

## THEORETICAL STUDY OF ANNULENES STRUCTURE [14], [16] AND [18] ANNULENES

Dušan LOOS and Jaroslav LEŠKA

*Chemical Institute,*

*Department of Organic Chemistry, CH-2, 842 15 Bratislava*

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The quantum-chemical methods EHT, CNDO/2, MINDO/2 and the method of empirical potentials have been used for calculation of equilibrium geometry of six isomers of [14] annulene, four isomers of [16], and three isomers of [18] annulenes. The bond strengths and degree of delocalization are characterized by the overlap populations and the Wiberg indices. Relative stabilities have been determined by comparison of enthalpies of formation calculated by the MINDO/2 and empirical potential methods. Influence of internal strain of the molecules on their stability lowering is discussed. The degree of aromaticity has been determined by calculation of several aromaticity indexes.

The first communication<sup>1</sup> of this series dealt with equilibrium geometry, stability, internal strain, and aromaticity of geometrical isomers of [10] and [12] annulenes. An analogous study has been carried out for [14], [16] and [18] annulenes which constitute the second part in the range of annulene rings having considerable distortions from natural structure. Importance of studies of real, three-dimensional annulene structures is also indicated by the calculations of chemical shifts in [14] and [18] annulenes<sup>2</sup> which show an agreement between the calculated and measured values only when non-plane and nearly plane geometries were used for [14] and [18] annulenes, respectively. This communication presents results of our study.

We chose the same methods except for MINDO/3 which, according to some results of our previous work, seems to be less convenient for studies of strained molecules; serious objections were also raised against application of the MINDO methods to studies of annulenes in ref.<sup>3</sup>. Therefore, the calculation of the aromaticity indexes  $HOMA_w$  was based on the Wiberg indices calculated by the CNDO/2 method. These indices are systematically (with few exceptions) higher by about 0.1 than those calculated by the MINDO/3 method. For comparison of the aromaticity indices in the whole set of [10] to [18] annulenes we also give, in conclusion of this communication, the  $HOMA_w$  indexes of [10] and [12] annulenes calculated by the CNDO/2 method.

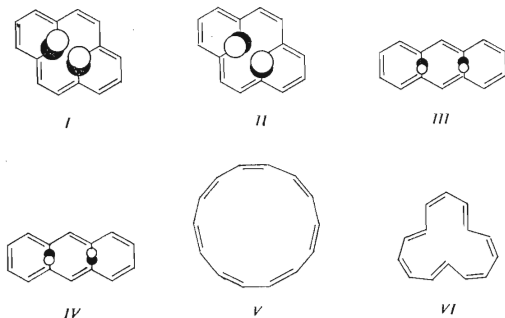
The geometrical parameters, *i.e.* valence, torsion, and deviation angles, were optimized as in ref.<sup>1</sup>. The bond lengths were optimized\* by the CNDO/2 method

\* The communication<sup>1</sup> does not give the bond optimization method.

in such a way that, starting from equal lengths 0.1400 nm, single bonds were uniformly lengthened and double bonds shortened, and the optimum bonds were then found by parabolic interpolation. Only in some cases the bonds were also optimized by the MINDO/2 method for comparison.

### CALCULATION AND DISCUSSION

[14] *Annulene*. This ring fulfils the Hückel aromaticity rule. In spite of that it is relatively stable at low temperatures only. From crystallographic studies<sup>4</sup>, NMR spectra<sup>5,6</sup>, and electronic absorption spectra it follows that in [14] annulene the shape of perimeter resembles that of pyrene, two structures being possible with different arrangement of the internal carbon atoms (Scheme 1). Sondheimer presumed also a structure with three internal hydrogen atoms (VI). Our theoretical approach also takes into account the structures III, IV, and V.

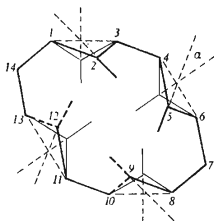


SCHEME 1

Two models were considered for the structures *I* to *IV*. In analogy to [10] and [12] annulenes<sup>1</sup> the model A presumes plane arrangement of outer carbon atoms of the perimeter, the inner carbons being deviated above and below the plane by the angle  $\alpha$ . The second model (B) presumes a space arrangement caused by repulsion interaction of the inner atoms and realized by torsion around the single bonds by the angles  $\alpha$ . Simultaneously some other valence angles are deformed, too (denoted as  $\delta$  and  $\omega$  in Schemes).

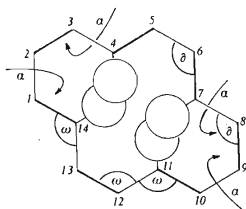
The values 33, 40, 29, and 42° of the deviation angle  $\alpha$  (Scheme 2) in structure *Ia* (model A) follow from the energy minima obtained by the methods EMP, EHT,

CNDO/2, and MINDO/2, respectively. The values of overlap populations (0.894 to 0.916 and 1.213 to 1.227) and Wiberg indices (1.101 to 1.109 and 1.802 to 1.828) indicate regular bond alternation. The bond lengths C—C and C=C are 0.1466 and 0.1334 nm, respectively.



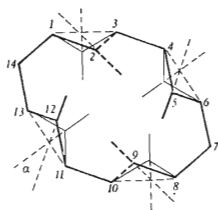
SCHEME 2

The values (in degrees) of the torsion angle  $\alpha$  in *Ib* isomer (model B) and valence angles  $\delta$  and  $\omega$  (Scheme 3) from the individual methods are following: EMP 46, 118.5, 121.5; EHT 46, 118.5, 121.5; CNDO/2 36, 119.2, 120.8; MINDO/2 51, 117.9, 122.1. The overlap populations (0.902 to 0.924; 1.206 to 1.218) and Wiberg indices (1.095 to 1.110; 1.804 to 1.834) indicate bond alternation. The bond lengths C—C and C=C are 0.1447 and 0.1353 nm (CNDO/2) and 0.1455 and 0.1345 nm (MINDO/2), respectively.



SCHEME 3

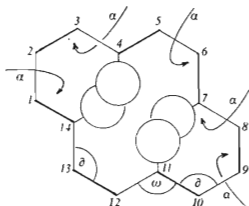
For the isomer *Ila* (model A) the angle  $\alpha$  (in degrees) obtained from the individual methods with the optimum geometry (Scheme 4) is: EMP 29, EHT 38, CNDO/2 28, MINDO/2 55. The overlap populations (0.936 to 1.011 and 1.086 to 1.144) and Wiberg indexes (1.200 to 1.243 and 1.623 to 1.648) indicate an only smaller bond alternation



SCHEME 4

and, hence, partial delocalization. The bond lengths C—C and C=C are 0.1419 and 0.1381 nm, respectively.

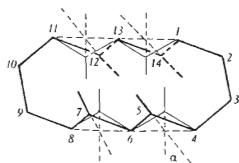
The isomer *IIb* (model B) has the torsion angle  $\alpha$  and the valence angles  $\delta$  and  $\omega$  (Scheme 5) in the optimum geometry (in degrees): EMP 44, 118.6, 121.4; EHT 44, 118.7, 121.3; CNDO/2 34, 119.4, 120.6; MINDO/2 45, 118.5, 121.5. The calculation results obtained by the different methods show a good agreement. Only the CNDO/2



SCHEME 5

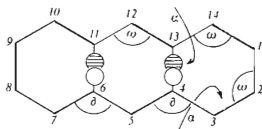
method gives the torsion angle smaller by  $10^\circ$ . The overlap populations (0.885 to 0.905; 1.227 to 1.241) and Wiberg indices (1.075 to 1.110; 1.804 to 1.836) show obviously a bond alternation. The bond lengths C—C and C=C are 0.1456 and 0.1344 nm, respectively.

In the isomer *IIIa* (model A) the values (in degrees) of the deviation angle  $\alpha$  (Scheme 6) in the optimum structure are: EMP 56, EHT 67, CNDO/2 41, MINDO/2 69. The overlap populations (1.071, 1.078) and Wiberg indices (1.337, 1.451) indicate partial delocalization in the bonds C<sub>5</sub>—C<sub>6</sub>, C<sub>6</sub>—C<sub>7</sub> and those symmetrical therewith. The other bonds alternate with the overlap populations 0.892 to 0.992 and 1.071 to 1.176 and the Wiberg indices 1.068 to 1.070 and 1.454 to 1.801. The bond lengths are 0.1416 and 0.1384 nm.



SCHEME 6

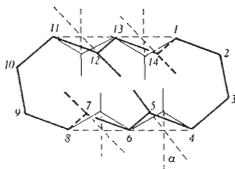
The isomer *IIIb* (model B) has the torsion angle  $\alpha$  and the valence angles  $\delta$  and  $\omega$  (Scheme 7) in the optimum geometry (in degrees): EMP 88, 110.9, 129.1; EHT 89, 110.8, 129.2; CNDO/2 77, 114.6, 125.4; MINDO/2 90, 110.8, 129.2. Again good agreement can be seen between the results of the different methods. The CNDO/2 method gives the torsion angle lower by about  $10^\circ$ , too. The overlap populations (1.029, 1.052, 1.112) and the Wiberg indices (1.203, 1.419, 1.687) indicate partial delocalization in the bonds  $C_4-C_5$ ,  $C_5-C_6$ ,  $C_6-C_7$  and those symmetrical there-



SCHEME 7

with. The other bonds alternate (the overlap populations 0.855 to 0.891 and 1.172 to 1.180; the Wiberg indices 1.063 to 1.122 and 1.804 to 1.825). The bond lengths were not calculated, because variation of bonds did not reach convergency of the SCF procedure for some combinations of bond lengths.

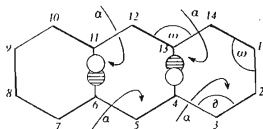
In the isomer *IVa* (model A) the values (in degrees) of the deviation angle  $\alpha$  (Scheme 8) in the optimum geometry are: EMP 49, EHT 57, CNDO/2 34, MINDO/2 55.



SCHEME 8

Again the CNDO/2 method gives a value lower by about 20°. The overlap populations (0.903 to 0.994 and 1.006 to 1.112) and the Wiberg indices (1.529 and 1.377) indicate a partial delocalization in the bonds C<sub>5</sub>—C<sub>6</sub>, C<sub>6</sub>—C<sub>7</sub> and those symmetrical therewith. In the other bonds the Wiberg indices vary within the limits 1.070 to 1.143 and 1.711 to 1.814. The bond lengths are 0.1425 and 0.1375 nm.

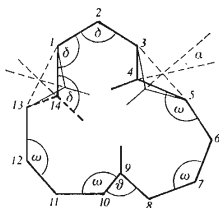
The isomer IVb (model B) has the torsion angle  $\alpha$  and the valence angles  $\delta$  and  $\omega$  (Scheme 9) in the optimum geometry (in degrees): EMP 86, 110.8, 129.2; EHT 89,



SCHEME 9

109.8, 130.2; CNDO/2 84, 111.7, 128.3; MINDO/2 90, 109.6, 130.4. A good agreement between the results of all the methods is obvious. The overlap populations (0.866 to 0.946 and 1.095 to 1.183) and the Wiberg indices (1.054 to 1.169 and 1.599 to 1.722) indicate regular bond alternation. The bond lengths could not be calculated, because the SCF procedure did not reach convergency on variation of bonds.

The isomer V is a regular tetradecagon with valence angle 154.3°. The overlap populations in all the bonds have close values (0.917 and 1.027). The Wiberg indices also show smaller differences than those of isolated single and double bonds, which indicates a partial delocalization. The bond lengths C—C and C=C are 0.1427 and 0.1374 nm, respectively. Smaller equalization of bond lengths than that in the analogous structure of [10] annulene is due to natural tendency to bond alternation<sup>7,8</sup>.



SCHEME 10

The isomer *VI*, suggested by Sonderheimer<sup>9</sup>, has its perimeter as if it were composed of equal parts of the regular octagon and parts of the regular hexagon. Out of the three inner carbon atoms of the perimeter two must be deviated above and below the plane by the angle  $\alpha$  (Scheme 10). In the plane section of the molecule there are three pairs of different valence angles  $\delta = 120^\circ$ ,  $\omega = 134.4^\circ$  and  $\vartheta = 110.3^\circ$ . For the optimum structure the values (in degrees) of the angle  $\alpha$  are: EMP 30, EHT 39, CNDO/2 27, MINDO/2 38. Smaller differences in the overlap populations (0.971 to 1.127) and the Wiberg indices (1.246 to 1.608) indicate a partial bond delocalization. The C—C and C=C bond lengths are 0.1420 and 0.1380 nm, respectively.

Comparison of the deviation and torsion angles of all the isomers shows that the greatest and the smallest values are obtained by the MINDO/2 and CNDO/2 methods, respectively, the difference being  $10-20^\circ$  (in two cases almost  $30^\circ$  (*IIa*, *IIIa*)). Only in the isomer *IVb* the CNDO/2 method gives the torsion angle lower by mere  $6^\circ$  than that given by the MINDO/2 method. This fact results obviously from overestimation of non-bonding repulsion interactions in the MINDO methods<sup>10</sup>. The EMP and EHT methods give generally close values to those of MINDO/2. Only in some cases the DMP method gives substantially lower values close to those of CNDO/2 (*Ia*, *IIa*, *VI*). If the difference between the angles is about  $5^\circ$ , then the data are considered to be approximately identical with respect to semiempirical character of the methods. When deciding which one of the torsion angle values is the best and nearest to the correct value, we can take the MINDO/2 values as exaggerated (with respect to the mentioned reason), the same being true of the EHT

TABLE I

Calculated values of enthalpy of formation of geometrical isomers of [14] annulenes ( $\text{kJ mol}^{-1}$ )

Geometrical isomer	$\Delta H_f$	
	EMP	MINDO/2
<i>Ia</i>	680.7	663.1
<i>Ib</i>	532.4	635.6
<i>IIa</i>	640.1	658.7
<i>IIb</i>	514.6	646.4
<i>IIIa</i>	900.7	749.0
<i>IIIb</i>	883.0	786.2
<i>IVa</i>	1 259.2	801.7
<i>IVb</i>	906.9	801.7
<i>V</i>	1 836.1	1 210.1
<i>VI</i>	718.7	673.6

and EMP values which are mostly close to the MINDO/2 values. The CNDO/2 values are considered to be most probable. If the difference between the MINDO/2 and CNDO/2 values is large, then the latter are considered to be much too low.

Relative stability of the geometrical isomers is given by the calculated enthalpies of formation (Table I). Both the MINDO/2 and EMP methods ascribe the highest stability to the *Ib* isomer having a skeleton of fully space shape, which agrees with the crystallographically determined structure of [14] annulene<sup>4</sup>. The *Ia* isomer is less stable in spite of greater bond delocalization. This fact is obviously due to greater strain energy in the molecule (Table II). The geometrical isomer *Ib* is more stable than *Iib* by 10.8 kJ mol<sup>-1</sup>. Allinger<sup>10</sup>, using the VESCF method, found the difference 10.5 kJ mol<sup>-1</sup>.

The bond lengths of the *Ib* isomer calculated by the CNDO/2 and MINDO/2 methods show a lower delocalization degree ( $R_{C-C} - R_{C=C} = 0.0094$  and  $0.0110$  nm according to CNDO/2 and MINDO/2, respectively) than those found by Allinger<sup>10</sup> ( $R_{C-C} = 0.1411$  nm,  $R_{C=C} = 0.1405$  nm). Chiang and Paul<sup>4</sup> found experimentally the values  $R_{C-C} = 0.1407$  nm and  $R_{C=C} = 0.1378$  nm, however, in this ref.<sup>4</sup> the bond alternation was not found (in contrast to our results). This fact can be explained by different arrangement of the molecule in crystalline state and in isolated molecule calculated by quantum-chemical methods. Similar result was obtained by Dewar<sup>11</sup> in calculation of [18] annulene by the MINDO/3 method.

The aromaticity indices *A* and HOMA<sub>d</sub> of the *Ib* isomer have the respective values 0.673 and 0.715 (MINDO/2), 0.745 and 0.780 (CNDO/2), 0.999 and 0.987

TABLE II

Values of non-bonding interaction energies ( $U_{vw}$ ), deformation energies of valence angles ( $U_{angle}$ ), and strain energies ( $U_{str}$ ) of [14] annulene (kJ mol<sup>-1</sup>)

Geometrical isomer	$U_{vw}$	$U_{angle}$	$U_{str}$
<i>Ia</i>	697.8	10.5	887.1
<i>Ib</i>	682.5	6.7	708.5
<i>IIa</i>	762.4	4.1	846.5
<i>IIb</i>	626.8	14.0	720.2
<i>IIIa</i>	763.8	10.6	1 080.9
<i>IIIb</i>	1 010.4	22.8	1 149.9
<i>IVa</i>	718.1	18.8	1 465.7
<i>IVb</i>	919.1	92.8	1 113.4
<i>V</i>	938.9	1 101.2	2 040.1
<i>VI</i>	670.6	147.2	925.0



(VESCF calculation<sup>12</sup>), 0.959 and 0.931 (from experiment<sup>4</sup>). Hence from the values of aromaticity indices according to the results by Allinger and crystallographical structure, [14] annulene should be an aromatic compound. However, the aromaticity indices obtained from bond lengths calculated by us indicate lowered aromatic properties of [14] annulene, which was found experimentally by other way, too<sup>13</sup>. High negative DRE value ( $-151.8 \text{ kJ mol}^{-1}$ ) represents another evidence of lowered aromatic properties.

The geometrical isomer *I* in solution is in thermodynamic equilibrium with the isomer *II* or *VI* (ref.<sup>6</sup>). Our results show, that *VI* is less stable than *II*. Ratio of relative stability favours the *II* isomer.

The values of enthalpies of formation of the isomers calculated by the EMP method agree well with the MINDO/2 values. Greater differences are only observed in the case of the *IV* and *IIIb* isomers which have high values of strain energy (Table II). The high strain energy values of the *VI* isomer are due to great deformation energy value of valence angles, whereas in the case of the *IIIb* isomer they are due to energy of non-bonding interactions.

For comparison of aromatic properties of the mentioned geometrical isomers of [14] annulene we calculated the aromaticity indices of all the isomers (Fig. 1). The values of  $\text{HOMA}_d$  index calculated from bond lengths (CNDO/2) indicate a quite high aromaticity degree in the isomers *IIa*, *IIIa*, *IVa*, *V*, and *VI* (similar conclusion follows also from the value of the factor *A*). However, the values of  $\text{HOMA}_w$  index calculated from the Wiberg CNDO/2 indices indicate a much lower aromaticity degree reaching a value close to 0.8 for the *V* and *VI* isomers only. This difference can be explained by the  $\text{HOMA}_d$  index (which is a function of bond lengths) being unable to express the strain in the molecule. On the contrary, the  $\text{HOMA}_w$

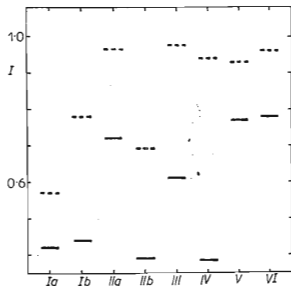
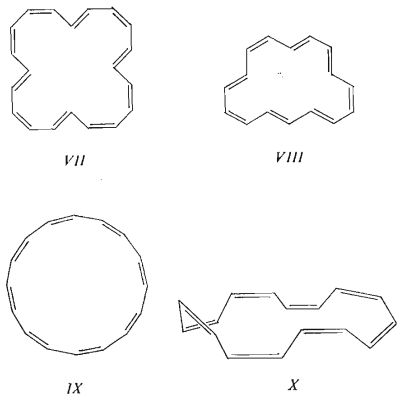


FIG. 1  
Aromaticity indices of [14] annulenes

index (which is a function of the Wiberg indices) can express the aromaticity lowering due to the strain which is implicitly involved in values of the Wiberg index. In spite of the values of  $HOMA_d$  and  $HOMA_w$  indices indicating an only smaller lowering of aromaticity of some structures, high negative values of the Dewar resonance energy (from  $-113$  to  $1436$ ) show small stability of these compounds.

[16] *Annulene*. This ring is relatively stable, and its structure was studied crystallographically<sup>14</sup> and by NMR spectroscopy<sup>15</sup>. We studied four geometrical isomers (Scheme 11), out of which *VII* and *VIII* were studied experimentally, too<sup>16</sup>. The isomer *VII* has valence angles  $135^\circ$ , if plane structure is presumed. The optimum plane structure was calculated by the EMP, EHT and CNDO/2 methods. The overlap popula-

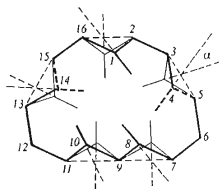


SCHEME 11

tion values (0.909, 0.919 and 1.165, 1.175) and the Wiberg indices (1.124 and 1.802) indicate obviously bond alternation. Also alternating are the bond lengths according to the CNDO/2 (0.1356 and 0.1444 nm) and MINDO/2 calculation (0.1342 and 0.1458 nm), which agrees with the VESCF calculation by Allinger<sup>10</sup> (0.1351 and 0.1475 nm) and with experimental measurements<sup>14</sup> (0.1332 and 0.1456 nm). A very good agreement is obvious. However, the VESCF method and experiment give a small space distortion, *i.e.* deviation of the inner carbon atoms of perimeter by the angle  $15.9$  and  $12.8^\circ$ , respectively, and the bond angles  $123.9$  and  $126.1^\circ$ , respectively.

The isomer *VIII* (Scheme 12) has the outer carbon atoms of perimeter in plane and the outer ones deviated by the angle  $\alpha$ , the atoms  $C_1$ ,  $C_8$  and  $C_{10}$  being above

the plane and the atoms  $C_4$  and  $C_{14}$  below the plane. The individual methods give the optimum geometry angle (in degrees): EMP 30, EHT 39, CNDO/2 29, MINDO/2 38. The overlap populations (0.933 to 0.966 and 1.154 to 1.163) and the Wiberg



SCHEME 12

indices (1.146 to 1.177 and 1.693 to 1.741) indicate bond alternation. The C—C and C=C bond lengths calculated by the CNDO/2 method (0.1426 and 0.1374 nm, respectively) and by the MINDO/2 method (0.1455 and 0.1345 nm) agree well with the VESCF calculation by Allinger<sup>10</sup> (0.1460 and 0.1365 nm). The VESCF calculation gives the out-of-plane deviation angle  $57^\circ$ . The corresponding values obtained by us for this angle by calculation by four methods are substantially lower (maximum by  $20^\circ$ ) and mutually close (with maximum deviation  $10^\circ$ ). The average value of these results is considered to be most probable, *i.e.* about  $35^\circ$ .

The isomer *IX* is a regular hexadecagon with valence angles  $157.5^\circ$ . Pairs of different values of overlap populations (0.833 and 1.077) and Wiberg indices (1.162 and 1.748) indicate bond alternation, which agrees with the Hückel rule. The bond lengths are 0.1426 and 0.1374 nm.

The isomer *X* is constructed, as a molecular model, by connecting (with a single bond) the terminal carbon atoms of the respective all-*trans* polyene. The molecule has a space shape with uniform torsion angle at single bonds ( $127.6^\circ$ ). Pairs of different values of the overlap populations (0.881 and 1.238) and the Wiberg indices (1.072 and 1.865) indicate a marked alternation, which is also determined by the space shape of the molecule. The C—C and C=C bond lengths calculated by the CNDO/2 method (0.1449 and 0.1351 nm, respectively) and by the MINDO/2 method (0.1459 and 0.1341 nm).

Table III gives enthalpies of formation reflecting relative stability of the isomers. Both the EMP and MINDO/2 methods give the stability order  $X > VII > VIII > IX$ , *i.e.* the most stable is the *X* isomer not yet prepared. This isomer is free of strain and by  $54.5 \text{ kJ mol}^{-1}$  (according to MINDO/2) more stable than the *VII* isomer which is the most stable according to Allinger<sup>10</sup>. The isomer *VII* is more stable than *VIII* by  $44.4 \text{ kJ mol}^{-1}$  ( $30.3 \text{ kJ mol}^{-1}$  according to Allinger<sup>10</sup>). The EMP

and MINDO/2 methods give close values of enthalpies of formation in spite of their different nature. Only the isomer *IX* exhibits a great difference, which can be ascribed to the strong strain due to great deformation of valence angles (Table II).

Aromatic properties of [16] annulenes are characterized by aromaticity indices (Fig. 2). The given values show that not all isomers of [16] annulene have aromatic properties. The DRE index has high negative values ( $-110$  to  $-2004$ ), which indicates low stability of these compounds.

[18] *Annulene*. This compound is relatively stable, almost plane (according to crystallographical analysis<sup>14,15</sup>), the carbon atoms of perimeter being deviated

TABLE III  
Heats of formation ( $\Delta H_f$ ) of geometrical isomers of [16] and [18] annulenes ( $\text{kJ mol}^{-1}$ )

Geometrical isomer	$\Delta H_f$	
	EMP	MINDO/2
<i>VII</i>	696.1	702.8
<i>VIII</i>	891.1	747.2
<i>IX</i>	2 461.4	1 580.7
<i>X</i>	567.1	648.3
<i>XI</i>	3 123.3	1 979.8
<i>XII</i>	2 364.5	1 530.2
<i>XIII</i>	643.3	761.3

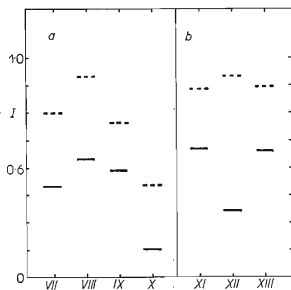
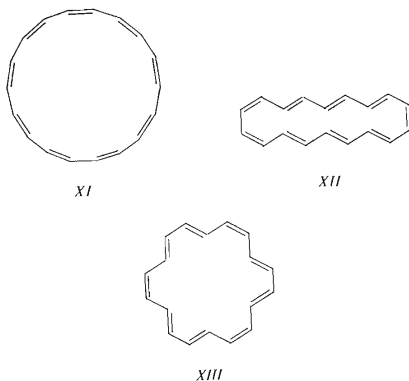


FIG. 2  
Aromaticity indices of all geometric isomers.  
*a* [16] annulene, *b* [18] annulene

only slightly out of plane (the inner ones by 0.025 nm, the outer ones by 0.0085 nm). The crystalline structure is close to  $D_{6h}$  symmetry. However, calculations indicate that structure  $D_{3h}$  with alternating bonds is more stable<sup>17-21</sup>. This fact agrees with natural tendency of rings with conjugated bonds systems to bond alternation as the size of the ring increases<sup>7,8</sup>.

It is, however, necessary to mention a surprising result obtained by Baumann<sup>3</sup> in calculation of annulenes by the MINDO methods. By involving several thousands biexcited configurations in configuration interaction he obtained a lower energy value for the  $D_{6h}$  isomer than for  $D_{3h}$ . This finding introduced an interfering element into the available knowledge about monotonous aromaticity decrease with increasing ring size which was obtained mainly by HMO type methods and graphical theoretical methods<sup>22-25</sup>. Also the result of an *ab initio* calculation by Haddon<sup>18</sup> gives higher stability for the  $D_{3h}$  isomer, however, in this case correlation energy can be significant. The results by Baumann are not quite reliable, as they were obtained on semi-empirical level.

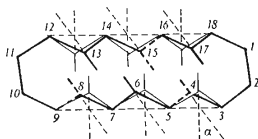
We studied three geometrical isomers (Scheme 13). The *XI* isomer is regular octadecagon with valence angle  $160^\circ$ . The overlap populations (0.874 and 1.012)



SCHEME 13

and the Wiberg indices (1.234 and 1.664) indicate considerable bond alternation – greater than in analogous [14] annulene – in spite of the Hückel rule being fulfilled. In this case, too, it is presumed that the reason consists in natural tendency to bond alternation with increasing ring size.

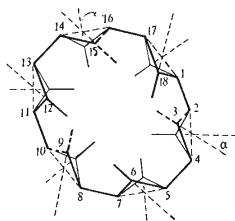
In the isomer *XII* the outer carbon atoms of perimeter are in plane (Scheme 14) and the inner ones are deviated alternatively above and below the plane by the angle  $\alpha$



SCHEME 14

For the optimum geometry the  $\alpha$  values (in degrees) calculated are: EMP 46, EHT 55, CNDO/2 46, MINDO/2 52. The overlap populations (0.856 to 0.956 and 1.161 to 1.199) and the Wiberg indices (1.082 to 1.123 and 1.718 to 1.882) indicate bond alternation.

The isomer *XIII* again has its outer carbon atoms of perimeter in plane, the inner ones being deviated by the angle  $\alpha$  (Scheme 15) for which the calculations in the



SCHEME 15

optimum geometry give the following values (in degrees): EMP 11, EHT 12, CNDO/2 0, and MINDO/2 10. The optimum C—C and C=C bond lengths calculated by the CNDO/2 method are 0.1433 and 0.1368 nm, respectively, and are alternating. However, the bond lengths optimized by the MINDO/2 method are equal (0.1400 nm). The optimum bond lengths in the *ab initio* calculation by Haddon<sup>18</sup> are 0.1479 and 0.1330 nm, respectively. Hence the MINDO/2 method does not give a correct result for the bond lengths. We also optimized the geometrical isomer of  $D_{6h}$  symmetry which has the total energy higher by 66.6 kJ mol<sup>-1</sup> (149.3 kJ mol<sup>-1</sup> according to the *ab initio* calculation<sup>18</sup> in STO 3G base). The bond lengths are 0.1405 and

0.1368 nm, the *an initio* calculation<sup>18</sup> gives 0.1400 and 0.1391 nm, respectively. The values found experimentally<sup>16,17</sup> are 0.1418 and 0.1382 nm. The experimental values are average, as the symmetry in the crystal structure is slightly disturbed. These results show that the bond lengths from the CNDO/2 calculation are comparable with the *ab initio* and experimental values within the accuracy limits of the semi-empirical methods. The overlap populations (0.978 to 0.998 and 1.132 to 1.155) and the Wiberg indices (1.225 and 1.646) in the  $D_{3h}$  isomer indicate an only partial delocalization. In the  $D_{6h}$  isomer the delocalization is substantially higher.

Relative stability is given by enthalpy of formation (Table III). Both the EMP and MINDO/2 methods give the same stability order  $XIII > XII > XI$ . The enthalpy of formation of the  $XIII$  isomer obtained by Dewar<sup>11</sup> is  $541.0 \text{ kJ mol}^{-1}$  (the MINDO/3 method with full optimization) *i.e.* by  $220.3 \text{ kJ mol}^{-1}$  less than our MINDO/2 value (according to Baumann<sup>3</sup>  $615.4 \text{ kJ mol}^{-1}$  and with CI  $381.1 \text{ kJ mol}^{-1}$ ). As the MINDO/2 method generally gives good values of enthalpies of formation, the above-mentioned considerable difference must be ascribed to the fact that our structure is not completely optimized. If the number of bonds is high, then errors in bond lengths can cause considerable difference in enthalpy of formation. For the isomers  $XI$  and  $XII$  the EMP and MINDO/2 methods give very different values of enthalpy of formation, which is obviously due to high energy values of bond angle deformations and strain energy (Table IV).

Aromatic properties of geometrical isomers of [18] annulene are determined by the aromaticity indexes  $HOMA_d$  and  $HOMA_w$  (Fig. 2). The Julg A factor is not given, because its values are close to those of the  $HOMA_d$  index. The values of the  $HOMA_d$  aromaticity index obtained by the CNDO/2 calculation for the  $D_{3h}$  and

TABLE IV

Values of non-bonding interaction energies ( $U_{vw}$ ), deformation energies of valence angles ( $U_{angle}$ ), and strain energies ( $U_{str}$ ) of isomers of [16] and [18] annulenes ( $\text{kJ mol}^{-1}$ )

Geometrical isomer	$U_{vw}$	$U_{angle}$	$U_{str}$
VII	691.2	240.9	932.0
VIII	763.2	7.8	1 008.4
IX	1 191.8	1 505.5	2 697.3
X	706.8	0	803.4
XI	1 461.7	1 927.1	3 388.7
XII	1 528.3	253.1	2 630.0
XIII	835.9	0.2	908.7

$D_{6h}$  isomers and the experimental structure are 0.875, 0.997, and 0.965, respectively. The  $HOMA_d$  index is seen to predict a high aromaticity degree for the  $D_{6h}$  isomer and for the experimental structure, too; for the  $D_{3h}$  isomer it predicts a lowered aromaticity. The  $HOMA_w$  index gives for all the isomers lower values than in the above cases, which reflects non-coplanarity and strain (which are implicitly involved in the Wiberg indices). The *XI* and *XII* isomers have high negative DRE values which indicate their instability. Only the *XIII* isomer exhibits a low negative value close to zero (-8) corresponding to its stability.

Values of the  $HOMA_w$  index of [10] and [12] annulenes calculated by the CNDO/2 method (the structures given in ref.<sup>1</sup>):

[10] annulenes: *Ia* 0.336, *Ib* 0.467, *II* 0.807, *III* 0.878, *IV* 0.327, *Va* 0.336, *Vb* 0.329, *Vc* 0.259

[12] annulenes: *VIa* 0.318, *VIb* 0.395, *VII* 0.244, *VIIIa* 0.297, *IX* 0.343, *X* 0.389, *XI* 0.240, *XII* 0.451.

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