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The Conjugated-Circuit Model Revisited*

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Two formulae for computing resonance energies of benzenoid hydrocarbons within the conjugated-circuit model are considered. The first is Randić's original formula developed in 1976 and the second is the result of the analysis of the foundations of the conjugated-circuit model in terms of the Simpson-Herndon model Hamiltonians. Both formulae produce very similar resonance energies. This analysis thus justifies Randić's initial choice of circuits and their parameters.

A dozen years ago Randić introduced a resonance-theoretical model named the conjugated-circuit model[1] which was motivated from an empirical point of view elaborating Armit-Robinson-Clar aromatic sextet ideas.[2,3] This model has been used rather successfully for the study of aromaticity and conjugation in a great variety of π-electronic systems such as benzenoid and nonbenzenoid hydrocarbons,[1,4–6] corannulenes,[7] benzoannelated annulenes,[8] helicenes,[5,9] macrocyclic benzenoid systems,[10] benzenoid polymers,[11] polycyclic conjugated hydrocarbon (di)cations and (d)anions,[12] the lowest excited states of polyacenes,[13] Möbius structures,[14] heterocyclic conjugated systems,[15] buckminsterfullerene and elemental carbons.[16]

A graph theoretical analysis of Kekulé valence structures led to the concept of conjugated circuits.[1,17,18] A conjugated circuit of lenght 21 is a cycle of $2l$ edges alternating between single and double bonds within a Kekulé structure. Conjugated circuits are used for the computation of π-electron resonance energies, *RE*. Below we give, for example, the *RE* expression for benzenoid hydrocarbons[1]

$$RE = \frac{1}{K} \Sigma \varrho_n \, \#^{(4n+2)} \qquad (1)$$

where K is the number of Kekulé structures, the ϱ_n are parameters which decrease in magnitude nearly geometrically with increasing n[1,15a] and $\#^{(4n+2)}$

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is the total number of 4n+2 conjugated circuits summed over all Kekulé structures. Note that ρ_n measures the extent to which a specific conjugated circuit of size 4n+2 influences the thermodynamic stability of the conjugated molecule. There are several sets of ρ_n parameters (with truncation at different n values) available in the literature.[1,15a,19] In addition, the conjugated-circuit model turns out to be closely related[20] to Herndon's so-called »structure-resonance theory«,[21] so that parametrization from this approach might also be used. For the ρ_n, expressed in eV, Randić originally gave[1]

$$RE = \frac{1}{K}\,(0.869\,\#^{(6)} + 0.246\,\#^{(10)} + 0.100\,\#^{(14)} + \ldots) \tag{2}$$

Representative shapes of the first three lowest conjugated circuits that are used by Randić are depicted in Figure 1.

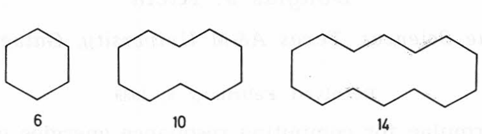

Figure 1. Representative shapes of the first three lowest conjugated circuits.

Recently we analyzed the foundations of the conjugated-circuit model[22] in terms of the Simpson-Herndon model Hamiltonians.[21,23] Via derivation from the Pauling-Wheland VB model[4] we found

$$RE = \frac{3J}{2K}\left(\frac{39}{64}\,\#^{(6)} + \frac{9}{64}\,\#^{(10)} + \frac{3}{64}\,\#^{(14a)} + \frac{3}{128}\,\#^{(14b)} + \frac{7}{64}\,\#^{(14c)} + \ldots\right) \tag{3}$$

or by using for the exchange parameter the following value[21b,26]

$$J = 1.857 \text{ eV} \tag{4}$$

eq. (3) is finally given as

$$RE = \frac{1}{K}\,(1.697\,\#^{(6)} + 0.392\,\#^{(10)} + 0.131\,\#^{(14a)} + 0.065\,\#^{(14b)} + 0.305\,\#^{(14c)} + \ldots) \tag{5}$$

Eq. (5) is somewhat different from Randić's original *RE* expression (2) and (by derivation[22]) leads to *RE* values close to those of Pauling-Wheland resonance theory.

Eqs. (3) and (5) indicate, for example, that there are three types of conjugated circuits of size 14. These are shown in Figure 2.

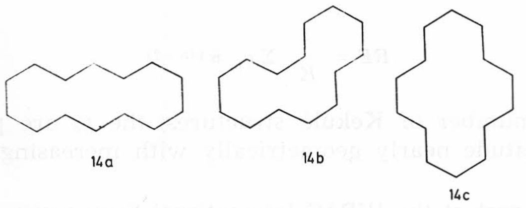

Figure 2. Shapes of three types of conjugated circuits of size 14.

Randić in his initial work did not independently differentiate between these three types of conjugated circuits which are of the same size 14 but of different shape.

Eqs. (3) and (5) have some appealing features. For example, they fulfil the minimum condition for the intrinsic consistency of ρ_n parameters[18,19]

$$\varrho_1 > \varrho_2 > \varrho_3. \tag{6}$$

The ratio of ρ_2 to ρ_1 ($\rho_2/\rho_1 \cong 0.23$) is also rather close to the value (0.28) of Randić.[1]

In this work we wish to reinvestigate Randić' original *RE* in terms of the difference between the shapes of the conjugated circuits of size 14. We will also truncate the set of 4n+2 circuits at size 14 (n=3). In considering only the smallest three conjugated circuits, we followed the empirical[1] and semiempirical[22] findings that only the smallest circuits make appreciable contributions to the *RE*. Eq. (5) may consequently be rewritten as

$$RE = \frac{1}{K}\ \varrho_1 \,\#^{(6)} + \varrho_2 \,\#^{(10)} + \varrho_{3a} \,\#^{(14a)} + \varrho_{3b} \,\#^{(14b)} + \varrho_{3c} \,\#^{(14c)} \tag{7}$$

Parameters ρ_n, $n = 1, 2, 3a, 3b, 3c$ can be determined by »inversion« from the SCF π-MO *REs* of benzene (B), naphthalene (N), anthracene (A), phenanthrene (Ph) and pyrene (Py). These values are available from Dewar and de Llano[27]

$$\begin{aligned} RE(\mathrm{B}) &= 0.869 \text{ eV} \\ RE(\mathrm{N}) &= 1.323 \text{ eV} \\ RE(\mathrm{A}) &= 1.600 \text{ eV} \\ RE(\mathrm{Ph}) &= 1.933 \text{ eV} \\ RE(\mathrm{Py}) &= 2.098 \text{ eV}. \end{aligned} \tag{8}$$

The *RE* expressions for these five benzenoid hydrocarbons are as follows

$$\begin{aligned} RE(\mathrm{B}) &= (2\varrho_1)/2 \\ RE(\mathrm{N}) &= (4\varrho_1 + 2\varrho_2)/3 \\ RE(\mathrm{A}) &= (6\varrho_1 + 4\varrho_2 + 2\varrho_{3a})/4 \\ RE(\mathrm{Ph}) &= (10\varrho_1 + 4\varrho_2 + 2\varrho_{3b})/5 \\ RE(\mathrm{Py}) &= (12\varrho_1 + 8\varrho_2 + 4\varrho_{3b} + 2\varrho_{3c})/6 \end{aligned} \tag{9}$$

Combination of (8) and (9) gives the numerical values for the ρ_n (n = 1, 2, 3a, 3b, 3c) parameters

$$\begin{aligned} \varrho_1 &= 0.869 \text{ eV} \\ \varrho_2 &= 0.247 \text{ eV} \\ \varrho_{3a} &= 0.099 \text{ eV} \\ \varrho_{3b} &= -0.006 \text{ eV} \\ \varrho_{3c} &= 0.104 \text{ eV} \end{aligned} \tag{10}$$

Thus, eq. (7) with the above parameter set becomes

$$RE = \frac{1}{K}\,(0.869\,\#^{(6)} + 0.247\,\#^{(10)} + 0.099\,\#^{(14a)} - 0.006\,\#^{(14b)} + 0.104\,\#^{(14c)}) \tag{11}$$

This equation also fulfils the minimum conditions for the intrinsic consistency of ρ_1, ρ_2 and ρ_3, whilst the ratio ρ_1/ρ_2 is 0.28 as expected because ρ_1 and ρ_2 are the same in Randic's original work[1] and here. Also, up to a scale factor, this expression is similar to that of eq. (5).

A further point of some difference occurs in Randić's use[1] of the so-called »linearly independent« conjugated circuits. This distinction makes a single modification in the present description with $\#^{(14b)}$ always being half as great as we would otherwise take it. Thence, if one used this modified value in eqs. (9), one would obtain $\rho_{3b} = -0.012$ eV in eqs. (10) and (11); but continuing to use these modified ρ_{3b} and $\#$,$^{(14b)}$ the product would be unchanged so that the *REs* computed therefrom would also be unchanged.

Randić's original *RE* expression and (11) will differ for those benzenoid hydrocarbons which contain 14b and 14c conjugated circuits such as, for example, anthanthrene (dibenzo[def,mno]chrysene) shown in Figure 3.

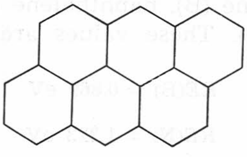

Figure 3. Diagram corresponding to anthanthrene.

Anthanthrene, a known benzenoid hydrocarbon,[28] has 10 Kekulé structures and the following circuit count: $\#^{(6)} = 24$, $\#^{(10)} = 18$, $\#^{(14a)} = 4$, $\#^{(14b)} = 8$ and $\#^{(14c)} = 4$. The two *RE* expressions are as follows

$$RE(\text{Randić}) = \frac{1}{10}\,(24\varrho_1 + 18\varrho_2 + 12\varrho_3) = 2.648 \text{ eV} \tag{12}$$

$$RE(\text{this work}) = \frac{1}{10}\,(24\varrho_1 + 18\varrho_2 + 4\varrho_{3a} + 8\varrho_{3b} + 4\varrho_{3c}) = 2.607 \text{ eV} \tag{13}$$

Here Randić's $\#^{(14)}$ has been taken as $\#^{(14a)} + (1/2)\,\#^{(14b)} + \#^{(14c)}$ because of his use of »linearly independent« conjugated circuits. Thence, though the introduction of this modified count makes no difference in our *RE* of eq. (11) via inversion, it does make a slight diference in Randić's original scheme.

In comparing Randić's *REs* with those obtained by eq. (11), we selected 17 benzenoid hydrocarbons from Dewar and de Llano's list[27] and calculated their *REs* by both formulae. These *REs* are reported in Table I.

Both sets of *RE* values are similar and close to the *REs* computed by Dewar and de Llano.[27] We compared both sets of *REs* to one another and to the *REs* of Dewar and de Llano via linear regression

$$RE(\text{model I}) = p\; RE(\text{model II}) + q \tag{14}$$

In Table II the statistical parameters for the linear relationships between *Re* (Randić) and *RE* (this work), *RE* (Randić) and *RE* (Dewar-de Llano) and *RE* (this work) and *RE* (Dewar-de Llano) are given.

TABLE I

Resonance energies (in eV) of selected benzenoid hydrocarbons

Molecule	RE(Randić)	RE(this work)	RE(Dewar-de Llano)[27]
Benz[a]anthracene	2.311	2.295	2.291
Benzo[c]phenanthrene	2.506	2.478	2.478
Chysene	2.506	2.478	2.483
Triphenylene	2.708	2.670	2.654
Dibenz[a,j]anthracene	2.986	2.949	2.948
Dibenz[a,h]anthracene	2.985	2.949	2.948
Benzo[b]chysene	2.808	2.808	2.823
Dibenz[a,c]anthracene	3.111	3.085	3.058
Dibenzo[c,g]phenanthrene	3.092	3.049	3.072
Benzo[c]chrysene	3.092	3.049	3.071
Picene	3.092	3.049	3.071
Dibenzo[b,g]phenanthrene	2.828	2.808	2.822
Benzo[e]pyrene	2.905	2.856	2.853
Benzo[a]pyrene	2.585	2.550	2.584
Benzo[ghi]perylene	3.150	3.109	3.128
Anthranthrene	2.648	2.607	2.665
Coronene	3.502	3.415	3.524

TABLE II

The leasts-squares parameters for linear relationships (14)

Linear relationship	Statistical parameters					
	n^a	p	q	r^b	SD^c	F^d
RE(this work) vs *RE*(Randić)	17	0.9632(±0.0990)	0.0687(±0.0287)	0.9996	0.0120	9381
RE(Dewar-de Llano) vs *RE(Randić)*	17	1.0049(±0.0190)	—0.0355(±0.0547)	0.9973	0.0228	2810
RE(Dewar-de Llano) vs *RE*(this work)	17	0.9522(±0.0236)	0.1206(±0.0675)	0.9954	0.0286	1635

a_n = the number of points

b_r = the correlation coefficient

c_{SD} = the standard deviation

d_F = the ratio between the variances of values by the two models considered

It appears that *RE* (Randić) and *RE* (this work) reproduce well the SCF π-MO *REs*, and *RE* (Randić) and *RE* (this work) are linearly correlated with a high value (0.9996) of the correlation coefficient (see Figure 4.)

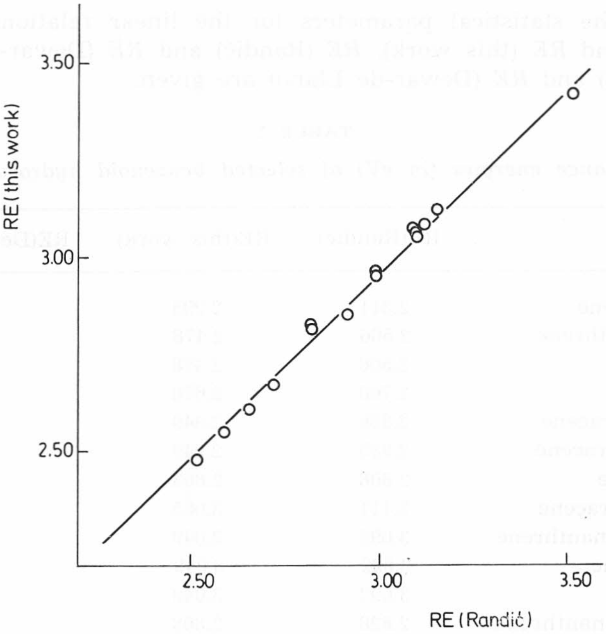

Figure 4. A plot of *RE*(this work) vs *RE*(Randić).

This result also supports Randić's initial selection of the three lowest conjugated circuits and his choice of parameters. Therefore, we recommend both ways (e. g., Randić's and eq. (11)) for further use in the chemistry of benzenoid hydrocarbons. However, it is nice to know that this truly empirical model can be justified by rigorous development from the VB model. Our associated Simpson-Herndon model[22] may have applications to further properties.[29]

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SAŽETAK

Kritičko razmatranje modela konjugiranih krugova

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Razmatrane su dvije formule za računanje rezonancijskih energija benzenoidnih ugljikovodika u okviru modela konjugiranih krugova. Prvu formulu predložio je 1976. Randić, dok je druga rezultat analize modela konjugiranih krugova u okviru Simpson-Herndonovog hamiltoniana. Obje formule daju vrlo slične rezonancijske energije, što potvrđuje ispravnost modela konjugiranih krugova kao i vrijednosti odgovarajućih parametara što ih je predložio Randić.