MINDO/3 Study of [18]Annulene

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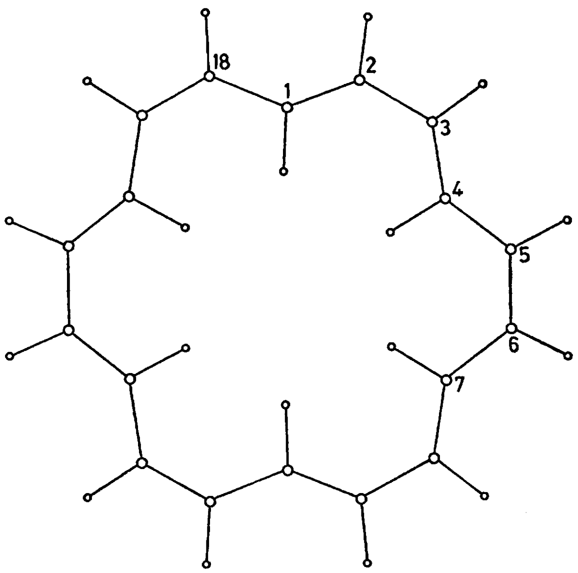
Summary The geometry of [18]annulene has been calculated by minimising the energy with respect to all 102 internal co-ordinates, using the MINDO/2 and MINDO/3 semiempirical SCF MO methods; the bond lengths are predicted to alternate, in agreement with calculations by the π approximation and molecular mechanics and the predicted heat of formation agrees with that from the π approximation, implying little aromatic stabilization.

[18]Annulene (I)[1] is the smallest annulene after benzene that can attain planarity without severe nonbonded interactions. It would be of interest therefore to determine whether the bonds in the ring alternate in length.

An X-ray structure determination[2] has shown that crystalline (I) has the D_{6h} structure with bonds of 'aromatic' length (Table I). On the other hand the proton chemical shifts in the n.m.r. spectrum[3] of (I) in solution indicate that the ring current is much smaller than would be expected[4] for such a structure. The electronic spectrum of (I) also leads to no unambiguous decision. Thus while the recent discovery[5] of a new band in the i.r. spectrum invalidates earlier conclusions[4a,6] that (I) has the 'polyene' D_{3h} structure with bonds of alternating length, the relationship between the wavelengths of the various absorption bands still seems to suggest[5] bond alternation.

Theoretical studies of (I) have mostly predicted[6a,7] bond alternation. Table 1 shows bond lengths calculated by two studies, one[7a] using an SCF π approximation and the other[7b] a recent extension of the molecular mechanics approach. In the former[7a], the molecule was assumed to be planar. The latter,[7b] however, predicted it to be nonplanar with D_3 symmetry, due to nonbonded interactions between the internal hydrogen atoms.



All these calculations[6a,7] have, however, been based on the Hückel σ, π approximation using parameters derived from polyenes and benzenoid hydrocarbons. It is uncertain whether such an approach can be extended to large rings. We therefore decided to study (I) using a recently

Table 1

Calculated structure of [18]annulene (I)

Bold length (Å) or bond angle (degrees)	X-Ray crystallography[2]	Molecular mechanics	SCF π-MO[7a]	MINDO/2′		MINDO/3	
	ca. D_{6h}	D_3	D_{3h}	D_{6h}	D_{3h}	D_{6h}	D_{3h}
C1–C2	1·381	1·463	1·462	1·412	1·469	1·399	1·458
C2–C3	1·419	1·361	1·352	1·412	1·365	1·405	1·355
C3–C4	1·383	1·463	1·462	1·421	1·472	1·399	1·458
C4–C5		1·357	1·353		1·360		1·351
C5–C6		1·467	1·458		1·477		1·466
C6–C7		1·357	1·354		1·361		1·350
C1-H	1·01			1·096	1·108	1·117	1·116
C2–H	1·00			1·110	1·096	1·111	1·110
C3–H	1·00			1·096	1·096	1·111	1·111
C4-H					1·108		1·116
C5–H					1·095		1·111
C6–H					1·095		1·111
C18–C1–C2	127·5	125·7		127·6	126·8		137·5
C1–C2–C3	123·8	123·4		134·2	126·6		128·1
C2–C3–C4	123·8	123·4		127·6	122·0		128·6
C3–C4–C5		125·7			135·0		136·9
C4–C5–C6		123·0			119·8		129·0
C5–C6–C7		122·7			131·4		128·8
C18–C1–H	116·8			116·2	116·6	111·1	112·7
C1–C2–H	117·9			112·9	116·7	116·2	114·8
C2–C3–H	118·6			116·2	119·0	114·9	117·0
C3–C4–H				112·0	112·5		110·0
C4–C5–H					120·1		117·9
C5–C6–H					114·3		113·2
H1–H4	1·97	2·22		2·074	1·861	2·044	1·968
H4–H7					2·037		2·104

developed and thoroughly tested semiempirical all-valence-electron SCF MO method (MINDO/3[8]). The molecule was not assumed to be planar or to have any symmetry, the geometry being calculated by minimizing the energy with respect to all 102 internal co-ordinates. This is by far the largest molecule for which such a calculation has been attempted; it was made possible only by the recent development of a procedure[9] based on the Davidon-Fletcher-Powell algorithm.[10] The molecule is predicted to be planar with D_{3h} symmetry and alternating bond lengths that agree well with those from the two earlier calculations (Table 1). The Figure shows a scale drawing plotted[11] by the computer. Calculations were also carried out for (I) constrained to D_{6h} symmetry (Table 1).

While MINDO/3 is generally superior to the earlier MINDO/2[12] and MINDO/2′[13] approximations, it does tend to underestimate the stability of aromatic rings. If this is due to an underestimate of resonance interactions, it could lead to a corresponding overestimate of the importance of bond alternation in compounds such as (I). We therefore adapted our geometry procedure[9] to MINDO/2′ and repeated the calculations. The resulting geometry (Table 1) agrees very closely with the three other estimates. These results therefore strongly reinforce the growing body of evidence that the bonds in (I) do alternate in length.†

The heats of formation calculated by MINDO/2′ and MINDO/3 are also in quite good agreement (Table 2). The differences between them and the value for the π approximation can be attributed to repulsions between the internal hydrogen atoms. There seems in any case no doubt that the only reported[14] experimental value for the heat of formation of (I) (*ca.* -280 kJ mol^{-1}) is in error, probably as a result of autoxidation of (I) in the bomb prior to combustion. The aromatic energy of (I) is probably very small, 7·5 kJ mol^{-1} according to the π approximation‡

TABLE 2

Energetics of [18]annulene

Heat of formation (ΔH_f) or reaction (ΔH)/kJ mol^{-1}	SCF π-MO[7a]	Molecular mechanics[7b]	MINDO/2′	MINDO/3
ΔH_f (D_{6h})	609·2	a	636·8	648·5
ΔH_f (D_{3h})	488·7	a	539·1	541·0
ΔH $D_3 \rightarrow D_{3h}$)	—	37·2	b	b
ΔH ($D_{3h} \rightarrow D_{6h}$)	130·5	5·3	97·7	107·5

[a] No value quoted. [b] Very little energy gain on deforming the molecule from coplanarity.

This work was supported by the Air Force Office of Scientific Research and the Robert A. Welch Foundation.

(*Received*, 30*th April* 1974; *Com.* 491.)

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† While *X*-ray diffraction studies could normally distinguish very easily between structures with such dissimilar bond lengths, the situation here is complicated by the fact that the alternating form of (I) would form crystals in which the two Kekulé structures were randomly oriented and might moreover undergo rapid equilibrium. To a first approximation, the diffraction pattern from such a crystal would be the same as that from one of the 'aromatic' (I) with D_{6h} symmetry. While this possibility was considered and rejected,[2] we feel that the present results would justify a re-examination of the crystal structure.

‡ Aromatic energy is the difference in energy between a cyclic conjugated compound and a corresponding structure with bond alternation, the 'single' and 'double' bonds being similar to those in a corresponding linear system. This is the quantity termed 'resonance energy' in ref. 7a.

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