BOND LENGTH ALTERNATION IN HEPTALENE

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Abstract—Using LCAO-MO theory it is shown that the heptalene molecule possesses only a centre of symmetry instead of two mutually perpendicular twofold axes in the molecular plane. Charges and free valence numbers indicate that the 1-position should be the most reactive.

INTRODUCTION

In a recent paper Dauben and Bertelli[1] describe the successful synthesis of the non-alternant hydrocarbon heptalene and mention its properties. From the point of view of the molecular orbital theory the bridged ring molecules heptalene $C_{12}H_{10}$ (I) and the still unknown pentalene C_8H_6 (II) should be closely related. Craig,[2] assuming

molecular symmetry D_{2h} discussed the electronic structures at length and for reasons of symmetry assigned both planar hydrocarbons to a special class of compounds: the pseudo-aromatics. It may be remarked that if the central bonds in pentalene and heptalene are omitted, cyclic polyenes result with general formula $C_{4n}H_{4n}$.

Longuet-Higgins and Salem[3] performed a theoretical analysis of bond lengths in cyclic and long chain polyenes. Using the molecular orbital method they were able to show that for rings larger than $C_{18}H_{18}$, bond length alternation should be expected. Coulson and Dixon[4] arrived at similar conclusions within the valence bond approximation. The more stable energy situation for such structures of lowered symmetry may be ascribed to a pseudo-Jahn-Teller effect—i.e. distortion of the molecular framework introduces mixing of the ground state with a low lying excited state.

Recently it could be shown[5] that for pentalene such an interaction becomes possible if a distortion from the familiar D_{2h} symmetry to C_{2h} symmetry is introduced. In other words a structure of the conventional type should be less favourable energetically than one in which bond lengths alternate. If the same approach is followed for heptalene, a similar behaviour appears, so that it was decided to verify whether the first experimental data available now might confirm the results of such calculations.

[1] H. J. Dauben Jr. and D. J. Bertelli, *J. Amer. Chem. Soc.* **83**, 4659 (1961).
[2] D. P. Craig, *J. Chem. Soc.* 3175 (1951).
[3] H. C. Longuet-Higgins and L. Salem, *Proc. Royal Soc.* **251A**, 172 (1959).
[4] C. A. Coulson and W. T. Dixon, *Tetrahedron* **17**, 215 (1962).
[5] P. C. den Boer-Veenendaal and D. H. W. den Boer, *Mol. Physics* **4**, 33 (1961).

ELECTRON ENERGIES

Using an iterative procedure known as the ω-technique[6,7] "self-consistent" values for charges, bond orders and bond lengths were calculated for symmetrical (D_{2h}) and asymmetrical (C_{2h}) heptalene. This method proceeds as follows. After having solved a first determinant—e.g. of the Hückel type—a new determinant is set up in which the Coulomb integrals (α) and resonance integrals (β) have been corrected with the aid of charges q and bond orders p obtained from the solution of the first one. The relations used here are:

$$\alpha_i' = \alpha_i^\circ + \omega(1 - q_i)\beta^\circ$$

$$\beta = \beta^\circ \exp\left(\frac{+1\cdot40 - l}{0\cdot3106}\right)$$

$$l = 1\cdot51 - 0\cdot16p$$

The proportionality coefficient ω is taken to be unity.[8] The expression for the exponential dependence of the resonance integral on the bond length l is taken from a paper by Longuet-Higgins and Salem.[3]

The figures considered to be final for charges, bond orders and free valence numbers are summarized in Table 1. For comparison the values obtained by solving the simple Hückel type equations are tabulated as well. The corresponding energies and symmetry assignments for the molecular orbitals are collected in Table 2. From these data the total π-electron energy for the ground states of the correspondingly treated models can be obtained. For the model with molecular symmetry D_{2h}—which entails the presence of the twofold axes C_2^x and C_2^y—a value of $(12\alpha^\circ + 14\cdot90\beta^\circ)$ is found. If an asymmetrical distortion, leading to symmetry C_{2h}, is introduced, the structure possesses only a centre of symmetry. In that case a more favourable π-electron results namely $(12\alpha^\circ + 15\cdot22\beta^\circ)$.

TABLE 1. CHARGES, BOND ORDERS AND FREE VALENCE NUMBERS IN HEPTALENE

charges				bond orders				free valence numbers			
atom	a	b	c	bond	a	b	c	atom	a	b	c
11	0·867	0·896	0·960	11–1	0·536	0·515	0·751	11	0·158	0·160	0·207
1	1·125	1·076	1·074	1–2	0·672	0·690	0·457	1	0·524	0·527	0·524
2	0·882	0·935	0·973	2–3	0·619	0·609	0·814	2	0·441	0·433	0·461
3	1·119	1·081	1·027	3–4			0·409	3	0·494	0·514	0·509
4			0·969	4–5			0·847	4			0·476
5			0·998	5–12			0·362	5			0·523
				11–12	0·502	0·542	0·412				

[a] Hückel scheme. [b] ω-technique molecular symmetry D_{2h}. [c] idem C_{2h}.

It should be remarked that compared with the Hückel method, the iterative procedure—as any method that takes into account electron repulsion—smoothes out the charge densities. This tendency is most pronounced where bond lengths alternate.

So far the π-electrons have been considered, though in fact the σ-electrons enter

[6] R. Daudel, R. Lefebvre and C. Moser, *Quantum Chemistry* p. 78. Interscience, New York (1959).
[7] A. Streitwieser, *Molecular Orbital Theory for Organic Chemists* p. 115. Wiley, London (1961).
[8] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* 17, 264 (1949).

into the calculations through the order-length relation. A comparison of stabilities should of course be based upon the total electron energies. It has been derived[8] for polyenes with an even charge distribution that the total energy v of a bond in equilibrium is given by:

$$v = -2aP' + \text{constant}$$

where $P' = -(0\cdot16)^{-1}$ and $a = 0\cdot3106$ Å. So one may compare the sums of the total energies V of all bonds in a symmetrical and asymmetrical (subscripts s and a respectively) nonalternant hydrocarbon through:

$$V_{(s)} - V_{(a)} = -2aP' \sum_{i<j} [\beta_{ij(s)} - \beta_{ij(a)}] + (\sum_i q_i\alpha_i)_{(s)} - (\sum_i q_i\alpha_i)_{(a)}$$

Though the figure obtained $-0\cdot08\beta°$—is rather small and may be subject to a large error, it indicates that a "deformation" of heptalene may be favoured by a stabilization energy of a few kcal/mole.

DISCUSSION

Similar to what has been found for pentalene,[5] the distortion of the nuclear framework of heptalene has the effect that in the ground state the highest occupied— i.e. the sixth— and the lowest unoccupied level do acquire the same symmetry. The resulting interaction of these orbitals is demonstrated by the data of Table 2. The top occupied orbital is lowered by the deformation, in contrast to the seventh that rises. So, in passing from the symmetrical to the asymmetrical molecule, the lowest electronic transition—a forbidden one—increases from $0\cdot17\beta°$ to $0\cdot43\beta°$, which is equivalent to a large shift to the blue. In a qualitative way this is in agreement with the observations of Dauben and Bertelli.[1]

TABLE 2. ENERGIES AND SYMMETRY ASSIGNMENTS OF MOLECULAR ORBITALS OF HEPTALENE*

Hückel	D_{2h}	C_{2h}	
$-2\cdot170\ b_{2g}$	$-1\cdot995\ b_{2g}$	$-2\cdot014\ b_g$	unoccupied
$-1\cdot891\ b_{1u}$	$-1\cdot837\ b_{1u}$	$-1\cdot840\ a_u$	in
$-1\cdot732\ b_{3g}$	$-1\cdot696\ b_{3g}$	$-1\cdot688\ b_g$	
$-1\cdot000\ a_{1u}$	$-1\cdot009\ a_{1u}$	$-1\cdot002\ a_u$	
$-0\cdot705\ b_{1u}$	$-0\cdot662\ b_{1u}$	$-0\cdot705\ a_u$	ground
$-0\cdot311\ b_{2g}$	$-0\cdot252\ b_{2g}$	$-0\cdot363\ b_g$	state
$0\quad b_{3g}$	$-0\cdot082\ b_{3g}$	$+0\cdot067\ b_g$	occupied
$+1\cdot000\ a_{1u}$	$+0\cdot999\ a_{1u}$	$+1\cdot003\ a_u$	in
$+1\cdot317\ b_{1u}$	$+1\cdot265\ b_{1u}$	$+1\cdot259\ a_u$	ground
$+1\cdot481\ b_{2g}$	$-1\cdot415\ b_{2g}$	$+1\cdot440\ b_g$	state
$+1\cdot732\ b_{3g}$	$+1\cdot683\ b_{3g}$	$+1\cdot691\ b_g$	
$+2\cdot278\ b_{1u}$	$+2\cdot171\ b_{1u}$	$+2\cdot152\ a_u$	

* The energies are characterized by the coefficients c in $E = \alpha + c\beta$.

Predictions for the chemical reactivity may be based upon ground state properties and as such the free valence numbers or the electronic charges are relevant. Inspection of Table 1 suggests that the asymmetrical structure accentuates clearly a charge difference at positions 1 and 3 which does not emerge from the symmetrical model. The free valence numbers in all three cases indicate that the highest reactivity

is to be expected at positions 1 and 5. So, in agreement with experiment, the 1-position should be the most reactive. It should be remarked that in the asymmetrical molecule the positions 1,5,6, and 10 are of course no longer equivalent.

For nonalternants a prediction for the chemical reactivity from charge densities and free valence numbers is not always in agreement with conclusions drawn from the computation of localization energies.[9] Therefore the three types of localization energy were calculated according to a Hückel scheme in which all the resonance integrals are taken equal, and are shown in Table 3 in units of the resonance integral β°. Obviously for these calculations the phenomenon of bond alternation is no longer of interest. Except for nucleophilic substituents where position 2 should be favoured, again the 1-position is predicted to be the most reactive.

TABLE 3. LOCALIZATION ENERGIES FOR
HEPTALENE

position	Ae	An	Ar
1	1·659	2·193	1·926
2	2·032	2·032	2·032
3	1·715	2·337	2·026

[9] See also *Dictionary of Values of Molecular Constants* (Edited by C. A. Coulson and R. Daudel).