Hückel Molecular Orbital Calculations of Aromatic Stabilization of Annulenes

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Annulenes were studied using the concept of aromatic stabilization. A simple expression is presented for the calculation of aromatic stabilization of annulenes. The index of aromatic stabilization differentiates correctly between the [4n + 2] — and [4n] —annulenes. The analysis of the approach of Kruszewski and Krygowski shows that their KK index differs only by a constant from the value of aromatic stabilization of a particular annulene. Similarly, the relation between REPE values of Hess and Schaad and indices of aromatic stabilization is discussed.

Recently we[1-3] developed the concept of aromatic stabilization within the framework of the Hückel molecular orbital (HMO) theory. The aromatic stabilization (A_S) has been defined as the difference between the HMO energy of a given cyclic conjugated molecule and the HMO energy of the corresponding reference structure. The HMO energy of the reference structure is equal to the sum of the effective energy of the polyene carbon-carbon »double« bonds and the effective energy of the polyene carbon-carbon »single« bonds. This approach has been applied to a number of polycyclic conjugated molecules giving in all cases an excellent correlation between calculated A_S values and chemical behaviour[1-3].

We thought that the annulenes would be an interesting group of monocyclic conjugated molecules to test our approach. The reference structure of the particular annulene (cyclic polyene) is best approximated by the corresponding linear polyene. Therefore, the index of aromatic stabilization of annulenes is equal to the difference between the HMO energy of a given annulene and that of a corresponding linear polyene. Thus, the index of aromatic stabilization of annulenes really corresponds to the energy change resulting from the ring closure.

In the past a number of authors studied these compounds from various aspects[4-12]. Especially interesting are studies of Dewar and Gleicher[13], and Figeys[14], who predicted resonance energies of annulenes, the former using a variant[13,15] of the SCF π-molecular orbital method[16,17] and the latter using the LCAO-BETA method[18].

CALCULATION AND RESULTS

The total π-electron energy (E_π) of the annulene is evaluated using the following simple expression[9]:

$$E_\pi \text{ (annulene)} = \begin{cases} 4 \cosec \dfrac{\pi}{N}, \text{ for } [4n+2]\text{-annulenes} \\ \\ 4 \cotan \dfrac{\pi}{N}, \text{ for } [4n]\text{-annulenes} \end{cases} \tag{1}$$

Similarly, the total π-electron energy of the corresponding linear polyene is calculated from the expression:

$$E_\pi \text{ (polyene)} = 2 \cosec \dfrac{\pi}{2N+2} - 2 \tag{2}$$

In above expressions N is the number of carbon atoms in annulenes (1) or polyenes (2). The energies obtained from the expressions (1) and (2) are given in units of β.

Aromatic stabilization is then given as follows:

$$A_S = \begin{cases} 4 \cosec \dfrac{\pi}{N} \\ \text{or} \\ 4 \cotan \dfrac{\pi}{N} \end{cases} - 2 \cosec \dfrac{\pi}{2N+2} + 2 \tag{3}$$

The HMO energies of annulenes from [4] to [30] and that of the corresponding linear polyenes with the values of aromatic stabilization are summarized in the Table. Similarly, the REPE values of Hess and Schaad[19], the KK values of Krygowski[12], the resonance energies (E_R) calculated by Figeys[14] using the LCAO-BETA method[18], and by Dewar and Gleicher[13] using the SCF MO method[113,15] are also given in the Table. The Table is divided in two parts: the first part contains results for [4n]-annulenes, while the second part contains results for [4n + 2]-annulenes.

The geometries of the investigated annulenes are shown in Fig. 1. All annulenes are assumed to be planar. This assumption is not completely correct[20,21], because in some cases the repulsion between the annulene inner hydrogen atoms might be considerable. Therefore, the molecule, in order to avoid the effect of hydrogen interference, might distort from planar conformation. In fact, there is some experimental evidence[22-25] that up to [18]--annulene the nonplanarity of the molecules is significant, but not exceptionally great.

The plot of A_S as a function of the annulene ring size is shown in Fig. 2. We note that A_S as a function of the ring size divides the annulenes in two groups: aromatic [4n + 2] — and non-aromatic [4n]-annulenes. Our result is in agreement with earlier theoretical studies (REPE, KK, E_R)[12,14,19] and with the predictions obtained by considering NMR spectra of annulenes. The proton chemical shifts are sensitive to the magnetic properties of the π-electrons and therefore, NMR also differentiates between the [4n + 2]- and [4n]-annulenes[26].

Because our approach is very simple we cannot predict when the change of the aromaticity of the [4n+2]-annulenes should occur. Such a change should be the result of the bond alternation which appears in higher annulenes.[8] Dewar and Gleicher[13] predicted that the critical size of the annulene, at which

TABLE I

HMO Energies (E_π) of Annulenes and Corresponding Linear Polyenes

Indices of aromatic stabilization (A_S), REPE and KK values, and resonance energies (E_R) calculated by Figeys (LCAO-BETA method), and by Dewar and Gleicher (SCF MO method).

[N]-annulene		E_π (annulene) [β]	E_π (polyene) [β]	A_S [β]	REPE [β]	KK [β]	E_R (Figeys)[13] [kcal/mole]	E_R (Dewar and Gleicher)[12] [eV]
[4n]	[4]	4.000	4.472	—0.472	—0.2680	2.000	—24.34	—0.534
	[8]	9.657	9.518	0.139	—0.0609	2.669	—10.78	—0.108
	[12]	14.928	14.593	0.335	—0.0239	2.875	—6.58	0.131
	[16]	20.109	19.676	0.433	—0.0111	2.975	—4.47	0.043
	[20]	25.255	24.762	0.493	—0.0520	3.035	—3.11	—0.120
	[24]	30.383	29.852	0.531	—0.0020	3.075	—2.03	—0.305
	[28]	35.501	34.944	0.557	—0.00001	3.105	—1.33	—0.339
[4n + 2]	[6]	8.000	6.988	1.012	0.0653	3.528	10.01	1.318
	[10]	12.944	12.053	0.891	0.0264	3.426	6.30	1.061
	[14]	17.976	17.134	0.842	0.0161	3.383	4.89	0.689
	[18]	23.035	22.220	0.815	0.0118	3.359	4.26	0.382
	[22]	28.106	27.308	0.798	0.0096	3.344	3.86	0.229
	[26]	33.187	32.396	0.791	0.0090	3.335	3.76	—0.054
	[30]	38.267	37.486	0.781	0.0080	3.323	3.57	—0.263

the bond alternation occurs, is between [22]- and [26]-annulene (see Table I, last column.) They predicted [26]-annulene to be a non-aromatic molecule. There are some indications in the literature[26] that they may be correct in their prediction. For example, the NMR spectrum of tridehydro-[26]-annulene[27] indicated that this compound is non-aromatic. Apparently, the bond alter-
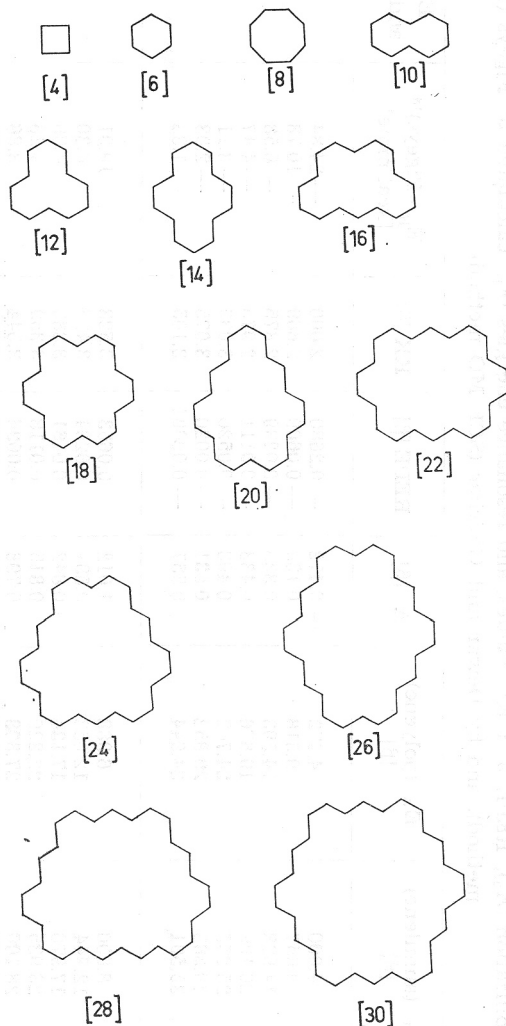

Fig. 1. Geometries of annulenes [4]—[30].

nation appearing in [26]-annulene quenches the ring current, and therefore, the NMR spectrum of tridehydro-[26]-annulene does not show discrete inner and outer proton resonances; its NMR spectrum consists of broad multiplets at τ 2.0 to 4.5. A typical aromatic annulene NMR spectrum would be that of [18]-annulene[28], taken at — 60° C with the band of the six inner protons at τ 12.99 and the band of the twelve outer protons at τ 0.72. The NMR results[26] support the theoretical results of Dewar and Gleicher[13], according
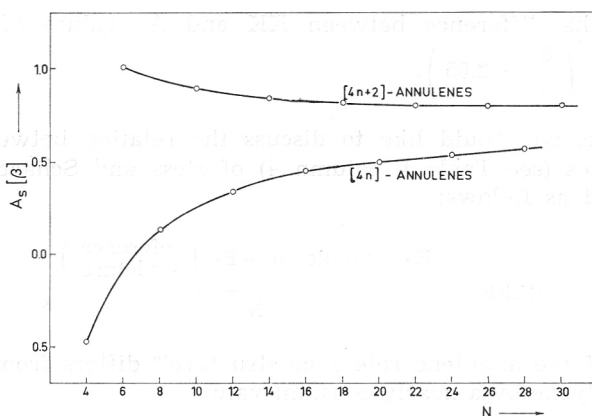
Fig. 2. Index of aromatic stabilization (A_s) *vs.* the annulene ring size.

to which the [4n + 2]-annulenes up to n = 5 are aromatic, while the [4n + 2]-annulenes with n > 5 are non-aromatic.

Finally, we would like to discuss an additional interesting point. Our results agree also well with the approach of Kruszewski and Krygowski[29]. They introduced the KK index as a measure of aromaticity of a particular conjugated molecule, and it was defined as the resistance of a conjugated molecule to addition reactions. The KK index can be calculated from the expression:

$$KK = E_\pi \left(\begin{array}{c} conjugated \\ molecule \end{array} \right) - E_\pi \text{ (product)} \qquad (4)$$

which is describing the π-energy change during the course of the addition reaction:

$$(5)$$

conjugated   product
molecule
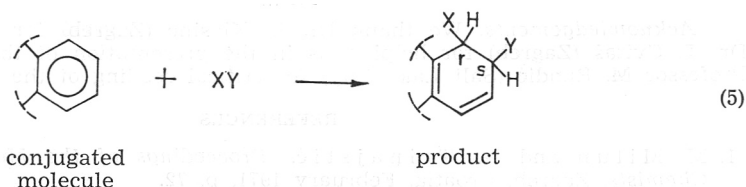
as a result of the formation of new bonds C-X and C-Y in the positions r and s.

E_π (product) is the π-energy of the most favourable product of addition. Proof that 1,2 addition product is the most favourable one in the annulene addition reactions will be reported elsewhere[30].

It is not surprising that our results are very close to those by Krygowski[12] (see Table I, column 5) obtained using the KK index[29], because the expression (4) written in a different form is very similar to our expression (3):

$$KK = \left\{ \begin{array}{c} 4 \cosec \dfrac{\pi}{N} \\[12pt] 4 \cotan \dfrac{\pi}{N} \end{array} \right\} - 2 \cosec \dfrac{\pi}{2N-2} + 2 \qquad (6)$$

Consequently, the difference between KK and A_S values of annulenes is nearly constant $\left(\dfrac{8}{\pi} \sim 2.55 \right)$.

To conclude, we would like to discuss the relation between A_S indices and REPE values (see Table I, column 4) of Hess and Schaad[19]. The REPE index is defined as follows:

$$REPE = \frac{E_\pi \text{ (annulene)} - E_\pi \left(\begin{array}{c} \text{reference} \\ \text{structure} \end{array} \right)}{N} \tag{7}$$

The π-energy of the annulene reference structure[19] differs from the π-energy of the linear polyene by a nearly constant value:

$$E_\pi \left(\begin{array}{c} \text{reference} \\ \text{structure} \end{array} \right) - E_\pi \text{ (polyene)} = 0.0052N - 0.73 \approx \text{Constant} \tag{8}$$

Combining eqs. (7) and (8) and utilizing the definition of A_S one obtains the following relation between A_S and REPE values:

$$A_S - n. \text{ REPE} \approx \text{Constant} \tag{9}$$

This expression can be simplified by using:

$$n. \text{ REPE} = RE \tag{10}$$

Thus, eq. (9) becomes:

$$A_S - RE \approx \text{Constant} \tag{11}$$

It can be easily shown that the constant in the above expressions is independent of the choise of bond energies in the reference structure.

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IZVOD

Aromatička stabilizacija anulena izračunata Hückelovom metodom molekularnih orbitala

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Anuleni su studirani pomoću indeksa aromatičke stabilizacije (A_S). Izveden je jednostavan izraz za numeričko računanje A_S-indeksa. A_S-indeks točno razlikuje [4n + 2]-anulene od [4n]-anulena. Analizirana je također metoda Kruszewskog i Krygowskog, i pokazano je da se njihov KK-indeks razlikuje od A_S-indeksa odgovarajućeg anulena samo za konstantnu vrijednost. Također je pokazano da se REPE-vrijednosti Hessa i Schaada razlikuju od A_S-indeksa promatranog anulena za gotovo konstantnu vrijednost.

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