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Note

The Conjugated-Circuits Model: On the Selection of the Parameters*

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Four sets of parameters that are used in the framework of the semi-empirical VB resonance-theoretic model named the conjugated-circuits model are compared. The basis of the comparison was statistical analysis of the linear relationship between the REs obtained by the Dewar's SCF π -MO model and the REs obtained by the conjugated-circuits model. All four sets of parameters lead to the linear relationships with similar statistical characteristics. Since the value of the R_4 parameter is rather uncertain the three-parameter model is recommended to be used.

INTRODUCTION

The conjugated-circuits model is a semi-empirical VB resonance-theoretic model which was introduced by Milan Randić in 1976¹ for the study of aromaticity and conjugation in polycyclic conjugated systems.² This model was motivated³ from an empirical point of view elaborating Fries' ideas on the stability of aromatic systems⁴ and Clar's aromatic sextet ideas.⁵ By using the tools of chemical graph theory⁶ Randić quantified these ideas into his conjugated-circuits model.

The conjugated-circuits model may be rigorously derived⁷ from the Pauling-Wheland VB resonance theory⁸ by means of the Simpson-Herndon model.⁹ The model also introduces a novel superposition principle not recognized before within quantum chemistry.¹⁰

In this paper we will discuss the selection of the parameters for computing the resonance energies of benzenoid and coronoid hydrocarbons. It was stimulated by some reports in the literature¹¹ in which, we are afraid, the authors did not quite comprehend how the parameters used in the conjugated-circuits model were chosen.

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The report is structured as follows. In the next section we will give a brief outline of the conjugated-circuits model. The third section contains the parametrization procedure. In the fourth section we will compare several sets of the parameters that are used in the literature. The report will end with concluding remarks.

OUTLINE OF THE CONJUGATED-CIRCUITS MODEL

The model is based on the concept of conjugated circuits. A graph-theoretical analysis of Kekulé valence structures led to this concept.¹ The conjugated circuits are those circuits within the individual Kekulé structure in which there is a regular alternation of formal CC single and double bonds. Thence, the conjugated circuits are necessarily of even length.

The circuit decomposition of individual Kekulé structures of polycyclic conjugated hydrocarbons gives conjugated circuits of size $4n+2$ and/or $4n$ ($n = \text{integer}$). There are possible linearly dependent, linearly independent and disjoint conjugated circuits. Linearly independent conjugated circuits are those that cannot be represented by superposition of conjugated circuits of smaller sizes. Disjoint conjugated circuits are composites of two or more single conjugated circuits no pair of which share a site. The total number of all conjugated circuits disjoint or not, within a single Kekulé structure is equal to $K-1$,¹² where K is the number of Kekulé structures of a polycyclic conjugated hydrocarbon. The $4n+2$ carbon conjugated circuits are denoted by R_n and similarly the $4n$ carbon conjugated circuits by Q_n . In Figure 1 we give as an example, the Kekulé structures of naphthalene and their circuit decomposition.

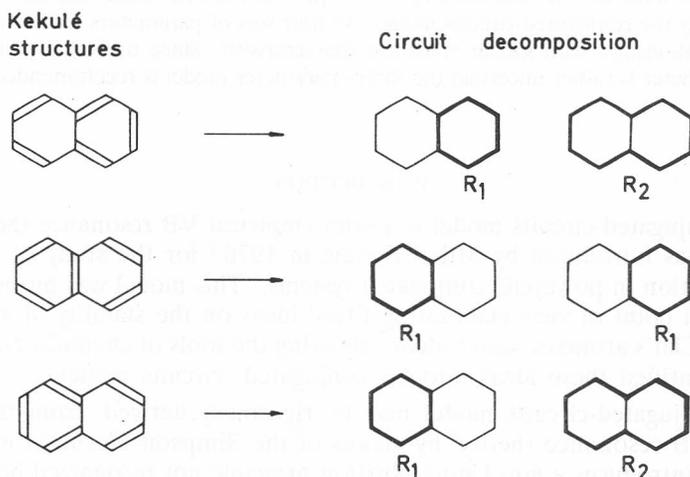


Figure 1. The decomposition of Kekulé structures of naphthalene into the corresponding conjugated circuits

The total circuit decomposition of naphthalene is given by:

$$4 R_1 + 2 R_2 \quad (1)$$

The conjugated circuits may be used to calculate π -resonance energies (REs) of polycyclic conjugated systems. This is related to the basic assumption of the conjugated-circuits model according to which the conjugated circuits are dominant structural features determining the stabilities and, in particular, the REs of conjugated systems. The REs can be expressed as simple additive functions of the conjugated circuits, and only the size of a conjugated circuit has to be taken into consideration. Hence, the formula for computing REs is:

$$RE = \frac{1}{K} \sum_{n \geq 1} (r_n R_n + q_n Q_n) \quad (2)$$

where K is the number of Kekulé structures, R_n and Q_n are, respectively, the oppositely-signed parametric values corresponding to $4n+2$ and $4n$ circuits, and r_n and q_n are, respectively, the total numbers of R_n and Q_n circuits summed over all Kekulé structures of the molecule. The parameter R_n (Q_n) measures the extent to which a specific conjugated circuit of size $4n+2$ ($4n$) influences the thermodynamic stability of the polycyclic conjugated molecule. The R_n circuits contribute towards the aromatic stability of a polycyclic system, whilst the Q_n circuits have a destabilizing effect on the aromatic stability of the system.

Eq. (2) reduces to

$$RE = \frac{1}{K} \sum_{n \geq 1} r_n R_n \quad (3)$$

for benzenoid systems. This is so because benzenoid hydrocarbons contain only R_n circuits.

NUMERICAL VALUES OF THE R_n PARAMETERS

The RE expression (3) is the result of a formal graph-theoretical analysis of molecular graphs representing benzenoids. In order to "introduce" chemistry into this analysis one has to adopt some outside source in the form of the numerical values for the R_n parameters. Here we will follow the parametrization procedure of Randić.^{1,13}

The parameters R_n are derived from the REs calculated by Dewar and de Llano¹⁴ via Dewar's original variant¹⁵ of the SCF π -MO model of Pople.¹⁶ Dewar's REs for benzene (B), naphthalene (N), anthracene (A) and tetracene (T), that are given below, are used as standards to which the R_n were adjusted accurately:

$$\begin{aligned} RE(B) &= 0.869 \text{ eV} \\ RE(N) &= 1.323 \text{ eV} \\ RE(A) &= 1.600 \text{ eV} \\ RE(T) &= 1.822 \text{ eV} \end{aligned} \quad (4)$$

The RE expressions for the four linear benzenoids are:

$$\begin{aligned}
 RE(B) &= (2 R_1)/2 \\
 RE(N) &= (4 R_1 + 2 R_2)/3 \\
 RE(A) &= (6 R_1 + 4 R_2 + 2 R_3)/4 \\
 RE(T) &= (8 R_1 + 6 R_2 + 4 R_3 + 2 R_4)/5
 \end{aligned}
 \tag{5}$$

These equations for our purpose could more conveniently be written as:

$$\begin{aligned}
 R_1 &= RE(B) \\
 R_2 &= (3/2) RE(N) - 2 RE(B) \\
 R_3 &= RE(B) - 3 RE(N) + 2 RE(A) \\
 R_4 &= (3/2) RE(N) - 4 RE(A) + (5/2) RE(T)
 \end{aligned}
 \tag{6}$$

Introduction of (4) into (6) gives¹³

$$\begin{aligned}
 R_1 &= 0.869 \text{ eV} \\
 R_2 &= 0.247 \text{ eV} \\
 R_3 &= 0.100 \text{ eV} \\
 R_4 &= 0.140 \text{ eV}
 \end{aligned}
 \tag{7}$$

There are several more sets of the R_n parameters available in the literature. We will list below all of them. Randić's original set¹ is the following:

$$\begin{aligned}
 R_1 &= 0.869 \text{ eV} \\
 R_2 &= 0.247 \text{ eV} \\
 R_3 &= 0.100 \text{ eV} \\
 R_4 &= 0.041 \text{ eV}
 \end{aligned}
 \tag{8}$$

Herndon's resonance-structure model^{9a,9b} which is closely related^{7,17} to the conjugated-circuits model uses only two-parameters:

$$\begin{aligned}
 R_1 &= 0.841 \text{ eV} \\
 R_2 &= 0.336 \text{ eV}
 \end{aligned}
 \tag{9}$$

Finally, Randić and co-workers^{2d,18} have recently advocated the use of the following three parameters in the conjugated-circuits model:

$$\begin{aligned}
 R_1 &= 0.869 \text{ eV} \\
 R_2 &= 0.247 \text{ eV} \\
 R_3 &= 0.100 \text{ eV}
 \end{aligned}
 \tag{10}$$

RESULTS AND DISCUSSION

We calculated REs of 32 benzenoid hydrocarbons for which Dewar's REs^{14} are available. Diagrams of these benzenoids are given in Figure 2.

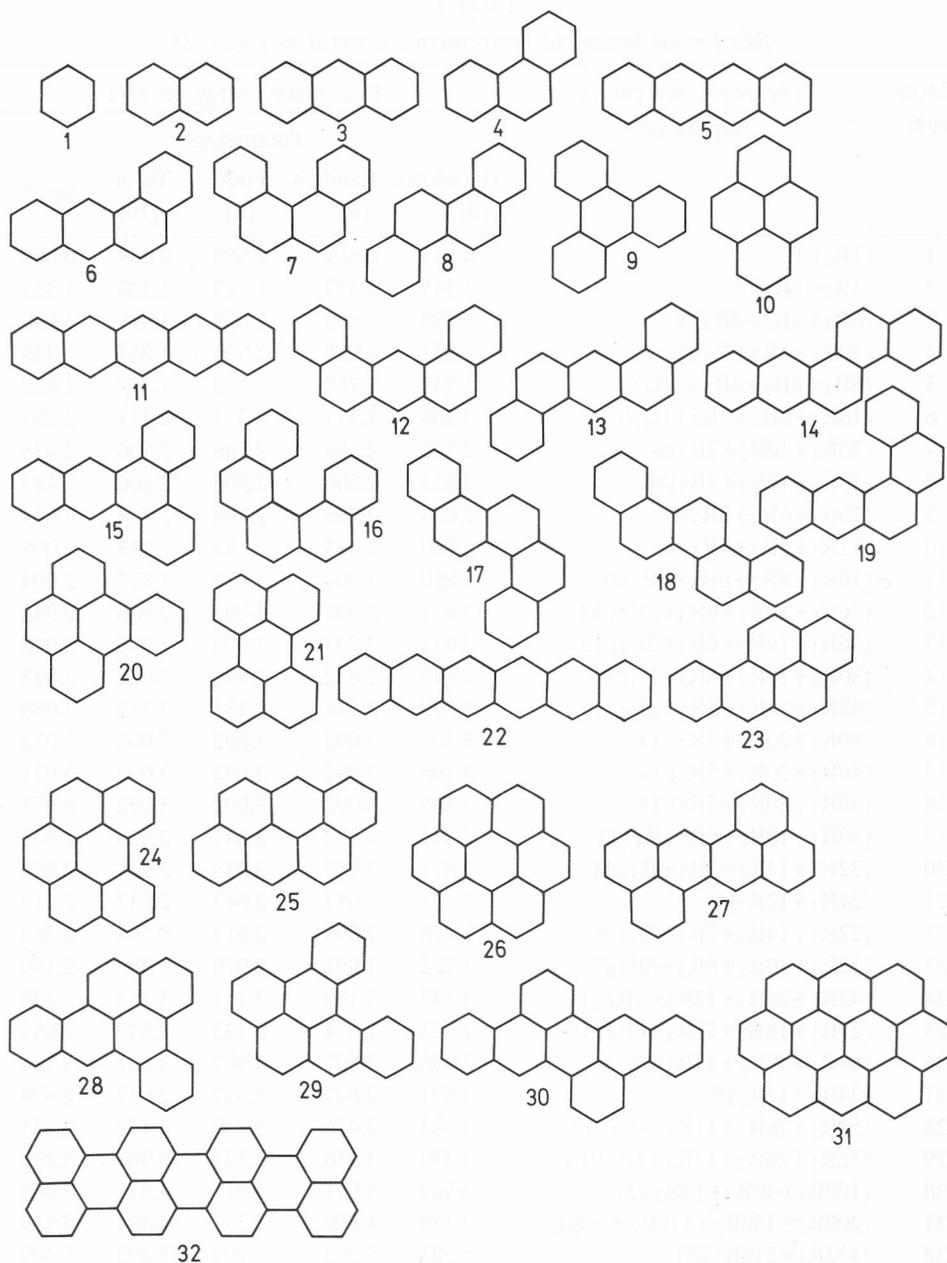


Figure 2. Diagrams of the studied benzenoid hydrocarbons

The RE values for these benzenoid hydrocarbons obtained using four sets of the R_n parameters are reported in Table I. This table also contains the SCF π -MO REs of Dewar and de Llano.¹⁴

TABLE I
REs for the benzenoid hydrocarbons depicted in Figure 2

Mole- cule	The resonance energy expression	Resonance energy (in eV)				SCF ^a
		Parameters				
		Herndon's (9)	Randić's (8)	Four (7)	Three (10)	
1	(2R ₁)/2	0.841	0.869	0.869	0.869	0.869
2	(4R ₁ +2R ₂)/3	1.345	1.323	1.323	1.323	1.323
3	(6R ₁ +4R ₂ +2R ₃)/4	1.598	1.600	1.600	1.600	1.600
4	(10R ₁ +4R ₂ +R ₃)/5	1.951	1.955	1.955	1.955	1.933
5	(8R ₁ +6R ₂ +4R ₃ +2R ₄)/5	1.749	1.782	1.822	1.766	1.822
6	(16R ₁ +8R ₂ +3R ₃ +R ₄)/7	2.306	2.317	2.331	2.311	2.291
7	(20R ₁ +10R ₂ +2R ₃)/8	2.523	2.506	2.506	2.506	2.478
8	(20R ₁ +10R ₂ +2R ₃)/8	2.523	2.506	2.506	2.506	2.483
9	(26R ₁ +6R ₂ +3R ₃)/9	2.654	2.708	2.708	2.708	2.654
10	(12R ₁ +8R ₂ +4R ₃)/6	2.130	2.133	2.133	2.133	2.098
11	(10R ₁ +8R ₂ +6R ₃ +4R ₄)/6	1.850	1.904	1.970	1.877	2.004
12	(36R ₁ +16R ₂ +6R ₃ +2R ₄)/12	2.971	2.993	3.009	2.986	2.948
13	(36R ₁ +16R ₂ +6R ₃ +2R ₄)/12	2.971	2.993	3.009	2.986	2.948
14	(30R ₁ +18R ₂ +6R ₃ +R ₄)/11	2.843	2.832	2.841	2.828	2.823
15	(42R ₁ +14R ₂ +5R ₃ +2R ₄)/13	3.079	3.118	3.133	3.112	3.058
16	(40R ₁ +20R ₂ +5R ₃)/13	3.105	3.092	3.092	3.092	3.072
17	(40R ₁ +20R ₂ +5R ₃)/13	3.105	3.092	3.092	3.092	3.071
18	(40R ₁ +20R ₂ +5R ₃)/13	3.105	3.092	3.092	3.092	3.071
19	(30R ₁ +18R ₂ +6R ₃ +R ₄)/11	2.843	2.832	2.841	2.828	2.823
20	(32R ₁ +14R ₂ +7R ₃ +R ₄)/11	2.874	2.909	2.918	2.905	2.853
21	(24R ₁ +12R ₂)/9	2.691	2.647	2.647	2.647	2.619
22	(22R ₁ +14R ₂ +7R ₃ +2R ₄)/9	2.578	2.595	2.617	2.585	2.584
23	(12R ₁ +10R ₂ +8R ₃ +6R ₄)/7	1.922	1.991	2.076	1.956	2.160
24	(42R ₁ +26R ₂ +12R ₃ +3R ₄)/14	3.147	3.159	3.181	3.151	3.128
25	(24R ₁ +18R ₂ +12R ₃ +6R ₄)/10	2.623	2.674	2.733	2.649	2.665
26	(64R ₁ +48R ₂ +27R ₃)/20	3.498	3.507	3.507	3.507	3.524
27	(24R ₁ +12R ₂)/9	2.691	2.647	2.647	2.647	2.694
28	(58R ₁ +26R ₂ +11R ₃ +4R ₄)/17	3.383	3.416	3.440	3.407	3.375
29	(52R ₁ +26R ₂ +13R ₃ +4R ₄)/16	3.279	3.316	3.341	3.306	3.283
30	(100R ₁ +40R ₂ +10R ₃)/25	3.902	3.911	3.911	3.911	3.862
31	(200R ₁ +160R ₂ +110R ₃ +26R ₄)/50	4.439	4.506	4.557	4.484	4.539
32	(432R ₁ +216R ₂)/81	5.381	5.293	5.293	5.293	5.309

^a M. J. S. Dewar and C. de Llano, *J. Am. Chem. Soc.* **91** (1969) 789.

The RE s obtained by four sets of parameters were tested against Dewar RE s by means of the following linear correlation:

$$RE(\text{Dewar}) = p RE(\text{conjugated-circuits model}) + q \quad (11)$$

In Table II we give statistical parameters for the linear relationships between the $RE(\text{Dewar})$ values and the $RE(\text{conjugated-circuits model})$ values computed via the four sets of parameters considered in this report.

TABLE II
Least-squares parameters for linear relationship (11)

Model	Statistical parameters						
	n	p	q	r	SD	t	χ^2
Herndon's	32	0.979(0.013)	0.059(0.036)	0.998	0.061	78.1107	0.0519
Randić's	32	0.989(0.010)	0.023(0.028)	0.999	0.047	103.0769	0.0284
Four-parameter	32	0.990(0.007)	0.004(0.021)	0.999	0.036	134.4640	0.0145
Three-parameter	32	0.988(0.011)	0.032(0.031)	0.998	0.053	90.2153	0.0384

On the basis of these statistical parameters, the conjugated-circuits model using four parameters (with $R_4 = 0.140$ eV) best agrees with the Dewar RE s. The second in this sense is the conjugated-circuits model with Randić's original selection of parameters. Randić selected for R_4 the value of 0.041 eV in order to obey the monotonic behaviour of the R_n parameters: $R_1 > R_2 > R_3 > R_4$ (see Figure 3). His selection is also based on the reasonable assumption that the larger circuits have smaller contributions to the stabilization energy.^{1,2a,2b}

From the practical point of view all four sets of parameters may be used in the conjugated-circuits model when applied to benzenoid hydrocarbons. For example, Klein and co-workers¹⁹ in their elegant reports on the stabilities of fullerenes and other large π -networks such as graphite have used Herndon's parameters. Randić and co-workers^{2d,12,18,20} have used in a variety of the recent applications of the conjugated-circuits model the three-parameter version of the model. There are several reasons for this practice. We will list some below:

(a) The empirical findings indicate that only the smallest circuit make appreciable contributions to the RE .^{9c}

(b) The value of the parameter R_4 is rather uncertain and its value ranges from 0.041 eV to 0.140 eV, depending on the source of the SCF π -MO calculation and the type of parametrization procedure.⁷

(c) There is only a slight difference between the three-parameter and the four-parameter versions of the conjugated-circuits model.

(d) The three-parameter version of the model may be relatively easily extended to heteroconjugated systems.^{18a,21}

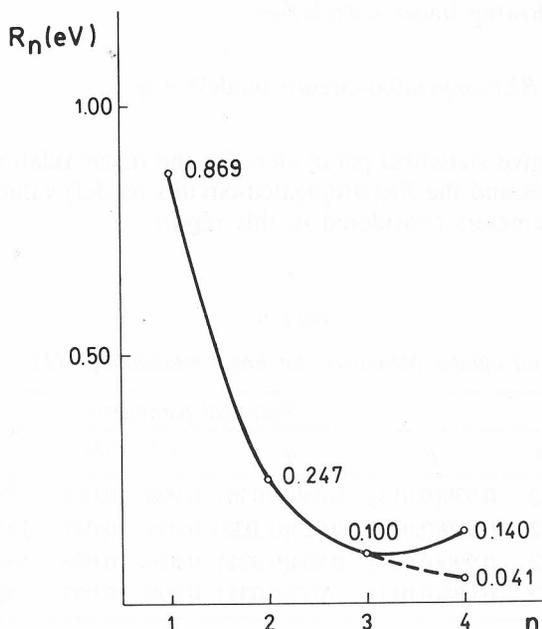


Figure 3. A plot of R_n vs n

The present level of the development of the conjugated-circuits model allows one to treat a variety of organic and inorganic conjugated systems^{22,23} such as polycyclic conjugated hydrocarbons, elemental carbon cages, fractal conjugated structures, heterocyclic conjugated systems, extended conjugated systems, high-temperature superconductors, conjugated radicals, cations and anions, Möbius structures and lowest excited states of benzenoid hydrocarbons. The key step in this development was the reduction of the number of parameters to three (and in some cases to two) and a parametrization approach based on the expression:^{9c,13,18a,19a,21b,23}

$$(CC)_n = (R_n/R_1) (CC)_1; \quad n = 1,2,3 \quad (12)$$

where $(CC)_n$ stands for parameters corresponding to carbon conjugated circuits or heteroatomic conjugated circuits. To use this formula one needs to know only the numerical value for the $(CC)_1$ parameter for each case considered. The above formula is based on the assumption that the same relationship that exists between the parameters for $(4n+2)$ carbon conjugated circuits holds also for other kinds of circuits.²⁴ The set of parameters is truncated at $n = 3$ because only R_1 , R_2 and R_3 are known rather accurately and as such they can be used for generating other types of conjugated circuits, i.e., $4n$ carbon conjugated circuits, $4n+2$ and $4n$ conjugated circuits containing divalent sulphur, etc.

CONCLUDING REMARKS

Four sets of numerical values for the R_n parameters are used for the conjugated-circuits calculations of the REs for 32 benzenoid hydrocarbons with the known Dewar's REs . All four set of parameters may be used for predicting the REs of unknown benzenoids. However, the three-parameter set is recommended to be used because it is simple enough and gives accurately enough the REs . Besides, it is shown to be easily extendable to other kinds of conjugated circuits, i.e., circuits containing other types of atoms besides carbon.

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SAŽETAK

Model konjugiranih krugova. O izboru parametara

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Uspoređivana su četiri skupa parametara koja se upotrebljavaju unutar semiempirijskog VB rezonancijsko-teorijskog modela nazvanog model konjugiranih krugova. Temelj usporedbe bila je statistička analiza linearnog odnosa između rezonancijskih energija dobivenih Dewarovim SCF π -MO modelom i onih dobivenih modelom konjugiranih krugova. Sva četiri skupa parametara pokazuju linearnu ovisnost sa sličnim statističkim karakteristikama. Budući da je vrijednost parametra R_4 nepouzdana, preporučuje se upotreba modela sa tri parametra.