STUDY OF THE INTERCONVERSION OF ISOMERS OF [16]ANNULENE BY THE AM1 METHOD

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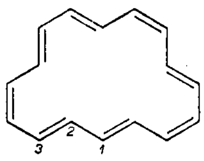
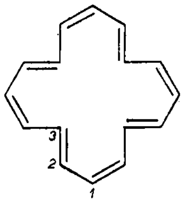
The AM1 method was used to carry out a theoretical study of different isomers of [16]annulene and of the reversible transformation between them preserving the molecular periphery. Transition states were located on the corresponding potential energy hypersurface.

The molecule of [16]annulene, which bears 4π electrons, was first synthesized by Sondheimer and Gaoni[1]. It is quite stable notwithstanding the clustering of the hydrogens lying within the molecular ring. Structures *I* and *II* show the two most representative isomers of this molecule. While isomer *I* has five inner hydrogen atoms (H(2), H(6), H(12), and H(16)), isomer *II* has only four (H(3), H(7), H(11), and H(15)).



I



II

Isomer *I* was synthesized[2] later than isomer *II* and its geometry is consistent with that postulated by Dewar and Gleicher[3]. Bond lengths and valence angles were obtained from crystallographic data[4]. Experiments carried out in solution[5] showed the two isomers to be in equilibrium, though in the ratio *I* : *II* of about 3 : 7.

This paper reports on a theoretical study of the two isomers by using the semi-empirical AM1 method[6]. The energy barriers between the two isomers for each of their peripheries are also reported. No other isomers of this molecule were studied because of the lack of literature references to their synthesis and because of the results found in an earlier study[7] by CNDO/2 and MINDO/3 methods. MINDO/3 results showed that the other isomers are less stable than the two isomers studied. This point was also confirmed by the findings of Loos and Leška[8].

CALCULATIONS

All calculations were performed by the standard version of the program MOPAC (ref.[9]). The minimum-energy points on the potential hypersurface were determined by Davidon–Fletcher–Powell (DFP) optimization technique[10,11].

Concerning the reliability of AM1 in its aplication to annulenes, it is necessary to point out the two following considerations. On one hand, and as a rule, the AM1 technique offers more accurate predictions on molecules with high bond strains[6] (e.g. [n]annulenes) than earlier semiempirical methods. On the other hand, Baumann has shown[12] that the objections to the fact that semiempirical methods do not take into account properly the electronic correlation effect are not so important for [4n]annulenes, for which the π-electron correlation energy is not so dependent on symmetry.

Evaluation of the interconversion barriers was carried out by the determination of the corresponding transition states on the AM1 hypersurface. The calculation procedure used for this purpose was recently developed by Dewar et al.[13] for the study of elemental processes and had already been successfully applied to theoretical studies of similar reactions (e.g. the interconversion of isomers of [14]annulene with a pyrene periphery[14]). This method enables an approximate point within the true transition-state zone to be localized by starting from the geometries of the two minima situated on both sides of the saddle point. The approximate points obtained in this way were subsequently refined by minimizing the Euclidean norm of the energy gradient and were later characterized by calculating force constants and transition vectors[15]. The method described here is of proven efficiency in treating processes occuring on potential hypersurfaces with very small energy differences between their stationary points, as is the case with the interconversions between isomers of large molecules (e.g. annulenes), particularly if the molecular periphery is preserved in the process.

RESULTS AND DISCUSSION

For each of the two above-mentioned potential peripheries of [16]annulene, *I* and *II*, we located two minima on the respective potential energy hypersurface. In accordance with Dewar and Gleicher, we refer to the minima corresponding to *I* to as *A* and *B*, and to those corresponding to *II* to as *C* and *D*. We also located saddle points for the interconversions $A \rightleftharpoons B$ and $C \rightleftharpoons D$. Full information about optimum geometries of the stationary points located are available from authors on request.

Figure 1 shows the calculated structures for *A*, *B*, *C*, and *D*, with indication of the most relevant atomic vertical shifts, which were calculated by taking arbitrarily the plane containing the largest number of them as reference. Table I summarizes energies and some other properties for all the calculated points. In agreement with X-ray diffraction data of [16]annulene and with our previous theoretical studies on different members of the [n]annulene family by the AM1 method[14], the structures obtained feature alternant C—C bond lengths, so that the four isomers are faithfully described by formulae such as *I* and *II*, with eight double and eight single bonds in perfect alternancy. Structures deviating somewhat from planarity are energetically more favourable for all four isomers; this can be checked on their vertical shifts (Fig. 1). This result is also in agreement with the crystallographic data mentioned above.

In [16]annulenes the strain of valence angles seems to determine the relative stability of the isomers, and thus the deviation from the ideal 120° for an sp^2 carbon atom provides a criterion for qualitative discussion in this context. This fact, which was already proved by our group in the above-mentioned studies on members of the [n]annulene family, may be evident from the values of the valence angles. On the one hand, our predictions for the bond angles of isomer *D*, the most stable, are quite consistent with the experimental values found[4] ranging from 122° to 129° (isomer *A* 120·4° – 125·6°; isomer *B* 119·4° – 126·4°; isomer *C* 122·1° – 129·2°; isomer *D* 122·3° – 127·7°). On the other hand, the most stable isomer for each periphery (*I* and *II*), i.e. isomer *D* and *A*, respectively, feature lesser variation and smaller deviation from ideal value to 120°.

Bond strain in annulenes arises from the repulsive interaction between inner hydrogen atoms, which compels them to deviate from the planarity one would a priori postulate. The shifts of these hydrogen atoms, which determine those of the other atoms of the molecule and hence structural distortion, may lead to different results and thus to different isomers. Thus, type *II* structures, like in [14]annulene, may occur with their four shifted hydrogen atoms in alternate (isomer *D*) or adjacent

TABLE I

AM1 heat of formation, ionization potential (IP) and dipole moment (DM) for four isomers and two transition structures of the [16]annulene

Parameter	*A*	*B*	*C*	*D*	TS($A \rightleftarrows B$)	TS($C \rightleftarrows D$)
ΔH_f°, kcal/mol	114·7	116·9	117·4	114·4	123·6	118·8
IP, eV	8·032	8·216	8·313	8·076	7·966	8·152
DM, D	0·133	0·080	0·182	0·000	0·218	0·123

position (isomer *C*). In this case the alternate isomer is more stable; this is in clear contrast with the behaviour of [14]annulene with a pyrene periphery. With type *I* structures, the most stable one (*A*) arises from the downward shift of H(2) and H(16) and the upward shift of H(6) and H(12), while H(9), owing to its greater distance from the two adjacent inner hydrogen atoms, H(6) and H(12), scarcely interacts and is not shifted appreciably. Therefore, H(9) excluded, isomer *A* has its inner hydrogen atoms arranged as the most stable conformation of [14]annulene. Isomer *B* represents the other possibility: H(6) and H(16) are markedly shifted upwards,

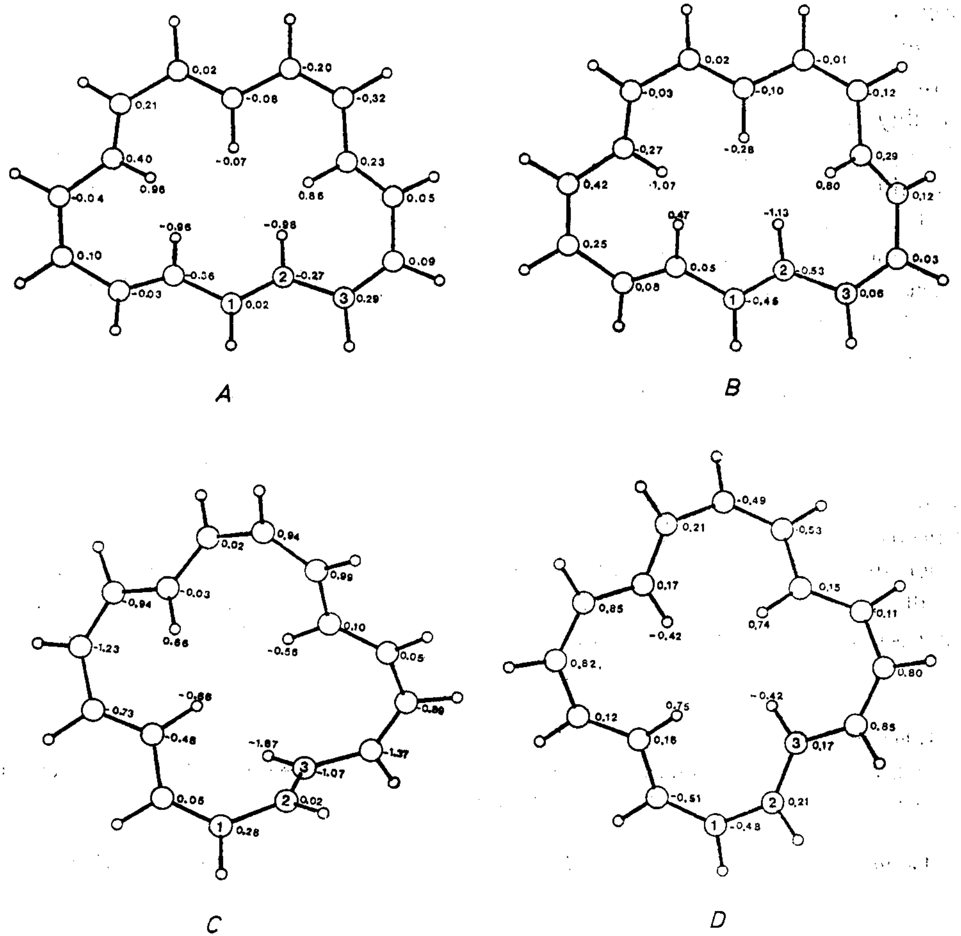


FIG. 1

Calculated structures for isomers *A*, *B*, *C*, and *D* of [16]annulene, with indication of significant atomic vertical shifts (in Å)

while H(2) and H(12) are shifted downwards and the fragment containing H(9) is scarcely distorted.

As far as the calculated vertical shifts are concerned, we should emphasize that, as a rule, those obtained for type *I* structures were smaller than those found for type *II* structures which unlike the former, do not correspond to any classical valence structure, and which would be planar in the absence of clustering. The values obtained for geometries *A* and *B* are fairly consistent, the former being somewhat more symmetrical. In fact, in *A*, shifts of clustered hydrogens are of the same order (+0·860, −0·985; +0·958; −0·960), and, as stated above, one of them is scarcely shifted with respect to the reference plane. This situation is analogous to that found in ref.[16], although the values obtained in that case for the positive shifts of the clustered hydrogens were much more divergent from the negative values. On the other hand, the geometry of *B* does not appear to be so easily predicted a priori, as the three negative shifts (−1·130, −1·074, −0·279) are opposed by two positive shifts (0·800 and 0·466), with a clear lack of homogeneity.

Geometries *C* and *D* behave similarly. The latter gives rise to values better matching the expectation that, in addition to the expected consistency, the shifts of the clustered hydrogen atoms are somewhat symmetrical, as in the case with the atoms departing from the clustering zone. In contrast to isomer *D*, which could be labelled "− + − +", isomer *C* would be "− − + +", despite the fact that the calculated *z* coordinate of its H(15) atom is negative; in fact, the position of H(15) with respect to H(3) and the *z* coordinates of the carbon atoms lying close to H(15) – all negative – provide a better understanding of the arrangement of the four inner hydrogen atoms in isomer *C*, and support the denomination we proposed above. We should note that the *z* coordinates for each isomer were calculated by using a reference plane which was not necessarily common for all isomers (i.e. it need not contain the same atoms of the carbon skeleton); hence, the calculated values only provide an intuitive picture of the structure of each isomer. Any comparison between the values found for two different isomers or between these and those calculated for the transition states should be taken with caution.

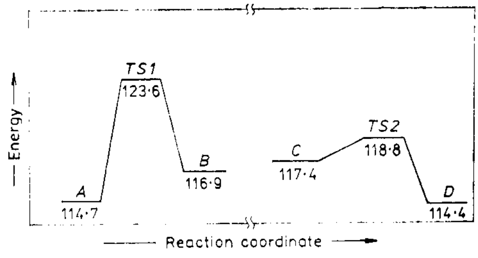


Fig. 2

Energy profiles for the two interconversion processes considered

We calculated the activation barriers for each of the isomerization processes studied at 298·15 K and found them to be 8·9 and 6·7 kcal/mol for the direct and reverse process, respectively, involving isomers with type *I* structure, and 1·4 and 4·4 kcal/mol, respectively, for those involving type *II* structures (Fig. 2). The interconversion process was thus easier for the structure having a smaller number of clustered hydrogen atoms. With the reservations noted above, the vertical shift values calculated for the saddle points show that in transition structure TS*1*, which relates the minima of *A* and *B*, H(12) and H(16) are the actual hydrogen atoms which exchange their positions, while H(9) is shifted slightly. Likewise, in TS*2*, which relates the other two minima, H(7) and H(11) are the atoms involved. The interconversion is associated with a relaxation in the ring zone closest to the inner hydrogen atoms directly involved. Thus the bond angles C(13)–C(12)–C(11) and C(15)–C(14)–C(13) are larger than their counterparts in isomers *A* and *B*. This is also the case with angles C(6)–C(5)–C(4) and C(7)–C(6)–C(5) in TS*2*.

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