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QUANTITATIVE APPROACH TO HÜCKEL RULE

THE RELATIONS BETWEEN THE CYCLES OF A MOLECULAR GRAPH AND THE THERMODYNAMIC STABILITY OF A CONJUGATED MOLECULE

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Abstract—Contribution of the rings to the total π-electron energy (CE) is calculated for a number of polycyclic conjugated hydrocarbons. The Hückel 4m + 2 rule is tested quantitatively in this way. It is shown that (4m)-membered rings always destabilize, while (4m + 2)-membered rings almost always stabilize the molecule. The magnitude of this effect is, however, subject to considerable variations. The main factors which determine the magnitude of CE are discussed. Examples of the alternant hydrocarbons are found for which the (4m + 2)-membered cycles have a destabilizing effect, and therefore violate the Hückel rule. The odd membered cycles are shown to have a negligibly small effect on the stability of the conjugated molecules.

It was recognized[1] long ago that rings which are present in a π-electron network, cause stabilization (aromaticity) or destabilization (antiaromaticity) of the corresponding conjugated compound. In the monocyclic systems (annulenes) this effect can be demonstrated by comparing the total π electron energy of a particular annulene with that of its open-chain analogue—the linear polyene.[2-5] This open-chain analogue is determined unequivocally because of the high symmetry of the annulene topology.

The main conclusions of the Refs. 2–5 are

(a) (4m + 2)-membered cycles stabilize and

(b) (4m)-membered cycles destabilize the corresponding annulene molecule.

The properties (a) and (b) are usually called the Hückel rule. It was conjectured some time ago[6] that they hold for an arbitrary conjugated molecule. The conjecture was later supported by graph-theoretical arguments.[7]

Further properties of the annulenes, which were expected to hold also in the polycyclic case are the following.

(c) Both the stabilization and the destabilization effects decrease and vanish with increasing m.

(d) Odd-membered cycles have a negligibly small effect on total π-electron energy.

In the case of the polycyclic molecules, the choice of an "open-chain analogue" is by no means unique and the approach of the Refs. 2–5 cannot be simply extended. Recent graph-theoretical analysis[7-10] resulted in a deeper insight into the way the cycles inflence total π-electron energy and thus[11] the thermodynamic stability of the conjugated compounds. Finally, the Hückel rule was proved[8] for an arbitrary alternant hydrocarbon *under certain assumptions* (see Appendix).

The Hückel rule is *qualitative* by its nature, namely it predicts only whether the effect caused by a cycle is stabilization or destabilization, but says nothing about the magnitude of this effect. Therefore, *quantitative* studies on the Hückel rule were a natural continuation of the theory elaborated in the Ref. 9. In the present work we would like to report the results of such a quantitative approach to the Hückel rule.

THEORY AND RESULTS

Theoretical background of the present analysis is given in more details elsewhere.[9,10] For our purposes only the following few graph-theoretical notions are required.[12] A conjugated molecule is presented by a molecular graph G with n vertices. The characteristic polynomial[12-14] of G is P(G, x). Let C be a cycle contained in the graph G, the size of which is γ. Then G–C is the graph obtained by deletion of the vertices of C from G. Of course, G–C has $n-\gamma$ vertices.

Assuming the usual relations[12] between the graph theory and the HMO model, it can be shown[9] that the HMO total π-electron energy (in β units) is expressed as

$$E(G) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{dx}{x^2} \log |P(G, 1/ix)| \tag{1}$$

where $i = \sqrt{(-1)}$. According to the Sachs theorem,[14] the characteristic polynomial of a graph G can be calculated from a set S(G) of its certain subgraphs, which are usually called[12] the Sachs graphs (of G). Since we will not be interested in the actual form of this calculation, it will suffice to write the Sachs theorem as

$$S(G) \xrightarrow{f} P(G, x) \tag{2}$$

were *f* is a complicated, but algebraically completely defined mapping.

The Sachs graphs consist of cycles.[12-14] This fact gives it a convenient and consistent procedure to take into account the effect of a particular cycle C. Let S(G/C) be the set of those Sachs graphs from S(G) which do not contain the cycle C as a component. Then by analogy to eqns (1) and (2) we define a polynomial P(G/C, x) and a number E(G/C) as

$$S(G/C) \xrightarrow{f} P(G/C, x)$$

$$E(G/C) = \frac{1}{\pi}\int_{-\infty}^{+\infty} \frac{dx}{x^2} \log |P(G/C, 1/ix)|. \tag{3}$$

Note that P(G/C, x) is not the characteristic polynomial of any graph (although it is a polynomial of degree n with integer coefficients). The quantity E(G/C) have obviously the same algebraic structure as E(G). Because of the definition of the set $S(G/C)$, the difference

$$CE = E(G) - E(G/C) \tag{4}$$

can be interpreted as *that contribution to total π-electron energy, which comes from the presence of the cycle C in the molecular graph G.* We propose the name "cycle energy" for this quantity.

The described formalism was developed to prove the Hückel rule[9] (see Appendix). In order to enable evaluation of CE's, the formulas (1), (3) and (4) are to be transformed into a more convenient form[10]

$$CE = \frac{1}{\pi}\int_{-\infty}^{+\infty} \log \left| \frac{P(G, ix)}{P(G, ix) + 2P(G-C, ix)} \right| dx. \tag{5}$$

Proof of the eqn (5) and further computational details are given in Ref. 10.

We give Table 1 the CE values of a representative set of polycyclic conjugated hydrocarbons, shown in Chart 1.

The rings in Table 1 are labelled in the following manner. If the rings a and b are indicated in Chart 1, a + b denotes the ring which is generated from those edges of a and b which do not belong simultaneously to both a and a. Further, a + b + c means (a + b) + c, etc.

DISCUSSION

Quantitative Hückel rule. The most striking property of the ring energies in Table 1 is that they are always positive for (4m + 2)-membered rings and negative for the rings of the size 4m. This confirms the validity of the (qualitative) Hückel rule, at least in the great majority of cases.

Since the HMO energies are reliable up to approximately 0.1β, one can accept this value for a conventional differentiation between the chemically significant (greater than 0.1β) and chemically negligible (smaller than 0.01β) ring effects. From Table 1 is deduced that the CE values are not determined solely by the size of the rings, but are rather sensitive to the various details of the molecular structure. Therefore we conclude that *the Hückel rule is in some cases very important, but in the others has no significance for organic chemistry.* The actual effect of a ring depends on a delicate balance of different topological factors. Our numerical experience can be summarized as follows.

Rule 1. CE's in general decrease with the increasing size of the ring, although there exists a large number of exceptions. While the effects of 4- and 6-membered rings are almost always significant, 14-, 16-, etc. rings have a negligibly small effect in all the studied cases.

This regularity can be easily noticed when the CE's of the rings of a particular conjugated system are compared.

Rule 2. In systems with similar structure, the CE's decrease with the increasing size of a molecule.

Rule 3. The larger the stability of a conjugated compound (i.e. the larger E(G)), the smaller are the ring energies.

This is demonstrated by comparing the isomers of similar structure (e.g. the two diphenzopentalenes 27 and 28, the first being much less stable than the second one[14]).

Rule 4. In similar molecules, those rings which are conjugated[15] have much larger values of CE than the non-conjugated ones.

Table 1. Ring energies (CE's) in β units of conjugated systems which are presented in Chart 1

No	cycle	size	cycle energy
1	a	4	-1.2257
2	a	4	-0.1628
3	a	4	-0.2482
4	a	4	-0.0718
5	a	5	+0.0200
6	a	6	+0.2726
7	a	6	+0.1554
8	a	6	+0.0612
9	a	6	+0.0958
10	a	6	+0.0090
11	a	7	+0.0091
12	a	8	-0.5948
13	a	4	-0.4956
	a+b	6	+0.5152
14	a	6	+0.4252
	b	4	-0.4287
	a+b	8	-0.2641
15	a	5	+0.1480
	a+b	8	-0.2756
16	a	6	+0.1211
	a+b	10	+0.0709
17	a	7	-0.0109
	b	5	-0.0017
	a+b	10	+0.1467
18	a	8	-0.2506
	b	4	-0.4432
	a+b	10	+0.3202
19	a	6	+0.2153
	b	5	+0.0062
	a+b	9	+0.0039
20	a	6	+0.0801
	b	5	+0.0152
	a+b	9	+0.0116
21	a	7	+0.0987
	a+b	12	-0.1816
22	a	6	+0.4596
	b	4	-0.1597
	a+b	8	-0.0678
	a+b+c	12	-0.0480
23	a	6	+0.1050
	c	5	+0.0124
	a+b	10	+0.0567
	a+c	9	+0.0049
	a+b+c	11	-0.0026
24	a	6	+0.0862
	a+b	10	+0.0261
	a+b+c	12	-0.0125
25	a	6	+0.0952
	b	6	+0.0652

Table 1. (*Contd*)

No	cycle	size	cycle energy
	a+b	10	+0.0369
	a+b+c	14	+0.0279
26	a	6	+0.1586
	b	6	+0.0534
	a+b	10	+0.0275
	a+b+c	14	+0.0198
27	a	6	+0.2534
	b	5	+0.0253
	a+b	9	+0.0173
	b+c	8	−0.0392
	a+b+c	12	−0.0291
	a+b+c+d	16	−0.0248
28	a	6	+0.0966
	b	5	+0.0585
	a+b	9	+0.0478
	b+c	8	−0.0656
	a+b+c	12	−0.0549
	a+b+c+d	16	−0.0501
29	a	6	+0.0528
	b	6	+0.1063
	a+b	10	+0.0198
	a+c	10	+0.0056
	a+b+c	12	−0.0023
	a+b+d	14	+0.0128
	a+b+c+d	14	+0.0128
30	a	6	+0.1909
	b	6	+0.0242
	a+b	10	+0.0102
	a+b+c	14	+0.0068
	a+b+c+d	18	+0.0053
31	a	6	+0.1093
	c	6	+0.0218
	a+b	10	+0.0586
	a+b+c	12	−0.0018
	a+b+c+d+e	18	+0.0003

For example, the smallest observed CE values (for a given size of a ring) are those in the radialenes. As another example, one can compare the CE's of the 6-membered rings in the two benzfulvenes **19** and **20** (the ring a is resonant in **19** but not in **20**).

Randić[16] found that the SCF MO resonance energies of conjugated hydrocarbons can be calculated with an unexpected accuracy from a simple additive scheme

$$RE = \sum_j n_j R_j. \qquad (6)$$

In formula (6) the R_j's are empirical parameters and the n_j's are the number of times the j-membered rings are resonant in the Kekulé structures of a molecule. R_j can be interpreted as an average value of CE's for the rings of a size j.

Formula (6) is in agreement with our finding that the contributions of the resonant rings to the total π-electron energy (and thus also to the resonance energy) are the most important ones. However, since the CE's are found to be far from constant, our theory gives no explanation for the success of eqn (6).

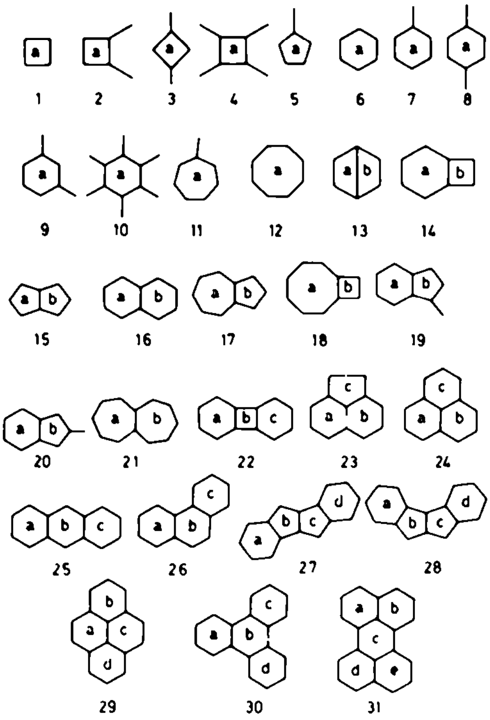


Chart 1.

In connection with Rule 4 are the relations which exist between the Clar formulas[17,18] and the CE's of benzenoid hydrocarbons.

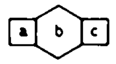
Rule 5. The larger the benzoid (or local aromatic[19]) character of a 6-membered ring, the larger is the CE.

As an example one can compare the CE values of the rings a and b in triphenylene **30**. Consequently, the rings which are "empty" in all Clar formulas (e.g. the ring c in perilene, **31**) have unusually small values of CE. Therefore, we see that the use of Clar formulas can be justified also from an energetic point of view: the circles in Clar's notation can be understood as indicating those six-membered rings which have the largest contributions to the total π-electron energy.

Violations of the Hückel rule. It is shown in the Appendix that the Hückel rule is valid for all (4m)-membered rings of alternant hydrocarbons. The Hückel rule holds for a (4m + 2)-membered ring if certain additional conditions are fulfilled. In the general case, alternant molecules can be designed which violate the Hückel rule, namely which have CE < 0 for a (4m + 2)-membered ring.

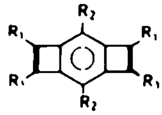
A detailed analysis gives that the necessary condition for a negative ring energy of a (4m + 2)-membered ring is $a_n = 0$ and $b_{n-1} \neq 0$. On the other hand, the relation $a_n = 0$ implies the existence of non-bonding molecular orbitals in the corresponding molecule.[12] Since such conjugated systems are known to be extremely unstable and/or reactive,[20] we conclude that the violations of the Hückel rule may occur in the case of the least stable (usually nonexistant) alternant species.

The simplest case of such conjugated system is the molecule 32, in which the central 6-membered ring exhibits a destabilizing effect of 0.13β. Since all the other rings in **32** are of the size 4m, it is easily understood that



32

a	−0.7664
b	−0.1284
a+b	−0.5746
a+b+c	−0.1797



33

$R_1 = C_6H_5$, $R_2 = (CH_3)_3C$

this compound should be thermodynamically very unstable. It is interesting to note that a polysubstituted derivative **33** of the molecule **32** was recently obtained by classical synthetic methods[21] and was found to be fairly stable. It would be, therefore, very interesting to try to prepare further derivatives of **32** without sterically and electronically protecting substituents.

CE's of odd-membered rings. Our calculations completely confirm the previous expectation that the odd-rings have rather small influence on the stability of a conjugated molecule. The only known case where an odd-ring has a CE greater than 0.1β is the 5-membered ring in pentalene **15**. This exception is explained simply as a combined effect of the small size (Rule 2) and low stability[22] (Rule 3) of pentalene.

Rules can be formulated which determine whether an odd cycle causes stabilization or destabilization, but these are not simple.[23] Since the effects are very small, these rules are not expected to be of any use in practice.

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[15] A ring C is conjugated[16] if there exists a Kekulé structure of the molecule, such that the edges of C correspond successively to single and double bonds of this Kekulé structure. Odd rings are therefore never conjugated. Congugated rings play an important role in a theory recently developed by Randić.[16]

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APPENDIX

Formula (5) enables the evaluation of CE from the knowledge of the spectra (or, which is the same, of the characteristic polynomials) of graphs G and G–C. If G is the molecular graph of an alternant hydrocarbon, P(G, x) can be written as

$$P(G, x) = \sum_{j=0}^{n/2} (-1)^j a_{2j} x^{n-2j}. \qquad \text{(A1)}$$

Then $a_{2j} \geq 0$ for all j. By analogy, P(G–C, x) will be denoted by

$$P(G-C, x) = \sum_{j=0}^{(n-\gamma)/2} (-1)^j b_{2j} x^{n-\gamma-2j} \qquad \text{(A2)}$$

where γ is the size of the ring C. Consequently, $b_{2j} \geq 0$. By substituting (A1) and (A2) back into (5), one obtains

$$CE = \frac{1}{\pi} \int_{-\infty}^{+\infty} \log \frac{x^n + a_2x^{n-2} + a_4x^{n-4} + \cdots + a_n}{x^n + c_2x^{n-2} + c_4x^{n-4} + \cdots + c_n} dx \qquad \text{(A3)}$$

where

$$c_{2j} \begin{cases} a_{2j} & \text{for } 2j < \gamma \\ a_{2j} + 2(-1)^{\gamma/2} b_{2j-\gamma} & \text{for } 2j \geq \gamma. \end{cases}$$

If C is a (4m)-membered ring, then $c_{2j} \geq a_{2j} \geq 0$ and from the eqn (A3) it follows that

$$\frac{x^n + a_2x^{n-2} + \cdots + a_n}{x^n + c_2x^{n-2} + \cdots + c_n} \leq 1$$

for all values of x. Therefore,

$$CE < 0 \qquad \text{(A4)}$$

for all (4m)-membered rings.

A similar argument shows that if C is a (4m + 2)-membered ring, $c_{2j} \leq a_{2j}$ for all j. Assuming further that c_{2j}'s are non-negative quantities, it follows from (A3) that

$$CE > 0 \qquad \text{(A5)}$$

for all rings of the size 4m + 2. The statements (A4) and (A5) are equivalent to the Hückel rule.

Although the inequalities $c_{2j} \geq 0$, i.e.

$$a_{2j} \geq 2b_{2j-\gamma}$$

hold in the overwhelming majority of cases, there exist exceptions. If some of the c_{2j}'s are negative, the expression

$$\log \frac{x^n + a_2x^{n-2} + \cdots + a_n}{x^n + c_2x^{n-2} + \cdots + c_n}$$

can have both positive and negative values and in the general case the sign of the integral (A3) cannot be predicted. In particular, it can happen that for certain (4m + 2)-rings the corresponding ring energy has a negative value, which is a violation of the Hückel rule.