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Conference Paper

## Why are the Properties of Polycyclic Hydrocarbons Additive over Conjugation Circuits?\*

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Properties as different as resonance energies and magnetic ring-currents are investigated and a non-empirical system of increments is proposed. It is shown that the  $\pi$ -electron properties of conjugated, polycyclic hydrocarbons are additive over all conjugation circuits that can be identified in the molecule. The contribution from each individual conjugation circuit is calculated non-empirically on a simple, free-electron model for the associated annulene.

Within a special form of the resonance theory, it is shown that all conjugation circuits should contribute with equal weight, and not only the »independent circuits« as proposed earlier by Randić or certain lower circuits as postulated by Herndon. Contributions from higher circuits turn out quite naturally, however, to be small.

Results for a wide variety of polycyclic hydrocarbons, alternant and non-alternant, are presented. Both for resonance energies and for magnetically-induced ring-currents, very satisfactory agreement with conventional calculations has been obtained.

### RESONANCE THEORY

Consider a basis set formed by the functions associated with all the Kekulé structures which can be drawn for a given conjugated molecule. In the valence-bond approach, the groundstate energy is calculated as the lowest root,  $E$ , of the secular determinant

$$|H_{ij} - ES_{ij}| \quad (1)$$

where  $H_{ij}$  and  $S_{ij}$  are, respectively, the hamiltonian and overlap matrix elements between structures  $i$  and  $j$ .

When exchange integrals between neighbouring centres alone are considered, and these are assumed to be all equal to a quantity  $\alpha$ , the matrix element  $H_{ij}$  may be put<sup>1</sup> in a simple form

$$H_{ij} = 2^{x-n} \left\{ Q + \frac{3}{2} \alpha \sum_{\text{all cycles}} [(\text{no. of bonds in the cycle}) - (\text{no. of even kisses in the cycle})] - \frac{1}{2} \alpha (\text{total no. of bond in the molecule}) \right\} \quad (2)$$

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where  $x$  is the number of cycles (counting an isolated island (o—o) as a cycle of one side),  $n$  is the number of pairs of orbitals in the molecule, and  $Q$  is the Coulomb integral. The overlap integral,  $S_{ij}$ , is in the zero differential approximation given by

$$S_{ij} = 2^{x-n} \quad (3)$$

For even hydrocarbons, the general term of the secular matrix may be written as

$$(H_{ij} - ES_{ij}) = 2^A \left\{ -E_R + \frac{3}{2} \alpha \sum_{\text{cycles}} \left[ \frac{m}{2} - (\text{no. of even kisses}) \right] \right\} \quad (4)$$

with

$$A = \sum_{\text{cycles}} \left( 1 - \frac{m}{2} \right)$$

Summations run over all cycles in superimposed structures,  $m$  is the number of sides in the cycle, and the resonance energy,  $E_R$ , is defined as

$$E_R = E_{\text{Kekulé}} - E \quad (5)$$

Each cycle formed by the superimposition of any two Kekulé structures gives, according to (4), a well-defined contribution to the general term in the secular determinant.

An estimate of the resonance energy may easily be obtained when we take into consideration the fact that the coefficients  $c_j^{(0)}$  of the groundstate function are of similar magnitude. These coefficients satisfy the secular equations

$$\sum_j (H_{ij} - E^{(0)} S_{ij}) c_j^{(0)} = 0 \quad (6)$$

The energy may be given by

$$E^{(0)} = \frac{\sum_{i,j} c_i^{(0)} H_{ij} c_j^{(0)}}{\sum_{i,j} c_i^{(0)} S_{ij} c_j^{(0)}} \quad (7)$$

and this is simplified if the  $c_i^{(0)}$  are assumed to be all equal:

$$E^{(0)} \approx E_{RT} = \frac{\sum_{i,j} H_{ij}}{\sum_{i,j} S_{ij}} \quad (8)$$

This is the fundamental expression of the resonance theory considered here.

#### CONJUGATION CIRCUITS

In the former section, consideration was given to all cycles formed by superimposition of the Kekulé structures. In a molecule with  $K$  Kekulé structures, one must inspect the  $K(K-1)/2$  superimpositions to identify all cycles formed and then calculate the elements of the secular determinant. We shall now show this task may be simplified by inspecting the  $K$  individual Kekulé

structures and to identifying the so-called »conjugation circuits« in these structures.

Let us consider the expression for the matrix elements between Kekulé structures (equations (3) and (4)). The overlap term may be written

$$S_{ij} = 2^A \quad (9)$$

with

$$A = \sum_{\text{cycles}} \left( 1 - \frac{m}{2} \right)$$

This quantity decreases very quickly when more than one cycle is formed in the superimposition. The same may be said about the matrix element  $H_{ij}$ , for its expression (equation (2) or (4)) contains a factor equal to the quantity given by equation (9).

Notice that the contribution from a superimposition with two cycles of the same size, such as  $m = 6$ , is  $1/4 \times 1/4$  while each of the cycles will occur separately in other superimpositions with a factor  $1/4$ .

When all superimpositions in which more than one cycle is formed are disregarded, we are reduced to counting the cycles in a way equivalent to finding all conjugation circuits in all the Kekulé structures.

The concept of a conjugation circuit was considered by the present author<sup>2,3</sup> in the context of the calculation of ring-currents, which are also discussed below, and by Randić<sup>4,5</sup> in his method of estimating resonance energies. This author works from a purely topological point of view and is therefore led to consider »independent circuits« only. This idea is not corroborated by the derivation currently presented. Herndon<sup>6,7</sup> considers certain conjugation circuits as giving the main contributions to the resonance energies. In all these approaches, some analysis of the topology of the molecule is made in order to break it down into a set of constituent circuits; the increments from these circuits are determined empirically for the best fit of the property being calculated.

In order to avoid the introduction of empirical data and thus to give the method maximum generality, it was decided to identify the contribution from each conjugation circuit with the calculated value of the property for the associated annulene in a simple, free-electron model.

Calculated<sup>8</sup> delocalization energies of annulenes in a free-electron theory with a Kuhn harmonic potential<sup>9</sup> of 2.40 eV are given in Figure 1, where they are plotted against the estimates obtained by the resonance theory (given by  $H_{ij}/(1 + S_{ij})$ ).

Application of this system of conjugation-circuit increments implies the following steps:

1. Writing all the Kekulé structures for the molecule;
2. Identifying in each Kekulé structure all conjugation circuits, i. e., circuits with alternating single and double bonds;
3. Summing the increments (given in Figure 1, from a free-electron theory) from all circuits identified in 2;
4. Dividing the result by the number of Kekulé structures to obtain the final estimate of the resonance energy.

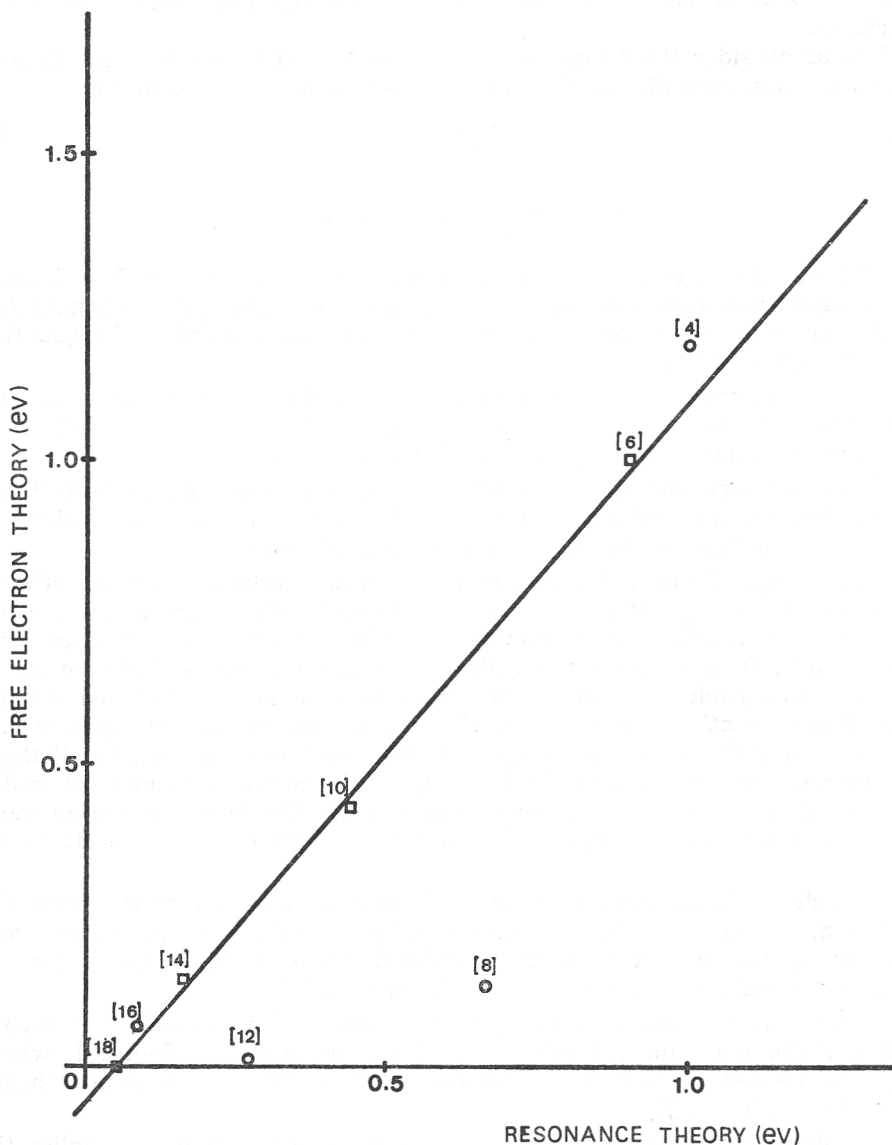


Figure 1. Delocalization energies of [4]- to [16]-annulenes as calculated by a free-electron theory<sup>8</sup> and by the resonance theory (Eq. (8)).

Comparison of the present results with those of the SCF-MO calculation by Dewar and deLlano<sup>10</sup> may be seen in Figure 2, where these results are plotted for the twenty molecules in Figure 3. A linear-regression correlation-coefficient of 0.982 is obtained for the 20 points plotted (regression line:  $+ 0.004 + 1.206 \chi$ ).

Comparison of the results of the present method with those of Randić<sup>4,5</sup> can be made by examining the linear-regression correlation-coefficients. Regres-

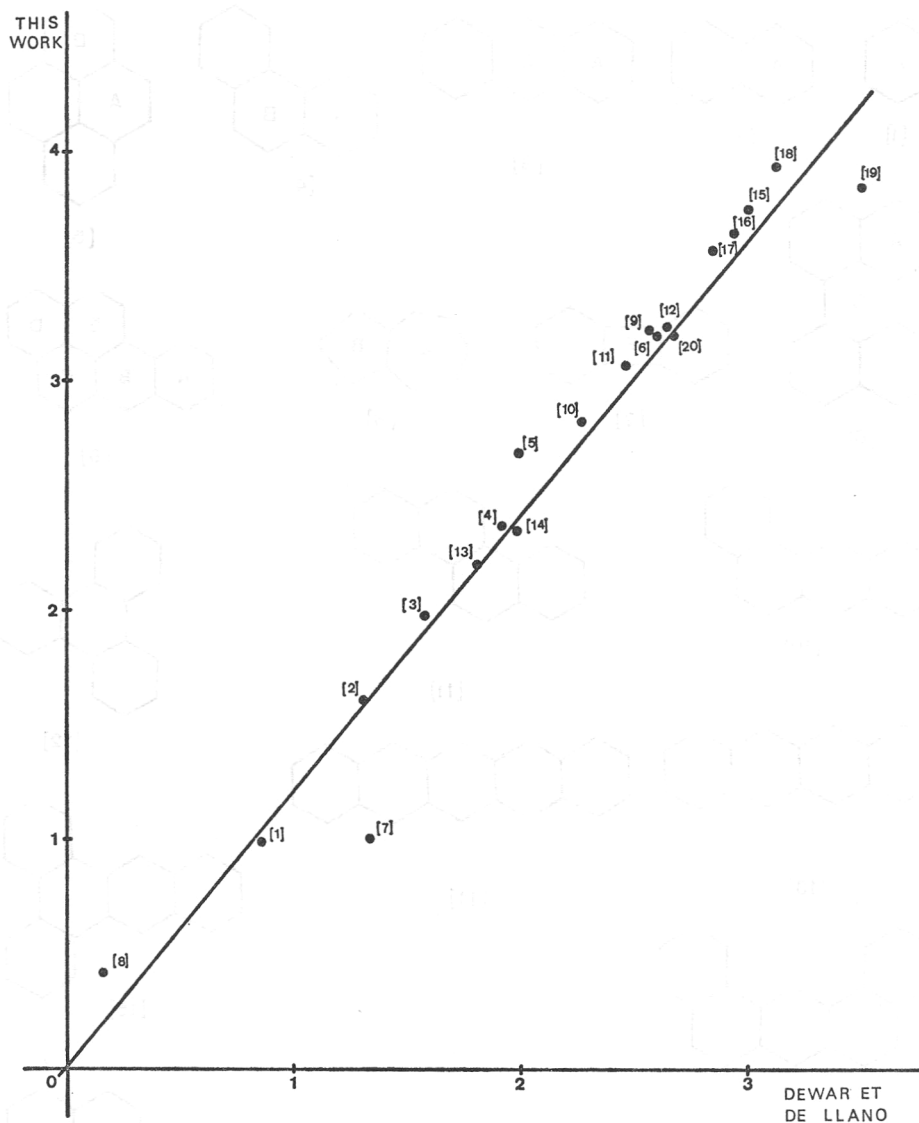


Figure 2. Plot of estimated resonance energies vs. calculated resonance energies by Dewar and deLlano<sup>10</sup>, in eV units.

sion of the present results vs. those of Dewar and deLlano<sup>10</sup> gives a linear-regression correlation-coefficient of 0.982, while for Randić's results (excluding molecules (1)—(3) for which the fit was made) the correlation-coefficient is 0.965. We find, therefore, that the current method is marginally better than that of Randić<sup>4,5</sup> when judged by linear regression against SCF-MO results. The actual differences from the SCF-MO results are in some cases larger for the method proposed here, but this is not unexpected as no fitting parameters were introduced.

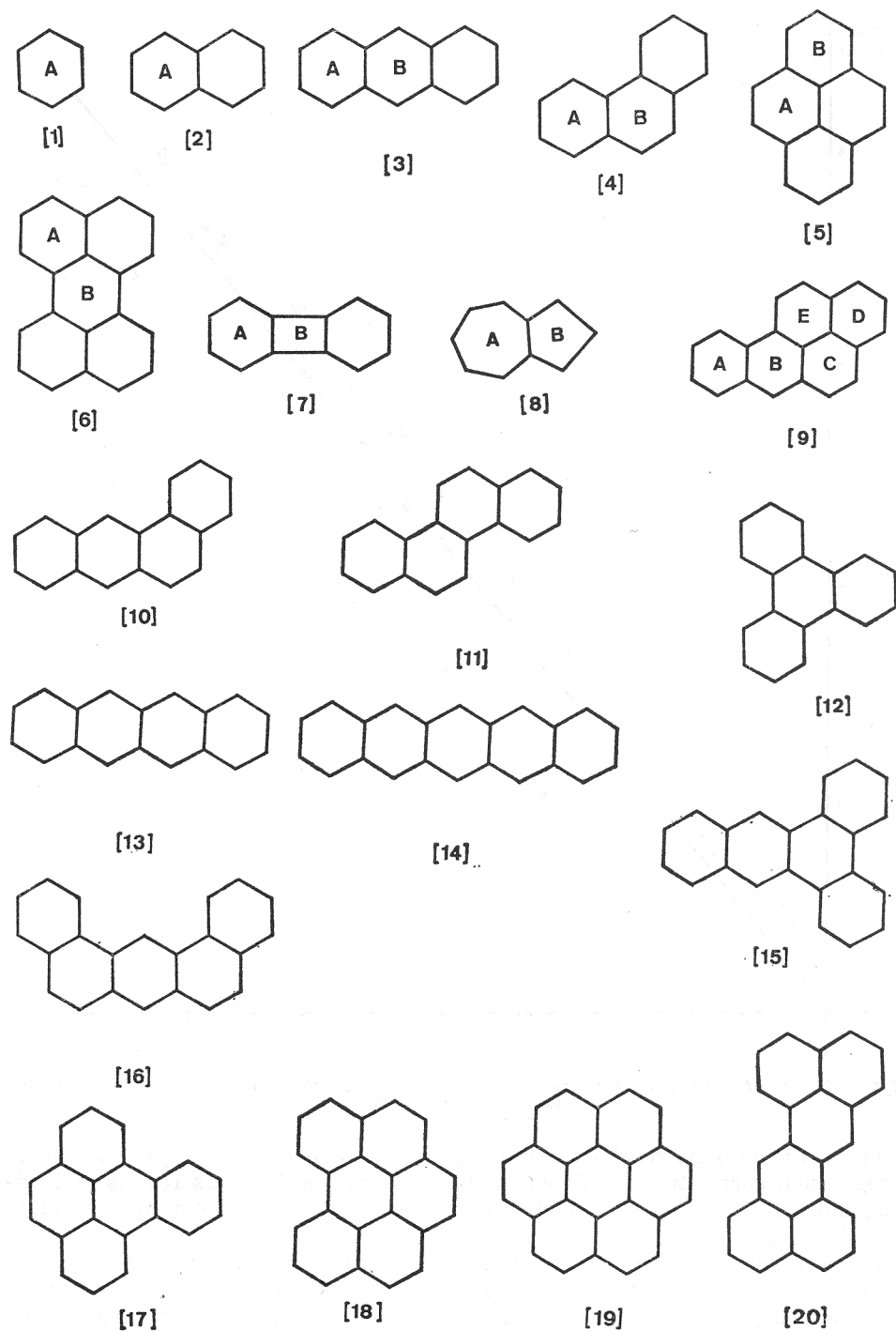


Figure 3. Skeletons of the molecules in which the new system of increments was tested.

## MAGNETIC RING-CURRENTS

The same philosophy as was used in Section Conjugation Circuits for the calculation of resonance energies may, in principle, be applied to any other property. In this section we shall consider its application to the estimation of magnetic ring-currents.

The increment,  $j$ , to the local ring-current from a conjugation circuit with  $N$  bonds is calculated from the ring-current (see Figure 4.) for the associated regular annulene by the expression

$$j = J_N \times \frac{a_N}{A_N} \times \frac{1}{K} \quad (10)$$

where  $J_N$  is the standard ring-current in the  $[N]$ annulene,  $a_N$  and  $A_N$  are the actual area and the area of the regular  $[N]$ annulene, and  $K$  is the number of Kekulé structures that may be written for the molecule.

In Table I the results of an application of this system of increments to some of the molecules in Figure 3. are compared with the ring currents calculated by standard methods.

TABLE I

*Ring-Currents Obtained by the Conjugation-Circuits System of Increments and Standard Methods. (All the Currents are Given by the Ratios to those in Benzene.)*

Molecule	Ring	This Work	Integrated $\pi$ -electron current <sup>a</sup>	London-Pople-McWeeny <sup>b</sup> ring current
1	A	1	1	1
2	A	0.99	1.07	1.09
3	A	0.84	1.05 (0.96)	1.08
	B	1.08	1.28 (1.32)	1.28
4	A	1.07	1.13	1.13
	B	1.86	0.95	0.97
5	A	0.80	0.94	0.96
	B	1.20	1.34	1.33
6	A	0.99	1.03	0.97
	B	0.0	0.22	0.23
7	A	0.27	0.40	0.25
	B	-1.79	-1.76	-1.81
8	A	0.50	1.03	1.07
	B	0.50	1.28	1.15
9	A	0.94		1.08
	B	1.18		1.29
	C	1.01		1.20
	D	1.15		1.28
	E	0.61		0.84

<sup>a</sup> Calculated by Coulson et al.<sup>12</sup> who give the absolute value of the integrated current in<sup>11</sup> benzene:  $(e^2B/2m_0) \times 94.6$  A pm. The results of an iterative calculation by Gomes and Mallion are given in parentheses.

<sup>b</sup> Ratios of  $\pi$ -electron ring-currents calculated by the London-Pople-McWeeny method (see Ref. 3 for detailed references).

The values calculated by the currently proposed method of conjugation-circuit increments compare very well with those obtained by the more orthodox methods of calculation. Full details leading to the results that are summarized in this contribution are being published elsewhere.

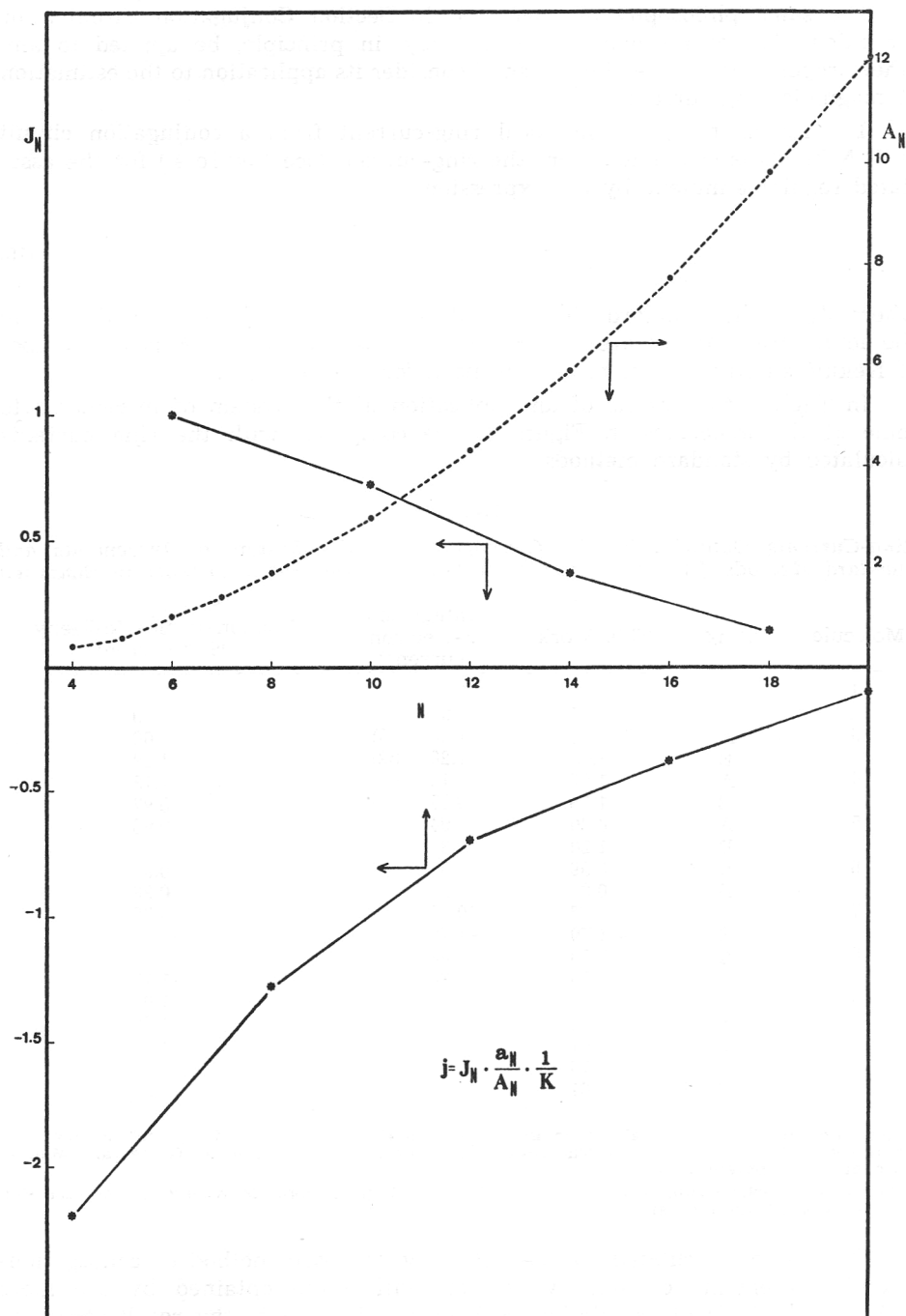


Figure 4. Ring-currents,  $J_N$ , and ring areas,  $A_N$ , of [4]- to [20]-annulenes.



An attempt to apply Randić's theory of conjugation-circuit increments to the estimation of magnetic susceptibility exaltations in polycyclic, conjugated hydrocarbons has been reported quite recently by Gayoso<sup>13</sup>. Eight fitted parameters were used, and application to 19 test molecules lead to a semi-quantitative agreement with experimental data.

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## SAŽETAK

Zašto su svojstva policikličkih ugljikovodika aditivna po krugovima konjugacije

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Istraživana su tako raznovrsna svojstva kao što su resonancijske energije i struje u prstenovima te je predložen neempirijski sustav računanja doprinosa tim veličinama. Pokazano je da su pi-elektronska svojstva konjugiranih policikličkih ugljikovodika aditivna po svim konjugiranim prstenovima što se mogu u molekuli raspoznati. Na temelju računa unutar modela slobodnih elektrona za pridruženi anulen izračunani su neempirijski dopinosi individualnih konjugiranih prstenova.

Unutar posebnog oblika teorije resonancije pokazano je da bi svi konjugirani krugovi mogli pridonositi s istom težinom a ne samo oni »nezavisni« kao što je ranije predložio Randić ili samo neki niži prstenovi kao što je postulirao Herndon. Ipak, potpuno prirodno, dolazi do toga da su dopinosi velikih krugova maleni.

Prikazani su rezultati za velik broj policikličkih, alternantnih i nealternantnih ugljikovodika. Dobiveno je vrlo zadovoljavajuće slaganje za resonancijske energije i magnetski inducirane struje u prstenovima u usporedbi s rezultatima uobičajenih računa.

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