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AROMATICITY IN POLYCYCLIC ANNULENES[1]

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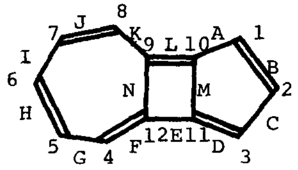
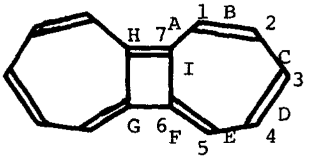
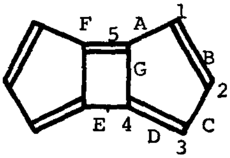
A favourite pastime of theoreticians has been the naming of hitherto unknown cyclic polyenes and related compounds on the grounds that Hückel calculations predicted that they would prove to be aromatic; pentalene[3,4] and heptalene[3,4] are classical examples. In nearly all cases the predictions of aromaticity have proved to be unfounded and it is now well recognized that the HMO method is hopelessly unreliable in this connection. In spite of this, the trivial name "zurlene" has recently been suggested for the tricyclic hydrocarbon I on the grounds that HMO calculations predict[6] a large resonance energy (4.2 β) for it, and attempts directed towards its synthesis are reported[5] to be in progress.



I



III



II

Recent work in these laboratories has led to an improved version[7] of an earlier[8] semiempirical SCF MO treatment which seems to give very good estimates of heats of formation and bond lengths for conjugated molecules of all types. In particular, it correctly predicts which of them are, and which are not, aromatic. We have now applied this procedure to I, and to the related tricyclic compounds II and III.

If I-III are aromatic, they should possess planes of symmetry bisecting the three rings; if they are not aromatic, the bonds in them should alternate as indicated in I-III. The calculations were accordingly carried out for both types of structures, by using different initial geometries. For the "aromatic" case (A) all bonds were assumed equal initially (1.397 Å), while for the nonaromatic case (B), the lengths of single and double bonds in the initial structures were taken to be 1.46 and 1.35 Å respectively. If the initial structure is symmetrical, this symmetry will of course be retained throughout our SCF procedure, so (A) must lead to a symmetrical solution. If this is in fact the stable form of the molecule, i.e. if the molecule is aromatic, both (A) and (B) should then converge to the same symmetrical solution, while in the case of a nonaromatic molecule, B should lead to a solution with alternating bonds and a lower energy than that given by A.

Table I shows that in all three cases it is the unsymmetrical structure B that is the more stable, implying that none of these compounds is aromatic. A further check is provided by a comparison of the heat of atomization with that calculated for a corresponding classical polyene with localized double and single bonds. Using the "polyene" bond energies of ref.[8], we find the values for these energy differences ("resonance energies") listed in Table I. The symmetrical structures have negative resonance energies, implying that I, II and III are all antiaromatic. The bond lengths calculated for IB, IIB, and IIIB are listed in Table II; it will be seen that they correspond to those[8] for a classical polyene. Calculated π charge densities are shown in Table III.

Table I. Heats of Atomization (ΔH_a) and Resonance Energies (RE) of I-III.

Compound	IA	IB	IIA	IIB	IIIA	IIIB
ΔH_a*	103.23	103.58	84.72	84.87	121.70	122.28
RE†	-6.7	1.2	-1.2	2.5	-13.4	-0.2

* In eV at 25° C. † In kcal/mole at 25° C.

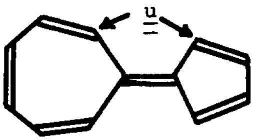
Table II. Calculated Bond Lengths (Å) for IB, IIB, and IIIB.

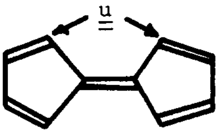
Compoun	A(J)	B(K)	C(L)	D(M)	E(N)	F	G	H	I
IB	1.456	1.358	1.447	1.361	1.474	1.359	1.453	1.357	1.454
	(1.356)	(1.458)	(1.371)	(1.464)	(1.463)				
IIB	1.451	1.361	1.445	1.361	1.461		1.477		
IIIB	1.453	1.355	1.456	1.356	1.456	1.357	1.471	1.366	1.470

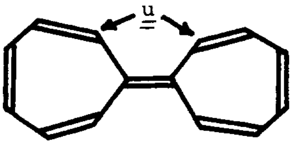
Table III. Calculated π Electron Densities for IB, IIB, and IIIB.

Compound	1(8)	2(9)	3(10)	4(11)	5(12)	6	7
IB	0.978	1.041	1.001	1.034	0.942	1.037	0.949
	(1.046)	(0.946)	(1.070)	(1.066)	(0.890)		
IIB	1.073	0.950	1.057	1.001	0.913		
IIIB	0.983	1.013	0.979	1.025	0.966	1.044	0.991

In conclusion, it should be pointed out that similar conclusions could be reached more simply by the PMO method,[9] a treatment which also seems to give reliable predictions for aromaticity.[10] Thus I, II and III can be derived, as indicated, from sesquifulvalene (IV), fulvalene (V), and heptafulvalene (VI) respectively, by intramolecular union[10] between positions separated by three (=4n-1, with n=1) bonds. The bond order between positions in a classical polyene separated by (4n-1) bonds is always negative, so such union leads to an increase in energy. Since IV, V, and VI are nonaromatic, being classical polyenes, it follows that I, II, and III must be antiaromatic.







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1. This work was supported by the Air Force Office of Scientific Research through Grant No. AF-AFOSR-1050-67.
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