The Conjugated-Circuit Model Revisited*

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Received February 6, 1989

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 which was motivated from an empirical point of view elaborating Armit-Robinson-Clar aromatic sextet ideas. 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, corannulenes, benzoannelated annulenes, helicenes, macrocyclic benzenoid systems, benzenoid polymers, polycyclic conjugated hydrocarbon (di)cations and (dianions), the lowest excited states of polyacenes, Möbius structures, heterocyclic conjugated systems, buckminsterfullerene and elemental carbons.

A graph theoretical analysis of Kekulé valence structures led to the concept of conjugated circuits. A conjugated circuit of length 21 is a cycle of 21 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:

\[ RE = \frac{1}{K} \sum \rho_n \#(n - 2) \]  

where \( K \) is the number of Kekulé structures, the \( \rho_n \) are parameters which decrease in magnitude nearly geometrically with increasing \( n \).

is the total number of $4n+2$ conjugated circuits summed over all Kekulé structures. Note that $\rho_n$ 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 $\rho_n$ parameters (with truncation at different $n$ values) available in the literature.\textsuperscript{1,15a,19} In addition, the conjugated-circuit model turns out to be closely related\textsuperscript{89} to Herndon's so-called »structure-resonance theory«,\textsuperscript{21} so that parametrization from this approach might also be used. For the $\rho_n$, expressed in eV, Randić originally gave\textsuperscript{1}

\[ RE = \frac{1}{K} (0.869 \#^{10} + 0.246 \#^{10} + 0.100 \#^{10} + \ldots) \]  

(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.](image)

Recently we analyzed the foundations of the conjugated-circuit model\textsuperscript{22} in terms of the Simpson-Herndon model Hamiltonians.\textsuperscript{21,23} Via derivation from the Pauling-Wheland VB model\textsuperscript{24} we found

\[ RE = \frac{3J}{2k} \left( \frac{39}{64} \#^{10} + \frac{9}{64} \#^{10} + \frac{3}{64} \#^{140} + \frac{3}{128} \#^{140} + \frac{7}{64} \#^{140} + \ldots \right) \]  

(3)

or by using for the exchange parameter the following value\textsuperscript{21b,26}

\[ J = 1.857 \text{ eV} \]  

(4)

Eq. (3) is finally given as

\[ RE = \frac{1}{K} (1.697 \#^{10} + 0.392 \#^{140} + 0.131 \#^{140} + 0.065 \#^{140} + 0.065 \#^{140} + \ldots) \]  

(5)

Eq. (5) is somewhat different from Randić's original $RE$ expression (2) and (by derivation\textsuperscript{89}) 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.](image)
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 fulfill the minimum condition for the intrinsic consistency of $\rho_n$ parameters\cite{18,19}:

$$\rho_1 > \rho_2 > \rho_3.$$ \hspace{1cm} (6)

The ratio of $\rho_1$ to $\rho_3$ ($\rho_2/\rho_1 = 0.23$) is also rather close to the value (0.23) of Randić\cite{1}.

In this work we wish to reinvestigate Randić’s 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\cite{21} and semiempirical\cite{22} findings that only the smallest circuits make appreciable contributions to the RE. Eq. (5) may consequently be rewritten as

$$RE = \frac{1}{K} \rho_1 \#^{(10)} + \rho_2 \#^{(14)} + \rho_{1b} \#^{(14)} + \rho_{1b} \#^{(14)}$$ \hspace{1cm} (7)

Parameters $\rho_n$, $n = 1, 2, 3a, 3b, 3c$ can be determined by a method from the SCF $\pi$-MO REs of benzene (B), naphthalene (N), anthracene (A), phenanthrene (Ph) and pyrene (Py). These values are available from Dewar and de Llano\cite{27}:

$$RE(B) = 0.869 \text{ eV}$$
$$RE(N) = 1.323 \text{ eV}$$
$$RE(A) = 1.600 \text{ eV}$$
$$RE(Ph) = 1.933 \text{ eV}$$
$$RE(Py) = 2.098 \text{ eV}.$$ \hspace{1cm} (8)

The RE expressions for these five benzenoid hydrocarbons are as follows

$$RE(B) = \frac{(2\rho_1)}{2}$$
$$RE(N) = \frac{(4\rho_1 + 4\rho_2)}{3}$$
$$RE(A) = \frac{(6\rho_1 + 4\rho_2 + 2\rho_{1b})}{4}$$
$$RE(Ph) = \frac{(10\rho_1 + 4\rho_2 + 2\rho_{1b})}{5}$$
$$RE(Py) = \frac{(12\rho_1 + 8\rho_2 + 4\rho_{1b} + 2\rho_{1b})}{6}.$$ \hspace{1cm} (9)

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

$$\rho_1 = 0.869 \text{ eV}$$
$$\rho_2 = 0.247 \text{ eV}$$
$$\rho_{1b} = 0.099 \text{ eV}$$
$$\rho_{2b} = -0.006 \text{ eV}$$
$$\rho_{1c} = 0.104 \text{ eV}.$$ \hspace{1cm} (10)
Thus, eq. (7) with the above parameter set becomes

\[
RE = \frac{1}{K} \left( 0.869 \#(6) + 0.247 \#(10) + 0.099 \#(14') - 0.006 \#(14b) + 0.104 \#(14') \right)
\]

(11)

This equation also fulfills the minimum conditions for the intrinsic consistency of \( \rho_1, \rho_2 \) and \( \rho_3 \) whilst the ratio \( \rho_1/\rho_2 \) is 0.28 as expected because \( \rho_1 \) and \( \rho_2 \) are the same in Randić'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. Hence, 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 \( \rho_{3b} \) 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,\(^{10}\) 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

\[
RE(\text{Randić}) = \frac{1}{10} \left( 24q_1 + 18q_2 + 12q_3 \right) = 2.648 \text{ eV}
\]

(12)

\[
RE(\text{this work}) = \frac{1}{10} \left( 24q_1 + 18q_2 + 4q_{3b} + 8q_{3b} + 4q_{3c} \right) = 2.607 \text{ eV}
\]

(13)

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

\[
RE(\text{model I}) = p \cdot RE(\text{model II}) + q
\]

(14)
In Table II the statistical parameters for the linear relationships between Re (Randíć) and Re (this work), Re (Randíć) 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

<table>
<thead>
<tr>
<th>Molecule</th>
<th>RE(Randíć)</th>
<th>RE(this work)</th>
<th>RE(Dewar-de Llano)*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benz[a]anthracene</td>
<td>2.311</td>
<td>2.295</td>
<td>2.291</td>
</tr>
<tr>
<td>Benzo[c]phenanthrene</td>
<td>2.506</td>
<td>2.478</td>
<td>2.478</td>
</tr>
<tr>
<td>Chrysene</td>
<td>2.506</td>
<td>2.478</td>
<td>2.483</td>
</tr>
<tr>
<td>Triphenylene</td>
<td>2.708</td>
<td>2.670</td>
<td>2.654</td>
</tr>
<tr>
<td>Dibenzo[a,j]anthracene</td>
<td>2.986</td>
<td>2.949</td>
<td>2.948</td>
</tr>
<tr>
<td>Dibenzo[a,h]anthracene</td>
<td>2.985</td>
<td>2.949</td>
<td>2.948</td>
</tr>
<tr>
<td>Benzo[b]chrysene</td>
<td>2.808</td>
<td>2.808</td>
<td>2.823</td>
</tr>
<tr>
<td>Dibenzo[a,c]anthracene</td>
<td>3.111</td>
<td>3.085</td>
<td>3.058</td>
</tr>
<tr>
<td>Dibenzo[c,g]phenanthrene</td>
<td>3.092</td>
<td>3.049</td>
<td>3.072</td>
</tr>
<tr>
<td>Benzo[c]chrysene</td>
<td>3.092</td>
<td>3.049</td>
<td>3.071</td>
</tr>
<tr>
<td>Picene</td>
<td>3.092</td>
<td>3.049</td>
<td>3.071</td>
</tr>
<tr>
<td>Dibenzo[b,g]phenanthrene</td>
<td>2.828</td>
<td>2.808</td>
<td>2.822</td>
</tr>
<tr>
<td>Benzo[e]pyrene</td>
<td>2.905</td>
<td>2.856</td>
<td>2.853</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>2.385</td>
<td>2.550</td>
<td>2.564</td>
</tr>
<tr>
<td>Benzo[ghi]perylene</td>
<td>3.150</td>
<td>3.109</td>
<td>3.128</td>
</tr>
<tr>
<td>Anthracene</td>
<td>2.648</td>
<td>2.697</td>
<td>2.665</td>
</tr>
<tr>
<td>Coronene</td>
<td>3.502</td>
<td>3.415</td>
<td>3.524</td>
</tr>
</tbody>
</table>

TABLE II

The least-squares parameters for linear relationships (14)

<table>
<thead>
<tr>
<th>Linear relationship</th>
<th>n²</th>
<th>p</th>
<th>q</th>
<th>r²</th>
<th>SD²</th>
<th>F²</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE(this work) vs RE(Randíć)</td>
<td>17</td>
<td>0.9632</td>
<td>±0.0990</td>
<td>0.0687</td>
<td>±0.0287</td>
<td>0.9986</td>
</tr>
<tr>
<td>RE(Dewar-de Llano) vs RE(Randíć)</td>
<td>17</td>
<td>1.0049</td>
<td>±0.0190</td>
<td>-0.0355</td>
<td>±0.0547</td>
<td>0.9973</td>
</tr>
<tr>
<td>RE(Dewar-de Llano) vs RE(this work)</td>
<td>17</td>
<td>0.9322</td>
<td>±0.0236</td>
<td>0.1206</td>
<td>±0.0675</td>
<td>0.9954</td>
</tr>
</tbody>
</table>

a = the number of points
b = the correlation coefficient
csd = the standard deviation
df = the ratio between the variances of values by the two models considered

It appears that Re (Randíć) and Re (this work) reproduce well the SCF π-MO Res, and Re (Randíć) and Re (this work) are linearly correlated with a high value (0.9986) of the correlation coefficient (see Figure 4.)
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 may have applications to further properties.

Acknowledgements. — DP and NT are grateful to the Republic of Croatia Science Fund and DJK to the Robert A. Welch Foundation of Houston, Texas for financial support. We thank Dr Sonja Nikolić (Zagreb) for helpful discussions.

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SAZETAK

Kritičko razmatranje modela konjugiranih krugova

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