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THE PROPERTIES OF POLYCYCLIC HYDROCARBONS: ON THE THEORY OF INCREMENTAL METHODS

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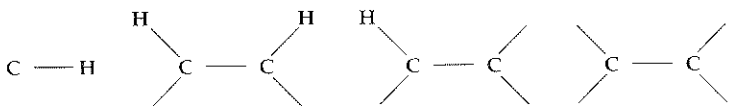
ABSTRACT

A short review of some incremental methods of estimating the properties of polycyclic conjugated hydrocarbons is given in order to introduce the conjugation circuits model. A quantum derivation of this model is outlined and its applications to the prediction of resonance energies and magnetic ring currents are discussed briefly. An extension of the conjugation circuits model is presented to improve on the description of the magnetically induced currents in benzenoid polycyclic hydrocarbons.

INTRODUCTION

Incremental methods for the calculation of molecular properties are used extensively in chemistry. For the calculation of thermodynamic properties and, particularly, of binding energies, the method [1] which is followed usually consists of considering (i) the sum of bond energies, (ii) the destabilization energies associated with steric hindrance or angular strain, and (iii) the stabilization energies such as those due to electron delocalization.

Condensed polycyclic hydrocarbons constitute a class of molecules where electron delocalization over the whole molecule is well known to play an important role. However, bond-energy schemes have been used with considerable success. Tatevskii et al. [2] and McGinn [3] have proposed a scheme where three types of aromatic carbon–carbon bonds are considered (Scheme 1).



Using the values proposed by Cox and Pilcher [1] for these increments, the estimated binding energies of molecules up to four rings may deviate by as much as 6 kcal mol^{-1} (in the case of 3,4-benzphenanthrene). Bernstein [4]

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proposed a more elaborate method, where the carbon–carbon bond increments are made to depend on the π-bond order of that particular bond and the adjacent ones; the results [1], however, do not show any improvement relative to the previous one.

Further improvement in the quantitative description and, especially, in the understanding of the behaviour of these systems does not appear possible if the idea of adding up regional increments is preserved. The alternative consists of some sort of global analysis. This is done implicity, when a standard method of calculation is used. Even in the simple Hückel molecular-orbital method, the adjacencies matrix used covers the whole molecule, as do the state functions built as a result of the calculation. In the valence-bond method, each structure considered also covers the whole molecule and no regional incremental method seems to be devisable to describe the molecular properties.

The method of conjugation circuits counting [5–8] is the most successful attempt at devising a simple system of increments for the properties of polycyclic conjugated hydrocarbons. Increments are not associated with particular regions or fragments of the molecule but with paths that may extend over the entire molecule. These paths are devised from the Kekulé structures associated with the molecule. The method has been used for resonance energies [7–9] and magnetic ring currents [5,6], either in the framework of a simplified version of valence-bond theory [9], or in graph-theory language [8].

Another graph-theory inspired concept is the so-called topological resonance energy [10]. Here, the always ambiguous definition of a reference energy, E_{ref}, to compute the resonance energy, E_{R}, as the difference $E_{\text{R}}=E-E_{\text{ref}}$ is solved by special use of the Sachs' formula [11] for the coefficients of the characteristic polynomial (which is associated with, and has the same roots as, the determinant of the adjacencies matrix). This formula allows the construction of the characteristic polynomial by the enumeration of certain subgraphs of the molecular graph. By suppression of the subgraphs that contain cycles, an acyclic polynomial is obtained. The difference between the roots of the two polynomials gives a measure of the effect of the cycles upon the energy, the so-called topological-resonance energy. This quantity correlates well in most cases with more conventional measures of the resonance energy [12,13]; it may be argued that the method evaluates the effect of the cyclic structures uncontaminated by other effects. However, it should be stressed that it is not possible, in general, to associate a graph with the acyclic polynomial and thus a reference chemical structure may not exist.

In the following section, an outline of the quantum theory of the conjugation circuits model is presented and in the final section an extension of this model is introduced for the case of benzenoid polycyclic hydrocarbons.

QUANTUM THEORY OF THE CONJUGATION-CIRCUITS MODEL

A simplified version of valence-bond theory may be used to lead to the model of the conjugation circuits. The great simplifications required may raise sus-

picion about their justification or the soundness of the final results in relation to the initial formalism. This type of difficulty has been raised about resonance theories [14,15] which do sometimes appear to follow molecular-orbital theory more closely than (more) rigorous valence-bond theories. There is, however, agreement about the good quality of the results obtained through this type of approach and, for the present application, an invaluable insight to the problem is gained.

Consider $2n$ π-electrons in a structure with N C–C conjugated bonds. From the ensemble of valence-bond structures, consider at this stage the Kekulé structures only. The ground-state energy may be obtained as the lowest root of the secular determinant $|H_{ij}-E\ S_{ij}|$. To compute the Hamiltonian and overlap matrix elements, the superposition of structures i and j is examined to identify the cycles (or circuits, as we prefer to call them in this context) of double bonds that are found. Circuits may have any size with an even number of sides, $m=4, 6, 8, \ldots$, etc. The case of a superimposed double bond will be also considered as a degenerate circuit with $m=1$.

The H_{ij} matrix element is then easily calculated [16] as

$$H_{ij}=2^{c-n}\{Q+3/2\alpha\textstyle\sum_{\nu}(m_{\nu}-e_{\nu})-1/2\alpha\ N\} \tag{1}$$

where the summation in ν runs over all the c circuits identified in the superposition ij and e_{ν} is the number of bond connections between nodes of the circuit ν such that the number of sides in each fragment of the circuit is even (e.g. $e_{\nu}=1$ for the 10-sided circuit, $m=10$, of azulene). The overlap-matrix element is simply given by

$$S_{ij}=2^{c-n} \tag{2}$$

If we assume that the ground-state wavefunction is well represented by an admixture of all Kekulé structures with equal weights, its energy, E_{RT}, is given by

$$E_{RT}=\textstyle\sum_{ij}H_{ij}/\sum_{ij}S_{ij} \tag{3}$$

This approximation has been shown [9] to give very good results, introducing errors typically not larger than 2% for the kind of systems we consider here. Equation (3) has been used for direct calculation in the resonance theories, giving results surprisingly close to more sofisticated SCF-MO formalisms [17].

As the matrix elements H_{ij} are computed in terms of the circuits found in the corresponding superposition, eqn. (3) lends itself to alternative forms in terms of increments associated with those circuits. It may be easily verified that the set of circuits of dimension $m=4, 6, 8, \ldots$, etc. found in all superpositions is the same as the set of conjugation circuits (i.e. circuits with alternating single and double bonds) found in all Kekulé structures taken individually. For the energy and the magnetic currents, the values of these increments have

been calculated non-empirically [5,6] and also estimated to best fit a set of known values [7,8].

The discussion above is centred on the assumption that the Kekulé structures alone are sufficient to describe the properties of interest. It is hoped that certain polar structures which, for benzene, Norbeck and Gallup [18] have found to be very important (with an energy 0.027 a.u. lower than that of the Kekulé admixture), will be automatically taken into account when the values of the increments are chosen as indicated above. The Dewar structures, however, may be of considerable importance; they are not considered in the most simplified methods only due to the much increased complexity introduced in the formalism.

Certain terms found in the magnetic current distribution do suggest that they may be relevant in the present context of a conjugation-circuits theory.

EXTENSION OF THE CONJUGATION-CIRCUITS MODEL

In this section, an extension of the conjugation-circuits model is proposed for the detailed description of the distribution of magnetic currents in benzenoid hydrocarbons.

Consider the five molecules depicted in Fig. 1 with the magnetic ring currents relative to benzene calculated using the method of Coulson et al. [19].

A comment should be given here about the way in which these ring currents are defined. From the π-electron ground-state SCF-MO wavefunction and its first-order perturbation induced by an external magnetic field, the current density is written as an $\mathscr{R}^3 \rightarrow \mathscr{R}^3$ function of the position. The expression of this function may be made to appear as a summation over pairs of centres, each centre of a p_z orbital being identified with a carbon atom. The term associated with a pair of atoms linked by a chemical bond, when integrated over all space, is called the integrated bond current. (It should be noted that this quantity has the dimensions of an electronic current times a length!). When we look at the set of integrated bond currents for a molecule, they show a very nice current

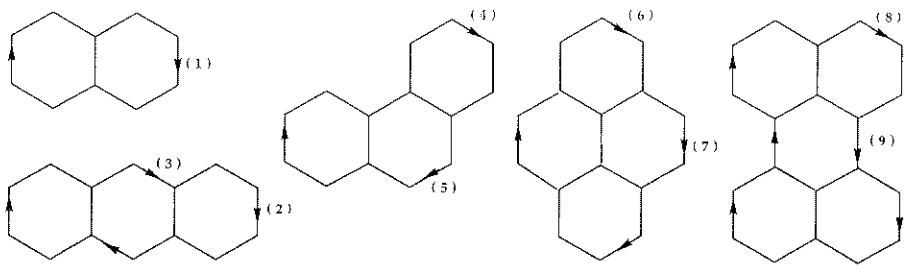

Fig. 1. Enumeration of the independent ring currents in naphthalene, phenanthrene, pyrene and perylene.

TABLE 1

Ring currents relative to benzene (calculated by the method described in ref. 19 and estimated by the conjugation circuits model in refs. 5 and 6)

Molecule	Ring	Ring current [19]	Ring current [5,6]
Naphthalene	1	1.074	0.99
Anthracene	2	1.055	0.84
	3	1.285	1.08
Phenanthrene	4	1.128	1.07
	5	0.952	0.86
Pyrene	6	1.337	1.20
	7	0.940	0.80
Perylene	8	1.030	0.99
	9	0.219	0.0

conservation, taking the molecular backbone as a Kirchhoff-type electrical network. It is this feature that allows the definition of the ring currents presented in Table 1.

A case of particular interest is perylene, where the conjugation-circuits model predicts a zero current in the central ring while the integrated current [19] (or the London–Pople–McWeeny ring current [20]) is small but significantly different from zero (22% of that found in benzene). This prediction of the conjugation circuit model is obviously associated with the fact that none of the nine Kekulé structures has double bonds between the two naphthalene fragments, which thus appear to be independent. Immediate consequences of this are: (a) a zero current across the central bonds, and (b) a resonance energy of perylene estimated to be exactly twice that of naphthalene.

Consequence (b) concerning the resonance energy introduces only a small error (2%, if the SCF-MO values of Dewar and Llano [21] are used). However, the error introduced in the prediction of the ring currents requires further attention.

If we repeat the calculation of the integrated currents following the method given in Ref. 19, small but non-vanishing currents are found between some non-bonded centres as shown in Figs. 2 and 3 and tabulated in Table 2.

In Fig. 2, all independent interactions between carbon atoms located in the 1 and 4 relative positions in a chain with *cis* conformation are shown. (Current terms which must vanish by symmetry are not mentioned.) In Fig. 3, the 1,4 interactions are shown similarly in chains in *trans* conformations. Inspection

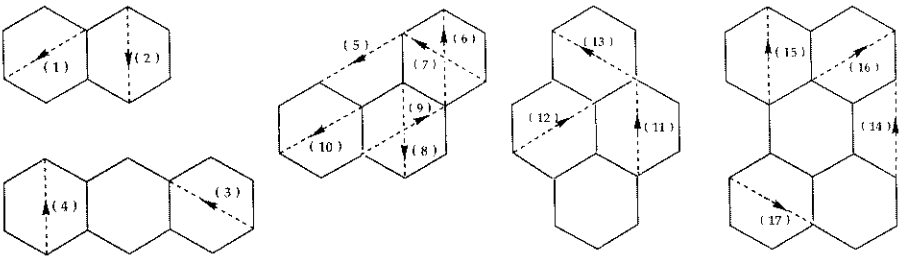

Fig. 2. Integrated currents between non-bonded centres in the diagonal 1,4-cis position.

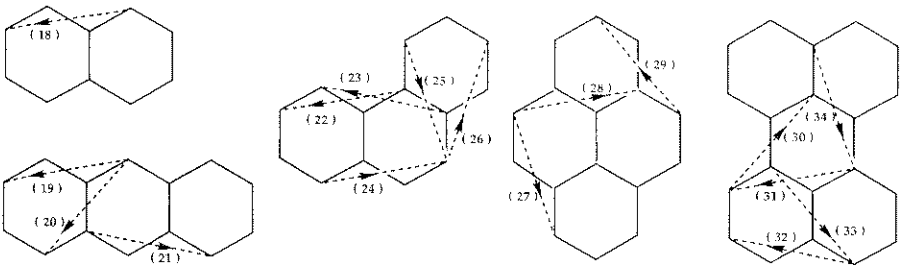

Fig. 3. Integrated currents between non-bonded centres in the 1,4-*trans* position.

of the values in Table 2 shows that 1,4-*trans* interactions produce currents which are about 1% of that in the benzene ring or smaller. However, for 1,4-*cis* interactions, values of 5% of the benzene current are common and larger values (up to 20%) do occur in more favourable cases. A common feature of these currents is their paramagnetic nature, partially compensating the dominant diamagnetic nature of these molecules.

One problem that may be raised about these non-bonded currents is their apparent non-conservation. In fact, while the bond currents represented in Fig. 1 do obey Kirchhoff's node-conservation law, the non-bonded currents in Figs. 2 and 3 do not. However, one must be careful in dealing with these quantities as they are the result of an integration of a current density term over all space. For the bond currents, the more important region in this integration is close to the mid-point between the two atoms or the bond, if this is understood as a straight line in three-dimensional space between the two centres. For the non-bonded currents, the situation is different. In the region of highest overlap, midway between the two centres, there are normally several other terms giving a contribution as sketched in Fig. 4.

Each term, individually cannot be expected therefore to satisfy some sort of electric-network-conservation law, while the resultant term for each molecular region suggests current density conservation. It should be noted, however, that, for a current density derived from a crudely approximated wavefunction, rig-

TABLE 2

Integrated currents between non-bonded centres (method of ref. 19), relative to benzene ring current

1.4-*cis* Interactions		1.4-*trans* Interactions	
No.	Current	No.	Current
1	0.0386	18	0.0101
2	0.0091	19	0.0119
3	0.0453	20	0.0012
4	0.0162	21	0.0099
5	0.1077	22	0.0088
6	0.0336	23	0.0029
7	0.0023	24	0.0101
8	0.0556	25	0.0023
9	0.0518	26	0.0087
10	0.0322	27	0.0118
11	0.0548	28	0.0022
12	0.0616	29	0.0086
13	0.0436	30	0.0092
14	0.2011	31	0.0093
15	0.0052	32	0.0082
16	0.0332	33	0.0016
17	0.0313	34	0.0017

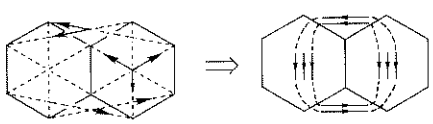

Fig. 4. Individual integrated currents between non-bonded centres in naphthalene (a) and their regional resultants (b), suggesting how the overall current density is conserved.

orous local conservation ($\nabla \cdot \mathbf{J} = 0$) is not expected, as discussed by Atkins and Gomes [22].

In an attempt to make predictions of integrated currents between 1,4-*cis*, non-bonded centres of the type shown in Fig. 2, an extension of the conjugation circuits model of Gomes and Mallion [6,5] is now devised. Currents of the type shown in Fig. 3 are left out in this attempt as they appear to be consistently smaller.

Let all conjugation circuits be considered that have one, and only one, side along a 1,4-*cis* non-bonded interaction as shown in Fig. 5 for naphthalene. This count is equivalent to considering the circuits in all superpositions between Kekulé and Dewar-type structures in a straightforward extension of the formal discussion in the previous section.

The conjugation circuit count for the 17 currents in Fig. 2 is presented in

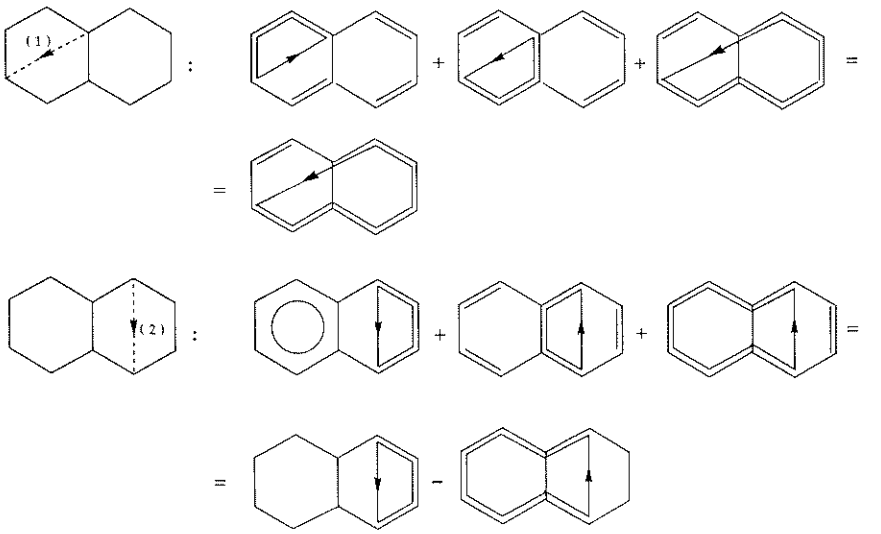

Fig. 5. Conjugation circuits count for non-bonded currents in naphthalene. Individual conjugation circuits are signed according to the Hückel rule that associates a paramagnetic current to $4n$-annulenes.

TABLE 3

Conjugation-circuit count for the integrated currents depicted in Fig. 2

n	j_n	K^a	ij							
			00	10	20	30	40	31	41	52
1	0.0365	3	0	1	0	0	0	0	0	0
2	0.0091		1	−1	0	0	0	0	0	0
3	0.0453	4	0	1	1	0	0	0	0	0
4	0.0162		2	−1	−1	0	0	0	0	0
5	0.1077	5	1	2	1	0	0	0	0	0
6	0.0336		0	1	1	0	0	0	0	0
7	0.0023		−1	1	1	0	0	0	0	0
8	0.0556		1	1	0	0	0	0	0	0
9	0.0518		0	2	1	0	0	0	0	0
10	0.0322		0	1	1	0	0	0	0	0
11	0.0548	6	0	2	1	0	0	1	0	0
12	0.0616		1	1	1	0	0	0	0	0
13	0.0436		−1	2	2	0	0	1	0	0
14	0.2011	9	4	5	3	1	1	3	2	1
15	0.0052		3	−3	0	0	0	0	0	0
16	0.0332		0	3	0	0	0	0	0	0
17	0.0313		0	3	0	0	0	0	0	0

[a]The number of Kekulé structures of the molecule.

Table 3, where the symbol f_{ij} represents a circuit that includes i benzene rings and has j internal double bonds. A circuit f_{ij} has, therefore, an area of $(i+1/2)$ benzene ring areas but a periphery equivalent to that of $(i-j+1/2)$ linearly arranged, condensed benzene rings.

The application of the model of the conjugation circuits requires the knowledge of the values of the increments. Their estimation by a non-empirical technique like that used in the standard model [5,6] is not possible; the alternative consists in fitting a set of expressions of the conjugation circuit count to known integrated currents. If line 14 in Table 3 is excluded, the other 16 currents may be fitted through their conjugation-circuits counts to just three parameters, f_{00}, f_{10} and f_{20} since parameter f_{31} may be related to f_{20} by the ratio of the corresponding circuit areas, $f_{31}=7.5\ f_{20}$. The values obtained through this fitting are: $f_{00}=0.1374$, $f_{10}=0.1106$ and $f_{20}=0.0611$, with a standard deviation of $\sigma=0.0050$. The model used does therefore explain 80% of the variation among the set of currents used.

ACKNOWLEDGEMENTS

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