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HÜCKEL RULE IN CATACONDENSED BENZENOID HYDROCARBONS

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Abstract: It is demonstrated that all cycles in a catacondensed benzenoid hydrocarbons exhibit a stabilizing effect on its overall thermodynamic stability. Because the cycles in a catacondensed benzenoid hydrocarbon are all of (4m+2)-type, our result implies that in the class of conjugated molecules considered the Hückel (4m+2)-rule is obeyed without exceptions.

INTRODUCTION

Slobodan Bosanac and the present author developed in 1977 [1,2] a method for the calculation of the effect of an individual cycle in a polycyclic conjugated π-electron system on the thermodynamic stability of the respective compound. This method is based on the application of certain mathematical techniques of graph spectral theory, by means of which it is possible to "extract" the contribution of each individual cycle to the total π-electron energy. The current version of the theory is formulated within the framework of the tight-binding (Hückel) molecular orbital approximation. Both its chemical and mathematical details have been outlined in earlier publications [1-4].

Thus if G denotes the molecular graph of a conjugated system and $\phi(G, x)$ stands for its characteristic polynomial [5,6], then the energy--effect of a cycle Z (in the units of the HMO resonance integral β) is given by [1-4]:

$$ef(G,Z) = \frac{2}{\pi} \int_0^{\infty} \ln \left| \frac{\phi(G, iy)}{\phi(G, iy) + 2\,\phi(G-Z, iy)} \right| dy \qquad (1)$$

where $i = \sqrt{-1}$ and where G-Z is the subgraph obtained by deleting from G the vertices that belong to the cycle Z. [In the case when Z embraces all the vertices of G i.e. when Z is a Hamiltonian cycle of G, then formula (1) remains valid provided the term $\phi(G-Z, iy)$ is set to be identically equal to unity.]

The cycle Z causes (thermodynamic) stabilization if ef(G,Z) is greater than zero. If ef(G,Z) is negative then the respective cycle diminishes the stability of the molecule examined [1-4]. In view of this the quantity ef(G,Z) provides the basis of a straightforward method for checking the validity of the Hückel (4m+2)-rule in the case of polycyclic conjugated molecules.

It seems that Michael Dewar [7] was the first to formulate the so--called "generalized Hückel rule" (GHR), according to which 6-, 10-, 14-, ...-membered cycles stabilize whereas 4-, 8-, 12-, ...-membered cycles destabilize the respective polycyclic conjugated molecule. Here "stabilization" and "destabilization" are understood in a thermodynamic sense i.e. as effects on the energy (enthalpy) of the conjugated compound considered.

The reasoning which led to the GHR were based on perturbation-molecular-orbital arguments [7-9] and could not be completely justified by

more sophisticated theoretical analyses. In particular, some difficulties in the Dewar's approach were pointed out a long time ago [10].

In the great majority of the conjugated molecules investigated so far, the ef-method was found to be in very good harmony with the **GHR**. In other words, we usually have $ef(G,Z) > 0$ if the size of the cycle Z is $4m+2$ and $ef(G,Z) < 0$ if the size of this cycle is $4m$. These regularities are, however, not without exceptions. Cases have been reported [2,11] in which the **GHR** was violated. These cases embrace alternant conjugated hydrocarbons containing cyclobutadiene fragments [2] as well as conjugated molecules with heteroatoms [11].

On the other hand, it has been shown [12] that in alternant conjugated hydrocarbons one half of the **GHR** is always obeyed. We namely have the following result, which could be proved in a mathematically rigorous manner and which, therefore, cannot have exceptions.

Theorem 1. If G is an arbitrary bipartite graph and Z its arbitrary cycle whose size is divisible by four, then $ef(G, Z) < 0$.

Because the molecular graphs of alternant hydrocarbons are necessarily bipartite, Theorem 1 means that all $(4m)$-membered cycles in an alternant hydrocarbon necessarily diminish its thermodynamic stability.

Curiously, however, it is not always true that $(4m+2)$-membered cycles in a bipartite graph have positive ef-values. Counterexamples have been discovered already in [2].

In this paper we demonstrate that if we restrict our consideration to catacondensed benzenoid hydrocarbons [13], then also the second half of the **GHR** is always satisfied. In particular, we offer the following result.

Theorem 2. If G is the molecular graph of an arbitrary catacondensed benzenoid hydrocarbons and Z is its arbitrary cycle, then $ef(G, Z) > 0$.

Bearing in mind that all cycles of a catacondensed benzenoid system are of (4m+2)-type [13,14], from Theorem 2 we readily conclude that catacondensed benzenoid hydrocarbons fully obey the **GHR**.

In order to prove Theorem 2 we need some preparations.

THE FUNCTION γ AND SOME OF ITS PROPERTIES

By introducing the substitution $y = 1/x$ into eq. (1) we obtain after some elementary calculus

$$ef(G,Z) = \frac{2}{\pi} \int_0^\infty x^{-2} \ln \left| \frac{\phi(G, i/x)}{\phi(G, i/x) + 2\,\phi(G-Z, i/x)} \right| dx$$

which can be rewritten in the form

$$ef(G,Z) = -\frac{2}{\pi} \int_0^\infty x^{-2} \ln |1 - \gamma(x)|\, dx \qquad (2)$$

where

$$\gamma(x) \equiv \gamma(G,Z,x) \equiv -2\,\phi(G-Z, i/x)/\phi(G, i/x) \quad . \qquad (3)$$

By means of eq. (3) we defined a novel graph function whose independent variable is x and which depends on the graph G and its particular cycle Z. In the general case γ is a complex-valued quantity. However, we have

Lemma 1. If G is a bipartite graph, then for all real values of the variable x, for which the function $\gamma(x)$ exists, $\gamma(x)$ is real-valued.

Proof. The characteristic polynomial of an n-vertex bipartite graph G can always be written in the form

$$\phi(G, x) = \sum_{k \geq 0} (-1)^k \, b(G, k) \, x^{n-2k} \qquad (4)$$

where the coefficients b(G, k) are non-negative. Formula (4) is an easy algebraic consequence of the pairing theorem [5,6], and has been used many times in the chemical literature.

Now, if G is bipartite then all its cycles are of even size. Further, for any cycle Z of G, the subgraph G-Z is also bipartite [5]. Hence,

$$\phi(G-Z, x) = \sum_{k \geq 0} (-1)^k \, b(G-Z, k) \, x^{n-|Z|-2k} \; . \qquad (5)$$

Here and later the size (= number of vertices) of the cycle Z is denoted by $|Z|$.

Substituting (4) and (5) back into (3) we obtain after straightforward calculation

$$\gamma(x) = -2 \, (-1)^{|Z|/2} \, x^{|Z|} \, \frac{\sum_k b(G-Z, k) \, x^{2k}}{\sum_k b(G, k) \, x^{2k}} \qquad (6)$$

form which the validity of Lemma 1 is obvious. □

From (6) we also immediately arrive at

Lemma 2. If G is a bipartite graph, then the function $\gamma(x)$ exists for all real values of the variable x, except for x = 0.

Proof. It is sufficient to recall that both the numerator and the nominator on the right-hand side of eq. (6) are polynomials whose coefficients are positive or zero. Because of b(G, 0) = 1 the nominator cannot

be equal to zero (in fact, it is always greater than or equal to unity). Hence, the right-hand side of formula (6) exists for all real values of x. For x = 0, however, the original definition (3) of $\gamma(x)$ would require division with zero. □

By introducing the auxiliary quantity

$$\zeta(Z) = \begin{cases} -1 & \text{if } |Z| \in \{4, 8, 12, \ldots, 4m, \ldots\} \\ +1 & \text{if } |Z| \in \{6, 10, 14, \ldots, 4m+2, \ldots\} \end{cases}$$

the expression (6) can be written in a somewhat more compact form

$$\gamma(x) = \zeta(Z) \frac{2 \sum_k b(G-Z, k)\, x^{2k+|Z|}}{\sum_k b(G, k)\, x^{2k}} . \qquad (6')$$

From eq. (6') we are able to straightforwardly deduce Theorem 1. Although Theorem 1 is not a new result [12], we deem that at this point it is instructive to repeat its (very short) proof.

Proof of Theorem 1. If the size of a cycle Z is divisible by 4 then Z is of (4m)-type i.e. $\zeta(Z) = -1$. Therefore for all $x \in (0,\infty)$ $\gamma(x)$ is greater than unity. This means that the integrand in (2) is positive in the entire domain of integration. Hence the left-hand side of (2) must be negative. □

From eq. (2) it is clear that if for all $x \in (0,\infty)$,

$$0 \leq \gamma(x) \leq 1 \qquad (7)$$

then ef(G,Z) will necessarily be positive. In what follows we prove Theorem 2 by showing that for G being the molecular graph of a catacondensed benzenoid hydrocarbon and Z its arbitrary cycle, the function $\gamma(G,Z,x)$ obeys the relations (7).

PROOF OF THEOREM 2

Let the molecular graph G possess cycles. Let Z be the cycle whose effect on total π-electron energy we are interested in and let e_{uv} be an edge of G, connecting the vertices u and v, lying on Z. The edge e_{uv} may (but needs not) belong to other cycles of G. If such cycles exist, we denote them by $Z_1, Z_2, \ldots, Z_r$.

According to a well known result of Heilbronner [5,15], the characteristic polynomial of the graph G conforms to the recursion relation:

$$\phi(G) = \phi(G-e_{uv}) - \phi(G-u-v) - 2\,\phi(G-Z) - 2\sum_{j=1}^{r}\phi(G-Z_j) \quad . \qquad (8)$$

If Z is the only cycle containing the edge e_{uv} (i.e. if r = 0), then the last summation on the right-hand side of (8) does not exist. In the case of benzenoid graphs, however, r is necessarily greater than unity. (Exceptionally, r = 0 for benzene and r = 1 for naphthalene.)

Now, if G is bipartite so are the subgraphs $G-e_{uv}$, G-u-v, G-Z and $G-Z_j$, j = 1,...r. Consequently, formulas of type (4)-(5) apply to all of them. From (8) we then deduce the following recurrence relation for the coefficients of the characteristic polynomial:

$$b(G, k) = b(G-e_{uv}, k) + b(G-u-v, k-1) + 2\,\zeta(Z)\,b(G-Z, k-|Z|/2) + 2\sum_{j=1}^{r}\zeta(Z_j)\,b(G-Z_j, k-|Z_j|/2) \quad . \qquad (9)$$

In order that the relation (9) hold for all values of k = 0,1,2,..., it is both consistent and convenient to set b(H, k') = 0 for all bipartite graphs H and all k' = -1, -2, -3,... . We assume that this condition is satisfied in all formulas that follow.

As already mentioned, all the cycles of a catacondensed benzenoid hydrocarbon are of size 4m+2. This makes possible to simplify (9) as

$$b(G, k) = b(G-e_{uv}, k) + b(G-u-v, k-1) + 2\, b(G-Z, k-|Z|/2) + 2 \sum_{j=1}^{r} b(G-Z_j, k-|Z_j|/2) \quad .$$

Bearing in mind that for all values of k, $b(G-e_{uv}, k) \geq 0$, $b(G-u-v, k-1) \geq 0$ and $b(G-Z_j, k-|Z|/2) \geq 0$, one arrives at

Lemma 3. If G is the molecular graph of a catacondensed benzenoid system and Z its arbitrary cycle, then the inequality

$$b(G, k) \geq b(G-Z, k-|Z|) \qquad (10)$$

is satisfied for all values of k, k = 0,1,2,... .

We are now prepared to show that the relations (7) are obeyed for all $x \in (0,\infty)$ provided G is a molecular graph of a catacondensed benzenoid hydrocarbon.

The validity of the left-hand inequality in (7) is obvious from (6') and the fact that $\zeta(Z) = +1$ for any cycle Z contained in a catacondensed benzenoid system.

In order to verify the right-hand side inequality in (7) we use eq. (6') and write $\gamma(x)$ in the form:

$$\gamma(x) = \frac{2 \sum_k b(G-Z, k)\, x^{2(k+|Z|/2)}}{\sum_k b(G, k)\, x^{2k}} = \frac{2 \sum_k b(G-Z, k-|Z|/2)\, x^{2k}}{\sum_k b(G, k)\, x^{2k}} \quad . \qquad (11)$$

Because of the Lemma 3 the right-hand side of (11) cannot exceed unity i.e. the the second inequality in (7) holds for all $x \in (0,\infty)$.

This completes the proof of Theorem 2. □

DISCUSSION

We computed a large number of ef-values of both cata- and pericondensed benzenoid hydrocarbons and found not a single case of violation of the Hückel rule. Therefore we are inclined to conjecture that the **GHR** (measured via its energy-effect) is satisfied not only in all catacondensed benzenoids (which we proved in this paper), but also in all pericondensed benzenoid systems.

Pericondensed benzenoid hydrocarbons possess both (4m+2)- and (4m)--membered cycles [13]. The validity of the **GHR** for the (4m)-cycles is ensured by means of Theorem 1. Hence what only remains, is to prove that all (4m+2)-cycles in a pericondensed benzenoid molecule have positive ef-values. For this it would suffice to show that the inequalities (7) are obeyed, which - as we just have seen - is the case provided the relation (10) holds.

At the first glance, deducing (10) from the Heilbronner identity (9) may look as a not too difficult task; in formula (9) we now would have $\zeta(Z) = +1$, but $\zeta(Z_j) = -1$ for some j. Nevertheless, the finding of a satisfactory proof of the below conjecture was not successful so far.

Conjecture. If G is the molecular graph of a benzenoid system and Z its arbitrary cycle of size 4m+2, then the inequality (10) is satisfied for all values of k, $k = 0,1,2,\ldots$.

If this Conjecture is true then the generalized Hückel (4m+2)-rule is obeyed without exception by all benzenoid hydrocarbons.

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