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The Conjugated-Circuit Model: Application to Benzenoid Hydrocarbon Radicals*

D. Plavšić and N. Trinajstić

The Rugjer Bošković Institute, P.O.B. 1016, 41001 Zagreb, Croatia, Yugoslavia

and

M. Randić and C. Venier

Department of Mathematics and Computer Science, Drake University, Des Moines, Iowa 50311, USA

We have applied the conjugated-circuit model to benzenoid hydrocarbon radicals and predicted their aromatic stabilities. Our predictions are supported by alternative theoretical schemes such as the structure-resonance approach and by available experimental data. This work points to a considerable potential of the conjugated-circuit model for qualitative and quantitative discussion of thermodynamic stabilities of polycyclic conjugated radicals.

INTRODUCTION

In this paper we wish to report the application of the conjugated-circuit model[1-4] to benzenoid hydrocarbon radicals. These radicals have been subject of a number of previous studies, experimental and theoreticals including the work of Streitwieser et al.[5] on protodetritiation of benzenoid hydrocarbons, the work of Unruch and Gleicher[6] on hydrogen abstractions from aryl-methanes, who also carried out the SCF π-MO computations on selected radicals and the work of Stein and Golden[7] on the π-bonding resonance stabilization of benzenoid radicals using the modified form of the structure-resonance theory[8]. The work by Herndon[9,10] on resonance energies and radical reactivities of benzenoid hydrocarbons and the work of Stein[11] on benzenoid radicals in coal conversion also belong here.

Since the thermodynamic (and kinetic) stabilities of benzenoid hydrocarbon radicals are related to a great extent to their π-electronic structures[5,6], we decided to apply the conjugated-circuit model to these systems in order to test the model and to compare it to some other models that have been used to compute the π-resonance energies of benzenoid radicals[6-10,12].

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The structure of the paper is as follows. In the next section the conjugated-circuit model is outlined. The third section reports the concept of conjugated circuits in benzenoid radicals. In the fourth section the resonance energies of selected benzenoid radicals are given and these are compared to those computed by the structure-resonance model. In this section we also compare our results with those obtained by the resonance stabilization energy model. The article ends with some concluding remarks.

THE CONJUGATED-CIRCUIT MODEL

The conjugated circuit-model allows one to calculate the resonance energies (REs) of conjugated molecules in a rather simple way. The RE is a theoretical quantity which appears to be a reliable criterion for predicting aromatic stabilities of conjugated systems[13,14]. It is defined as that part of the molecular binding energy which denotes deviation from the simple bond additivity.

A graph-theoretical analysis of Kekulé valence structures reveals that each Kekulé structure can be decomposed into several conjugated circuits. A conjugated circuit is defined as a circuit within an individual Kekulé structure in which there is a regular alternation of formal carbon-carbon single and double bonds. For this reason, the conjugated circuits are necessarily of even length.

The circuit decomposition of a Kekulé structure produces $4n+2$ and/or $4n$ linearly independent, linearly dependent and disconnected conjugated circuits. Linearly independent circuits are those which cannot be represented by a superposition of conjugated circuits of smaller size. We denote $4n+2$ conjugated circuits by R_n and $4n$ circuits by Q_n. The total number of all conjugated circuits within a single Kekulé structure is equal to SC-1 (or K-1)[15], where SC is the structure count (or the number of Kekulé valence structures K) for a polycyclic conjugated hydrocarbon. As an example, we give in Figure 1 all Kekulé structures and conjugated circuits for pyrene.

The conjugated circuits count for pyrene is given by:

$$12 R_1 + 8 R_2 + 6 R_3 + 4 R_1 \cdot R_1 \tag{1}$$

where the symbols have the following meaning: R_1 is a conjugated circuit of size 6 (i. e., a $4n+2$ circuit with $n=1$), R_2 a circuit of size 10 and R_3 a circuit of size 14, whilst $R_1 \cdot R_1$ stands for two disjoint circuits of size 6.

The π-resonance energy is given in terms of conjugated circuits as follows:

$$RE = \frac{1}{SC} \sum_{n \geqslant 1} [\varrho_n \#^{(4n+2)} + \xi_n \#^{(4n)}] \tag{2}$$

where $\rho_n (\xi_n)$ is the parametric value corresponding to $R_n (Q_n)$ circuits and $\#^{(4m+2)} (\#^{(4n)})$ is the count of $4n + 2$ $(4n)$ conjugated circuits. Note that $\rho_m (\xi_m)$ is the measure of the extent by which a specific conjugated circuit of size $4n+2$ $(4n)$ influences the thermodynamic stability of the conjugated molecule. We will use in (2) only linearly independent conjugated circuits of size 14 $(n=3)$ or less. In considering only the smallest three conjugated circuits, we have followed the empirical findings that only the smallest circuits make
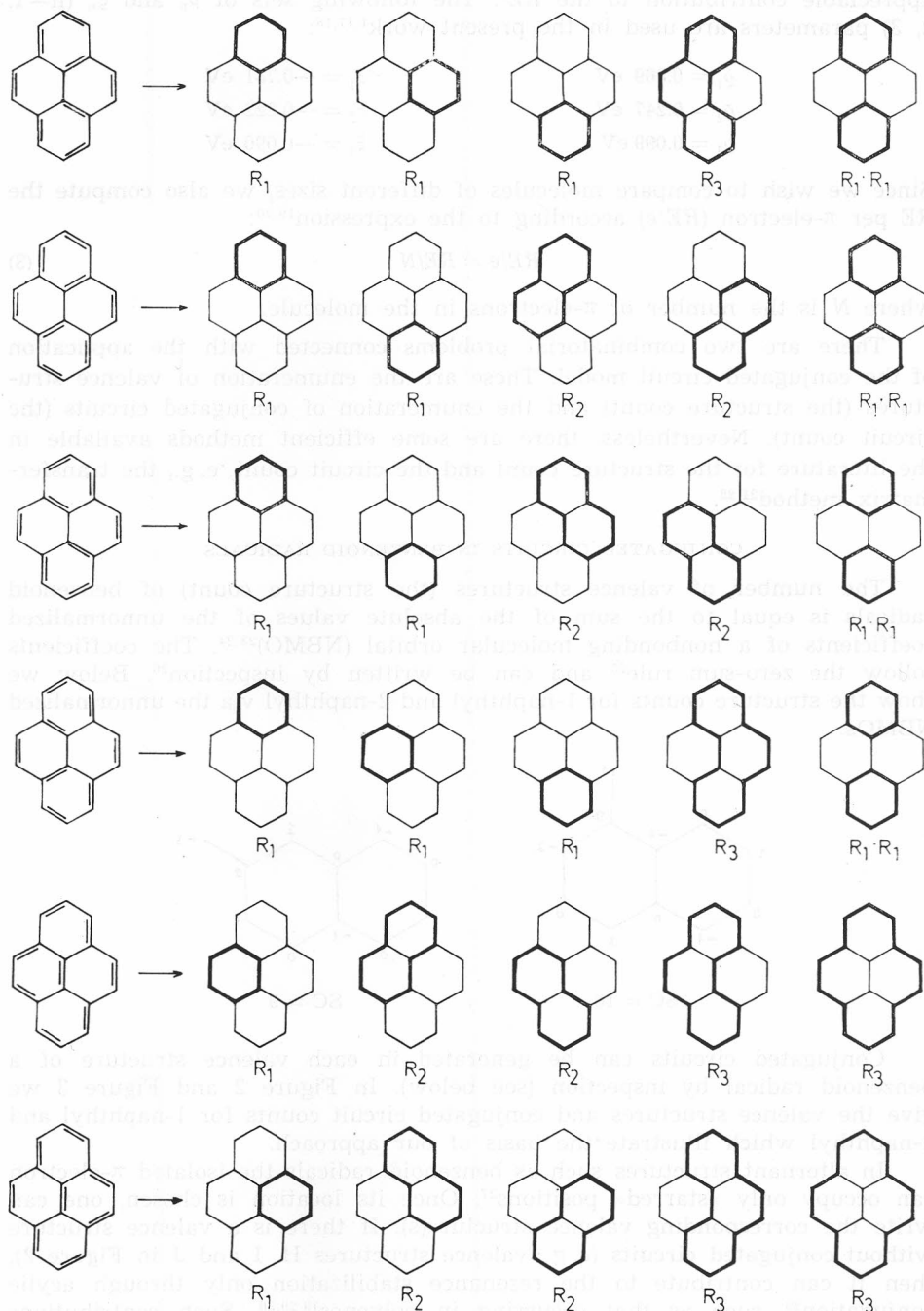
Figure 1. **Kekulé structures of pyrene and their decomposition into conjugated circuits**

appreciable contribution to the RE[8]. The following sets of ρ_n and ξ_n ($n=1$, 2, 3) parameters are used in the present work[1,17,18]:

$$\varrho_1 = 0.869 \text{ eV} \qquad\qquad \xi_1 = -0.781 \text{ eV}$$
$$\varrho_2 = 0.247 \text{ eV} \qquad\qquad \xi_2 = -0.222 \text{ eV}$$
$$\varrho_3 = 0.099 \text{ eV} \qquad\qquad \xi_3 = -0.090 \text{ eV}$$

Since we wish to compare molecules of different sizes, we also compute the RE per π-electron (RE/e) according to the expression[19,20]:

$$RE/e = RE/N \qquad\qquad\qquad (3)$$

where N is the number of π-electrons in the molecule.

There are two combinatorial problems connected with the application of the conjugated circuit model. These are the enumeration of valence structures (the structure count) and the enumeration of conjugated circuits (the circuit count). Nevertheless, there are some efficient methods available in the literature for the structure count and the circuit count, e. g., the transfer-matrix method[21,22].

CONJUGATED CIRCUITS IN BENZENOID RADICALS

The number of valence structures (the structure count) of benzenoid radicals is equal to the sum of the absolute values of the unnormalized coefficients of a nonbonding molecular orbital (NBMO)[23,24]. The coefficients follow the zero-sum rule[25] and can be written by inspection[26]. Below we show the structure counts for 1-naphthyl and 2-naphthyl via the unnormalized NBMOs.

SC = 10　　　　　　　　　　　　　SC = 9
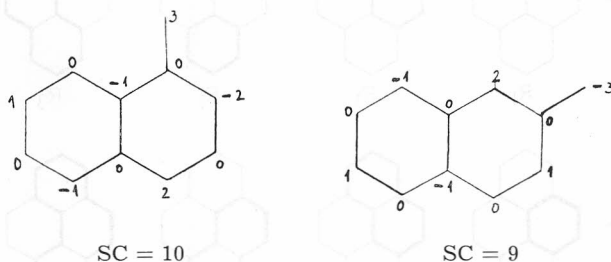
Conjugated circuits can be generated in each valence structure of a benzenoid radical by inspection (see below). In Figure 2 and Figure 3 we give the valence structures and conjugated circuit counts for 1-naphthyl and 2-naphthyl which illustrate the basis of our approach.

In alternant structures such as benzenoid radicals the isolated π-electron can occupy only »starred« positions[27]. Once its location is chosen, one can write the corresponding valence structure(s). If there is a valence structure without conjugated circuits (e. g., valence structures H, I and J in Figure 2), then it can contribute to the resonance stabilization only through acylic conjugation[28], such as that occurring in polyenes[19,29,30]. Such contributions will be neglected at this stage, since they could be considered as secondary in nature. Valence structures containing conjugated circuits contribute to
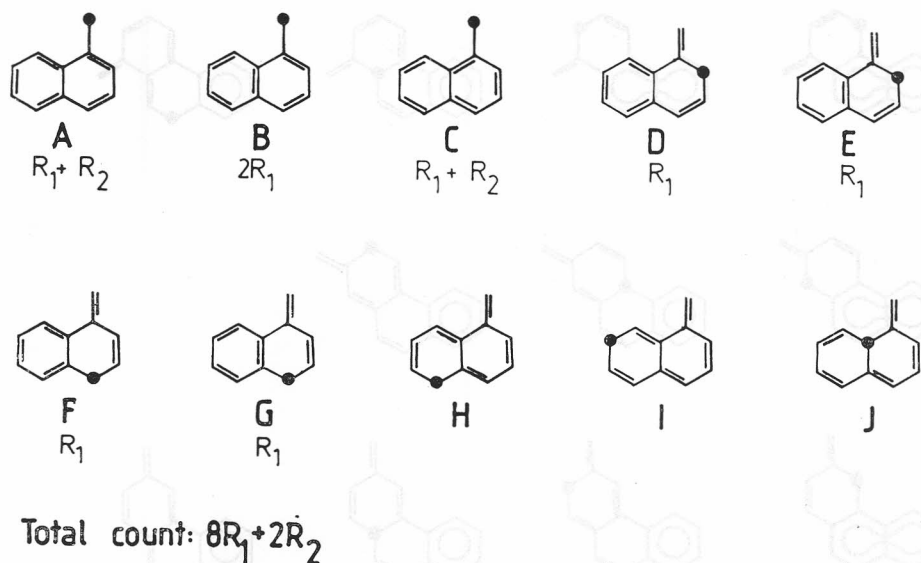
$$A \quad B \quad C \quad D \quad E$$
$$R_1 + R_2 \quad 2R_1 \quad R_1 + R_2 \quad R_1 \quad R_1$$

$$F \quad G \quad H \quad I \quad J$$
$$R_1 \quad R_1$$

Total count: $8R_1 + 2R_2$

Figure 2. The valence structures and conjugated circuits count for 1-naphthyl

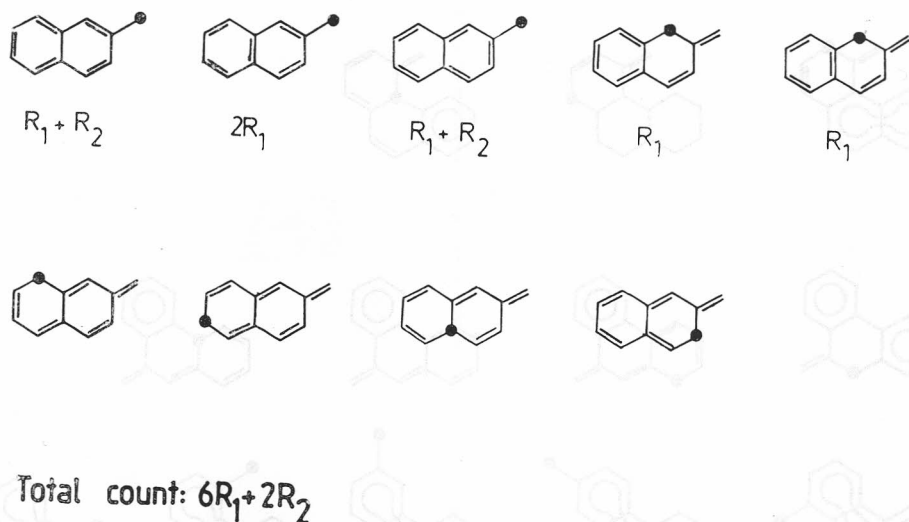
$$R_1 + R_2 \quad 2R_1 \quad R_1 + R_2 \quad R_1 \quad R_1$$

Total count: $6R_1 + 2R_2$

Figure 3. The valence structures and conjugated circuits count for 2-naphthyl

the RE; the amount of contribution is given by the count of conjugated circuits. Thus, the RE expressions for 1-naphthyl and 2-naphthyl are:

$$RE\ (1\text{-aphthyl}) = (8\,\varrho_1 + 2\,\varrho_2)/10$$
$$= 0.745\ \text{eV} \tag{4}$$

$$RE\ (2\text{-naphthyl}) = (6\,\varrho_1 + 2\,\varrho_2)/9$$
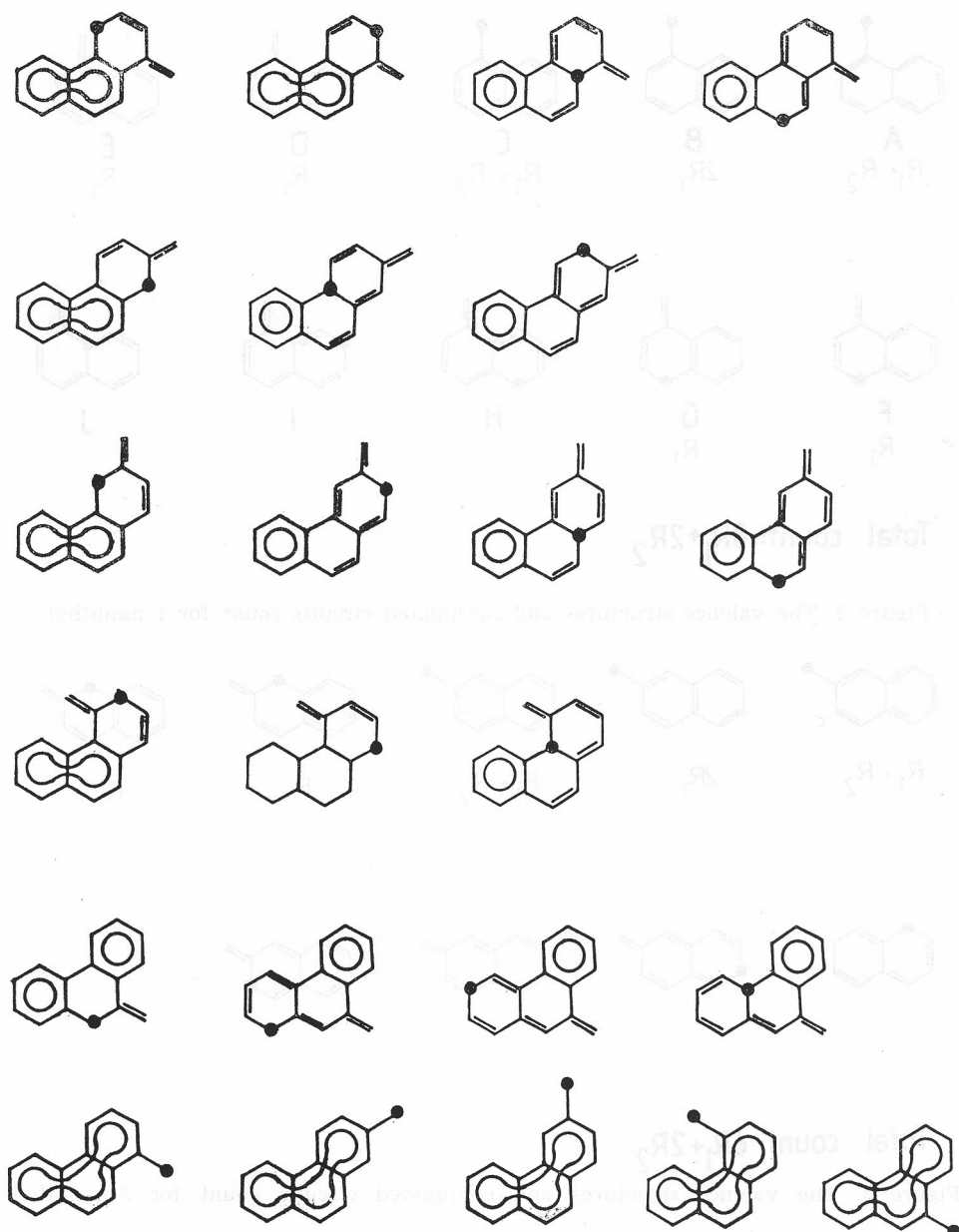$$= 0.634\ \text{eV} \tag{5}$$

Figure 4. Valence structures of different phenanthryl radicals which contain
conjugated circuits

This result favours 1-naphthyl as being more stable of the two and is in
agreement with experimental observations[6]. Other theoretical studies also
obtained the same result[6,7]. In Figure 4 we have collected only those valence
structures of different phenanthryl radicals which contain conjugated circuits.

In other words, the structures in which the location of odd π-electron uniquely determines the bond types for all other bonds, and thus excludes the possibility of having conjugated circuits, are omitted.

Below we give the conjugated circuits contents and the REs of phenanthryl radicals:

$$RE \text{ (1-phenanthryl)} = (22 \varrho_1 + 8 \varrho_2 + \varrho_3)/18$$
$$= 1.177 \text{ eV} \tag{6}$$

$$RE \text{ (2-phenanthryl)} = (18 \varrho_1 + 6 \varrho_2 + \varrho_3)/16$$
$$= 1.076 \text{ eV} \tag{7}$$

$$RE \text{ (3-phenanthryl)} = (20 \varrho_1 + 6 \varrho_2 + \varrho_3)/17$$
$$= 1.115 \text{ eV} \tag{8}$$

$$RE \text{ (4-phenanthryl)} = (20 \varrho_1 + 8 \varrho_2 + \varrho_3)/17$$
$$= 1.144 \text{ eV} \tag{9}$$

$$RE \text{ (9-phenanthryl)} = (24 \varrho_1 + 4 \varrho_2 + \varrho_3)/18$$
$$= 1.219 \text{ eV} \tag{10}$$

1-phenanthryl and 9-phenanthryl as well as 3-phenanthryl and 4-phenanthryl possess the same structure counts.

The RE criterion based on the conjugated circuits orders the phenanthryl radicals according to their aromatic stabilities in the following way:

9-phenantryl > 1-phenanthryl > 4-phenanthryl > 3-phenanthryl > 2-phenanthryl

$$\tag{11}$$

The same order is obtained if the REs are computed by the structure-resonance model[8]. However, the resonance stabilization energy model of Stein and Golden[7], which is based on modified resonance-theoretical ideas of Herndon, orders the phenanthryl radicals according to their Kekulé numbers:

9-phenanthryl ≈ 1-phenanthryl > 3-phenanthryl ≈ 4-phenanthryl > 2-phenanthryl

$$\tag{12}$$

RESONANCE ENERGIES OF BENZENOID RADICALS

In Table I. we give resonance energy expressions for 28 benzenoid radicals whose diagrams are given in Figure 5.

Numerical values of REs and REs/e are reported in Table II. In this Table we also list the π-bonding resonance stabilization energies ($E_{\pi RSE}$) and total stabilization energies (E_{RSE}) of benzenoid radicals[7]. These were calculated using the following expressions:

$$E_{\pi RSE} \text{ (eV)} = 0.9835 \ln [SC (R^{\cdot})] - 1.1851 \ln [SC (RH)] \tag{13}$$

where R˙ (RH) stands for benzenoid radical (benzenoid hydrocarbon). In a general case when 4n cycles appear, the SC should be replaced by the algebraic structure count (ASC)[31]. The ASC is defined as[32]:

$$ASC = SC^+ - SC^-; \quad SC^+ > SC^- \tag{14}$$

TABLE I

The resonance energy expressions for benzenoid hydrocarbon radicals

Label	Benzenoid radical[a]	Resonance energy expression
1	*Benzyl	$(2\varrho_1)/5$
2	*1-Naphthyl	$(8\varrho_1+2\varrho_2)/10$
3	*2-Naphthyl	$(6\varrho_1+2\varrho)/9$
4	*1-Phenanthryl	$(22\varrho_1+8\varrho_2+\varrho_3)/18$
5	*2-Phenanthryl	$(18\varrho_1+6\varrho_2+\varrho_3)/16$
6	*3-Phenanthryl	$(20\varrho_1+6\varrho_2+\varrho_3)/17$
7	*4-Phenanthryl	$(20\varrho_1+8\varrho_2+\varrho_3)/17$
8	*9-Phenanthryl	$(24\varrho_1+4\varrho_2+\varrho_3)/18$
9	*1-Anthryl	$(16\varrho_1+8\varrho_2+2\varrho_3)/16$
10	*2-Anthryl	$(12\varrho_1+6\varrho_2+2\varrho_3)/14$
11	*9-Anthryl	$(26\varrho_1+4\varrho_2+2\varrho_3)/20$
12	*1-Pyrenyl	$(40\varrho_1+22\varrho_2+4\varrho_3+2\xi_3)/29$
13	2-Pyrenyl	$(22\varrho_1+12\varrho_2+4\varrho_3)/19$
14	*4-Pyrenyl	$(32\varrho_1+16\varrho_2+5\varrho_3)/23$
15	1-Chrysyl	$(52\varrho_1+22\varrho_2+4\varrho_3)/31$
16	2-Chrysyl	$(42\varrho_1+18\varrho_2+3\varrho_3)/27$
17	3-Chrysyl	$(46\varrho_1+20\varrho_2+3\varrho_3)/29$
18	4-Chrysyl	$(48\varrho_1+20\varrho_2+4\varrho_3)/29$
19	5-Chrysyl	$(48\varrho_1+20\varrho_2+2\varrho_3)/29$
20	*6-Chrysyl	$(62\varrho_1+14\varrho_2+2\varrho_3)/34$
21	1-Tetracenyl	$(26\varrho_1+16\varrho_2+8\varrho_3)/23$
22	2-Tetracenyl	$(20\varrho_1+12\varrho_2+6\varrho_3)/20$
23	5-Tetracenyl	$(50\varrho_1+16\varrho_2+4\varrho_3)/32$
24	*1-Triphenylenyl	$(60\varrho_1+14\varrho_2+5\varrho_3)/32$
25	*2-Triphenylenyl	$(58\varrho_1+10\varrho_2+4\varrho_3)/31$
26	1-Perylenyl	$(88\varrho_1+40\varrho_2+6\varrho_3+2\xi_3)/48$
27	2-Perylenyl	$(54\varrho_1+24\varrho_2)/27$
28	3-Perylenyl	$(98\varrho_1+42\varrho_2+6\varrho_3+2\xi_3)/51$

[a] Asterisk denotes known benzenoid radicals

where SC^+ (SC^-) are valence structures of even (odd) parity. Note that $SC = SC^+ + SC^-$. For benzenoid hydrocarbons $SC = ASC$ because $SC^- = O$[33]. The E_{RSE} of benzenoid radicals is given by:

$$E_{RSE} \text{ (eV)} = E_{\pi RSE} - 0.1995 \qquad (15)$$

where 0.1995 eV is the correction for E_σ.

In Table II we furthermore give the *REs* of benzenoid radicals calculated by Herndon's formula obtained by the structure-resonance model

$$RE \text{ (SR)} = \frac{2}{SC} [n_1\gamma_1 + n_2\gamma_2 + n_3\beta_1 + n_4\beta_2] \qquad (16)$$

where γ_1 is the benzene (6-membered ring) resonance integral, γ_2 is the naphtalene (10-membered ring) resonance integral, β_1 is the allyl resonance integral and β_2 is the pentadienyl resonance integral, whilst n_1, n_2, n_3 and n_4 are the numbers of each type of the resonance integral. The following are the best correlative values of the resonance integral from above[8,12,34]
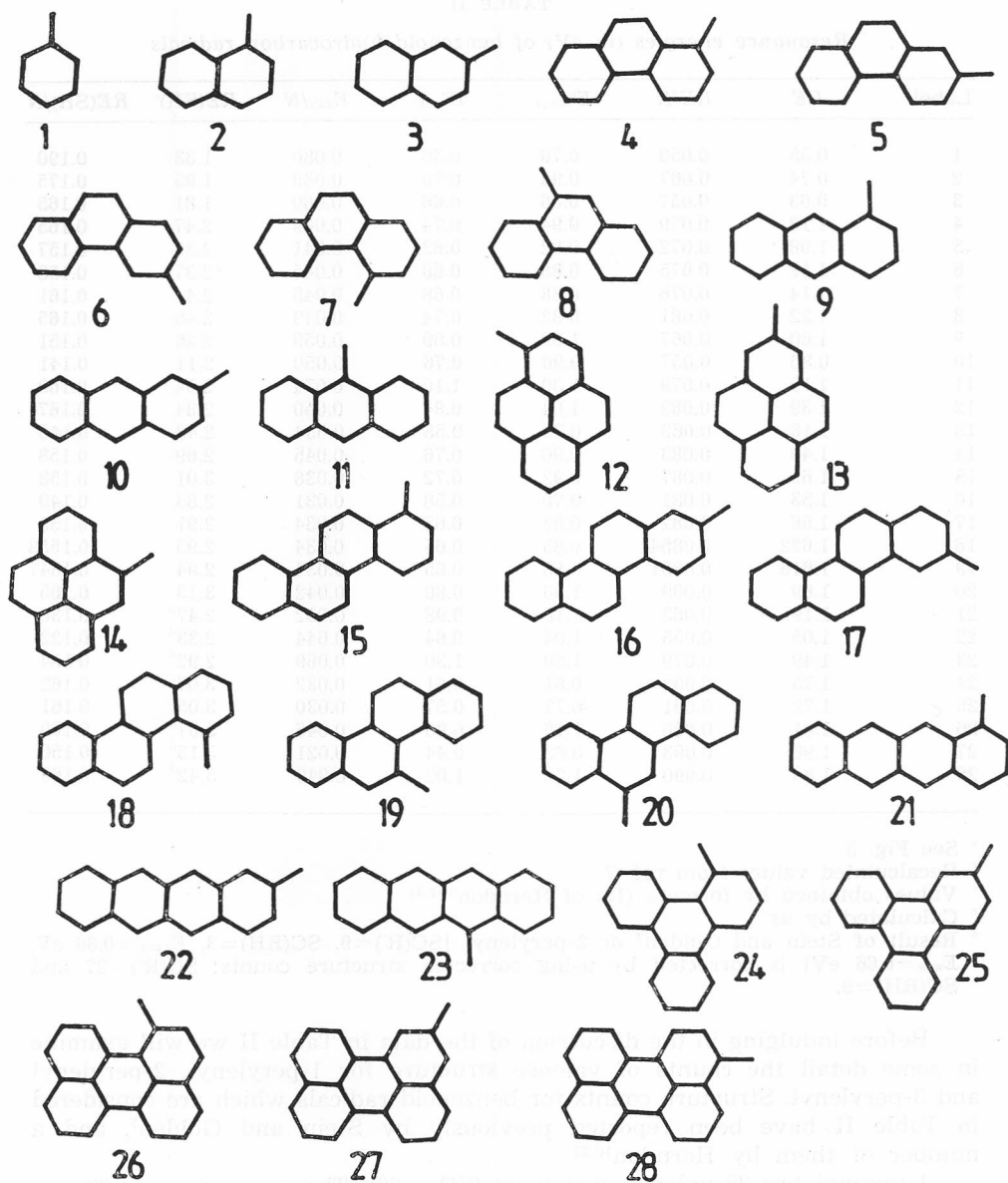
Figur 5. Diagrams of the investigated benzenoid radicals

$$\gamma_1 = 0.841 \text{ eV}$$

$$\gamma_2 = 0.336 \text{ eV}$$

$$\beta_1 = 0.501 \text{ eV}$$

$$\beta_2 = 0.159 \text{ eV}$$

TABLE II

Resonance energies (in eV) of benzenoid hydrocarbon radicals

Label[a]	RE	RE/N	$E^b_{\pi RSE}$	E^b_{RSE}	F_{RES}/N	$RE(SR)^c$	$RE(SR)/N$
1	0.35	0.050	0.76	0.56	0.080	1.33	0.190
2	0.74	0.067	0.96	0.76	0.089	1.93	0.175
3	0.63	0.057	0.86	0.66	0.060	1.81	0.165
4	1.18	0.079	0.94	0.74	0.049	2.47	0.165
5	1.08	0.072	0.82	0.62	0.041	2.35	0.157
6	1.12	0.075	0.88	0.68	0.045	2.37	0.158
7	1.14	0.076	0.88	0.68	0.045	2.41	0.161
8	1.22	0.081	0.82	0.74	0.049	2.48	0.165
9	1.00	0.067	1.09	0.89	0.059	2.26	0.151
10	0.86	0.057	0.96	0.76	0.050	2.11	0.141
11	1.19	0.079	1.30	1.10	0.074	2.54	0.169
12	1.39	0.082	1.04	0.84	0.050	2.84	0.167
13	1.18	0.069	0.78	0.58	0.034	2.48	0.146
14	1.40	0.083	0.96	0.76	0.045	2.69	0.158
15	1.65	0.087	0.92	0.72	0.038	3.01	0.158
16	1.53	0.081	0.78	0.58	0.031	2.83	0.149
17	1.56	0.082	0.85	0.65	0.034	2.91	0.153
18	1.622	0.0854	0.85	0.65	0.034	2.95	0.1553
19	1.616	0.0851	0.85	0.65	0.034	2.94	0.1547
20	1.69	0.089	1.00	0.80	0.042	3.13	0.165
21	1.19	0.063	1.18	0.98	0.052	2.47[d]	0.130
22	1.05	0.055	1.04	0.84	0.044	2.33[d]	0.122
23	1.49	0.079	1.50	1.30	0.069	2.92[d]	0.154
24	1.75	0.092	0.81	0.61	0.032	3.07	0.162
25	1.72	0.091	0.77	0.57	0.030	3.05	0.161
26	1.81	0.086	1.16	0.96	0.046	3.37[d]	0.160
27[e]	1.96	0.093	0.63	0.44	0.021	3.15[d]	0.150
28	1.88	0.090	1.22	1.02	0.049	3.42[d]	0.163

[a] See Fig. 5
[b] Recalculated values from ref. 7
[c] Values obtained by formula (16) of Herndon[8,12,34]
[d] Calculated by us
[e] Result of Stein and Golden[7] or 2-perylenyl [SC(R˙)=9, SC(RH)=3, $E_{\pi RSE}$=0.86 eV, E_{RSE}=0.66 eV] is corrected by using corrected structure counts: SC(R˙)=27 and SC(RH)=9.

Before indulging in the discussion of the data in Table II we will examine in some detail the counts of valence structure for 1-perylenyl, 2-perylenyl and 3-perylenyl. Structure counts for benzenoid radicals which are considered in Table II have been reported previously by Stein and Golden[7], and a number of them by Herndon[10,34].

1-pyrenyl has 29 valence structures (SC = 29). These are given in Figure 6 in the condensed form (superposing structures having the same delocalization as π-electron fragments).

As we can see, the last structure in Figure 6 involves the 12 π-electron delocalization (this is the origin of Q_3 terms in the RE expression of 1-pyrenyl in Table I). One can view such structures as being a combination of two valence forms of opposite parity (SC⁺ = 1, SC⁻ = 1) and thus effectively cancelling one another, making a netto count of 27 (ASC = 27). Let us briefly mention a simple way of diagnosing parity of valence structures.
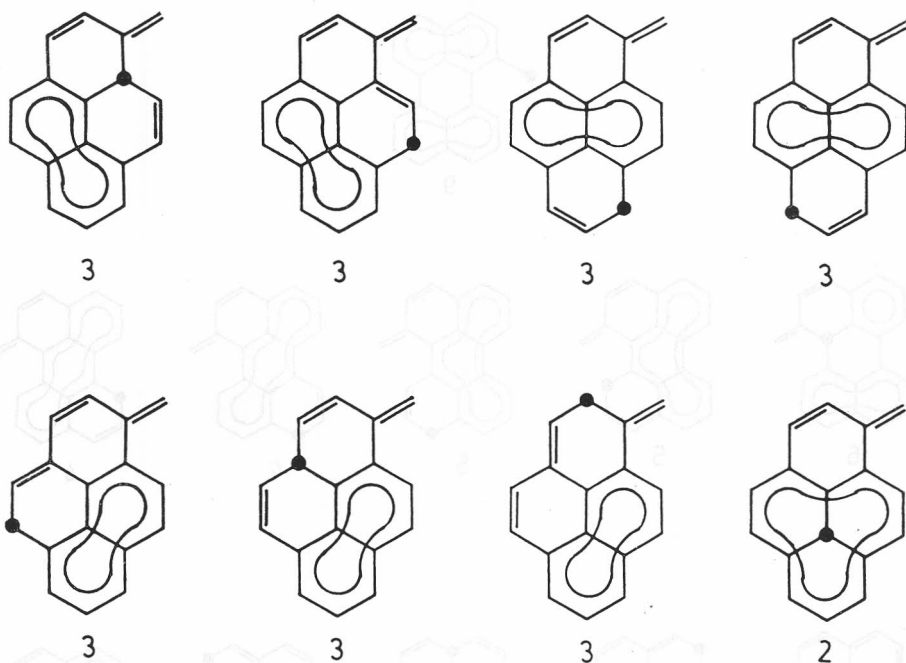
Figure 6. Valence structures of 1-pyrenyl in the condensed form, i. e., each structure is the result of superposition of several valence structures having the same delocalization of π-electron fragments. The number beneath each condensed structure indicates how many individual valence structures are superimposed.

Two different valence structures are of the same (opposite) parity if the number of the 4n-membered rings in their superposition is even (odd)[35,36].

In the case of perylenyl radicals we agree with counts reported by Stein and Golden[7] for 1-perylenyl (ASC = 46) and 3-perylenyl (ASC = 49), but disagree with their value of SC(9) for 2-perylenyl:

1-perylenyl has 48 valence structures (SC = 48). These are given in Figure 7 in the condensed form.

The last structure in Figure 7 involves 16 π-electron delocalization. It represents a superposition of three structures, two of which being of even parity and one of odd parity (SC$^+$ = 2, SC$^-$ = 1). Therefore, the count of structures for 1-perylenyl is 46 (ASC = 46).

3-perylenyl has 51 valence structures (SC = 51). These are given in the condensed form in Figure 8.

The same argument as for 1-perylenyl applies here. The netto count of structures for 2-perylenyl is 49 (ASC = 49).

The disagreement with Stein and Golden[7] is in the case of 2-perylenyl, for which they assign SC = 9. However, as seen in Figure 9, there are numerous valence structures for 2-perylenyl, a total of 27.

Interestingly, there is something unusual about 2-perylenyl radical in comparison with the other two perylenyl radicals: It has still relatively few valence structures, about half of those typifying other radicals of perylene. In addition, it has no 4n contributions, in fact it only has R_1 and R_2 conju-
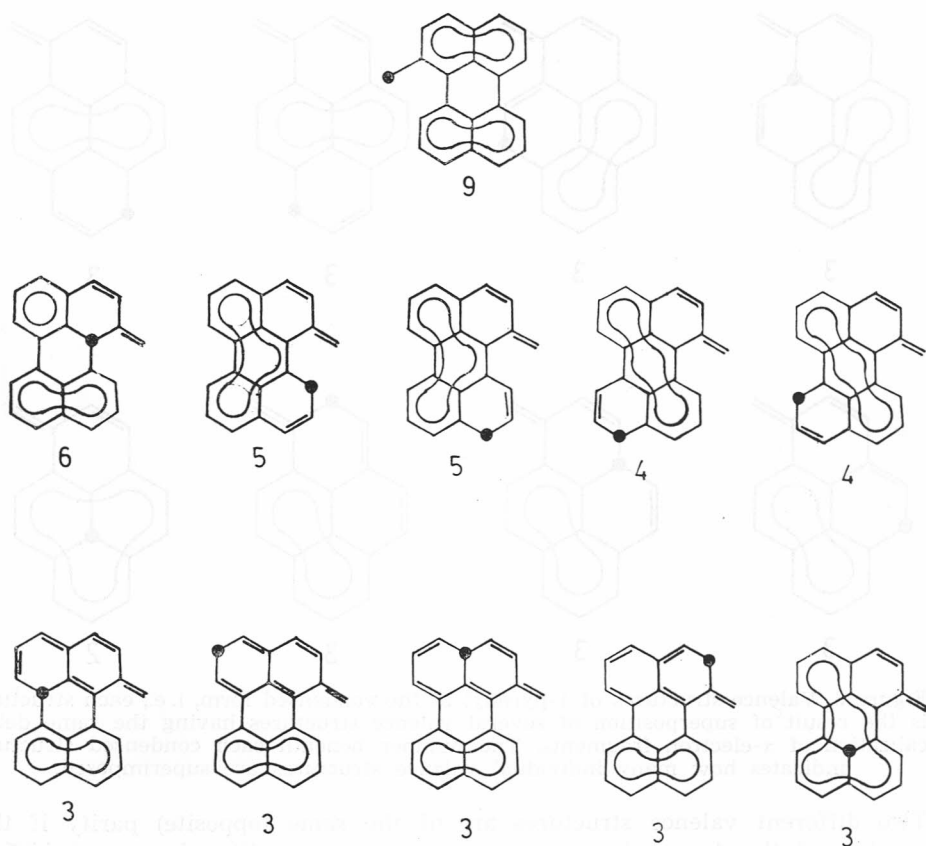
Figure 7 Valence structures of 1-perylenyl in the condensed form

gated circuits, just as naphthyl radicals, but in a somewhat different ratio: 26/9 rather than 8/9 as in 2-naphthylor 9/9 as in 1-naphthyl.

Here we also wish to say a few words about the isovalent structures. We will refer to molecules (ions and radicals included) as isovalent if they have the same number of valence structures or the same algebraic structure count.

In Table III we have collected all isovalent cases of this study. Inspection of Table III clearly shows that there is a considerable difference in the conjugation content (which we define as given by the count of conjugated circuits in the collection of valence structures of a molecule) for different cases. Differences in the count of R_1 will make up the major contribution to the anticipated differences among the isovalent systems. These contributions have to be normalized with ASC value, thus $\rho_1 \#^{(6)}$ ASC is an important parameter for indicating the possible differences among isovalent structures that the simple approach based on ASC alone cannot differentiate. From Table III we see that the ratio $\rho_1 \#^{(6)}$ ASC is greatest for the pair: 2-chrysyl and 2-perylenyl, followed by 5-tetracenyl and 1-triphenylenyl and the pair 9-anthryl and 2-tetracenyl. 2-perylenyl, as already stated, is unusual and
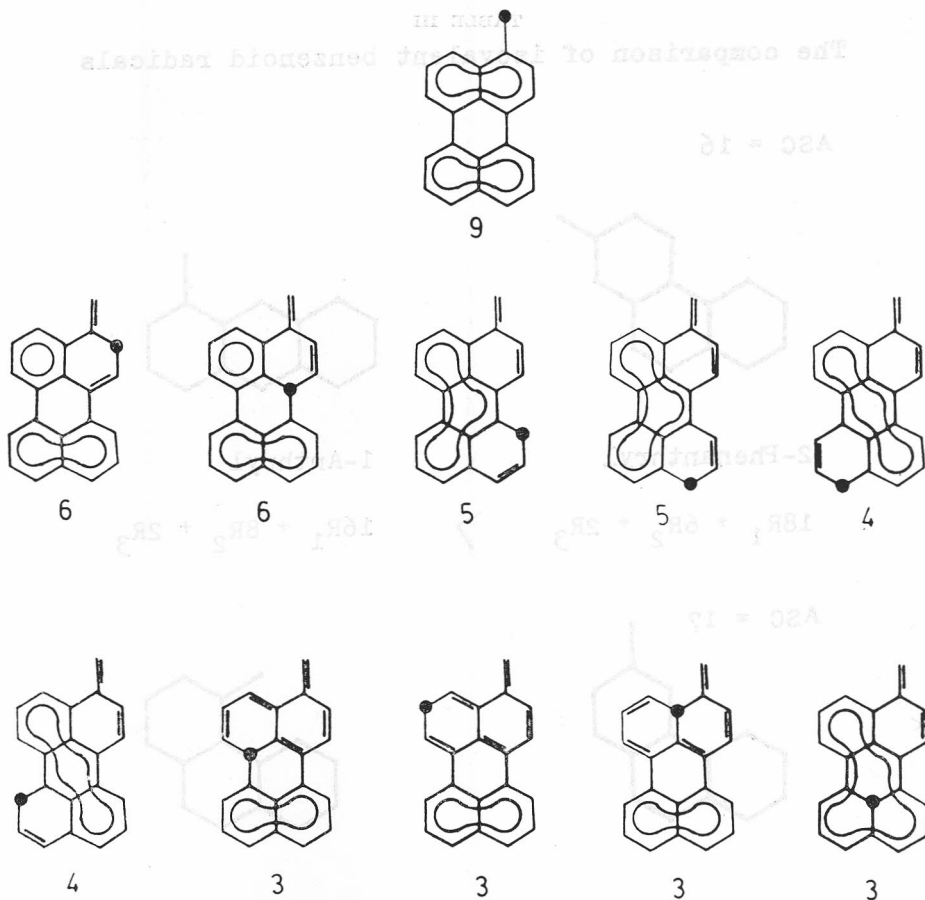
Figure 8. Valence structures of 3-perylenyl in the condensed form
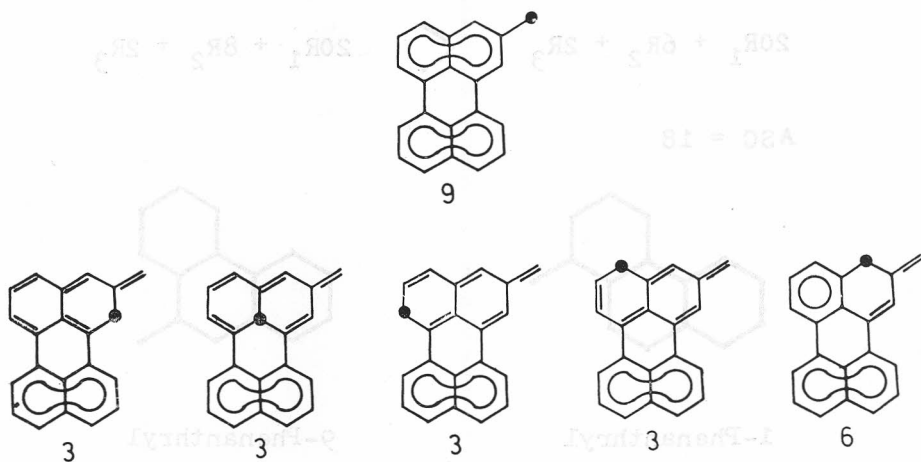
Figure 9. Valence structures of 2-perylenyl in the condensed form

D. PLAVŠIĆ ET AL.

The comparison of isovalent benzenoid radicals

ASC = 16
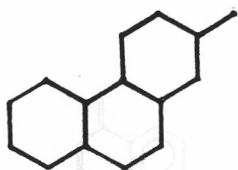
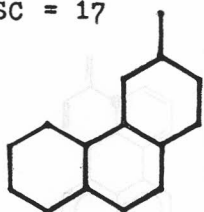

2-Phenanthryl

$18R_1 + 6R_2 + 2R_3$ > $16R_1 + 8R_2 + 2R_3$
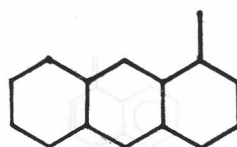
1-Anthryl

ASC = 17

3-Phenanthryl

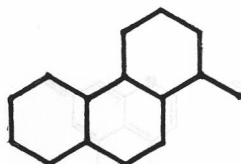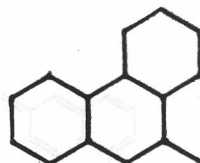$20R_1 + 6R_2 + 2R_3$ < $20R_1 + 8R_2 + 2R_3$

4-Phenanthryl

ASC = 18

1-Phenanthryl

$22R_1 + 8R_2 + 2R_3$ < $24R_1 + 4R_2 + 2R_3$

9-Phenanthryl

ASC = 20

9-Anthryl

$$26R_1 + 4R_2 + 2R_3 \quad > \quad 20R_1 + 12R_2 + 6R_3 + 2R_4$$
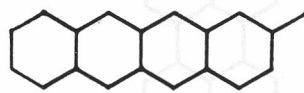
2-Tetracenyl

ASC = 23
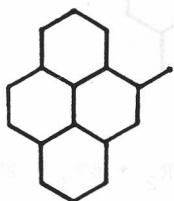
4-Pyrenyl

$$32R_1 + 16R_2 + 8R_3 \quad > \quad 26R_1 + 16R_2 + 8R_3 + 2R_4$$

1-Tetracenyl

ASC = 27
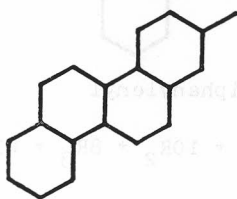
2-Chrysyl

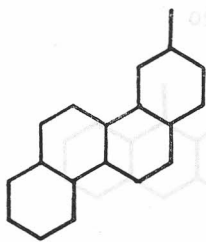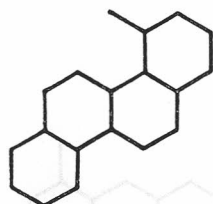$$42R_1 + 18R_2 + 6R_3 + 2R_4 \quad < \quad 54R_1 + 24R_2$$

2-Perylenyl

ASC = 29

1-Pyrenyl

$40R_1 + 22R_2 + 6R_3 + 2Q_3$
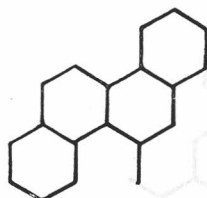
3-Chrysyl

$46R_1 + 20R_2 + 6R_3 + 2R_4$

4-Chrysyl
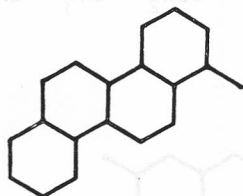
$48R_1 + 20R_2 + 8R_3 + 2R_4$

5-Chrysyl
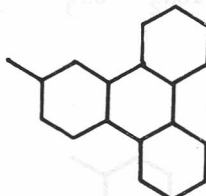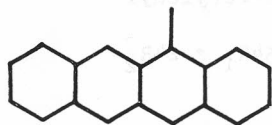
$48R_1 + 20R_2 + 4R_3 + 2R_4$

ASC = 31

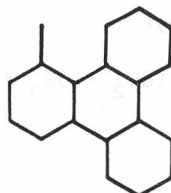1-Chrysyl

$52R_1 + 22R_2 + 6R_3 + 2R_4$

2-Triphenylenyl

$58R_1 + 10R_2 + 8R_3 + 2R_4$

ASC = 32

5-Tetracenyl

$50R_1 + 16R_2 + 4R_3 + 2R_4$

1-Triphenylenyl

$60R_1 + 14R_2 + 10R_3 + 2R_4$

can be viewed as naphthyl-naphthalene system which owes its additional resonance stability to naphthalene moiety. 1-Triphenylenyl gained resonance stabilization due to contributions of the conjugation of phenanthrene fragments and 9-anthryl is also known as unusually stable (compared to other anthryl radicals) primarily as all its valence structures contain conjugated circuits. The smallest differences among isovalent systems of Table III are found among 3-phenanthryl and 4-phenanthryl, the latter having a fraction higher resonance stabilization due to the larger count of R_2 conjugated circuits. With the current paucity of independent data on radicals it is difficult to examine how the above predictions fare. However, from the SCF MO calculation of Unruch and Gleicher[6] we see that for the only case they investigated that happens to have the same ASC, the case of 1-phenanthryl and 9-phenanthryl, the calculated ΔE_{RSE} (difference in resonance stabilization energies of the compound and benzyl) differ, being 3.21 kcal/mol and 4.10 kcal/mol. Thus, there is a definite difference in the two isovalent systems and 9-phenanthryl which has a greater $\rho_1 \#^{(6)}/ASC$ has a greater ΔE_{RSE}. This suggests that the ratio $\rho_1 \#^{(6)}/ASC$ may be an alternative (or additional) parameter of interest when discussiing resonance stabilizations of benzenoid hydrocarbon radicals.

To test this assumption we plotted in Figure 10 the quantity $\rho_1 \#^{(6)}/ASC$ which is shown in Table IV against RE in order to compare it with a plot

TABLE IV

Values of $\varrho_1 \#^{(6)}/ASC$ in eV

Label[a]	$\varrho_1 \#^6/ASC$
1	0.35
2	0.64
3	0.51
4	1.06
5	0.98
6	1.02
7	1.02
8	1.16
9	0.87
10	0.74
11	1.13
12	1.29
13	1.01
14	1.21
15	1.46
16	1.35
17	1.38
18	1.44
19	1.44
20	1.58
21	0.98
22	0.87
23	1.36
24	1.63
25	1.63
26	1.66
27	1.74
28	1.74

[a] See Figure 5

RE vs TSC (Figure 11) and to investigate a parallelism between conjugation content, the dominant term of which is given by the count of R_1 conjugated circuits and the algebraic structure count.
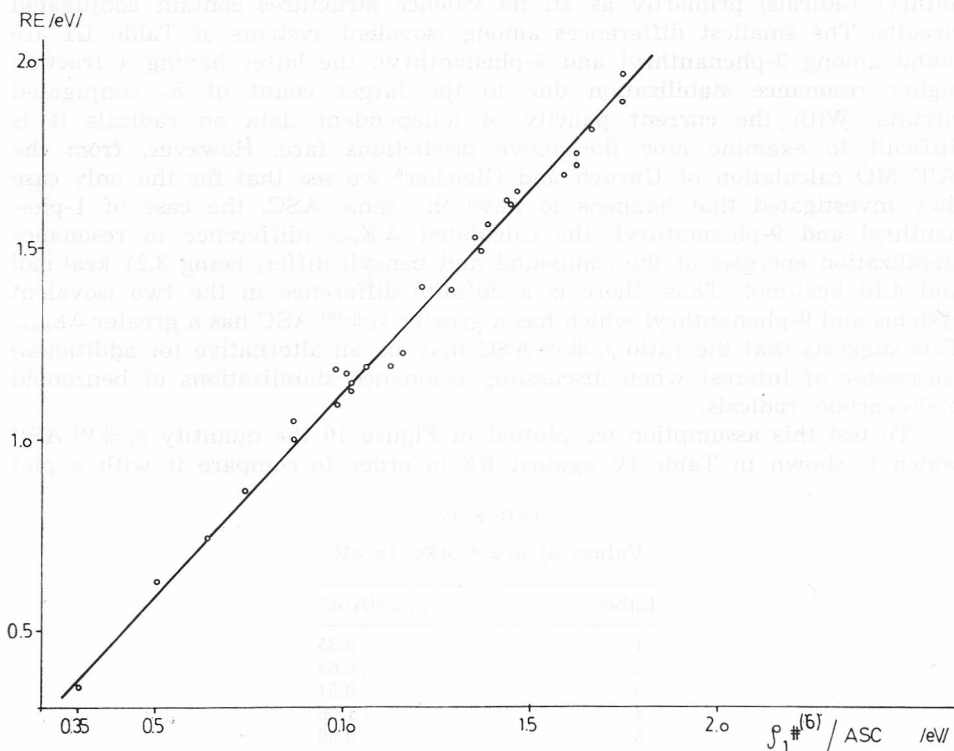

Figure 10. A plot of RE vs $\varrho_1 \#^{(6)}/ASC$

Inspection of Figure 10 and Figure 11 indicates that such parallelism exists, but a higher correlation is achieved with $\rho\#^{(6)}/ASC$ ($r = 0.993$) than by ASC ($r = 0.902$).

The advantage of $\rho\#^{(6)}/ASC$ is that it shows fewer accidental degeneracies (in fact for the sample considered only two have been spotted, the value of 1.02 for 3- and 4-phenanthryls and 1.44 for 4-and 5-chrysyl radicals). Thus, $\rho\#^{(6)}/ASC$ has »more flexibility« than ASC but, of course, further studies have yet to show if the diversification introduced by $\rho\#^{(6)}/ASC$ as compared to ASC is adding to the power of the simple empirical correlation between the conjugation content expressed in some simple way and RE or may not be warranted, or perhaps even introducing larger average deviation for quantities, such as ΔE_{RSE}, than that of the simple approach.

Since the RE based on conjugated circuits embraces both quantities, $\rho\#^{(6)}/ASC$ and ASC, the above results also indicate the importance of benzene-like circuits for the aromatic stability of benzenoid radicals.
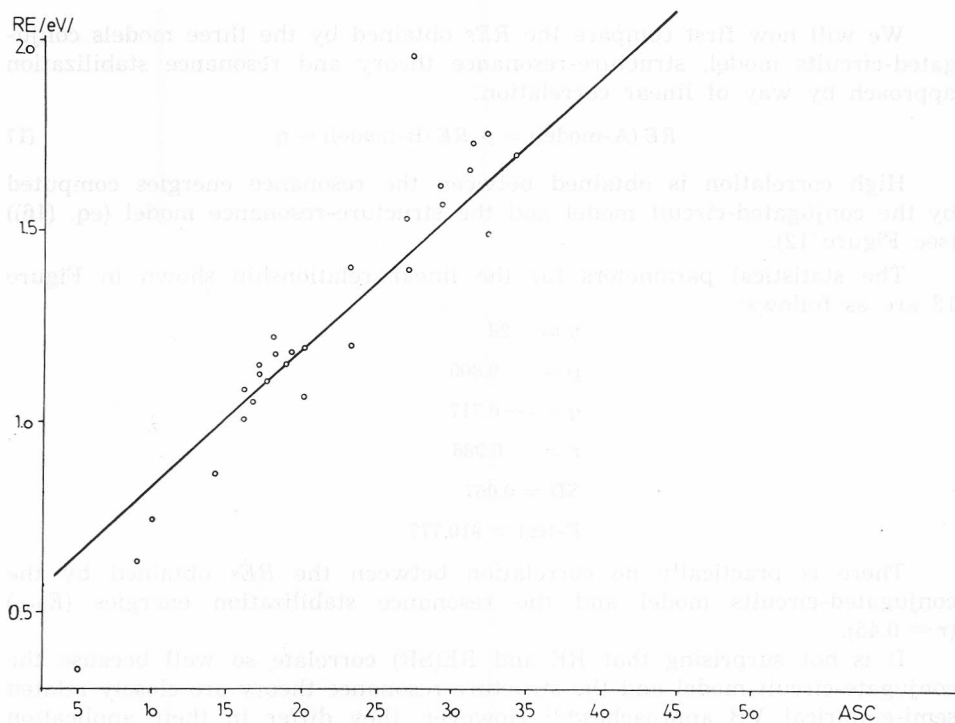
RE /eV/

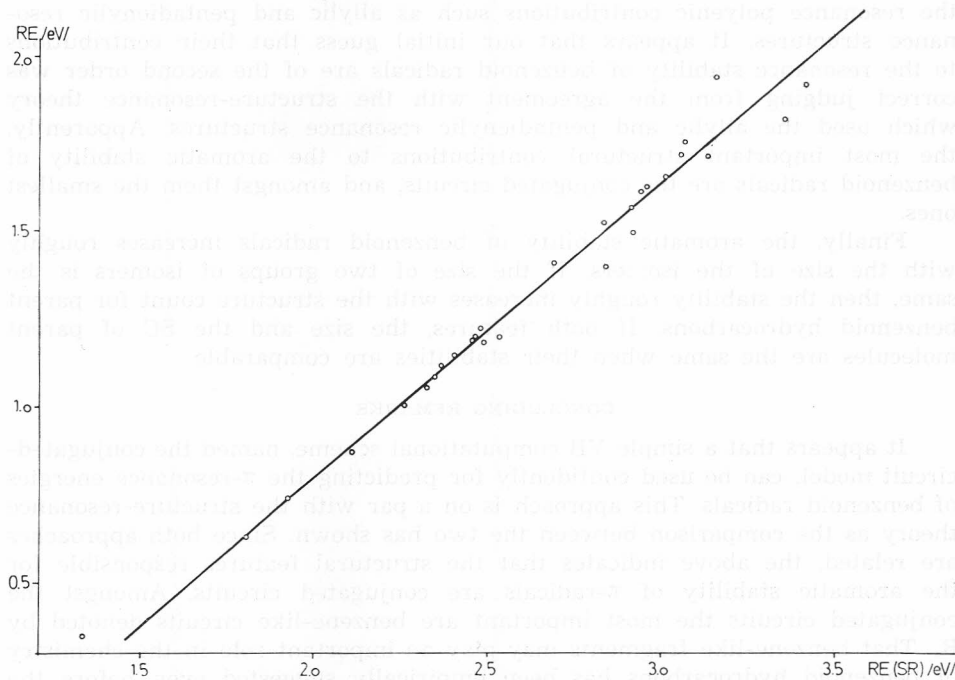
Figure 11. A plot of RE *vs.* ASC

RE /eV/

Figure 12. The linear correlation between resonance energies of benzenoid radicals computed using the conjugated-circuit model (RE) and structure-resonance model (RE(SR))

We will now first compare the REs obtained by the three models conjugated-circuits model, structure-resonance theory and resonance stabilization approach by way of linear correlation:

$$RE \text{ (A-model)} = p \; RE \text{ (B-model)} + q \qquad (17$$

High correlation is obtained between the resonance energies computed by the conjugated-circuit model and the structure-resonance model (eq. (16)) (see Figure 12).

The statistical parameters for the linear relationship shown in Figure 12 are as follows:

$$n = \quad 28$$
$$p = \quad 0.805$$
$$q = \quad -0.717$$
$$r = \quad 0.986$$
$$SD = 0.067$$
$$F\text{-test} = 910.777$$

There is practically no correlation between the REs obtained by the conjugated-circuits model and the resonance stabilization energies (E_{RSE}) ($r = 0.45$).

It is not surprising that RE and RE(SR) correlate so well because the conjugate-circuit model and the structure-resonance theory are closely related semi-empirical VB approaches.[4,37] However, they differ in their application to π-radicals because the conjugated-circuit model did not take into account the resonance polyenic contributions such as allylic and pentadienylic resonance structures. It appears that our initial guess that their contributions to the resonance stability of benzenoid radicals are of the second order was correct judging from the agreement with the structure-resonance theory which used the allylic and pentadienylic resonance structures. Apparently, the most important structural contributions to the aromatic stability of benzenoid radicals are the conjugated circuits, and amongst them the smallest ones.

Finally, the aromatic stability of benzenoid radicals increases roughly with the size of the isomers. If the size of two groups of isomers is the same, then the stability roughly increases with the structure count for parent benzenoid hydrocarbons. If both features, the size and the SC of parent molecules are the same when their stabilities are comparable.

CONCLUDING REMARKS

It appears that a simple VB computational scheme, named the conjugated-circuit model, can be used confidently for predicting the π-resonance energies of benzenoid radicals. This approach is on a par with the structure-resonance theory as the comparison between the two has shown. Since both approaches are related, the above indicates that the structural features responsible for the aromatic stability of π-radicals are conjugated circuits. Amongst the conjugated circuits the most important are benzene-like circuits denoted by R_1. That benzene-like fragments may play an important role in the chemistry of benzenoid hydrocarbons has been empirically suggested even before the

advent of quantum chemistry[38], thus anticipating perhaps the Hückel $4n+2$ rule. Therefore, the heart of the aromaticity of π-radicals (as well as of all polycyclic conjugated systems) may be in conjugative properties of small rings and not in the boundary of the collection of fused rings. The conjugated circuits belonging to larger boundaries ordinarily bring negligible contribution to the RE.

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SAŽETAK

Model konjugiranih krugova. Primjena na radikale benzenoidnih ugljikovodika

D. Plavšić, N. Trinajstić, M. Randić i C. Venier

Model konjugiranih krugova primijenjen je na radikale benzenoidnih ugljikovodika. Izračunane su njihove rezonancijske energije i upotrijebljene za predviđanje njihovih aromatičkih stabilnosti. Ta su predviđanja potvrđena i drugim teorijskim modelima kao što je npr. jednostavni strukturno-rezonancijski model. Teorijska su predviđanja također potvrđena eksperimentalnim podacima. Ovaj rad upućuje i na to da model konjugiranih krugova pruža velike mogućnosti za kvalitativno i kvantitativno proučavanje termodinamičke stabilnosti policikličkih konjugiranih radikala.