

THE CONJUGATED-CIRCUIT MODEL: THE OPTIMUM PARAMETERS FOR BENZENOID HYDROCARBONS

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Abstract

A search for the optimum set of parameters for the conjugated-circuit computations on benzenoid hydrocarbons is reported. The SCF π -MO resonance energies (REs) of Dewar and de Llano were used as standards for the determination of R_n ($n = 1, 2, 3$) parameters, which correspond to $4n + 2$ conjugated circuits. The following set of parameters: $R_1 = 0.827$ eV, $R_2 = 0.317$ eV and $R_3 = 0.111$ eV produced the best agreement between the REs calculated by the conjugated-circuit model and the REs calculated using the SCF π -MO model.

1. Introduction

The conjugated-circuit model is a semi-empirical VB resonance-theoretical model [1–3] which has been introduced using the tools of chemical graph theory [4] and is mainly employed for the study of aromaticity and conjugation in polycyclic conjugated molecules [5]. The model is based on classical chemical ideas of Armit and Robinson [6], Fries [7] and Clar [8]. It was also rigorously derived [9,10] from the Pauling–Wheland VB resonance theory [11,12] via the Simpson–Herndon model Hamiltonian [13,14].

In this work, we report an analysis of, and a search for optimum, parameters to be used within the framework of the conjugated-circuit model for computing the resonance energies (REs) of benzenoid hydrocarbons.

The work is structured as follows. In the second section, we briefly describe the conjugated-circuit model and the original selection of parameters. In the third section, we detail a search for the optimum set of parameters. The work ends with our concluding remarks.

2. A brief account of the conjugated-circuit model

A graph-theoretical analysis of Kekulé valence structures produced the concept of conjugated circuits [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.

The circuit decomposition of individual Kekulé structures of polycyclic conjugated molecules gives conjugated circuits of sizes $4n + 2$ and/or $4n$ ($n = \text{integer}$). There are possible linearly dependent, linearly independent and disjoint conjugated circuits. The total number of all conjugated circuits within a single Kekulé valence structure is equal to $K - 1$ ($K = \text{the number of Kekulé structures}$) [15]. The $4n + 2$ carbon conjugated circuits we denoted by R_n and similarly the $4n$ carbon conjugated circuit by Q_n [1 – 3].

The conjugated circuits are used to generate π -resonance energies of polycyclic conjugated molecules. This is related to the basic assumption of the conjugated-circuit model, according to which the conjugated circuits are dominant structural features determining the stabilities and, in particular, the REs of conjugated molecules. The REs can be expressed as simple additive functions of the conjugated circuits, and only the size of a circuit has to be taken into consideration. For example, the RE expression for benzenoid hydrocarbons is given by:

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

where K is the number of Kekulé valence structures of a given molecule, r_n is the total number of $4n + 2$ conjugated circuits summed over all Kekulé structures and R_n are corresponding empirical parameters. A given parameter R_n measures the extent to which a specific conjugated circuit of size $4n + 2$ influences the thermodynamic stability of the benzenoid hydrocarbon. The R_n 's are found [1, 16] to decrease in magnitude nearly geometrically with increasing n , so that only smaller circuits need to be counted to obtain a reasonable estimate of the resonance energy. Note that in eq. (1) appear only R_n circuits because benzenoid hydrocarbons do not contain Q_n circuits.

To make eq. (1) applicable in chemistry, the numerical values of the parameters R_n are needed. Initially, R_n parameters have been truncated at $n = 4$ and derived [1] from the SCF π -MO REs [17] for the first four linear benzenoids (benzene, naphthalene, anthracene, tetracene). However, later the use of only the first three R_n ($n = 1, 2, 3$) parameters was advocated [5, 18, 19].

Numerical values of the R_n ($n = 1, 2, 3$) parameters were obtained in the following way. Dewar and de Llano's REs [17] for benzene, naphthalene and anthracene are used as standards to which the R_n ($n = 1, 2, 3$) were adjusted accurately. The RE expressions for benzene (B), naphthalene (N) and anthracene (A) in terms of conjugated circuits are given as follows:

$$RE(\text{B}) = (2R_1)/2, \quad (2)$$

$$RE(\text{N}) = (4R_1 + 2R_2)/3, \quad (3)$$

$$RE(\text{A}) = (6R_1 + 4R_2 + 2R_3)/4. \quad (4)$$

Introduction of the SCF π -MO REs ($RE(B) = 0.869$ eV; $RE(N) = 1.323$ eV; $RE(A) = 1.600$ eV) into eqs. (2) – (4) produces the original set of parameters [1]:

$$R_1 = 0.869 \text{ eV}, \quad R_2 = 0.247 \text{ eV}, \quad R_3 = 0.100 \text{ eV}.$$

These parameters have been used in a number of papers employing the conjugated-circuit model [5, 19 – 22]. There are also some other proposals for the R_n parameters in the literature [23]. However, the evaluation of these are not the object of the present paper; they were considered in a separate report [24]. Here, our interest is directed to the search for the set of parameters which would give the best agreement between the REs obtained by the conjugated-circuit model and the SCF π -MO REs. In other words, our target is to reproduce the REs of Dewar and de Llano as closely as possible.

3. A search for the optimum set of parameters

There are 32 benzenoid hydrocarbons (see fig. 1) for which the SCF π -MO REs exist [17]. Their RE (conjugated circuits) expressions are given in table 1.

Benzenoid hydrocarbons in fig. 1 are partitioned into three groups according to their conjugated-circuit content. In the first group there is only benzene (1). In the second group there are naphthalene (2), perylene (3), zethrene (4) and quaterylene (5). These benzenoids contain R_1 and R_2 circuits in the ratio 2 : 1. In the third group there are all other benzenoids from 6 to 32. They contain R_1 , R_2 and R_3 parameters.

A search for the optimum set of parameters has been carried out in two ways. One way was to follow the methodology of Randić's original parametrization procedure [1]. For example, benzene (1), then one benzenoid from the second group, say zethrene (4) and one benzenoid from the third group, say coronene (15), were selected. Their RE conjugated-circuit expressions were set down and the corresponding SCF π -MO REs have been used as standards to which the R_n ($n = 1, 2, 3$) were adjusted accurately in the manner described earlier in the text. Altogether, 108 such triads for the benzenoids considered are possible. Amongst 108 possible sets of parameters, the triad consisting of benzene (1), perylene (3) and ovalene (32) led to the set of parameters producing the best agreement between the RE (conjugated circuits) and RE (SCF), i.e. the minimal value (0.07252) of $Q = \sum [RE(\text{conjugated circuits}) - RE(\text{SCF})]^2$. The values of these parameters are:

$$R_1 = 0.869 \text{ eV}, \quad R_2 = 0.226 \text{ eV}, \quad R_3 = 0.154 \text{ eV}.$$

It is interesting to note that close to this optimal set of parameters is the set identical to the original set chosen by Randić in the early days of the conjugated-circuit model [1 – 3]. The value of Q , for Randić's set of parameters, is 0.08757.

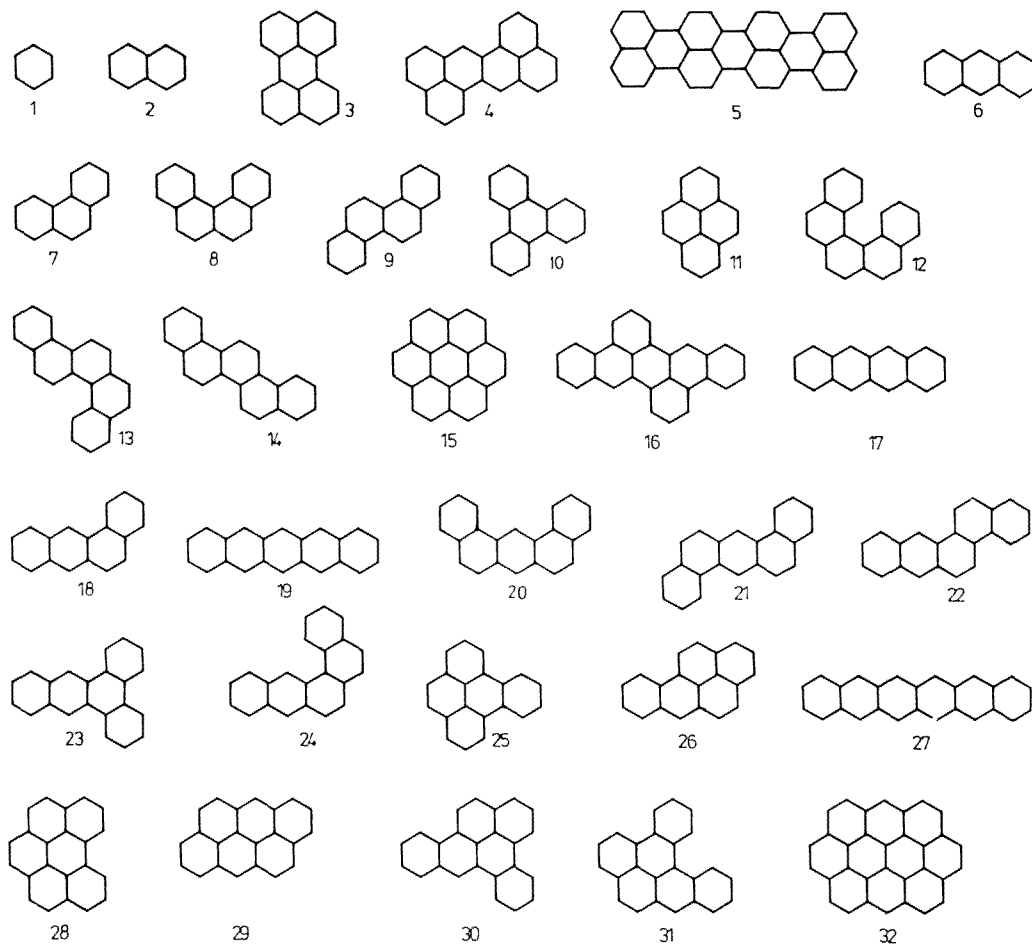


Fig. 1. Diagrams of the studied benzenoid hydrocarbons.

The second approach to a search for optimum parameters is based on the standard least-squares analysis on all the 32 data points. However, in this case we relaxed the requirement to reproduce exactly the $RE(SCF)$ of benzene. The set of parameters obtained in this way:

$$R_1 = 0.827 \text{ eV}, \quad R_2 = 0.317 \text{ eV}, \quad R_3 = 0.111 \text{ eV},$$

gives the value of Q (0.05383) at absolute minimum.

In table 1 are given the RE values computed by the conjugated-circuit model using the original set of parameters and the two sets of parameters listed above. For comparison purposes, the $RE(SCF)$ values are likewise given in table 1.

Table 1
REs (in eV) of the benzenoid hydrocarbons depicted in fig. 1

| Benzenoid hydrocarbon | RE expression | RE(I) ^a | RE(II) ^b | RE(III) ^c | RE(SCF) ^d |
|-----------------------|---------------------------------|--------------------|---------------------|----------------------|----------------------|
| 1 | $(2R_1)/2$ | 0.869 | 0.869 | 0.827 | 0.869 |
| 2 | $(4R_1 + 2R_2)/3$ | 1.323 | 1.309 | 1.314 | 1.323 |
| 3 | $(24R_1 + 12R_2)/9$ | 2.647 | 2.619 | 2.628 | 2.619 |
| 4 | $(24R_1 + 12R_2)/9$ | 2.647 | 2.619 | 2.628 | 2.694 |
| 5 | $(432R_1 + 216R_2)/81$ | 5.293 | 5.237 | 5.256 | 5.309 |
| 6 | $(6R_1 + 4R_2 + 2R_3)/4$ | 1.601 | 1.607 | 1.613 | 1.600 |
| 7 | $(10R_1 + 4R_2 + R_3)/5$ | 1.956 | 1.950 | 1.930 | 1.933 |
| 8 | $(20R_1 + 10R_2 + 2R_3)/8$ | 2.506 | 2.494 | 2.492 | 2.478 |
| 9 | $(20R_1 + 10R_2 + 2R_3)/8$ | 2.506 | 2.494 | 2.492 | 2.483 |
| 10 | $(26R_1 + 6R_2 + 3R_3)/9$ | 2.708 | 2.712 | 2.637 | 2.654 |
| 11 | $(12R_1 + 8R_2 + 4R_3)/6$ | 2.134 | 2.142 | 2.151 | 2.098 |
| 12 | $(40R_1 + 20R_2 + 5R_3)/13$ | 3.092 | 3.081 | 3.075 | 3.072 |
| 13 | $(40R_1 + 20R_2 + 5R_3)/13$ | 3.092 | 3.081 | 3.075 | 3.071 |
| 14 | $(40R_1 + 20R_2 + 5R_3)/13$ | 3.092 | 3.081 | 3.075 | 3.071 |
| 15 | $(64R_1 + 48R_2 + 27R_3)/20$ | 3.509 | 3.531 | 3.557 | 3.524 |
| 16 | $(100R_1 + 40R_2 + 10R_3)/25$ | 3.911 | 3.899 | 3.860 | 3.862 |
| 17 | $(8R_1 + 6R_2 + 4R_3)/5$ | 1.767 | 1.785 | 1.792 | 1.822 |
| 18 | $(16R_1 + 8R_2 + 3R_3)/7$ | 2.311 | 2.310 | 2.300 | 2.291 |
| 19 | $(10R_1 + 8R_2 + 6R_3)/6$ | 1.878 | 1.904 | 1.912 | 2.004 |
| 20 | $(36R_1 + 16R_2 + 6R_3)/12$ | 2.986 | 2.985 | 2.959 | 2.948 |
| 21 | $(36R_1 + 16R_2 + 6R_3)/12$ | 2.986 | 2.985 | 2.959 | 2.948 |
| 22 | $(30R_1 + 18R_2 + 6R_3)/11$ | 2.829 | 2.824 | 2.835 | 2.823 |
| 23 | $(42R_1 + 14R_2 + 5R_3)/13$ | 3.112 | 3.110 | 3.056 | 3.058 |
| 24 | $(30R_1 + 18R_2 + 6R_3)/11$ | 2.829 | 2.824 | 2.835 | 2.823 |
| 25 | $(32R_1 + 14R_2 + 7R_3)/11$ | 2.906 | 2.914 | 2.880 | 2.853 |
| 26 | $(22R_1 + 14R_2 + 7R_3)/9$ | 2.586 | 2.596 | 2.601 | 2.584 |
| 27 | $(12R_1 + 10R_2 + 8R_3)/7$ | 1.957 | 1.989 | 1.997 | 2.160 |
| 28 | $(42R_1 + 26R_2 + 12R_3)/14$ | 3.151 | 3.159 | 3.165 | 3.128 |
| 29 | $(24R_1 + 18R_2 + 12R_3)/10$ | 2.650 | 2.677 | 2.689 | 2.665 |
| 30 | $(58R_1 + 26R_2 + 11R_3)/17$ | 3.407 | 3.410 | 3.378 | 3.375 |
| 31 | $(52R_1 + 26R_2 + 13R_3)/16$ | 3.307 | 3.317 | 3.293 | 3.283 |
| 32 | $(200R_1 + 160R_2 + 110R_3)/50$ | 4.486 | 4.538 | 4.567 | 4.539 |

^a RE(I) is calculated using the original set of parameters: $R_1 = 0.869$ eV, $R_2 = 0.247$ eV and $R_3 = 0.100$ eV.

^b RE(II) is calculated using parameters: $R_1 = 0.869$ eV, $R_2 = 0.226$ eV and $R_3 = 0.154$ eV.

^c RE(III) is calculated using parameters: $R_1 = 0.827$ eV, $R_2 = 0.317$ eV and $R_3 = 0.111$ eV.

^d Ref. [17].

We compared all three sets of REs (conjugated circuits) to the REs of Dewar and de Llano [17] via the linear regression:

$$RE(\text{SCF}) = p \cdot RE(i) + q; \quad i = \text{I, II, III.} \quad (5)$$

In table 2, the statistical parameters for the linear relationships between $RE(\text{SCF})$ and $RE(\text{I})$, $RE(\text{SCF})$ and $RE(\text{II})$, and $RE(\text{SCF})$ and $RE(\text{III})$ are given. The $RE(\text{I})$'s are the resonance energies of the studied benzenoid hydrocarbons computed using the original set of parameters, whilst the $RE(\text{II})$'s and $RE(\text{III})$'s are obtained using the two novel sets of parameters.

Table 2
The least-squares parameters for the linear relationship (5)

| Linear relationship | n | p | q | r | SD | t | χ^2 |
|--|-----|----------------|----------------|--------|-------|---------|----------|
| $RE(\text{SCF})$ versus $RE(\text{I})$ | 32 | 0.988(± 0.011) | 0.031(± 0.31) | 0.9982 | 0.053 | 90.546 | 0.038 |
| $RE(\text{SCF})$ versus $RE(\text{II})$ | 32 | 0.992(± 0.010) | 0.020(± 0.029) | 0.9985 | 0.048 | 98.619 | 0.030 |
| $RE(\text{SCF})$ versus $RE(\text{III})$ | 32 | 0.989(± 0.009) | 0.034(± 0.024) | 0.9989 | 0.041 | 116.469 | 0.022 |

The comparison between the statistical characteristics of $RE(\text{SCF})$ versus $RE(\text{I})$, $RE(\text{SCF})$ versus $RE(\text{II})$, and $RE(\text{SCF})$ versus $RE(\text{III})$ is in favour of the $RE(\text{III})$ values. A plot of $RE(\text{SCF})$ versus $RE(\text{III})$ is given in fig. 2.

The molecules that yield the largest errors are zethrene (**4**), pentacene (**19**) and tetracene (**27**). In all these three cases, the $RE(\text{SCF})$ values are higher than the $RE(\text{III})$ values: $\Delta(\mathbf{4}) = 0.066$ eV, $\Delta(\mathbf{19}) = 0.091$ eV and $\Delta(\mathbf{27}) = 0.163$ eV, where $\Delta = RE(\text{SCF}) - RE(\text{III})$. It is interesting to note that the above benzenoids yield the largest errors even when the different sets of parameters are used to calculate REs (e.g. $RE(\text{I}) \rightarrow \Delta(\mathbf{4}) = 0.047$ eV, $\Delta(\mathbf{19}) = 0.126$ eV, $\Delta(\mathbf{27}) = 0.203$ eV; $RE(\text{II}) \rightarrow \Delta(\mathbf{4}) = 0.075$ eV, $\Delta(\mathbf{19}) = 0.100$ eV, $\Delta(\mathbf{27}) = 0.171$ eV). This result indicates that all the $RE(\text{SCF})$'s might not be of the same quality.

The analysis in this section points out the important fact that Randić's parameters for the conjugated-circuit calculations on benzenoid hydrocarbons can be improved on the basis of the same standards as he used in his original work. However, it also points out that the initial selection of parameters was a very good choice amongst many possibilities.

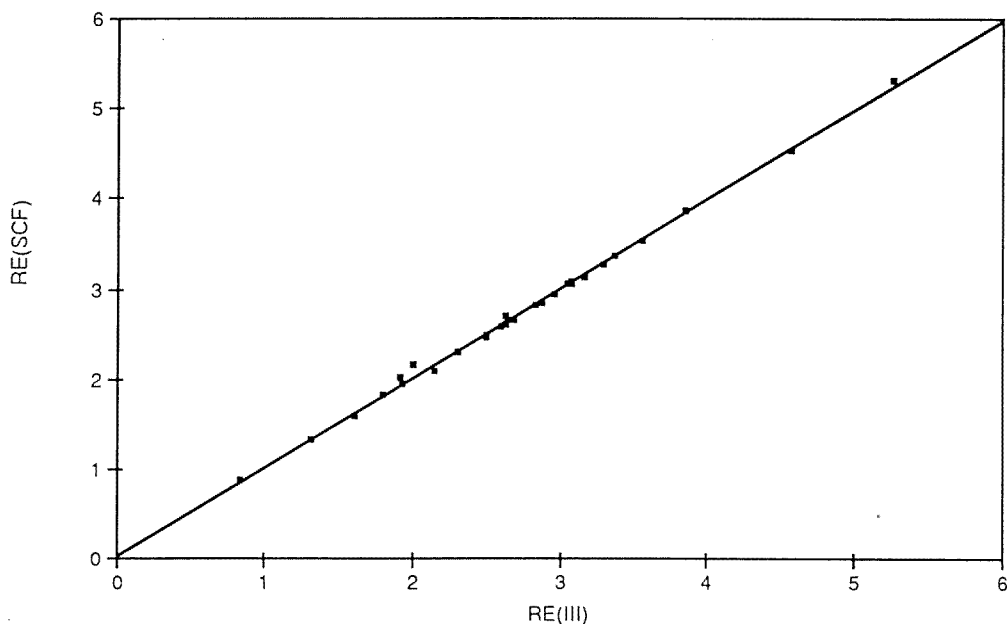


Fig. 2. A plot of $RE(SCF)$ versus $RE(III)$. $RE(III)$ are the conjugated-circuit resonance energies obtained using parameters $R_1 = 0.827$ eV, $R_2 = 0.317$ eV and $R_3 = 0.111$ eV.

4. Concluding remarks

A novel set of parameters for the conjugated-circuit model is obtained. This set of parameters ($R_1 = 0.827$ eV, $R_2 = 0.317$ eV, $R_3 = 0.111$ eV) produces a very good agreement between $RE(\text{conjugated-circuit model})$ and $RE(SCF)$ for benzenoid hydrocarbons. Thus, we recommend the present set of parameters for future use in conjugated-circuit computations.

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