*II*).

5. CONNECTION BETWEEN MOLECULAR-ORBITAL TREATMENT AND 'BOND-FIXATION' TERMINOLOGY

It was seen in § 3 (ii) (case (a)) that, in the context of simple MO-theory, when two even-alternant fragments are joined together in such a way as to form a new six-membered ring, like, for example, ring *C* in perylene (*II*), the »ring-current« intensity in that ring is small; conversely, it was shown in § 4 (i) (case (a)) that when *A* and *B* are both odd-alternant fragments the new ring (such as ring *C* in peropyrene (*I*)) bears a large »ring-current«. In general, even-alternant fragments have at least one Kekulé structure,[34] while odd-alternant fragments are radicals in the sense that no complete Kekulé-structure may be devised for them. We may therefore say immediately that when fragments *A* and *B* are linked together to form a six-membered ring (see, schematically, Figure 3), if fragments *A* and *B* both have a Kekulé structure then the »ring current« in ring *C* will be small, whereas if *A* and *B* are both radicals (*i. e.*, are therefore devoid of Kekulé structures) the »ring-current« intensity in ring *C* will be large. We may pursue this reasoning a little further in order to transgress the realms of MO-theory language into that of Valence-Bond Resonance-Theory and in order to say something about

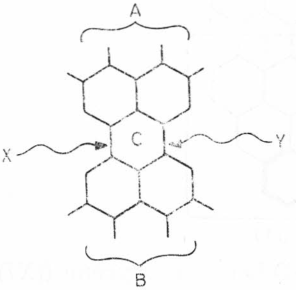


Figure 3. General scheme for linking together fragments *A* and *B* to form a 'new' ring, *C*, containing bonds *X* and *Y* that are shared with no other rings.

'bond fixation' in the central links *X* and *Y* of Figure 3. We may distinguish three cases:

1) If *A* and *B* are themselves independently possessed of a Kekulé structure, the connecting links *X* and *Y* will never appear other than as single links in any Kekulé structure that can be constructed for the composite molecule. (This is the 'perylene' case).

2) If *A* and *B* are both radicals, at least one Kekulé structure can always be devised for the composite molecule; furthermore, in this Kekulé structure, either *X* or *Y* will, of necessity, be represented as a *double* bond. (This is the 'peropyrene' case).

3) If, of *A* and *B*, one is possessed of a Kekulé structure and the other is a radical, then the composite molecule is also a radical and hence need not further concern us here.

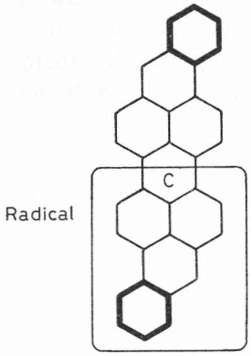
6. NUMERICAL EXAMPLES AND COMPARISONS WITH EXPERIMENT

(i) Examples Related to Perylene (II) and Peropyrene (I)

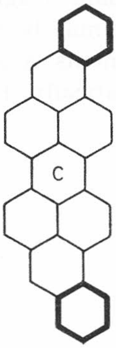
The points made in § 5 are illustrated by the following examples:

(a) 1,2;8,9- and 1,2;9,10-Dibenzoperopyrene ((*IX*) and (*X*))

If two further rings are added to peropyrene (*I*) in such a way as to preserve the radical nature of fragments *A* and *B*, giving, for example, (*IX*) or (*X*), the »ring-current« intensities in the central ring, *C*, remain large — a full calculation[40] predicts the intensity of the current in rings *C* of (*IX*) and (*X*) to be 1.377 and 1.345, respectively.



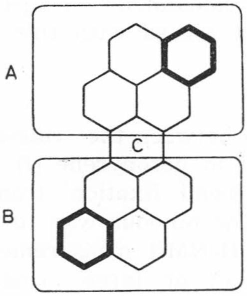
(IX)



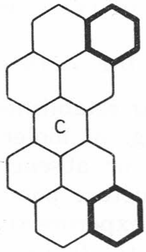
(X)

(b) 1,14;7,8- and 1,14;10,11-Dibenzoperopyrene ((*XI*) and (*XII*))

If two further rings are considered formally to be added to peropyrene (*I*) in such a way as to destroy the radical nature of the fragments *A* and *B*, so that Kekulé structures may then be written for them, the situation in § 4 (i) (case (a)) is transformed to that described in § 3 (ii) (case (a)) — *i. e.*, a 'peropyrene' arrangement has been converted to a 'perylene' one and, as a result, the »ring-current« intensity in the central ring, *C*, falls dramatically. Thus, if two rings are formally added to peropyrene to give (*XI*) or (*XII*), the fragments *A* and *B* that result both possess full Kekulé-structures



(XI)



(XII)

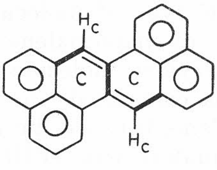
(in fact, *A* and *B* both have the carbon-atom connectivity of pyrene) and the »ring-current« intensity in ring *C* (calculated[40] to be 0.311 for both (*XI*) and (*XII*)) is, accordingly, very similar to that in the corresponding ring (*C*) in perylene (*II*). In fact, despite their names, (*XI*) and (*XII*) might, in this respect, more properly be regarded as being formally derived from perylene, rather than peropyrene.

(3) Other Examples: The molecule terrylene (*XIII*) might usefully be considered as one of the 'perylene' type of molecules, in which fragment *B* has the carbon-atom connectivity of naphthalene while fragment *A* has the carbon-atom skeleton of the perylene molecule itself. Accordingly, the »ring-current« intensity in ring *C* is calculated[40] to be 0.321 — not as low as in the corresponding ring in perylene, because the *B*-fragment is larger (§ 4 (iii)). In the same way, ring *C* in quaterrylene (*VIII*) may be considered to be of the 'perylene' type, since it is formed from fragments *A* and *B*, each of which has a Kekulé structure — in fact, in this case, both the fragments *A* and *B* have the carbon-atom skeleton of the perylene molecule itself! As discussed in § 4 (iii), however, both fragments are large and so the »ring-current« intensity in ring *C* of (*VIII*), though still quite small (0.447), is significantly larger than that (0.239) in the central ring, *C*, in perylene (*II*). This kind of argument can be taken further: ring *C′* of (*VIII*) might be thought of as being formed, *via* the sort of perturbation process we are considering, from a 'naphthalenic' fragment and from a fragment that had the carbon-atom connectivity of the terrylene molecule (*XIII*) — each of which is itself pos-

sessed of a Kekulé structure. The low calculated[40] »ring-current« intensity (0.353) in ring *C′* of (*VIII*) is entirely in accord with this view.

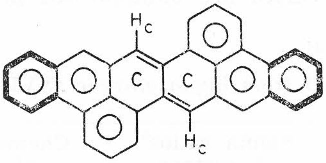
(*ii*) *Examples in the Zethrene Series*

We have so far established a relation between the »ring-current« intensity in the central rings of molecules related to peropyrene (*I*) and perylene (*II*) and the presence or absence of 'single-bond fixation' from the resonance-theory Kekulé-structure point of view. The obvious way to attempt to verify these predictions experimentally is by ^{1}H-NMR measurements. However, in molecules related to (*I*) and (*II*) the 'small' or 'large' »ring-current« is in a ring (the central one) which has *no* protons attached to it; hence, the »ring-current« intensity in this ring has only a second-order effect on the chemical shifts of the protons (all attached to other rings) in these molecules. We therefore attempt to extend these ideas to another series of hydrocarbons in which, on simple VB-Resonance-Theory concepts, there are fixed single *and* double bonds *in rings to which protons are directly bonded:* predictions on this type of molecule are, therefore, more susceptible to experimental test. Such a series is zethrene (*XIV*) — see also refs. 12 and 17b — and its homologues. In (*XIV*) the bonds in rings *C* indicated by double lines are always double, and those depicted with thick, single lines are always single, in any Kekulé structure that can be devised for the molecule as a whole.[43] The calculated »ring-current« in rings *C* is only[12,17b] 0.365; accordingly, the ratio[2] (B'_r/B'_{benzene}) for the protons (H_c) attached to rings *C* in zethrene is calculated[12] to be only 0.853; from equation (2) of ref. 10 this implies a chemical shift for this proton of about δ 7.0 — *i. e.*, upfield of benzene (δ 7.27[44]). Now formally condensing two further rings on to zethrene in such a way as to preserve the 'bond-fixation' — *e. g.* forming 4, 5; 11, 12 dibenzozethrene (*XV*) — leaves the »ring-current« intensity in the central rings (*C*) essentially unchanged[40] (0.363), and the 'sigma ratio'[2,10] (B'_r/B'_{benzene}) of the protons indicated, attached to these central rings, is now 0.915, implying (from equation (2) of ref. 10) a chemical shift of *ca* δ 7.1. The protons H_c in (*XIV*) and (*XV*) thus both have sigma ratios *lower* than the benzene proton (sigma ratio of unity) which is at the lower end of the range (1.0—2.1) of sigma ratios previously encountered.[10,12,13,22,45] If, however, two further rings are formally added to zethrene (*XIV*) in such a way as to *remove* the bond fixation — yielding, for example, 3,4;9,10 dibenzozethrene (*XVI*) — the calculated »ring-current« intensity in the central ring goes up dramatically to 1.355, and the sigma ratio of the proton attached to this central ring is as high as 2.170, which results (after application of equation (2) of ref. 10) in a predicted ^{1}H-NMR chemical-shift of δ 9.05. This is *also* outside the range (1.0—2.1) of previously encountered sigma-ratios — but in the *opposite* di-

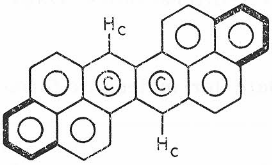


(XIV)

rection from that of H_c in (*XV*). We thus arrive at the rather entertaining observation that, by taking (*XV*) and simply changing slightly the position of substitution of two of the rings to give (*XVI*), the chemical shift of the protons marked »H_c« in (*XV*) and (*XVI*) is caused to leap-frog the entire range of previously calculated sigma-ratio values!



(XV)



(XVI)

The chemical-shift difference between the protons H_c in (*XV*) and (*XVI*) is thus predicted to be *ca.* 2.0 ppm. Since, under the appropriate experimental conditions,[44–47] chemical shifts in these molecules may be measured to within 0.005 ppm, this prediction in principle affords the opportunity of a singularly reliable experimental test. Proton chemical-shifts for zethrene (*XIV*) are available,[48] as are those for 4,5;11,12 dibenzozethrene (*XV*) (by the kind help of the late Professor E. Clar[49]); however, 3,4;9,10 dibenzozethrene (*XVI*) has, unfortunately, not been synthesised, and, according to Clar[49] and Schmidt,[50] it is likely to be a difficult molecule to make. It is hoped that the central importance of this molecule in testing the theoretical implications of »ring-current« theory discussed in the present paper may provide some incentive for its eventual synthesis.[51]

We have so far neglected to mention that the protons H_c in (*XV*) and (*XVI*) (as well as in (*XIV*)), all being what, on Martin's nomenclature,[52] are called 'Hα3' protons, will be involved in van der Waals steric-interactions which are thought[2,6,7,9,10,24,31,45,53] to displace the ^{1}H-NMR shifts of such protons *ca.* 0.6 ppm downfield (*i. e.*, to *higher* δ-values[54]). Since these steric interactions, if they are genuine, will be approximately the same for the protons H_c in both (*XV*) and (*XVI*), our prediction still stands that the chemical shifts of these two sets of protons should *differ* by *ca.* 2.0 ppm.

An exactly analogous trend is observed in a series of molecules ((*XVIII*) and (*XIX*)) similarly derived from heptazethrene (*XVII*). This series has the desirable feature that each molecule in it contains protons, H_d, attached to rings (*D*) bearing (in the case of (*XVII*) and (*XVIII*)) low, or (in the case of (*XIX*) high, »ring-currents«, which are not subject to any hydrogen-hydrogen steric-interactions. Data for this series are summarised in Table II.

TABLE II

Data for molecules formally derived from heptazethrene (XVII)

Molecule	»Ring current« in rings[a]		Sigma ratios[b] of protons		Chemical shifts[c] of protons	
	C	*D*	H_c	H_d	H_c	H_d
Heptazethrene (*XVII*)	0.577	0.410	0.985	0.810	δ 7.20[d]	δ 6.92
4,5; 12,13 Dibenzoheptazethrene (*XVIII*)	0.574	0.405	1.021	0.849	δ 7.25[d]	δ 6.98
3,4; 11,12 Dibenzoheptazethrene (*XIX*)	1.447	1.252	2.284	1.941	δ 9.22[d]	δ 8.69

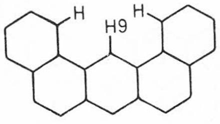
[a] By the full method described in note 40.

[b] From the calculated »ring-currents« in the previous two columns, equation (3) of ref. 22a, and the procedure described on page 793 of that reference.

[c] From the sigma ratios in the previous two columns, and equation (2) of ref. 10.

[d] Exclusive of a steric contribution of *ca.* 0.6 ppm downfield[10] (*i. e.*, the observed shift of H_c in heptazethrene would be expected to be *ca.* δ (7.20 + 0.60) = *ca.* δ 7.8).

From Table II it is seen that the chemical shifts of H_c in (*XVIII*) and (*XIX*) should differ by about 2.0 ppm, while those of H_d in the two molecules should differ by *ca.* 1.7 ppm. The H_c-protons suffer steric interactions and so the actual shift of H_c in (*XIX*) would be in the region of δ 9.8 — nearly as high a δ-value as that of proton 9 in 1,2;7,8 dibenzanthracene (*XX*) which partially achieves this high δ-value by experiencing a *double* steric-interaction.[9,10,53f] The H_c protons of (*XVII*) and (*XVIII*) appear from Table II to resonate to high field of benzene; in practice, because of the steric interactions just mentioned, they will be to low field of the benzene signal (δ 7.27[44]). The H_d-protons of (*XVII*) and (*XVIII*) are, however, sterically *unhindered* and hence would be expected to come into resonance at the δ-value indicated in the Table; these protons would thus resonate *ca.* 0.3 ppm to *high field* of benzene — a quite remarkable occurrence for a proton *in the molecular plane* of a *planar*, conjugated hydrocarbon composed entirely of

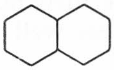


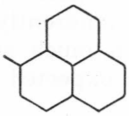
(XX)

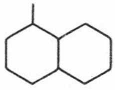
condensed, hexagonal rings and, furthermore, containing as many as *nine* of them! (*Cf*. refs. 12, 14 and 46).

(iii) Some Apparent Difficulties and Ambiguities with Zethrene

Having seen that trends in the zethrene series, deduced from complete »ring-current« calculations[40] *via* the McWeeny method, are particularly susceptible to experimental test, we investigate how far these predicted high and low »ring-currents« may be rationalised by the perturbation arguments of §§ 3 and 4. The first difficulty we encounter is that there appear to be two alternative (but ostensibly equivalent) ways of partitioning zethrene —


(XXI)


(XXII)


(XXIII)


(XXIV)

into two even-alternant fragments (naphthalene (*XXI*) and methylenephenalene (*XXII*), as in Figure 4(a), or into two odd-alternant parts (1-naphthyl methyl (*XXIII*) and phenalenyl (*XXIV*), as in Figure 4(b). In both cases, the new ring considered to be formed during the perturbation process in which such fragments are brought together is labelled *R*.

In the even-alternant/even-alternant dissection, t and v (Figure 4(a)) have the same parity, and u and w have the same parity. The situation is thus that described in § 3 (ii) (a) and $J^{\text{new ring}, R}$ is predicted to be *small* — as indeed is found from a simple »ring-current« calculation.[12,17b]

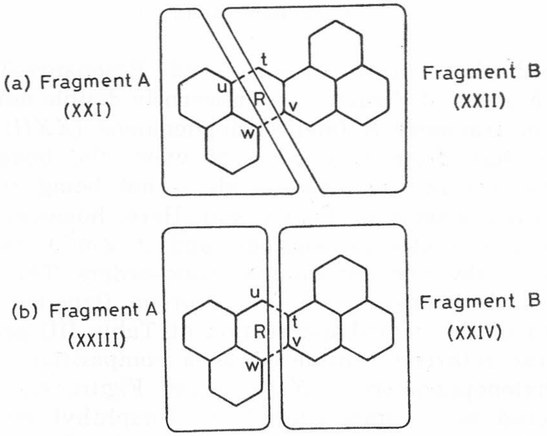


Figure 4. Alternative ways of fragmenting zethrene (*XIV*).

In the odd-alternant/odd-alternant decomposition, t and v (Figure 4(b)) have different parity, as do u and w. This is the arrangement described in § 3 (ii) (c) (β) and thus implies the prediction of a (diamagnetic) »ring-current« intensity, $J^{\text{new ring}, R}$, which is of 'normal' size — an incorrect deduction.[12,17b]

To resolve this apparent contradiction, we examine more closely which bonds are being broken when the composite molecule under investigation is fragmented in the perturbation process envisaged, in which we make the approximation:

$$\text{Molecule } M \approx \text{Fragment } A + \text{Fragment } B.$$

If, as in Figure 4(a), zethrene is split to give naphthalene (*XXI*) (*A*) plus methylenephenalene (*XXII*) (*B*), the bonds broken are inherently 'single' (see the Kekulé structure shown as (*XIV*)). This is therefore a weak perturbation and perturbation theory should hold well — this is in fact the case. If, however, as in Figure 4(b), the other pair (*tu*, *vw*) of available bonds in zethrene is severed, yielding 1-naphthyl methyl (*XXIII*) (*A*) and phenalenyl (*XXIV*) (*B*), the first bond broken (*tu*) is now inherently 'double' (and hence will have a larger bond-order). This is thus a much stronger perturbation, and perturbation theory may consequently be expected to hold less well — as, indeed, *a posteriori*, was found, above.

This is best illustrated by considering a detailed diagram of the newly created ring *R* in the molecule *M* for the 'zethrene' type of fragmentation, shown in Figure 5.

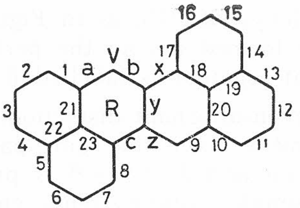


Figure 5. The newly created ring *R* in a general molecule *M* for the 'zethrene' type of fragmentation.

It may be noted that, in a Valence-Bond Resonance-Theory (VB—RT) approach, bonds *b* and *z* of Figure 5 are inherently double not only in zethrene (*XIV*), but also in fragment *B* (methylenephenalene (*XXII*)) of the scheme shown in Figure 4(a); from this point of view, the bonding structure in the immediate vicinity of the 'new' bonds is not being strongly perturbed in the fragmentation scheme of Figure 4(a). Here, however, we are actually performing molecular-orbital calculations, and it would, therefore, be more material to tabulate the relevant Coulson bond-orders. This is done in Table III, which lists such bond-orders[55] for zethrene (labelled as in Figure 5) (left-hand column of the right-hand section of Table III) and for the corresponding bonds for zethrene considered as a composition from naphthalene (*XXI*) plus methylenephenalene (*XXII*), as *per* Figure 4(a) (middle column), and also considered as a composition from 1-naphthyl methyl (*XXIII*) and phenalenyl (*XXIV*), as *per* Figure 4(b) (right-hand column of Table III). Of the bonds *a*, *b*, *x*, *y* and *z* in the vicinity of the 'new' bonds, changes in bond order are, in general, much larger for the scheme of Figure 4(b) than for that of Figure 4(a); and the new bond *b* in the former scheme is strong. Of the bonds more-distant from the newly created bonds, changes in bond order between the composite molecule and its fragments are significantly greater for scheme (b) of Figure 4 than for scheme (a) of that Figure in the case of

TABLE III

Coulson bond-orders[55] *in zethrene and its constituent fragments*

Bond[a] (Labelled as in Figure 5)	Zethrene (Figure 5)	Coulson bond-order of corresponding bonds[a]	
		Composition from naphthalene (*XXI*) plus methylene-phenalene (*XXII*), as *per* Figure 4(a)	Composition from 1-naphthyl methyl (*XXIII*) plus phenalenyl (*XXIV*), as *per* Figure 4(b)
a	0.51	—[b]	0.69
b	0.69	0.78	—[b]
c	0.42	—[b]	—[b]
x	0.42	0.40	0.55
y	0.47	0.46	0.67
z	0.69	0.80	0.67
1	0.60	0.72	0.53
2	0.65	0.60	0.67
3	0.69	0.72	0.67
4	0.55	0.55	0.54
5	0.55	0.55	0.56
6	0.70	0.72	0.71
7	0.64	0.60	0.62
8	0.63	0.72	0.69
9	0.51	0.47	0.55
10	0.60	0.63	0.55
11	0.65	0.64	0.67
12	0.69	0.70	0.67
13	0.55	0.55	0.55
14	0.55	0.55	0.55
15	0.70	0.71	0.67
16	0.64	0.63	0.67
17	0.63	0.64	0.55
18	0.54	0.54	0.53
19	0.53	0.52	0.53
20	0.51	0.52	0.53
21	0.51	0.55	0.43
22	0.53	0.52	0.53
23	0.54	0.55	0.61

[a] In columns 3 and 4, the bond orders are as calculated for the fragments, but are identified according to the corresponding bonds, as labelled in Figure 5.

[b] Bonds denoted '—' are those deleted in the particular fragmentation process under consideration!

bonds 17, 21 and 23; (though it may be observed that bonds 1 and 2 are more greatly perturbed in the even-alternant/even-alternant decomposition illustrated in Figure 4(a)). Overall, though, the first of the two alternative fragmentations shown in Figure 4 seems, on balance, to occasion the milder perturbation.

Consideration of heptazethrene (*XVII*) and appropriately annellated homologues (*e. g.*, (*XVIII*), but not (*XIX*)) shows clearly that the same arguments apply. In fact, they do so more strikingly; for, whereas naphthalene (*XXI*) has no inherently single- or double-bonds, when heptazethrene (*XVII*) is split into two even-alternant fragments, they are *both* methylenephenalene

(*XXII*), so that *two* sets of bonds similar to b and z, and x and y, in Figure 5, *retain* their inherently double- or single-bond character (see the structural formula of (*XVII*)).

To generalise further, it would appear that the choice of fragmentation available in zethrene occurs whenever there arises the arrangement depicted around the new ring R in Figure 5; ring R can be created either by forming bonds a and c, or bonds b and c. We are concerned only with molecules M that are *even* (and, here, actually, *even alternants*); thus, fragments A and B in the two cases — but not necessarily respectively — are even plus even or odd plus odd (in all cases, alternants). Therefore, the following generalisation can be made: if a composite molecule M can be formed by combining fragments A and B (in the process of which a new ring is created) with fragments A and B both even alternants *or* fragments A and B both odd alternants, the former should be chosen, because the perturbation approximation

$$\text{Molecule } M \approx \text{Fragment } A + \text{Fragment } B$$

will be better in that case. Furthermore, whenever carbon-atom V in Figure 5 bears a proton — the case in which we are especially interested — and R is an interior ring, this dichotomy *must* always occur.

7. CONCLUSIONS

In this paper we have succeeded in providing a theoretical basis for relating 'high' and 'low' »ring-current« intensities to intuitive Valence-Bond Resonance-Theory ideas about 'bond fixation'. It should be noted that this aim has *not* been achieved by devising a »ring-current« formalism that is itself actually based on a VB-RT wave-function. The philosophy that we have adopted here has been

(1) To identify, and classify, those situations in which simple MO-theory predicts specific rings in conjugated hydrocarbon-systems to have exceptionally high or low »ring currents«, and then

(2) To use what might be termed 'topological' arguments that rely simply on the carbon-atom connectivities of the conjugated systems in question to show that the situations identified in (1), above, are just those in which the absence or presence of VB-RT 'bond-fixation' is to be expected.

In invoking these topological considerations, we have implicitly been making use of, though have not specifically referred to, the techniques of graph theory (to which appeal was also made in the very recent work of Aihara[28] and Mizoguchi[29]). In ref. 17b, it was concluded that the »ring-current« index is *not* a completely graph-theoretical quantity, even when a purely topological wave-function[17b,56] (such as the simple Hückel one adopted in the present calculations) has been used to compute it. This is because the expression for the »ring-current« intensity based on such a wave function (equation (15) of ref. 17b) explicitly involves the *areas* of the various rings of the conjugated system, as well as the bond orders and imaginary bond-bond polarisabilities derived from the topological wave-function (see the Appendix of ref. 17b). Furthermore, before these bond orders and polarisabilities may be calculated from the eigenvectors and eigenvalues of the topological wave-function,[17b,20,56] some external prescription — 'external', that is, to the topological considerations — such as the *Aufbau* Principle is additionally required in order to distribute the π-electrons of the system amongst the available topological orbitals (eigenvalues). (This aspect has been investigated in some detail by one of the present authors and Rouvray, and others[57]). The point we wish to make in conclusion, however, is that in dealing entirely with the condensed, benzenoid hydrocarbons (to which class 20 of the 24 species specifically referred to in this paper belong) we assume that all ring areas are approximately the same as the area of a standard benzene-hexagon. In this very special case, therefore, *once given* the *Aufbau* Principle,[57] »ring-current« intensities calculated from a simple HMO ('topological') wave-function[17b,20,56] are dependent only on the carbon-atom connectivity (*i. e.*, the so-called 'topology') of the benzenoid system in question because *all* rings in such a molecule are taken to have unit area. A comparison between the predicted ^{1}H-NMR chemical-shifts of the protons attached to ring *C* in (*XVIII*) and (*XIX*) reveals just how dramatic the consequences of such changes in carbon-atom connectivity can be (§ 6 (ii)). Finally, if the occasional five-membered ring (area *ca.* 0.66 that of a benzene hexagon) and/or seven-membered ring (area *ca.* 1.40 benzene-hexagon units) were present in a molecule consisting predominantly of hexagonal, benzenoid rings, the error introduced into calculated »ring-current« intensities by neglecting these differences in ring area would never be greater than 40%, and, because of the way in which the ring-area factor plays its part in determining »ring-current« sizes, would usually be considerably less than this. That is why, in proposing the qualitative and semi-quantitative arguments about 'high' and 'low' »ring-currents« in §§ 3 and 4, it was not considered necessary to make explicit reference to invidual ring-areas.

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SAŽETAK

Racionalizacija relativnih veličina struje prstenova kod policikličkih konjugiranih ugljikovodika

C. W. Haigh i R. B. Mallion

Postavljen je teorijski okvir za proučavanje pojavljivanja relativno visokih i niskih intenziteta struje prstenova, koje se npr. susreću u središnjim prstenovima peropirena i perilena. Taj se teorijski pristup temelji na intuitivnim idejama teorije valentnih struktura i teorije molekulskih orbitala. Postupak se sastoji od dva koraka: *(i)* Najprije se identificiraju i klasificiraju oni slučajevi kod kojih je jednostavna teorija molekularnih orbitala predvidjela one prstenove kod konjugiranih ugljikovodika koji bi trebali imati izuzetno visoke i niske struje prstenova i *(ii)* Upotrebom topologijskih argumenata pokaže se da je gornji rezultat jednostavna posljedica naročite povezanosti atoma u pojedinom konjugiranom sustavu.