THEORETICAL STUDY OF [10] AND [12]ANNULENES

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Equilibrium geometries of various geometrical isomers of annulenes have been calculated by the quantum-chemical methods EHT, CNDO/2, MINDO/2, MINDO/3 and the method of empirical potentials. Automatic method of full optimization has been used for some [10]annulenes and all isomers of [12]annulene. The bond strengths and degree of delocalization have been determined from the bond overlap populations and the Wiberg indices. Relative stabilities of the isomers have been determined by comparison of the formation enthalpies calculated by MINDO/3, MINDO/2 and empirical potentials methods. Strain energy has been calculated, and degree of aromaticity of the isomers has been characterized by several aromaticity indices.

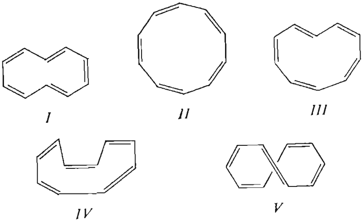
There exists a great number of theoretical papers on annulenes studying geometry and mainly stability of these cyclic polyenes with respect to properties of their conjugated bond system. The equilibrium geometry was studied by the method of Coulson and Senent[1–5] which also gave information about energy of valence angle deformation and non-bonding interactions. Calculation of atomization energies of cycloalkenes was carried out by the method of empirical potentials by Dashevskii[6]. The quantum-chemical MOLCAO methods of higher level were used relatively little. The *ab initio* calculations were realized for [4] and [8]annulenes[7,8]. The methods MINDO/2 and MINDO/3 were used by Dewar[9,10] and coworkers for [8] and [18]annulenes. We used the methods EHT, CNDO/2 and MINDO/2 for [10]annulenes[11]. There exist calculations based on combination of the methods of empirical potentials or molecular mechanics with the quantum-chemical methods in π-approximation[12–14]. A considerable number of papers are based on the simple HMO method, and the values thus obtained are used for construction of various indices characterizing stability of rings with various numbers of conjugated π-bonds. All these methods suffer from the insufficiency that they do not take into account real structure of the annulenes characterized by sterical strain and non-bonding interactions especially in the lower members. From the above brief survey of theoretical approaches to the problem of annulene structure it follows that the real structures need to be studied by uniform methods as MOLCAO. As annulenes are rather big molecules for *ab initio*" calculations, the semiempirical *all valence* methods seem to belong to the proper ones. However, reliability of the semiempirical methods is limited. Therefore, we used several methods, *viz.* EHT, CNDO/2, MINDO/2, MINDO/3 with standard parametrization and, in some cases, also the method of full optimization of geometry[15]. For our models we also used the method of empirical potentials by Dashevskii[6]. The quantum-chemical quantities were then used for calculation of various indices characterizing stability and degree of aromaticity[16–18].

CALCULATIONS AND DISCUSSION

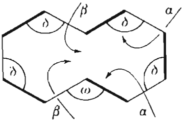
[10]*Annulene*

This part of the communication represents a continuation of our former study of [10]annulene[11]. Here we study the same isomers (Scheme 1), but the treatment is deeper and uses a greater number of methods. In the mentioned ref.[11] we considered all bonds to be equal with the length 0·1400 nm. In the present paper the bonds were varied and, in some cases, the geometry was fully optimized and compared with the result of the model approach. Besides that, stability was evaluated with the use of a greater number of criteria. Standard programs QCPE (64, 137, 141, 178, 279) were used.

SCHEME 1



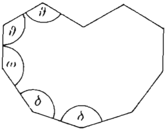
SCHEME 2



Two models were considered for the isomer *I*. The model *Ia* (Scheme 2) has spatial form resulting from rotation about single bonds by the angles α and β. Simultaneously the valence angles δ and ω are deformed, too. For a given angle α the angles β, δ and ω are also defined, if the ring is to be closed. The optimum values of these angles were found from the energy minimum. The individual methods give the following values for the angles α, β, δ and ω (in degrees): EMP 36, 58, 117·6, 122·4; EHT 38, 61, 117·5, 122·5; CNDO/2 36, 58, 117·6, 122·4; MINDO/2 38, 60, 117·8, 122·2; MINDO/3 38, 60, 117·8, 122·2. Obviously all the methods give almost identical torsion angles and equal bond angles. Variation of bond lengths does not change the bond angles. The optimum bond lengths C—C and C=C (in nm) are: MINDO/2 0·1452, 0·1358; MINDO/3 0·1450, 0·1358, respectively. Alternation of single and double bonds is also confirmed by overlap populations (0·920 to 0·959, 1·133 to 1·175) and by the Wiberg indices (CNDO/2 1·109 to 1·169, 1·761 to 1·785; MINDO/3 0·994 to 0·998, 1·830 to 1·851).

The isomer *Ib* is partially plane. The outside carbon atoms of perimeter lie in the plane, the inside ones are deviated by the angle α. Valence angles of the sp^2 hybridized carbon atoms are considered not to be deformed. For the deviation angle the following values (in degrees) were obtained by the individual methods: EMP 59, EHT 53, CNDO/2 35, MINDO/2 59 and MINDO/3 62. Except for CNDO/2 the values are close to each other. The overlap populations 0·926 to 1·000, 1·115 to 1·136 and the Wiberg indices (CNDO/2 1·153 to 1·271, 1·601 to 1·708; MINDO/3 1·005 to 1·049, 1·792 to 1·835) indicate bond alternation. The bond lengths C—C and C=C (in nm) calculated for the optimum α angle by the individual methods are: MINDO/2 0·1469, 0·1331; MINDO/3 0·1457, 0·1343, respectively. Again the both methods give identical results.

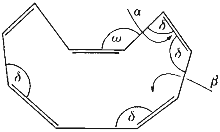
The isomer *II* is a regular decagon with valence angles 144°. Obviously it is very much strained, which is indicated by high value of deformation energy of valence angles (385·4 kJ/mol). As it is plane with high symmetry (D_{10h}) and its π-electron number fulfils the Hückel rule, full delocalization can be expected. It is confirmed by equal values of overlap populations (EHT 1·014) and the Wiberg indices (1·434) calculated by CNDO/2 method. But the Wiberg indices obtained by the more precise MINDO/3 method predict the bond alternation (1·667 to 1·114) with the bond lengths C—C and C=C (in nm) 0·1427 and 0·1373, according to MINDO/2 0·1437 and 0·1363, respectively. This indicates that the MINDO/3 parametrization is not suitable for extremely strained systems.



SCHEME 3

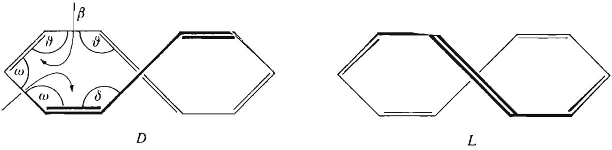
The isomer *III* (Scheme 3) is also plane with one double bond in *trans* arrangement. The model was formed in purely geometrical way, the two halves of the molecule having the shape of the isomers *I* and *II*, respectively. With this presumption it must be $\vartheta = 116·7°$, $\delta = 147·3°$, $\omega = 144·0°$. The overlap populations (1·005 to 1·070) and the Wiberg indices (CNDO/2 1·415 to 1·444) indicate a considerable degree of delocalization which is, however, smaller than with the isomer *II*. The Wiberg indices calculated by the MINDO/3 method do not indicate delocalization. The bond lengths C—C and C=C (in nm) according to individual methods are: MINDO/2 0·1454, 0·1346; MINDO/3 0·1445, 0·1355, respectively.

The isomer *IV* has a boat form (Scheme 4) with all the double bonds in cis arrangement. The bond angles are strongly distorted. From the geometrical conditions of the least deviations of the angles from 120° and of the closed ring the following values were found: $\delta = 132{\cdot}5°$, $\omega = 107{\cdot}5°$, $\alpha = 97°$, $\beta = 72°$. The overlap populations (0·899 to 0·900, 1·136 to 1·171) and the Wiberg indices (CNDO/2 1·028 to 1·177, 1·765 to 1·818, MINDO/3 0·985 to 1·011, 1·844 to 1·875) indicate considerable alternation of bonds. The bond lengths C—C and C=C (in nm) are: MINDO/2 0·1455 and 0·1345, MINDO/3 0·1446 and 0·1334, respectively. Full optimization according to McIver and Komornicki[15] gives for them the values* 0·1462, 0·1373.. Obviously all the methods give identical values corresponding to the bonds of the polyene.



SCHEME 4

The isomer *V* is propeller-shaped („chelene" could be suitable name for it), hence it is chiral and can exist in dextrorotatory (D) or laevorotatory (L) forms in mechanical sense (Scheme 5). Its geometry is determined unambiguously by a pair out of the valence angles δ, ϑ and ω and by the condition of coplanarity[11] for the three bonds C—C=C—C. The three geometrical forms *Va–c* have the following angles α, β, δ, ϑ, ω (in degrees): *Va* 51, 32, 149, 120, 120; *Vb* 50, 33, 128, 112, 128; *Vc* 55, 71, 93, 93, 147. The overlap populations (*Va* 0·930 to 0·934, 1·144 to 1·189; *Vb* 0·892 to 0·934, 1·144 to 1·183; *Vc* 0·742 to 0·923, 1·149 to 1·173) and the Wiberg indices CNDO/2 *Va* 1·123 to 1·147, 1·768 to 1·785; *Vb* 1·116 to 1·144, 1·734 to 1·807; *Vc* 1·025 to 1·131, 1·503 to 1·785) indicate considerable bond alternation in all the three structures. The



SCHEME 5

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* The bond lengths are average values, the maximum deviation being ±0·0009 nm.

Wiberg indices obtained by the MINDO/3 method indicate a still more marked bond alternation. The bond lengths C—C and C=C (in nm) according to MINDO/2 and MINDO/3 methods have the following values: *Va* 0·1452, 0·1348, 0·1452, 0·1348; *Vb* 0·1455, 0·1345, 0·1454, 0·1346; *Vc* 0·1438, 0·1362, 0·1437, 0·1363. It is seen that the isomers *Va* and *Vb* have almost identical bond lengths. Somewhat different are the bond lengths of the *Vc* isomer indicating greater delocalization.

Degree of aromaticity was determined from several indices known as DRE (Dewar resonance energy[16]), A (the Julg factor[17]), $\mathrm{HOMA_d}$ (the Kruszewski and Krygowski factor[18]). The index $\mathrm{HOMA_p}$ (Krygowski and Kruszewski[18]) was modified for the *all valence* methods by the relation

$$\mathrm{HOMA_W} = 1 - 1/n\left(a \sum_{kl} (\mathrm{W}^0 - \mathrm{W}_{kl})^2 + b \sum_{mn} (\mathrm{W}^{\circ} - \mathrm{W}_{mn})^2\right)$$

where W^0 is the Wiberg bond index in benzene, and the constants a, b were determined from the conditions that $\mathrm{HOMA_W}$ should equal to unity for benzene and zero for isolated single and double bonds (ethane, ethene). In the CNDO/2 method $\mathrm{W}^0 = 1{\cdot}447$, $a = 2{\cdot}6569$, $b = 6{\cdot}5645$ and in the MINDO/3 method $\mathrm{W}^0 = 1{\cdot}397$, $a = 2{\cdot}8963$, $b = 6{\cdot}1238$. W_{kl} and W_{mn} are the Wiberg indices for single and double bonds, respectively, n is total number of C—C bonds. From the values of the indices A, $\mathrm{HOMA_d}$ and $\mathrm{HOMA_W}$ it is seen that only the isomers *II* and *III* could have aromatic properties, but according to DRE they are not stable. From the diagram of the indices $\mathrm{HOMA_d}$ and $\mathrm{HOMA_W}$ (Fig. 1) it is obvious that they both give the same aromaticity order of the isomers except for *Ia* and *Ib*. However, all the values of the $\mathrm{HOMA_W}$ index give a substantially lower aromaticity than those of $\mathrm{HOMA_d}$.

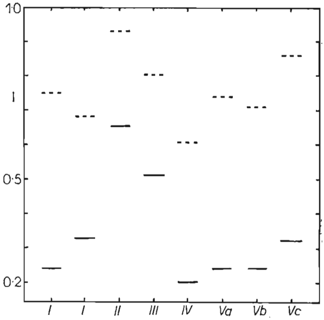


FIG. 1

Diagram of Aromaticity Indexes of [10]Annulenes MINDO/3: $\mathrm{HOMA_W}$ ———, $\mathrm{HOMA_d}$ – – –

Generally, the index $HOMA_w$ calculated by the CNDO/2 method is somewhat higher than the corresponding MINDO/3 values. Its MINDO/3 values are generally lower than the values of the $HOMA_d$ index. The Julg factor A has its values near those of $HOMA_d$. The index DRE has in general high negative values (*e.g.* MINDO/3 $-55{\cdot}7$ to $-1\,245{\cdot}7$), which indicates slight stability of all isomers.

The formation enthalpy, which is an absolute measure of stability, was calculated by the methods MINDO/2, MINDO/3 and empirical potentials (Table I). According to Dewar[19,20] inaccuracy of the MINDO/3 formation enthalpies depends on molecular strain, and it can reach about 120 kJ/mol for little strained systems. Therefore, such inaccuracy can be anticipated with the enthalpies calculated by us, too. Obviously, this inaccuracy is also responsible for different stability order according to the enthalpies calculated by different methods. The values obtained by MINDO/2 seem to be more reliable, which is indicated by the fact that MINDO/3 presents the isomer *II* as most stable, the latter having, however, strongly distorted bond angles and, hence, a high strain energy decreasing its stability. Again this fact indicates that the MINDO/3 method is not suitable for study of strongly strained molecules. The method of empirical potentials presents *Vb* as the most stable isomer which is, however, strongly strained, too. On the contrary, the MINDO/2 method ascribes the highest stability to the isomer *IV* which is the most stable also according to the presumptions of Masamune[21]. In our previous study[11] where the bonds were not varied the isomer *IV* turned out to be the most stable. Difference in the formation enthalpy value 62·03 kJ/mol corresponds to the distorsion energy. In spite of the isomer *IV* being presented as the most stable it contains two strongly weakened bonds as far as the overlap population (0·899) is considered a bond strength criterion. Only the least stable isomers *Vb* and *Vc* contain pairs of even weaker bonds.

TABLE I

Enthalpies of Formation of [10]Annulene

Geometrical isomer	ΔH_f, KJ mol^{-1}		
	EMP	MINDO/2	MINDO/3
Ia	585·7	508·8	676·0
Ib	787·6	448·8	587·1
II	746·7	509·1	341·4
III	797·3	534·1	522·1
IV	509·7	384·1	461·9
Va	522·9	465·8	618·0
Vb	431·6	435·7	613·3
Vc	1 478·9	983·0	1 531·4

Table II gives energies of the van der Waals interactions, valence angles deformations and total strain (involving also energies of rotations about the bonds). The isomers having the highest strain energy are *II* and *Vc*, both have high deformation of valence angles.

From the above considerations of the enthalpies according to various methods and strain in the isomers it is concluded that the isomer *IV* is to be considered the most stable.

[12]*Annulene*

[12]Annulene belongs to the most interesting compounds containing 4n π-electrons. Its high instability prevents experimental study of the isomers, and, therefore, quantum-chemical methods and other theoretical methods are valuable in this case. [12]Annulene can be prepared[22-24] and is stable at extremely low temperatures only. Its structure could be studied by NMR spectra[25] only at such low temperatures as −80 to −170°C. NMR spectrum of the prepared annulene indicates the structure *VI* (Scheme 6) with very rapid interchange of hydrogen atoms between periphery and interior of the molecule. This process has very low activation energy[25] due to repulsion between overlapping internal hydrogen atoms. The repulsion also determines out-of-flatness of the molecule.

Scheme 6 presents seven geometrical isomers of [12]annulene, out of which the structures *VI*, *VIII* and *XI* were described in literature. Furthermore, models of *VII*, *IX* and *X* can be constructed from molecular models. We took into account also the fully flat cyclic structure *XII*, analogous to the similar structure of [10]annulene

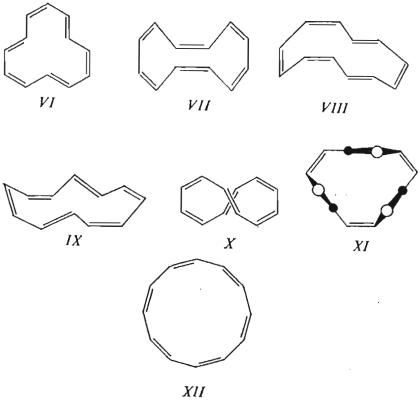
TABLE II

Values[a] of Non-Bonding Interactions (U_{VW}), Deformation Energies of Valence Angles (U_{angle}) and Strain Energies (U_{strain}) of [10]Annulene

Geometrical isomer	U_{VW}	U_{angle}	U_{strain}
Ia	629·2	16·8	737·8
Ib	556·4	53·2	935·0
II	508·8	385·4	894·2
III	691·6	230·4	947·1
IV	521·2	116·8	657·2
Va	534·6	116·6	671·9
Vb	517·5	44·9	576·4
Vc	1 185·6	435·6	1 625·5

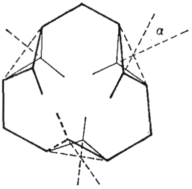
[a] The values are given in KJ mol^{-1}.

which exhibits relatively good stability in spite of great deformation of valence angles. The structures *VI–IX* have spatial arrangement, the structures *VII* and *XI* are strainless and can be easily constructed from molecular models. The other rings suffer from considerable strain. Two models were considered for the structure *VI*.



SCHEME 6

In one of them *VIa* plain arrangement was considered for the external carbon atoms of perimeter, the other *VIb* having spatial arrangement of all the carbon atoms. Deviation of the internal carbon atoms out of the plane is determined by the angle α (Scheme 7). The individual methods gave the following values of α: EMP 46°, EHT 48°, CNDO/2 67°, MINDO/2 58°, MINDO/3 52°. These values agree well with the estimate 50–60° based on experiment. The bond overlap populations (0·969, 1·120 to 1·129) and the Wiberg indices (CNDO/2 1·130 to 1·153, 1·768 to 1·778; MINDO/3

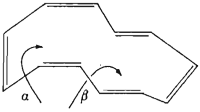


SCHEME 7

1·011 to 1·019, 1·823 to 1·830) indicate considerable bond alternation. Good agreement is encountered with the bond lengths values (in nm) obtained by the method MINDO/2 ($R_{C-C} = 0{\cdot}1466$, $R_{C=C} = 0{\cdot}1334$) and MINDO/3 ($R_{C-C} = 0{\cdot}1459$, $R_{C=C} = 0{\cdot}1341$).

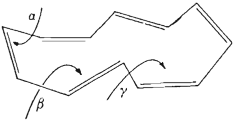
Spatial distorsion of the second model *VIb* results in deformation of its valence angles. The individual methods EMP, EHT, CNDO/2, CNDO/2 with full optimization, MINDO/2, MINDO/3 gave the following values (in degrees) of the torsion angle about single bond: 65, 64, 56, 62, 67, 75, respectively. The valence bond deformation in the ring ranges within 1·5 to 3°. The bond lengths R_{C-C} and $R_{C=C}$ (in nm) are: CNDO/2 0·1436, 0·1338, MINDO/2 0·1457, 0·1343, MINDO/3 0·1455, 0·1345. These values agree well with the VE SCF calculation[14] giving $\alpha = 54°$, valence angle deformations 2·7° and bond lengths 1·1487 and 0·1357 nm. The overlap populations (0·919, to 0·941, 1·164 to 1·165) and the Wiberg indices (CNDO/2 1·081 to 1·092, 1·853 to 1·866, MINDO/3 0·994 to 0·996, 1·875 to 1·888) give evidence for alternation of bonds.

The geometrical isomer *VII* can be constructed from the Dreiding models in such a way that in the open-chain polyene with all-*trans* double bond arrangement the end carbon atoms are connected with single bond. Two values of overlap populations (0·906 and 1·183) and two values of the Wiberg indices (CNDO/2) 1·062 and 1·892; MINDO/3 0·994 and 1·877) indicate two types of bonds with high alternation. The calculated bond lengths C—C and C=C (in nm): CNDO/2 0·1442, 0·1332; MINDO/2 0·1458, 0·1342; MINDO/3 0·1455, 0·1345. The bond lengths obtained by all three methods stand in good agreement.



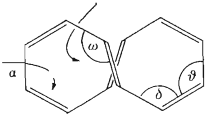
SCHEME 8

The isomer *VIII* is considered[22] to be in dynamical equilibrium with *VI*; the former was optimized by varying the torsion angles α and β (Scheme 8). Two optimum forms were found by all the methods: one of them *VIIIa* has smaller β angle and the other *VIIIb* a greater one. Bond alternation is indicated, too. The torsion angles α, β (in degrees) obtained by the individual methods are for *VIIIa*: EMP 85, 32; EHT 85, 31; CNDO/2 90, 18; MINDO/2 85, 32; MINDO/3 85, 32. For *VIIIb*: EMP 86, 202; EHT 88, 207; CNDO/2 93, 224; MINDO/2 90, 215; MINDO/3 89, 210. The bond lengths (in nm) of C—C and C=C are: *VIIIa* MINDO/2 0·1455, 0·1345; MINDO/3 0·1452, 0·1348; *VIIIb* has equal bond lengths, the difference for MINDO/3 being 0·0001 nm. Full optimization (CNDO/2) gave for the isomer *VIIIa* the torsion angles 87°, 36°, bond lengths 0·1446, 0·1331 nm. The overlap populations and the Wiberg indices change within the intervals: EHT 0·901 to 1·187, CNDO/2 1·036 to 1·889, MINDO/3 0·985 to 1·882.



SCHEME 9

In the isomer *IX* there are three different torsion angles α, β, γ (Scheme 9). For a fixed angle α the angles β and γ are unambiguously determined, if the symmetry is to be maintained. Therefore, only the angle α was varied. The angles α, β, ω corresponding to equilibrium geometry are for the individual methods as follows (in degrees): EMP 127, 60, 137; EHT 134, 59, 130; CNDO/2 113, 58, 152; MINDO/2 126, 60, 138; MINDO/3 132, 58, 133. Full optimization by the method CNDO/2 gave the values 123, 57, 137. Obviously the methods EMP, EHT, MINDO/2 and MINDO/3 give identical results with small deviations. The method CNDO/2 gives close values only in the case of full optimization. The overlap populations (0·929 to 0·941, 1·160 to 1·169) and the Wiberg indices (CNDO/2 1·077 to 1·089, 1·853 to 1·861) indicate bond alternation. The calculated bond lengths (in nm): CNDO/2 0·1438, 0·1335; MINDO/2 0·1453, 0·1347; MINDO/3 0·1448, 0·1352. Agreement between the individual methods is very good (max. deviation 0·0017 nm).



SCHEME 10

The isomer *X* can be constructed from molecular models and has a helix structure. It shows two torsion angles α, β (Scheme 10). For the coplanarity of the neighbourhood of double bonds to be maintained the valence angles ω, δ and ϑ must be deformed. It is interesting that the methods EMP, EHT, CNDO/2 and MINDO/2 do not find the energy minimum. However, the method MINDO/3 and CNDO/2 with full optimization give the energy minimum for this form. The Wiberg indices indicate bond alternation (CNDO/2 1·091 to 1·125, 1·821 to 1·854; MINDO/3 1·003 to 1·017, 1·816 to 1·858). For the optimum angles α, β, ω, δ, ϑ CNDO/2gives the values (in degrees): 39, 59, 129·9, 132·6, 131·5; for the bond lengths C—C and C=C (in nm): 0·1430, 0·1333. The MINDO/3 method gives for the angles in the same order the following values (in degrees): 35, 60, 131·6, 131·6, 131·6, and for the bond lengths 0·1452 and 0·1348 nm. Again a good agreement is seen between the values of the both methods CNDO/2 and MINDO/3.

The isomer *XI* has explicitly spatial arrangement without strain, the torsion angles about single bonds being 83·3°. Hence the isomer shows bond alternation which is seen from the bond overlap populations (0·888 to 0·891, 1·188 to 1·194) and the Wiberg indices (CNDO/2 1·062 to 1·064, 1·900 to 1·903; MINDO/3 0·991 to 0·992, 1·883 to 1·885). The C—C and C=C bond lengths (in nm): CNDO/2 0·1441, 0·1331; MINDO/2 0·1461, 0·1339; MINDO/3 0·1452, 0·1348. Here also difference between the values of different methods is very small. The bond lengths obtained by full optimization are approximately average values of those from CNDO/2 and MINDO/3. The valence angles are 123·6°.

The isomer *XII* was taken into account, even though its valence angles are very deformed (150°C); in case of [10]annulene such structure was proved by NMR spectrum, and calculation showed a relatively good stability. This fact was explained by perfect resonance and full delocalization in the system[11]. In the isomer *XII* considerable bond alternation is encountered, which is proved by two values of the overlap populations (1·065 and 0·896) and those of the Wiberg indices of CNDO/2 with full optimization (1·117 and 1·826) and of MINDO/3 (1·013 and 1·804). This result is obviously due to the [12]annulene not fulfilling the Hückel rule. The bond lengths (in nm): CNDO/2 0·1434, 0·1336; MINDO/2 0·1455, 0·1345 and MINDO/3 0·1432, 0·1348.

The enthalpy of formation calculated by the methods EMP, MINDO/2 and MINDO/3 (Table III) give order of relative stability as well as an idea about their absolute stability.

TABLE III

Values of Enthalpies of Formation (ΔH_f) of Geometrical Isomers of [12]Annulene

Geometrical isomer	ΔH_f, KJ mol^{-1}		
	EMP	MINDO/2	MINDO/3
VIa	789·6	525·4	610·1
VIb	501·7	473·4	566·9
VII	415·6	395·6	553·9
VIIIa	588·0	570·4	882·4
VIIIb	457·7	499·1	741·2
IX	413·2	455·3	636·6
X	—	—	707·6
XI	380·3	393·0	530·1
XII	1 255·7	821·4	574·6

All the three methods present *XI* and *IX* as the most stable. According to EMP the third by stability is *VII*, whereas according to MINDO/3 it is *VIb*. Result of the two first methods seems to be more reliable, as the three most stable isomers predicted by them have the lowest value of strain energy (Table IV). MINDO/3 presents *VIb* as more stable than *VII*, although *VIb* shows an excessively greater total strain energy. From experimental results[22,25] and calculations by Allinger[14] it follows that the geometrical isomer *VI* is the most stable. The geometrical isomer *XI*, which was obtained as relatively the most stable by three methods, can easily be derived from the geometrical isomer *VI* by increasing rotation angle about all single bonds by less than 20°. This rotation provides a structure with very small value of deformation energy of valence angles (Table IV). The rotation angle is not quite 90°, but it has the value 83° for which a structure can be constructed without any internal strain. Therefore, in the methods MINDO/2 and MINDO/3 (where the electronic energy contribution to overall energy is relatively lower than that in CNDO/2) decrease of repulsion energy had a greater influence on overall energy of the molecule. The structures *VII* and *IX* represent also relatively stable geometrical isomers and were constructed from the Dreiding models. The both isomers are characterized by low values of deformation energy of valence angles. Values of non-bonding interactions are lowest for the geometrical isomers *XI*, *VII* and *IX*. A very high value of strain energy is observed in the isomer *XII* which represents a regular dodecagon. Substantial part of this energy is due to deformation energy of valence angles. The geometrical isomer *VIII* is presumed in the work by Oth and coworkers[22] to be an intermediate product in preparation of [12]annulene. The authors suppose it to be less stable than the geometrical isomer *VI*.

TABLE IV

Values (in KJ mol^{-1}) of Non-Bonding Interactions (U_{VW}), Deformation Energies of Valence Angles (U_{angle}) and Strain Energies (U_{strain}) of Geometrical Isomers of [12]Annulene

Geometrical isomer	U_{VW}	U_{angle}	U_{strain}
VIa	602·9	27·0	966·6
VIb	579·8	38·9	674·3
VII	525·5	—	595·3
VIIIa	714·0	18·1	761·2
VIIIb	577·5	21·6	626·8
IX	540·5	2·6	589·1
XI	514·4	5·4	553·4
XII	710·0	722·7	1 432·7

This presumption was confirmed by all the methods used by us. The values of enthalpy of formation calculated by the MINDO/3 method are higher than those obtained from EMP or MINDO/2. Only the isomer *XII* represents an exception.

Aromatic properties of [12]annulene are characterized by the indices of aromaticity. The diagram in Fig. 2 gives only the indices $\mathrm{HOMA_b}$ and $\mathrm{HOMA_W}$ again. The Julg factor has the values close to $\mathrm{HOMA_d}$. Here also the index DRE has high negative values, which gives evidence for low stability of all the isomers. But the interval within which its values are found is much smaller (−187·2, −539·4).

Comparison of the diagrams in Figs 1 and 2 shows a striking difference of the intervals within which values of the indices are found. In case of [10]annulene the indices $\mathrm{HOMA_d}$ and $\mathrm{HOMA_W}$ change within the intervals about 0·3 and 0·45, respectively. For [12]annulene the corresponding intervals are about 0·1 and 0·2. Furthermore the both indices generally have lower values with [12]annulene, which can be explained on the basis of the Hückel rule of aromaticity. As the [10]annulene fulfils the rule, whereas the [12]annulene does not, it can be expected that in the former case aromaticity will be considerably affected by geometrical shape of the molecule (which determines the degree of delocalization) and by strain (which compensates the delocalization energy). The $\mathrm{HOMA_W}$ index calculated by the CNDO/2 method has, for all the isomers of [12]annulene, the values close to the corresponding values obtained from MINDO/3, which is different situation from that of [10]annulene.

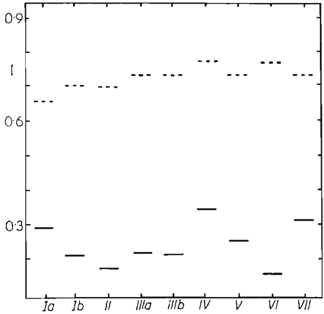


FIG. 2

Diagram of Aromaticity Indexes of [12]Annulenes MINDO/3: $\mathrm{HOMA_W}$ ———, $\mathrm{HOMA_d}$ — — —

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