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Clar Structures in Fractal Benzenoids*

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The aromaticity of fractal benzenoids was studied by the VB approach of Herndon and Hosoya based on the Clar structures. The results are compared with the logarithmic model and the conjugated-circuit model. It appears that the simplest model, *i.e.* the logarithmic model, is the most convenient one for use in this class of benzenoids.

Recently Klein *et al.*¹ have introduced a novel class of benzenoid hydrocarbons named fractal benzenoids. These are benzenoids in which a rigidly fixed pattern is systematically repeated on different scales. In other words, fractal benzenoids represent a benzenoid class of self-similar structures. As an illustrative example of fractal benzenoids we give in Figure 1 the first four members of a trigonal triphenylenoid family of self-similar structures with the fractal dimension $d = 1.5850$.

The fractal dimension d can be computed as

$$d = \lim_{n \rightarrow \infty} \frac{\ln \gamma_n}{\ln l_n} \quad (1)$$

where γ is the number of π -centers, l is the characteristic length and n is the stage number.

Klein *et al.*¹ have also discussed some possibilities of the synthesis of at least the early stages of fractal benzenoids. In this respect, the stability and aromaticity of these systems is of interest to prospective preparative chemists. We will consider three

* Dedicated to the heroic defenders of the city of Dubrovnik, the birthplace of Josip Rugjer Bošković (1711-1787), one of the greatest Croatian scholars of all time.

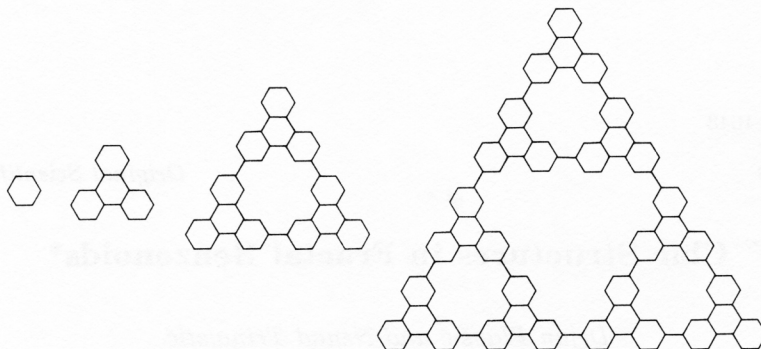


Figure 1. The first four stages of a trigonal triphenylenoid family of self-similar structures with the fractal dimension ≈ 1.585 .

models of aromaticity: the logarithmic model based on the count of Kekulé structures,² the conjugated-circuit model³ and the VB approach based on the Clar-structure count.⁴ The Kekulé structures of fractal benzenoids can be enumerated using the following recursive relations

$$K_{n+1} = K_n^3 + I_n^3 \quad (2)$$

$$J_{n+1} = K_n J_n^2 \quad (3)$$

$$I_{n+1} = I_n J_n^2 \quad (4)$$

Given the initial conditions for K_1 , J_1 and I_1 , one can compute the number of Kekulé structures up to any member of the series one wants. For the case of a trigonal triphenylenoid family, the initial conditions $K_1=2$ (the Kekulé count for benzene) and $J_1 = I_1 = 1$ (see Figure 2) lead to the following Kekulé numbers for other three members given in Figure 1: 9, 730 and 389017064.

The Kekulé count can be used for the computation of the resonance energy (RE) via the following expression²:

$$RE = A \ln K \quad (5)$$

where $A = 1.185$ eV. Then, the REs (in eV) of the initial members of the trigonal triphenylenoid family of self-similar structures are 0.821, 2.604, 7.812 and 23.438. If we normalize the RE by dividing it by the number of π -centers,⁵ then the RE/γ is constant for the whole series ($RE/\gamma = 0.145$ eV). In other words, the members of the whole series are predicted to be of comparable aromatic stability.

The resonance energies of fractal benzenoids can be also estimated by means of the two-parameter conjugated-circuit model^{3,6}

$$RE = (a_1 R_1 + a_2 R_2)/K \quad (6)$$

where R_1 and R_2 are parameters corresponding to the conjugated circuits of sizes 6 and 10 respectively, while a_1 and a_2 represent their total counts. If the R_1 and R_1 parameters of Randić³ are taken into account, then

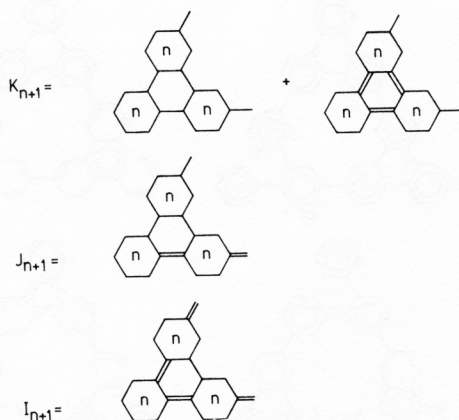


Figure 2. A diagrammatic development of the recursive relations (2)–(4) for counting the Kekulé structures of fractal benzenoids

$$R_2/R_1 = 1/3.5 \tag{7}$$

and

$$RE = R_1 (a_1 + 0.286 a_2)/K \tag{8}$$

The REs and REs/ γ of the first four members of a trigonal triphenylenoid family are given as follows:

| | | | | |
|--------------------|-------|-------|-------|-----------|
| n | 1 | 2 | 3 | 4 |
| γ | 6 | 18 | 54 | 162 |
| K | 2 | 9 | 730 | 389017064 |
| RE/eV | 0.869 | 2.675 | 8.014 | 24.041 |
| (RE/ γ)/eV | 0.145 | 0.149 | 0.148 | 0.148 |

The RE/ γ value for triphenylene is rather close to the SCF π -MO RE of Dewar and de Llano⁷ (RE(SCF)/ γ = 0.147 eV). The above results also parallel closely the predictions reached by the logarithmic formula (5).

Another way to study fractal benzenoids is by means of the Clar structures.⁸ The use of (orthonormal) Clar structures instead of the Kekulé structures in the VB model considerably reduces the numerical work,⁴ because the Clar structures represent a much smaller set than the Kekulé structures. For example, the Clar structure count (CSC) for the trigonal triphenylenoid family, depicted in Figure 1, is given by

$$CSC = \begin{cases} 1 & \text{,1st stage} \\ 2^{3^{(n-1)}} & \text{,nth stage} \end{cases} \tag{9}$$

This formula gives the following sequence for the numbers of the Clar structures for the first four members of the triphenylenoid family: 1, 2, 8 and 512, respectively. The Clar structures of the third member of the series are given in Figure 3.

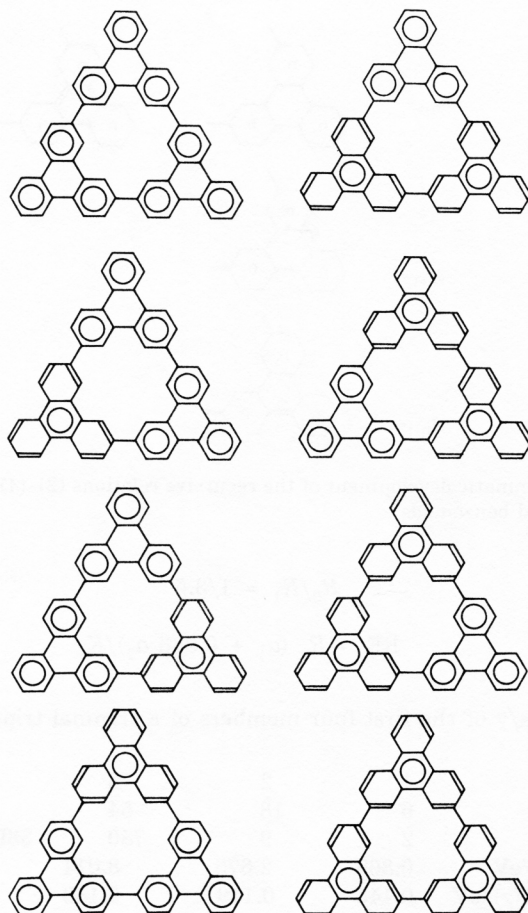


Figure 3. Diagrams of the Clar structures for the third member of the trigonal triphenylenoid family

The RE in terms of the Clar structures may be computed as the largest root of the polynomial resulting from the development of the secular determinant encoding the interaction between the Clar structures.⁴ As an example, we compute the RE of triphenylene using the Herndon-Hosoya procedure. Two Clar structures of triphenylene are shown in Figure 4. The parameters in the determinant in this figure signify the number of sextets⁸ (a), the number of double bonds (b) and the resonance interaction (k). Herndon and Hosoya have determined these parameters by adjusting the VB REs of selected benzenoids against the SCF π -MO REs of Dewar and de Llano.⁷ The values of these parameters (in eV) are as follows: $a = 0.8590$, $b = 0.0744$ and $k = 0.3176$. The secular determinant for the example of the triphenylene is therefore given by

$$\begin{vmatrix} 3a-x & k \\ k & a+6b-x \end{vmatrix} = 0 \quad (10)$$

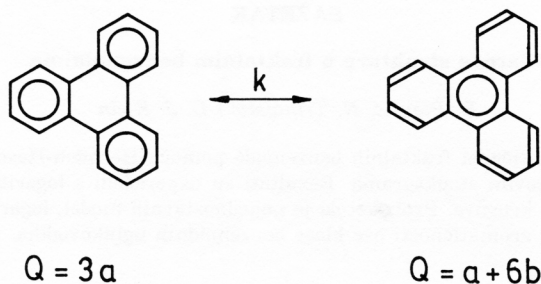


Figure 4. Clar structures of triphenylene

This determinant leads to the polynomial

$$(3a - x)(a + 6b - x) - k^2 = 0 \quad (11)$$

Introduction of the above values for the a , b and k parameters gives the largest root $x_1 = 2.652$ which represents the value of the Clar RE in eV and which is rather close to the SCF π -MO RE value of 2.654 eV. The REs using the Clar structures for the third and fourth members of the triphenylenoid family considered here are 7.938 eV and 23.814 eV, respectively. Because of the composition of the Clar-sextet Hamiltonian of Herndon and Hosoya⁴ for the triphenylene, the units in the present (stage 2 and higher) structures are non-interacting. Thence, the value of the RE/ γ (=0.147 eV) remains constant from stage 2 onward. It is interesting to note that all the three models of aromaticity used here produce very similar values for the REs and, consequently, for the REs/ γ . Therefore, the simplest model, *i.e.* the logarithmic model, is the most convenient because there are many methods available for estimating the number of Kekulé structures for any kind of benzenoid system.⁹⁻¹¹

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SAŽETAK

Clarove strukture u fraktalnim benzenoidima

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Studirana je aromatičnost fraktalnih benzenoida pomoću Herndon-Hosoyinog VB pristupa, koji se temelji na Clarovim strukturama. Rezultati su uspoređeni s logaritamskim modelom i modelom konjugiranih krugova. Proizlazi da je najjednostavniji model, logaritamski model, najpogodniji za studiranje aromatičnosti ove klase benzenoidnih ugljikovodika.