

Effect of a Ring on the Stability of Polycyclic Conjugated Molecules

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A graph theoretical method is developed which enables to calculate the contribution of a particular ring to the total π -electron energy of a conjugated molecule.

From the classical work of Hückel¹ it is known that the presence of the rings of various size ($4m$, $4m+1$, $4m+2$ or $4m+3$) in a π -electron network strongly influence the chemical and physical behaviour of the corresponding conjugated molecule. This led some time ago to the formulation² of the "extended Hückel rule", namely that in all conjugated molecules the presence of a $4m$ ring has a destabilizing, and the presence of a $4m+2$ ring a stabilizing effect, while odd membered rings have only a small, second order effect. Nevertheless, an exact proof of this statement has been obtained quite recently³ by applying graph theory within the framework of the HMO model.

The extended Hückel rule is qualitative by its nature since it distinguishes only between stabilization and destabilization. Therefore it is justified to pose the question: which is the actual numerical value of the effect of a particular ring? The problem was solved for the monocyclic case⁴ by comparison of total π -electron energies of annulenes with those of their open chain analogues – linear polyenes. However, such a procedure cannot be extended to polycyclic systems. In the present note we offer a method for quantitative evaluation of the contribution of a given ring to the total HMO π -electron energy (and hence⁵ stability) of an arbitrary polycyclic conjugated compound.

Let G be a molecular graph with $n = n(G)$ vertices⁶. The HMO total π -electron energy (in β units) of the corresponding conjugated system is

$$E(G) = 2 \sum_{j=1}^{n/2} x_j \quad (1)$$

where the x_j 's are the roots of the characteristic polynomial⁶ $P(G, x)$ of the graph G ($x_j \geq x_k$ for

$j < k$). Then the Coulson integral formula^{3, 7, 8} reads

$$E(G) = \left\langle n - i x \frac{P'(G, ix)}{P(G, ix)} \right\rangle \quad (2)$$

where we adopt the abbreviated notation^{8, 9}

$$\frac{1}{\pi} \int_{-\infty}^{+\infty} F(x) dx \equiv \langle F(x) \rangle.$$

The characteristic polynomial of a graph G can be calculated by means of the Sachs theorem⁶

$$P(G, x) = \sum_{S(G)} (-1)^{c(s)} 2^{r(s)} x^{n(G) - n(s)} \quad (3)$$

where $n(s)$, $c(s)$ and $r(s)$ are the number of vertices, components and cyclic components, respectively, of the Sachs graph s . The summation in Eq. (3) goes over the set $S(G)$ of all Sachs graphs of a molecular graph G ⁶. By substituting Eq. (3) back into (2) we see that $E(G)$ is completely determined with, and can be calculated from $S(G)$. We denote this fact symbolically by $E(G) = [S(G)]$.

Let us now consider a ring R of G . We can utilize the fact that R is itself a Sachs graph and therefore certain Sachs graphs from $S(G)$ contain R as a component. Let us further denote by $S(G/R)$ the set of those Sachs graphs of G which do not contain R as component. Then the contribution $E(G/R)$ of the ring R to $E(G)$ can be formulated as

$$E(G/R) = [S(G)] - [S(G/R)] \quad (4)$$

Generally speaking, formula (4) allows the computation of $E(G/R)$ via Eqs. (2) and (3). However, this would be an extremely tedious procedure. Fortunately, there exists a much more elegant way for evaluation of $E(G/R)$.

The quantities $[S(G)]$ and $[S(G/R)]$ are of the same algebraic structure and thus we can write

$$[S(G/R)] = 2 \sum_{j=1}^{n/2} y_j \quad (5)$$

where the y_j 's are the roots ($y_j \geq y_k$ for $j < k$) of a polynomial $P(G/R, x)$. Equation (5) is hence analogous to Eq. (1), and therefore

$$P(G/R, x) = \sum_{S(G/R)} (-1)^{c(s)} 2^{r(s)} x^{n(G) - n(s)}.$$

Now we proceed to show that

$$P(G/R, x) = P(G, x) + 2P(G - R, x) \quad (6)$$

where $G - R$ is the graph obtained by deletion of all vertices of the ring R from the graph G .

The Sachs graphs from $S(G)$ either contain the ring R as a component or not. Those Sachs graphs which do not contain R form the subset $S(G/R)$. Those which do contain R are obtained when the ring R is joined to the Sachs graphs of $S(G - R)$. Therefore, to every $s \in S(G)$ which contains the ring R , there corresponds a Sachs graph $s^* \in S(G - R)$ and vice versa. Then, of course, $c(s) = c(s^*) + 1$, $r(s) = r(s^*) + 1$, $n(G) - n(s) = n(G - R) - n(s^*)$, and

$$\begin{aligned} P(G, x) &= \sum_{S(G)} (-1)^{c(s)} 2^{r(s)} x^{n(G) - n(s)} \\ &= \sum_{S(G/R)} (-1)^{c(s)} 2^{r(s)} x^{n(G) - n(s)} \\ &\quad + \sum_{S(G-R)} (-1)^{c(s^*)+1} 2^{r(s^*)+1} x^{n(G-R) - n(s^*)} \\ &= P(G/R, x) - 2P(G - R, x) \end{aligned}$$

from which the Eq. (6) follows immediately.

Using another integral formula of Coulson^{9, 10} we can write Eq. (4) in the form

$$E(G/R) = \left\langle \log \left| \frac{P(G, i x)}{P(G/R, i x)} \right| \right\rangle. \quad (7)$$

Formula (7) together with the identity (6) results in the following algorithm for the evaluation of $E(G/R)$.

Step 1. Determine the spectra of the graphs G and $G - R$. (Since the spectra of numerous molecular graphs are tabulated, step 1 is often not necessary.)

Step 2. From the spectrum of G calculate $P(G, i x_0)$ for a given $x = x_0$ via the formula: $P(G, i x_0) = \prod_j (i x_0 - x_j)$. Calculate $P(G - R, i x_0)$ in the same manner.

Step 3. Determine $P(G/R, i x_0)$ and finally calculate $\log |P(G, i x_0)/P(G/R, i x_0)|$.

Step 4. Determine the integral in Eq. (7) using numerical integration. Thus steps 2 and 3 are to be

Table I. Contribution of a ring to the total HMO π -electron energy of selected conjugated systems.

Compound	Ring size	$E(G/R)$ (in β units)
cyclopropenium cation	3	+0.5359
[3]-radialene	3	+0.0091
cyclobutadiene	4	-1.2263
[4]-radialene	4	-0.0718
benzycyclobutadiene	4	-0.4287
cyclopentadienyl anion	5	+0.3168
[5]-radialene	5	+0.0009
azulene	5	-0.0017
benzene	6	+0.2726
[6]-radialene	6	+0.0090
benzycyclobutadiene	6	+0.4252
naphthalene	6	+0.1211
tropylium cation	7	+0.2253
[7]-radialene	7	+0.0000
azulene	7	-0.0109
cyclooctatetraene	8	-0.5948
[8]-radialene	8	-0.0013
benzycyclobutadiene	8	-0.2641
[10]-annulene	10	+0.1594
[10]-radialene	10	+0.0002
naphthalene	10	+0.0709
azulene	10	+0.1467

repeated for a number of appropriately chosen values of x . Fortunately, the integrand in formula (7) rapidly converges to zero with increasing $|x|$.

In Table I are presented characteristic values of $E(G/R)$ for a number of most frequently occurring types of rings. The most striking property of the $E(G/R)$'s is that they are always positive for $(4m+2)$ - and always negative for $(4m)$ -rings. The numerical values of $E(G/R)$'s within a particular ring size show, however, considerable variations (e.g. the effect of the 6-membered ring in benzene is 30 times larger than that in [6]-annulene). In the molecules of similar topology, a 4-membered ring has a larger destabilization effect than is the stabilization effect of a 6-membered ring (e.g. the destabilization in cyclobutadiene is nearly 5 times larger than the stabilization in benzene). With increasing ring size, the effect of a ring decreases.

Odd membered rings have in general a small, either stabilizing or destabilizing effect which is usually much smaller than 0.1β and thus chemically negligible (exceptions: cyclopropenium and tropylium cations and cyclopentadienyl anion).

Further numerical results together with a detailed analysis of the chemical relevance of the obtained results will be reported in a future paper.

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