A THEORETICAL SCHEME OF ANNULENES AROMATICITY

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An aromaticity scheme for annulenes is developed and applied on set of [6] to [18]annulenes. The dependence of annulenes aromaticity on the ring size, noncoplanarity and strain is considered which factors are in the aromaticity indices $\mathrm{HOMA_W}$ and $\mathrm{HOMA_M}$ implicitely included. The decrease in aromaticity index with increasing ring size was modelled for [4*n* + 2] and [4*n*] annulenes by the functions $A_{4n+2}(N)$ and $A_{4n}(N)$. Two quantities, $\varkappa_d$ and ν_s, as the average measures of noncoplanarity and strain have been defined. Significant correlations of the differences $A_x(N) - \mathrm{HOMA_W}$ and $A_x(N) - \mathrm{HOMA_M}$, which represent the decrease in aromaticity index by noncoplanarity and strain, with a function of the parameters $\varkappa_d$ and ν_s, have been obtained. The quantitative results show that not only the [4*n*]annulenes, but also the large part of the [4*n* + 2]annulenes are antiaromatic, even for the presence of noncoplanarity and strain in the molecules.

Annulenes have become a convenient subject of theoretical investigation, in the last decade, in connection with the development of various theories of aromaticity. A part of these theories is based on the Dewar concept of resonance energy[1] (DRE) and the treatments are mostly carried out in π-electron approximation on the level of the HMO and graph theoretical methods. It appears that to obtain a satisfactory agreement of the calculated and observed data, realistic structures are to be examined[2,3]. Namely, it is suggested that steric hindrance, occuring in all structures of [10] to [16] and partly in [18] annulenes causing the coplanarity perturbation and strain in electronic structure may appreciably influence the electronic distribution (delocaoization), lower the resonance energy of the species and thereby change also their other properties.

For this reason, we undertook an extensive study of realistic structures of annulenes[4,5] of various geometric forms, treated to date in some way in literature.* We characterized aromaticity of the species by calculating the DRE values. However, these values calculated by the all valence semiempirical methods are large negative numbers and do not give a good picture of annulenes aromaticity. Therefore, we selected the Kruszewski and Krygowski[6] $\mathrm{HOMA_d}$ index and reformulated it in order

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* At the finish of our work the *ab initio* calculations of [10] annulenes have been published by Farnell L., Radom L., Schaefer H. F.: J. Amer. Chem. Soc. *103*, 2147 (1981) and Haddon R. C.: J. Amer. Chem. Soc. *104*, 3516 (1982).

to be more sensitive to structural changes. Then we tried hard to find a relation, at least empirical, expressing the dependence of aromaticity on noncoplanarity and strain of these structure.

CALCULATION AND DISCUSSION

Aromaticity Characteristics

We selected 36 annulenes structures which we divided into 5 groups for the purpose of this study (Table I). Due to a large extent of calculations of big molecules we selected for the MOLCAO calculations the two simplest semiempirical methods with the oppositely different principles of approximation, *i.e.* the CNDO/2 and EHT methods with the standard parametriation[7]. We used the optimized geometries of the species published in our previous papers[4,5,8], In these papers some structures of [10] and all structures of [12] annulenes have been fully optimized by the variable metric method[9,10]. Since the optimal bond lengths cannot be calculated by the EHT method we used the CNDO/2 optimal geometries as the unified ones also in the EHT calculations.

In order to derive the atomaticity index, we recall briefly the basic ideas for the definition of the HOMA index. According to the harmonic oscillator theory[11] the energy change of a molecule caused by extension and compression of bonds from their optimal positions is interpreted as the energy of the harmonic oscillators distored from these positions. This idea, further elaborated using appropriate physical quantities, led to the definition $\text{HOMA}_d = 1 - a/N \sum(r_i - r_0)^2$, r_0, r_i being the benzene and annulene bond lengths, respectively, and N the total number of CC bonds. The constant a is determined from the condition $\text{HOMA}_d = 1$ for benzene and $\text{HOMA}_d = 0$ for the Kekulè benzene structure. We transformed the given expression in the following manner. We introduce for the bond lengths the correlation expression $r_i = a_1 + a_2 B_i$, where B_i is a quantum chemical bond index of the i-th bond. Then $r_i - r_0 = a_2(B_i - B^0)$. We use in the HOMA expression two adjustable constants, namely a, b for the single and double bonds, respectively, which corresponds to two required conditions concerning the value of the HOMA index for benzene and its Kekulè structure. Hence, the respective expression is

$$\text{HOMA}_X = 1 - 1/N\left[a \sum_{kl}(B^0 - B_{kl})^2 + b \sum_{mn}(B^0 - B_{mn})^2\right], \qquad (1)$$

where B_{kl} and B_{mn} are bond indices of the single and double bonds between atoms k, l and m, n respectively. When the bond index is the Wiberg index[12] equation (*1*) is HOMA_W, when B is the Mulliken bond overlap population, denoted θ, equation (*1*) is HOMA_M. The constants a, b for HOMA_W and HOMA_M are 2·6569, 6·5645,

TABLE I

Annulenes noncoplanarity and strain characteristics

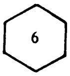
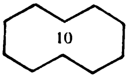
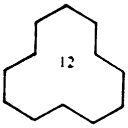
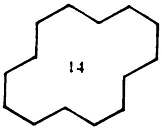
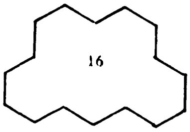
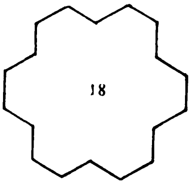
Group	No	Annulene	Symmetry	$\varkappa_d \cdot 10^2$	$\nu_s \cdot 10$
A	*I*		D_{6h}	0	0
	II		C_2	2·36	4·160
	III[a]		C_s	7·68	3·271
	IV		C_2	2·88	1·121
	V[a]		C_s	1·69	0·942
	VI		D_{3h}	0	0·394
B	*VII*	[8]	D_{4h}	0	0·803
	VIII[b]	[10]	D_{5h}	0	2·483
	IX	[12]	D_{6h}	0	4·113
	X	[14]	D_{7h}	0	5·675
	XI	[16]	D_{8h}	0	7·003
	XII	[18]	D_{9h}	0	8·090
C	*XIII*	[8]	C_{2v}	7·14	0·205
	XIV	[12]	C_{3v}	10·74	0·312
	XV	[16]	C_{4v}	8·38	0·324

TABLE I
(*Continued*)

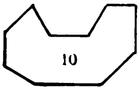
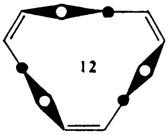
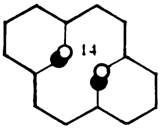
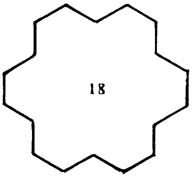
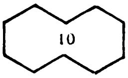
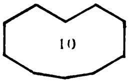
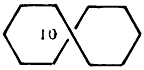
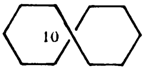
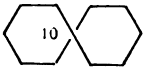
Group	No.	Annulene	Symmetry	$\varkappa_d . 10^2$	$\nu_s . 10$
D	*XVI*		C_s	7·14	0·998
	XVII		D_3	10·33	0·161
	XVIII[c]		C_s	3·83	0·628
	XV	[16]	C_{4v}	8·38	0·324
	XIX		D_{6h}	0	0·406
E	*XX*		C_2	5·95	1·763
	XXI		C_s	0	2·676
	XXII[d]		C_2	4·95	1·338
	XXIII[d]		C_2	7·77	0·834
	XXIV[d]		C_2	11·64	6·081

TABLE I
(*Continued*)

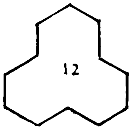
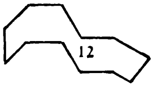
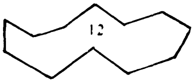
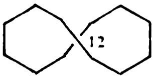
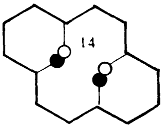
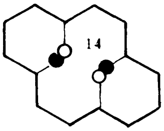
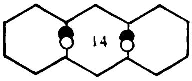
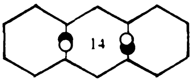
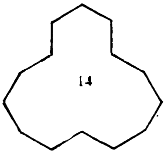
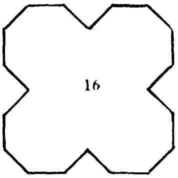
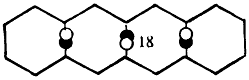
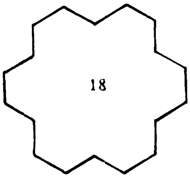
Group	No.	Annulene	Symmetry	$\varkappa_d \cdot 10^2$	$\nu_s \cdot 10$
	XXV		Symmetryless	4·71	0·586
	XXVI		C_s	10·25	0·939
	XXVII		C_2	6·61	0·328
	XXVIII		D_{2d}	4·70	1·350
	XXIX		C_s	1·73	0·883
	XXX[e]		C_2	5·23	0·737
	XXXI[e]		C_2	2·26	3·126
	XXXII[e]		C_2	3·95	7·083
	XXXIII[a]		C_2	0·85	1·143

TABLE I
(*Continued*)

Group	No.	Annulene	Symmetry	$\varkappa_d \,.\, 10^2$	$\upsilon_s \,.\, 10$
	XXXIV		D_{2h}	0	0·754
	XXXV		C_2	6·33	5·385
	XXXVI[e]		C_3	0·12	1·077

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[a] The bond length differences are not taken into account. [b] There is only a very small difference in the bond lengths. [c] The carbon perimeter is not partially planar. [d] About the structural differences see in[4]. [e] Experimental geometry.

26·0308, 6·3448, respectively. The values of the Wiberg index and of the bond overlap population for benzene are $W^0 = 1{\cdot}4470$, $\theta^0 = 1{\cdot}0713$.

$HOMA_X$ indices defined in this manner are much more sensitive to structural changes than the $HOMA_d$ index and especially noncoplanarity and strain are very sensitively reflected in their values.

Into group A belong the species the carbon skeleton of which has shape resembling the perimeter of the benzenoid aromatic hydrocarbons. Due to the repulsion of the inner hydrogen and carbon atoms, the carbon skeleton is distorted and the inner atoms are deviated above and under the plane which is determined by the outer carbon atoms. All these structures may be considered either as totally distorted, *i.e.* also outer carbon atoms are deviated from the plane, or they may be only partially distorted so that the outer carbon atoms lie in the plane. We considered both models in our calculations assuming the latter to be more favourable, due to a better delocalization. However, this is only valid for [10] and [18] annulenes. The more favourable structures of [12] and [14] annulenes are totally distorted due to a more advantageous arrangement of inner hydrogen atoms, connected with the lower repulsion energy value. In order to compare the quantities of the species, we selected for group A the isomers of all species with the planar arrangement of the outer carbon atoms and with respect to the arrangement of the inner atoms always the more stable isomers according to the heat of formation (ΔH_f). Group B is represented by annulenes the carbon skeleton of which has the form of a polygon with optimized bond lenghts which are not equal. Such a form of [10] annulenes has been found and proved by NMR spectroscopy[13], the calculation have also shown[5,8] the relatively good stability of this isomer. Therefore, we calculated such forms also for higher annulenes. However, the stability of the rings decreases rapidly with the number of atoms[5]. The species with the molecular shape of a crown[5] constitute a special group of annulenes (C). They differ from the others by the strainless valence angles in the carbon skeleton and also the hydrogen atoms have a very favourable mutual position which is seen from the small values of v_s (Table I). Since the rings are only of the type [4*n*] the aromaticity indices are low values, increasing with the increasing ring size from [12] to [16]. The species which are most stable according to the ΔH_f value in each set of molecules of the particular ring size are arranged into group D. All the other annulenes of various egometric forms which may not be arranged according to a common structural regularity belong to group E. For the sake of the unambiguous definition of the geometric isomers, we also introduce in Table I the symmetries of the species. In several cases in order to distinguish the similar geometric isomers, we do not take into account the bond length differences, *i.e.* we consider the higher symmetry.

In groups A, B and D both indices $HOMA_W$ and $HOMA_M$ sensitively distinguish between annulenes that obey the Hückel rule and those that do not. That is, Figs 1 – 3 show the characteristic zig-zag shape between [4*n* + 2] and [4*n*] annulenes.

Figs 1 to 3 reveal the aromaticity of [4*n* + 2] annulenes to be lower than expected. This may be explained for most species by the presence of appreciable non-coplanarity and strain, (Table I). However, there are some anomalies. Comparing geometric isomers *IV* and *XXIX* of [14] annulene it is seen that although the former has greater non-coplanarity and strain the latter possesses a much larger value of $HOMA_W$. We conclude that this may be an artifact of the CNDO/2 method, remembering the failure of this method in the determination of conformations of conjugated system[14-16]. The same ratio of the $HOMA_M$ indices of the species *IV* and *XXIX* is obtained. It is also seen that [16]annulenes *V* and *XI* have excessively high $HOMA_W$ index. Anomalies among the other species will be clearly seen only in the frame of a correlation in the whole set of the molecules given below (Table II).

Concerning the problem of aromaticity of [18]annulene, often treated in literature, it is seen (Fig. 1) that $HOMA_W$ of the D_{3h} isomer, with the natural tendency to the bond alternation[17,18], is near the boundary for aromaticity and antiaromaticity, which agrees with several statements appearing in papers. However, the D_{6h} isomer, which is only by 66·6 kJ mol^{-1} higher in energy (CNDO/2), has highly matched bonds and cosequently a high value of the HOMA$_W$ index 0·985. The HOMA$_W$ for the crystal structure[19,20] geometry is also high 0·978. Therefore, the D_{6h} isomer would be highly aromatic. However, the matching of bonds in this isomer would be connected with the spending and not with the release of energy.

This may be explained by assuming that the D_{6h} structure may exist only in the crystal state, and by solving in a solvent, is converted into the energy lower D_{3h} isomer. Otherwise the datum on the opposite stability ratio between the D_{3h} and D_{6h} isomers, given in[21], must be accepted as the more probable than the other data[22].

TABLE II

Data on correlations $A_x(N)$ — HOMA$_X$ *vs* $h_1(\varkappa_d, \nu_s)$

Annulenes	Index	Coefficients of the polynomial $h_1(\varkappa_d, \nu_s)$							
		a_{22}	a_{21}	a_{11}	a_{20}	a_{01}	a_{00}	r	s
[4n + 2]	HOMA$_W$	−26·903	−2·356	0·036	9·076	−0·058	0·007	0·921	0·104
	HOMA$_M$	31·904	−3·201	−0·126	5·626	−0·086	−0·016	0·933	0·118
[4n]	MOMA$_W$	11·325	−0·234	−0·456	0·603	0·159	−0·037	0·931	0·046
	HOMA$_M$	14·576	−0·667	−0·628	1·348	0·046	−0·053	0·941	0·062

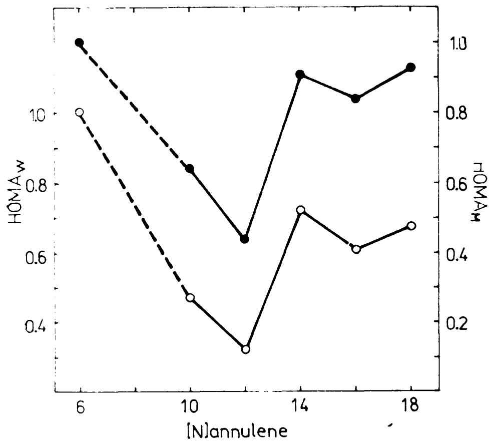

FIG. 1

Plot of the HOMA$_W$ (○) and HOMA$_M$ (●) indices *vs* the ring size, group A

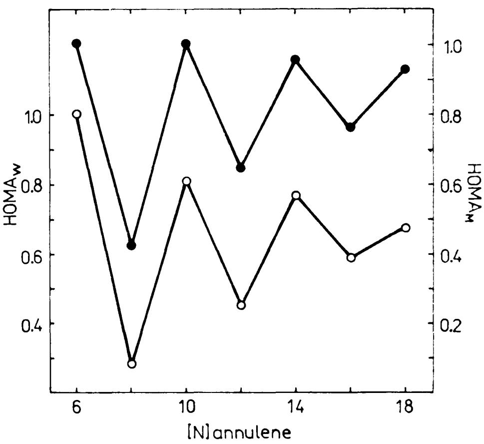

FIG. 2

Plot of the HOMA$_W$ (○) and HOMA$_M$ (●) indices *vs* the ring size, group B

The corresponding values of $HOMA_W$ and $HOMA_M$ are not identical. This may be understood because with the CNDO/2 best geometries in the EHT calculations the species appear to be more delocalized than they actually are. The $HOMA_M$ may be used in the *ab initio* calculations and we assume that the correct values of the $HOMA_M$ will be quantitatively compatible with the $HOMA_W$ values.

In diagram Fig. 2 belonging to the polygons which are planar and with regularly increasing strain, the aromaticity indices show the behaviour similar to that of the Dewar type resonance energies, *i.e.* that of the [4*n* + 2]annulenes decrease and that of the [4*n*]annulenes increase monotonically, approaching one another into a common limit. Estimating the accuracy of $HOMA_W$ ±0·1, this boundary is equal to the values 0·5 ± 0·1 Following this, we shall consider the annulenes with the index lower than 0·5 as antiaromatic and those, with the index higher than 0·5, as aromatic. It is seen (Figs 1 to 5) that not only all [4*n*] but also many [4*n* + 2]annulenes are antiaromatic.

Dependence of Aromaticity on Non-coplanarity and Strain

Let RE_a and RE_b be the Dewar resonance energy of an annulene and of benzene, respectively. It is sure that $RE_a < RE_b$ is always valid. Therefore, the difference $RE_b - RE_a$ is generally a nonzero value. It is assumed that this difference is a function of the ring size, non-coplanarity and strain of the respective annulene. We shall characterize aromaticity by resonance energy as Haddon[23,24].

With respect to the definition of the HOMA index[11] for any annulene $HOMA_X \leq 1$, whereby the equality sign is valid only for benzene. Assuming linear proportionality

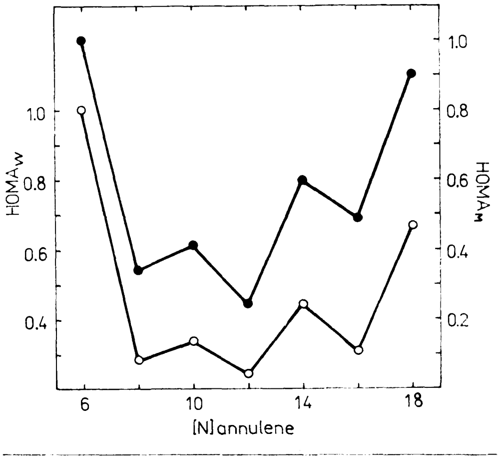

FIG. 3

Plot of the $HOMA_W$ (○) and $HOMA_M$ (●) indices *vs* the ring size, group D between $\mathrm{HOMA_X}$ and resonance energy it may be written $\mathrm{HOMA_X} = RE'_a/RE'_b$, where the dashed RE's mean the classical resonance energies, related to the energy of the Kekulè reference structure. Since only the upper half of the $\mathrm{HOMA_X}$ index interval characterizes aromaticity an appropriate linear transformation of this equation leads to

$$\mathrm{HOMA_X} = 1/2(1 + RE_a/RE_b)\,. \tag{2}$$

Due to relation (2) the index $\mathrm{HOMA_X}$ is also a function of the ring size, non-coplanarity and strain. For these function we make the folowing Ansatz

$$h[\Lambda(N), \varkappa, \nu] = \Lambda_x(N) - h_1(\varkappa, \nu) = \tag{3}$$

$$= \Lambda_x(N) - (a_{22}\varkappa^2 + a_{21}\varkappa\nu + a_{11}\nu^2 + a_{20}\varkappa + a_{01}\nu + a_{00})\,. \tag{4}$$

For $\Lambda_x(N)$ we set our empirical relations

$$\Lambda_{4n+2}(N) = \exp - \alpha[(N-6)/N]^{4/3}\,, \tag{5}$$
$$\Lambda_{4n}(N) = \exp \alpha'[(N-6)/N]^{1/4} - 1\,,$$

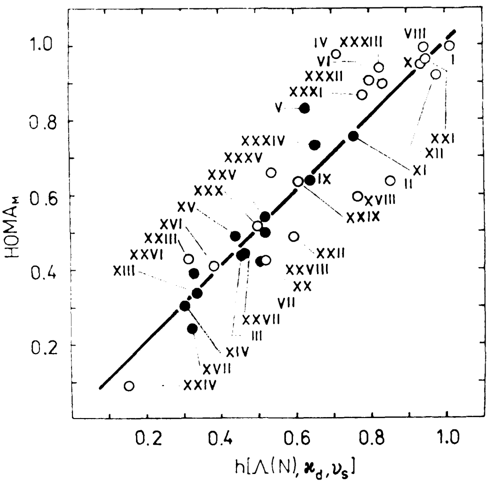

FIG. 4

Correlation of the $\mathrm{HOMA_W}$ indices of the whole set of molecules with the function $h[\Lambda(\mathrm{N}), \varkappa_d, \nu_s]$ ○ [4n + 2] annulenes, ● [4n] annulenes

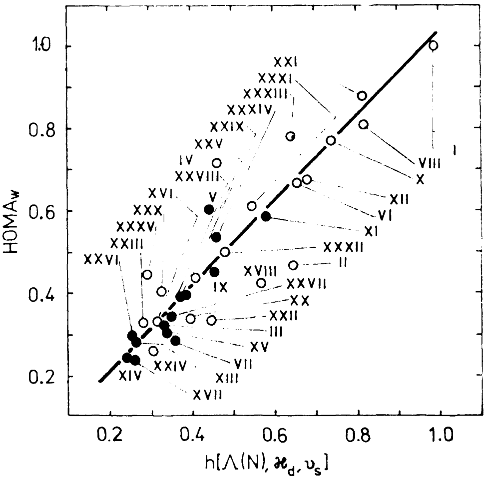

FIG. 5

Correlation of the $\mathrm{HOMA_M}$ indices of the whole set of molecules with the function $h[\Lambda(N)), \varkappa_d, \nu_s]$ ○ [4n + 2] annulenes, ● [4n] annulenes where α, α' are the normalization constants which ensure the common limit.

For $\varkappa$ we set

$$\varkappa_t = 1/2[1/N_s \sum_s (1 - \cos \alpha_s) + 1/N_d \sum_d (1 - \cos \alpha_d)] , \tag{6}$$

where α_s and α_d are the torsional angles about the single and the double bonds, respectively, and N_s and N_d are the respective numbers of single and double bonds. The summation runs over all bonds.

For ν we set

$$\nu_s = \nu'_s - \nu'_{s,b} ; \quad \nu'_s = (U_t/2N)/RE_b , \tag{7}$$

where U_t is the total strain including van der Waals interactions, valences angles deformations and torsion angles energies. $\nu'_{sb} = 0{\cdot}256$ is the benzehe value.

The functions (5) model the decrease and increase in HOMA_W of [4n + 2] and [4n] planar polygon type annulenes (group B) with increasing ring size N. Probably the strain in these molecules has no influence on aromaticity which arises from the comparison of HOMA_W of [18] annulenes of D_{3h} and D_{9h} symmetries. Both isomers have nearly the same HOMA_W although the former is almost strainless and the latter mostly strained. Therefore the quadratic polynomial for these molecules in Eq. (4) is nought.

Plotting HOMA_W of [4n + 2] annulenes of group B against the value $1/N$ and extrapolating this dependence for $1/N = 0$, we get exactly 0·5. Therefore, the function $\Lambda_{4n+2}(N)$ approximates well the respective HOMA_W dependence. However, plotting HOMA_W of [4n] annulenes of group B against $1/N$ and extrapolating $1/N = 0$, we get a larger value than 0·5. This is the consequence of excessively high HOMA_W of [16] and [12]annulenes, exaggerated by the CNDO/2 method. Therefore, we selected the function $\Lambda_{4n}(N)$ in order to approximate well the HOMA_W values of [8] and [12]annulenes in the accuracy limits ±0·05 and limiting the values 0·5 which is reasonable. The values of α, α' are $-\ln (1/2) = 0{\cdot}693$, $\ln (3/2) = 0{\cdot}405$, respectively. Obviously, the similar plottings of HOMA_M give a value different from 0·5. However, this value (0·7) is considered as quantitatively incorrect. The appropriate α, α' values are $-\ln (7/10) = 0{\cdot}357$ and $\ln (17/10) = 0{\cdot}531$, respectively.

The second part of Eq. (4) represents the decrease in the aromaticity index HOMA_X by noncoplanarity and strain, their average quantitative measures being $\varkappa$ and ν, respectively. Since the function (4) is dimensionless $\varkappa$ and ν have been selected as dimensionless quantities, too.

Since the torsional angles in distorted molecules may be indefinite, we transform the expression (6) in the folloving manner:

First let us consider three neigbouring bonds formed by carbon atoms numbered i, j, k, l with arbitrary bond lengths and arbitrary valence angles. Let the torsional angle about the central bond be α_t. Then the following expression holds

$$\sin \alpha_t = \Delta(i, j, k, l)/\Delta_{\max} \tag{8}$$

$$\Delta(i, j, k, l) = \begin{vmatrix} x_i - x_l, & y_i - y_l, & z_i - z_l \\ x_j - x_l, & y_j - y_l, & z_j - z_l \\ x_k - x_l, & y_k - y_l, & z_k - z_l \end{vmatrix}, \tag{9}$$

where $x_i, y_i, z_i, \ldots x_l, y_l, z_l$ are the Cartesian coordinates of the carbon atoms and $\Delta_{\max}$ is the value of the determinant (9) at the torsional angle $\alpha = 90°$. Now $\varkappa$ may be rewritten substituting (8) into (6).

$$\varkappa_d = 1 - 1/N \sum_{i,j,k,l} \{1 - [\Delta_{(i,j,k,l)}/\Delta_{\max}]^2\}^{1/2}, \tag{10}$$

where N is the total number of carbon atoms and the summation runs over all trinity bonds which are obtained by cyclic replacement of the indices i, j, k, l. Evidently the total number of all bond trinities is N. We denoted the new expression $\varkappa_d$, although in an undistorted molecule $\varkappa_t = \varkappa_d$ is exactly. However, in molecules deformed by steric hindrance, or in the bridged annulenes, where the determination of the torsional angles may be impossible, $\varkappa_t$ may not be evaluted, but $\varkappa_d$ may also be calculated in these cases. This quantity is generally the average quantitative measure of non-coplanarity of a cyclic molecule with a conjugated double bond system (non-coplanarity index)* and it is larger the larger the non-coplanarity of the respective system (with unity as the maximal value). It is convenient to use the 10^2 multiple of $\varkappa_d$ in qualitative non-coplanarity characterizations.

There are two kinds of non-coplanarity of a molecule. The first kind is the natural non-coplanarity given by structure, and it is not connected with strain. The second kind is enforced by steric hidrance, or by bridging and it is connected with strain. The first kind occurs at several structures of [4*n*] annulenes and the second kind is predominant at [4*n* + 2]annulenes. Nevertheless, these two kinds are not distinguished in our treatment.

There is not a simple relation between the elements of Δ and $\Delta_{\max}$ in a general position of the bond trinity in a Cartesian coordinate system and the calculation of $\Delta_{\max}$ is difficult. Therefore, in a routine use it is necessary for each bond trinity to transform the coordinate system in such a manner that three atoms which form the two neighbouring bonds are put into the xy plane and one random atom, say i^{th},

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* This quantity has a more general sense. It may be an average measure of spacity (spacity index) of an arbitrary flexible or rigid organic molecule, if α_t are the torsional angles about the single bonds.

is placed into the origin of the new coordinate system.The central bond is oriented parallel to the x axis. Then the determinant (*9*) may be expressed in the new coordinate system (ξ, η, ϑ) in the following form

$$\Delta = a \sin \alpha_t \begin{vmatrix} 1, & \xi_j \\ 1, & \xi_k \end{vmatrix} \qquad (11)$$

with

$$a = \eta_j[(\eta_l - \eta_k)^2 + \vartheta_l^2]^{1/2}$$

from which the simple relation between Δ and Δ_{max} is evident.

The evaluation of Δ_{max} may also be carried out by approximate ways. For example, a preliminary tabulation of Δ_{max} for different bond length trinities is made, in an appropriate interval of the bond length changes, and the values are stored. Then the value of Δ_{max} appropriate to the respective bond length trinity is used for the calculation of Δ/Δ_{max}. If the programs necessary to the described procedures are not available a fixed value of Δ_{max} may be used, namely this one corresponding to the trinity of the equal bond lengths 0·1400 nm. This is connected only with a small error because the values of Δ_{max} change only slightly (in our molecules about 5%, related to the average bond length). In our calculations, we used the former approximative procedure.

The quantity v_s means the average quantitative measure of strain of an annulene (strain index) related to the benzene value. We calculated the total strain U_t in (*7*) by the empirical method of Dashevski[25]. For RE_b we used the experimental[26,27] value 88·7 kJ mol^{-1}. It is convenient to use 10 multiple of v_s in qualitative strain characterizations.

The statistical characteristics of the correlations $\Lambda_x(N)$ – HOMA$_W$ and $\Lambda_x(N)$ – – HOMA$_M$ *vs* $h_l(\varkappa_d, v_s)$ are in the Table II.* The significance of the total correlations for [4*n* + 2] annulenes is 99·5% and for [4*n*] annulenes 97·5% (HOMA$_W$), 99·0% (HOMA$_M$). The comparison of the most significant terms in $h_l(\varkappa_d, v_s)$ shows that in [4*n* + 2]annulenes non-coplanarity is much more significant than strain, for both HOMA$_W$ and HOMA$_M$. In [4*n*]annulenes there is nearly an equal significance of these factors for HOMA$_W$, however, for HOMA$_M$ non-coplanarity is more significant than strain. The correlations HOMA$_W$ and HOMA$_M$ *vs* $h[\Lambda_x(N), \varkappa_d, v_s]$ (Figs 4 and 5) have the values of r and s 0·931, 0·071 (HOMA$_W$), and 0·935, 0·083 (HOMA$_M$), respectively. The significance is 99·5% for both. It may be stated, that significant influence of non-coplanarity and strain on annulenes aromaticity has been sufficiently proved.

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* The structures of [18] annulenes of the symmetries D_{6h} and C_3 (*XXIX*, *XXXVI*) were not include into the correlation because the definitions for their Λ(N) values are not known.

From the correlations mostly deviated structures are *II*, *IV*, *V*, *XVIII*, *XXII*, *XXXIII*, and *XXXV* in Fig. 4 and *II*, *IV*, *V* and *XXIX* in Fig. 5.

There are three factors which make the correlations worse. Namely *i*) the not quite optimal geometries of the structures which were not fully optimize, *ii*) the not quite correct or failed description of delocalization by the CNDO/2 method,* and *iii*) the quadratic polynomial $h_1(\varkappa_d, \nu_s)$ may be regarded as a truncated Taylor (or Mac Laurin) expansion of a function of two variables. Since it is not sure whether the cut-off of the series may be carried out after the second order terms the negleted rest of the series may deteriorate the correlations.

The Relation between the HOMA$_X$ *Indices and the Topological Resonance Energies*

There are excellent correlations of the resonance energies of annulenes [6] to [30] by Aihara[28], which are almost identical with the corresponding values from Haddon's "unified theory"[23], with the respective values of the functions $\Lambda_x(N)$. Similar correlations may be constructed with the other resonance energy indices[29–32].** It is seen that in spite of increasing strain in molecules, resonance energy may be computed using the same parameters in the HMO method and by the graph theoretical methods.

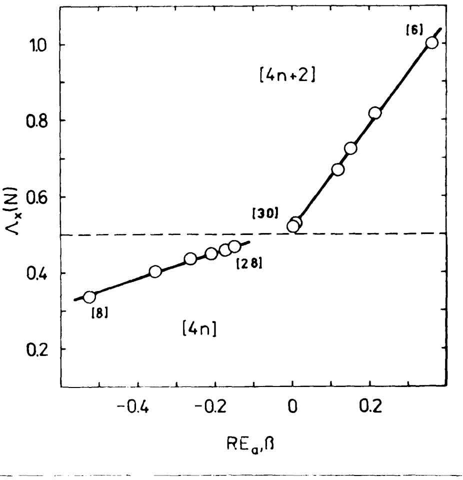

FIG. 6

Plot of the $\Lambda_{4n+2}(N)$ and $\Lambda_{4n}(N)$ functions *vs* the HMO resonance energies (Aihara[28])

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* Obviously these factors also caused that several differences Λ(N) — HOMA$_X$ are small negative numbers due to the inaccuracies of the HOMA$_X$ values; in three cases this value is rather large, about −0·1 and −0·15 (the structures of [16] annulene *V*, *XI* and *XXXIV*).

** These correlations have significant values of statistical characteristics but they are not of the same quality as that in Fig. 6.

This indicates that coplanarity of a molecule is the necessary and sufficient condition for the independence of resonance energy of a molecule on strain.

Following the expression (2) for $\mathrm{HOMA_X} = 1$ $RE_a = RE_b$ and for $\mathrm{HOMA_X} = 0{\cdot}5$ $RE_a = 0$, (the boundaries for aromaticity). It is assumed that (2) is also valid for all noncoplanar [4*n* + 2] annulenes even when they are antiaromatic, with $\mathrm{HOMA_X}$ lower than 0·5. Then DRE may be calculated simply as $(2\,\mathrm{HOMA_X} - 1)$ RE_b. This makes possible also to calculate at *ab initio* level the DRE value. For RE_b the experimental[26,27] or one correctly calculated value may be used.* However, the expression (2) may not be used for [4*n*]annulenes, as it is evident in Fig. 6. Following (2) the lower boundary for the antiaromatic DRE ($\mathrm{HOMA_X} = 0$) is $- RE_b$, *i.e.* the value for the antiaromatic structure of benzene (Kekulè structure). However, the antiaromatic DRE of [4*n*]annulenes changes much steeper with the change of $\mathrm{HOMA_X}$ and the boundary is much lower. The correct values of DRE of [4*n*] annulenes may be calculated using the expression

$$\mathrm{HOMA_X} = 1/2(1 + \eta RE_a/RE_b)\,, \qquad (12)$$

where η from the correlation in Fig. 6 is 1/4.

It is assumed that the Haddon's relation between resonance energy and the reduced ring currents of [4*n* + 2]annulenes[23] will also be valid for noncoplanar geometric isomers, if RE_a calculated from the respective $\mathrm{HOMA_X}$ index is used.

REFERENCES

1. Dewar M. J. S., de Llano C.: J. Amer. Chem. Soc. *91*, 789 (1969).
2. Vogler H.: J. Mol. Struct. *51*, 289 (1979).
3. Allinger N. L., Sprague J. T.: J. Amer. Chem. Soc.: *95*, 3893 (1973).
4. Loos D., Leška J.: This Journal *45*, 187 (1980).
5. Loos D., Leška J.: This Journal *47*, 1705 (1982).
6. Kruszewski J., Krygowski T. M.: Tetrahedron Lett. *1970*, 319.
7. QCPE programs No 137, 141.
8. Leška J., Loos D.: J. Mol. Struct. *21*, 245 (1974).
9. McIver, jr J. W., Komornicki A.: Chem. Phys. Lett. *10*, 303 (1971).
10. Pancíř J.: This Journal *40*, 2726 (1975).
11. Kruszewski J., Krygowski T. M.: Tetrahedron Lett. *1972*, 3839.
12. Wiberg K. B.: Tetrahedron Lett. *1968*, 1083.
13. Masamune S., Hojo K., Hojo Kiyomi, Bigam C., Rabenstein D. L.: J. Amer. Chem. Soc. *93*, 4966 (1971).
14. Davidson R. B., Jorgensen W. L., Allen L. C.: J. Amer. Chem. Soc. *92*, 749 (1970).
15. Perahia D., Pullman A.: Chem. Phys. Lett. *19*, 73 (1973).
16. Sierio C., Gonzales-Diaz P., Smeyers Y. G.: J. Mol. Struct. *24*, 345 (1975).

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* The more appropriate value of benzene DRE in our paper would be 77·0 kJ $\mathrm{mol^{-1}}$ given by Haddon[33] (one half of the classical value 150·6 kJ $\mathrm{mol^{-1}}$).

17. Longuet-Higgins H. C., Salem L : Proc. Roy. Soc. London *A251*, 172 (1959); *A257*, 445 (1960).
18. Buss V.: Chem. Phys. Lett. *22*, 191 (1973).
19. Bregman J., Hirschfeld F. L., Rabinovich D., Schmidt G. M. J.: Acta Crystalogr. *19*, 227 (1965).
20. Hirschfeld F. L., Rabinovich D.: Acta Crystallogr. *19*, 235 (1965).
21. Bauman H.: J. Amer. Chem. Soc. *100*, 7196 (1978).
22. Haddon R. C.: Chem. Phys. Lett. *70*, 210 (1980).
23. Haddon R. C.: J. Amer. Chem. Soc. *101*, 1722 (1979).
24. Haddon R. C., Fukunaga T.: Tetrahedron Lett. *1980*, 1191.
25. Dashevski V. G., Naumov V. A., Zaripov N. M.: Zh. Struct. Chim. *11*, 746 (1970).
26. George P., Trachtman M., Bock C. W., Brett A. M.: Theor. Chim. Acta *38*, 121 (1975).
27. George P., Trachtman M., Bock C. W., Brett A. M.: Tetrahedron *32*, 1357 (1976).
28. Aihara J. I.: Bull. Chem. Sod. Jap. *48*, 517 (1975).
29. Hess B. A., Schaad L. J.: J. Amer. Chem. Soc. *93*, 305, 2413 (1971).
30. Gutman I., Milun M., Trinajstić N.: Croat. Chem. Acta *44*, 207 (1972).
31. Figeys H. P.: Tetrahedron *26*, 4615, 5225 (1970).
32. Dewar M. J. S., Gleicher G. J.: J. Amer. Soc. *87*, 685 (1965).
33. Haddon R. C.: Tetrahedron *28*, 3613, 3635 (1972).

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