Graph Theory and Molecular Orbitals

IX. On the Stability of Cata-Condensed Hydrocarbons*

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A simple algorithm for the determination of the number of zeros in the molecular graphs of alternant cata-condensed conjugated hydrocarbons is derived. For non-branched hydrocarbons it is shown that, from the topological point of view, only *four* types of ring systems exist. The given algorithm enables the derivation of a number of general regularities relating the structural features of the molecule with its stability.

Key words: Cato-condensed hydrocarbons – Molecular graphs

1. Introduction

The presence of non-bonding molecular orbitals (NBMO's) in even alternant hydrocarbons leads to the prediction [2] (within the simple Hückel (topological [3]) MO approach) that such molecules should have a triplet ground state. Although the physical reality is much more complicated because of the action of the Jahn-Teller deformation forces in the cases of the triplet ground state [4], it is a fact that structures possessing NBMO's are rather rarely occuring in the chemistry of conjugated hydrocarbons [5] or they can be obtained as very unstable moieties under the drastic conditions of rigid-glass chemistry as, for example, cyclobutadiene [6].

It can be shown [7, 8] that the number of NBMO's is equal to the number of zeros in the molecular graph. Hence, the presence of zeros in the graph spectrum is sufficient for predicting an alternant hydrocarbon to be a reactive species. The number of zeros in the graph spectrum will be denoted as N_0.

There are mainly two techniques [9] used previously for determining whether $N_0 = 0$ or not: (a) the calculation of the determinant of the graph adjacency matrix [10] and (b) the actual construction of the NBMO's [2, 11], both being impractical for larger molecules. The approach we present here is the extension of the technique (b). The main idea of our approach is that instead of finding the NBMO of the whole molecule one has to determine the NBMO of a graph with two vertices only, this latter problem being, of course, trivial.

The topology of the cata-condensed hydrocarbons (CCH) is determined [12, 13] by the demand that no two rings possess more than one common edge

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* See Ref. [1].

and that no three rings possess a common vertex. Therefore, these molecules can be considered as "trees of rings". For instance, I is a branched CCH whereas II and III are non-branched CCH's.

(I)

(II)

(III)
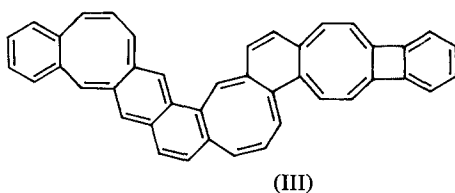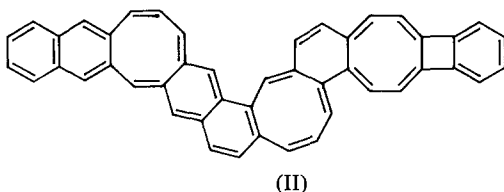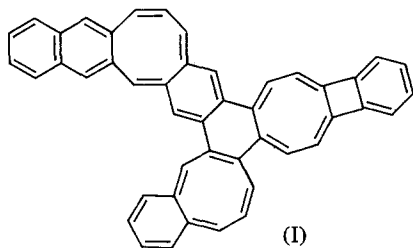
2. The Basic Equation

Let us consider (undirected) graphs with weighted edges, that is a non-zero number $a_{pq} = a_{qp}$ corresponds to every edge between the vertices p and q. If the weight of a particular edge is not indicated it is supposed to be unity. Note that $a_{pq} = 0$ means that there is no edge between p and q. The matrix $A = \|a_{pq}\|$ can be considered as a generalized adjacency matrix of the graph. If $C = (C_1, C_2, \ldots, C_N)$ is the eigenvector of the adjacency matrix corresponding to a zero eigenvalue, the following equations are fulfilled:
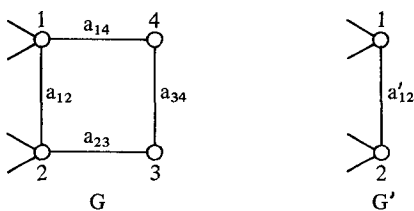
$$CA = 0 \tag{1}$$

or

$$\sum_j C_j a_{jp} = 0 \qquad p = 1, 2, \ldots, N \tag{2}$$

where the summation goes over all first neighbours of the vertex p.

Let G and G' be of the form

Then Eq. (2) gives:

$$R_1 + C_2 a_{12} + C_4 a_{14} = 0 \tag{3}$$

$$R_2 + C_1 a_{12} + C_3 a_{23} = 0 \tag{4}$$

$$C_2 a_{23} + C_4 a_{34} = 0 \tag{5}$$

$$C_1 a_{14} + C_3 a_{34} = 0. \tag{6}$$

R_1 and R_2 depend on the rest of the graph and are unimportant for the further discussion. Substituting (5) into (3) and (6) back into (4) one obtains the following equations:

$$R_1 + \left(a_{12} - \frac{a_{14} a_{23}}{a_{34}} \right) C_2 = 0 \tag{7}$$

$$R_2 + \left(a_{12} - \frac{a_{14} a_{23}}{a_{34}} \right) C_1 = 0. \tag{8}$$

These are just the Eq. (2) for the graph G' with

$$a'_{12} = a_{12} - \frac{a_{14} a_{23}}{a_{34}}. \tag{9}$$

Since the number of independent parameters in C is equal to N_0 [11] the principal relation of our procedure is given as follows:
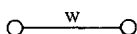
 (10)

This equation holds regardless the values of s, t, u, and v[1].

Every terminal ring in a graph can be eliminated by successively applying the Eq. (10), e.g.:

Every CCH can be in this manner reduced by a finite number of simple steps to a graph

$(w \neq 0)$ if $N_0 = 0$ or to a graph with N_0 isolated vertices if $N_0 > 0$. As an example consider the molecule I which is, according to the following study, predicted
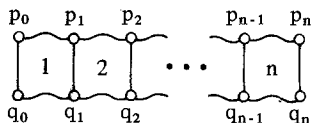
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[1] In order to avoid the formal complications which may arise in the case of $u = 0$, we shall use the symbol $1/0 = \infty$ like an ordinary number with the properties $\infty + x = \infty$ and $1/\infty = 0$.

to be an unstable species:

3. Application to Non-Branched CCH'S

The general form of a non-branched CCH with n rings is

The distance between the two vertices p and q is denoted by $d(p, q)$ [8]. Hence, $d(p_i, q_i) = 1$ $(i = 0, 1, 2, \ldots, n)$, the size of the k–th ring is $d(p_{k-1}, p_k) + d(q_{k-1}, q_k) + 2$ and since we consider alternant CCH's only (i.e. bipartite graphs [8]) all rings are of even size. A successive application of Eq. (10) gives the following:

Hence, the result is either $N_0 = 0$ (if $\alpha_n \neq 0$) or $N_0 = 2$ (if $\alpha_n = 0$), and the whole problem is reduced to the finding the values of α_n. This procedure can be also understood as if α_k is obtained by the action of an operator $\hat{o}_k = \hat{o}(x_k, y_k)$ on α_{k-1}:

$$\alpha_k = \hat{o}_k(\alpha_{k-1}) \qquad k = 1, 2, \ldots, n \tag{11}$$

while $\alpha_0 = 1$.

The operator $\hat{o}(x_k, y_k)$ is uniquely determined with $x_k = d(p_{k-1}, p_k)$ and $y_k = d(q_{k-1}, q_k)$, that is with the topology of the k–th ring. Evidently,

$$\alpha_n = \hat{o}_n \hat{o}_{n-1} \ldots \hat{o}_2 \hat{o}_1(1). \tag{12}$$

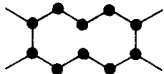Fortunately, the number of different types of $\hat{o}$'s is very much reduced because of the relations:

$$\hat{o}(x, y) = \hat{o}(y, x) \tag{13}$$

$$\hat{o}(x + 4, y) = \hat{o}(x, y) \tag{14}$$
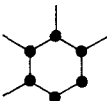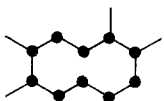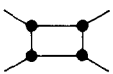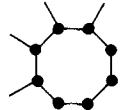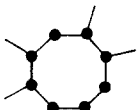
$$\hat{o}(x + 2, y + 2) = \hat{o}(x, y). \tag{15}$$

It can be now easily demonstrated that there are only four distinct possibilities for $\hat{o}$, and thus *non-branched CCH's are composed from four essentially different ring types* (from a topological point of view). This is indicated in Table 1.

Table 1.

$(x+y)/2$	x, y	$\hat{o}$	Examples of the corresponding ring constituents[a]
even	odd	$\hat{a}$	
even	even	$\hat{b}$	
odd	even	$\hat{c}$	
odd	odd	$\hat{d}$	

[a]Note that the size of $\hat{a}$– and $\hat{b}$–type rings is $4m+2$, whereas the size of $\hat{c}$– and $\hat{d}$–ones is $4m$

Direct calculation shows that

$$\hat{a}(\alpha) = 1 + \alpha$$

$$\hat{b}(\alpha) = 1 + 1/\alpha$$

$$\hat{c}(\alpha) = 1 - 1/\alpha \tag{16}$$

$$\hat{d}(\alpha) = 1 - \alpha .$$

An ordered n-tuple of symbols $\hat{a}$, $\hat{b}$, $\hat{c}$, and $\hat{d}$ can be properly related to every non-branched CCH. For example, for the Molecule II this symbolic sequence is: $\hat{a}\hat{a}\hat{d}\hat{a}\hat{a}\hat{b}\hat{d}\hat{b}\hat{c}\hat{c}\hat{a}$, which immediately gives $\alpha_n = 0$ and the prediction is that II should not be a stable molecule. For the Molecule III one obtains the opposite conclusion since $\alpha_n = \hat{a}\hat{d}\hat{a}\hat{b}\hat{d}\hat{b}\hat{c}\hat{c}\hat{a}(1) = -1$.
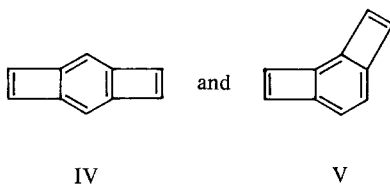
We will use as another illustration of our procedure the same two examples

IV   V

which were considered earlier by Wilcox [10b] and in our work [7]. The symbols $\hat{c}\hat{a}\hat{c}$ and $\hat{c}\hat{b}\hat{c}$ can be corresponded to molecules IV and V, respectively, and

$$\hat{c}\hat{a}\hat{c}(1) = \hat{c}\hat{a}(0) = \hat{c}(1) = 0 \Rightarrow N_0 = 2$$

$$\hat{c}\hat{b}\hat{c}(1) = \hat{c}\hat{b}(0) = \hat{c}(\infty) = 1 \Rightarrow N_0 = 0 .$$

Thus, the prediction is, in agreement with previous results, that the Molecule IV should be an unstable species.

The situation is quite opposite in the case of the three isomeric dibenzcyclo-octatetraenes:

VI   VII   VIII
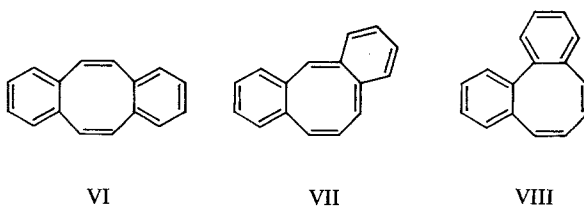
Here the corresponding symbols are $\hat{a}\hat{c}\hat{a}$, $\hat{a}\hat{d}\hat{a}$, and $\hat{a}\hat{c}\hat{a}$, respectively, and simple calculation gives that the isomers VI and VIII should be essentially more stable than VII. Besides, VI and VIII are topologically equivalent.

The operators $\hat{a}$, $\hat{b}$, $\hat{c}$, and $\hat{d}$ fulfill the following equations:

$$\hat{c}^3 = 1 \tag{17}$$

$$\hat{d}^2 = 1 \tag{18}$$

$$\hat{a}^{-1} = -\hat{d}, \quad \hat{b}^{-1} = -\hat{c}^2, \quad \hat{c}^{-1} = \hat{c}^2, \quad \hat{d}^{-1} = \hat{d} \tag{19}$$

$$\hat{a}\hat{c}^2\hat{a} = \hat{b}\hat{c}^2\hat{b} = \hat{d}\hat{c}^2\hat{d} = \hat{c} \tag{20}$$

$$\hat{a}\hat{c}^2\hat{b} = \hat{b}\hat{c}^2\hat{a} = \hat{d} \tag{21a}$$

$$\hat{a}\hat{c}^2\hat{d} = \hat{d}\hat{c}^2\hat{a} = \hat{b} \tag{21b}$$

$$\hat{b}\hat{c}^2\hat{d} = \hat{d}\hat{c}^2\hat{b} = \hat{a} \tag{21c}$$

$$\hat{a}\hat{d}\hat{a} = \hat{b}\hat{d}\hat{b} = \hat{c}\hat{d}\hat{c} = \hat{d} \tag{22}$$

$$\hat{a}\hat{d}\hat{b} = \hat{b}\hat{d}\hat{a} = \hat{c} \tag{23a}$$

$$\hat{a}\hat{d}\hat{c} = \hat{c}\hat{d}\hat{a} = \hat{b} \tag{23b}$$

$$\hat{b}\hat{d}\hat{c} = \hat{c}\hat{d}\hat{b} = \hat{a}. \tag{23c}$$

These equations can be used for further simplification of the procedure for determination of the N_0 value. For example, the symbol which corresponds to III can be transformed using Eqs. (18) and (22) as: $\hat{a}\hat{d}\hat{a}\hat{b}\hat{d}\hat{b}\hat{c}\hat{c}\hat{a} = \hat{d}\hat{b}\hat{d}\hat{b}\hat{c}\hat{c}\hat{a} = \hat{d}\hat{d}\hat{c}\hat{c}\hat{a} = \hat{c}\hat{c}\hat{a}$.

For the terminal operators of the ordered n-tuple it is $\hat{a} \equiv \hat{b}$ and $\hat{c} \equiv \hat{d}$. Moreover, one can delete from the ends of the n-tuple every combination $[\hat{a}, \hat{b}, \hat{c}, \hat{d}]$ of operators $\hat{a}$, $\hat{b}$, $\hat{c}$, and $\hat{d}$ with the property:

$$[\hat{a}, \hat{b}, \hat{c}, \hat{d}](1) = 1. \tag{24}$$

Such combination are, for instance: $\hat{a}\hat{c}$, $\hat{d}\hat{c}$, $\hat{c}\hat{a}^n\hat{c}\hat{c}$, etc.

4. Conclusions

Numerous general conclusions can be obtained from Eq. (16). Some of them we list below:

1. CCH's containing an arbitrary sequence of $\hat{a}$- and $\hat{b}$-type rings (that is $(4m + 2)$-membered ring systems) never possess NBMO's. This follows from the fact that $\hat{a}(\alpha) \geq 1$ and $\hat{b}(\alpha) \geq 1$ for $\alpha \geq 1$. Recently, a similar result was obtained by Bochvar and Stankevich [14] for non-branched CCH's containing only $\hat{a}$-type rings.

Therefore, the presence of $(4m)$-membered rings in the CCH is a neccesary condition for the existence of NBMO's.

2. Nevertheless, if the non-branched CCH is of the form $\hat{a}[\hat{a}, \hat{b}]\,\hat{a}\hat{c}[\hat{a}, \hat{b}]\,\hat{a}\hat{c}\ldots$ $\ldots[\hat{a}, \hat{b}]\,\hat{a}$, where $[\hat{a}, \hat{b}]$ denotes arbitrary sequences of $\hat{a}$- and $\hat{b}$-type rings, it is also $N_0 = 0$. To see this, note that $\hat{a}\hat{c}(\alpha) \geq 1$ for $\alpha > 1$.

3. The curious result that the $(4m)$-ring sequences $\hat{c}\hat{c}\hat{c}$, $\hat{c}\hat{d}\hat{c}\hat{d}$, $\hat{c}\hat{c}\hat{d}\hat{c}\hat{c}\hat{d}$, $\hat{d}\hat{d}$, etc. in arbitrary positions of the CCH's have no influence on the N_0 value follows immediately from Eqs. (17), (18), and (21).

Perhaps here is a good opportunity to emphasize that although $N_0 > 0$ indicated the reactive species, the condition $N_0 = 0$ is not a sufficient condition for

chemical stability. In this respect temperature and molecular environment, for example, are also important.

4. Suppose that a CCH is unstable. Then the annelation of an arbitrary ring in the terminal position will cause $N_0 = 0$. This follows from the simple fact that $\hat{o}(0) \neq 0$ for all $\hat{o}$'s.

5. Similarly, the deletion of the terminal ring from an unstable CCH will cause stabilization, regardless the type of the eliminated ring (compare II and III). This is a consequence of $\hat{o}(\alpha) = 0 \Rightarrow \alpha \neq 0$ for all $\hat{o}$'s.

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