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THE AROMATICITY OF PENTALENE, HEPTALENE AND RELATED BICYCLIC HYDROCARBONS

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Abstract—Using an internally consistent LCAO–MO method it is shown that pentalene and heptalene are not electronically stable and will tend to gain or lose two electrons, respectively. The treatment is generalized for bicyclic non-alternant hydrocarbons with a perimeter of $4n$ atoms by means of first-order perturbation theory and verified numerically. The energy levels of four selected molecules are presented.

A FULLY conjugated planar monocyclic hydrocarbon is electronically stable if it possesses $4n + 2$ π-electrons. This, the familiar Hückel rule, is based on the concept of closed shells; it follows from MO theory that this number of π-electrons is required to fill all available bonding orbitals. Molecules and ions of the $4n + 2$ type are called "aromatic", used in this context the term implies thermodynamic stability. It is not our present purpose to join in the perennial discussion on the exact meaning of "aromaticity", for the moment we adopt the closed-shell concept and state that a necessary condition for aromaticity is that all π-electrons in a molecule can be accommodated in all the available bonding molecular orbitals. In this Paper we examine whether bicyclic hydrocarbons with odd-membered rings and a perimeter of $4n$ atoms, a type which includes pentalene and heptalene, fulfill this condition.

In the Hamiltonian matrix for HMO calculations all Coulomb integrals α_j are assumed to be equal ($=\alpha$) and so are all resonance integrals between adjacent atoms ($\beta_{jk} = \beta$). This is justified by symmetry for planar monocyclic hydrocarbons; the calculations are internally consistent, and it is precisely for this type of molecule that the Huckel rule has been derived and to which it is strictly applicable. The assumption of uniform π-electron distribution holds for neutral alternant hydrocarbons generally,[1] and the matrix can be made fully self-consistent by iteratively relating[2] resonance integrals to bond orders, p_{jk}:

$$\beta_{jk} = \beta \exp (0{\cdot}48294\, p_{jk} - 0{\cdot}32196) \qquad (1)$$

For non-alternant hydrocarbons, in which π-electron densities, q_j, vary from atom to atom, Wheland and Mann's[3] ω-technique

$$\alpha_j = \alpha + \omega(1 - q_j)\beta \qquad (2)$$

is frequently used, and a combination of (1) and (2) ($\omega\beta$-method) leads to self-consistency. These methods (with $\omega = 1{\cdot}4$)[4] are now applied to pentalene and heptalene and shown to give reasonable results.

[1] C. A. Coulson and G. S. Rushbrooke, *Proc. Canbridge Phil. Soc.* **36**, 193 (1940).
[2] C. A. Coulson and A. Golebiewski, *Proc. Phys. Soc.* **78**, 1310 (1961).
[3] G. W. Wheland and D. E. Mann, *J. Chem. Phys.* **17**, 264 (1949).
[4] A. Streitwieser Jr., *Molecular Orbital Theory for Organic Chemists*, p. 115. Wiley, New York (1961).

TABLE 1. ENERGY LEVELS FOR PENTALENE (I)

	HMO	ω-Technique	$\omega\beta$-Technique
bonding	−2·343	−2·311	−2·199
	−1·414	−1·437	−1·433
	−1·000	−1·052	−0·959
	−0·471	−0·330	−0·349
		−0·161	−0·156
	0·000		
anti-bonding	1·414	1·406	1·392
	1·814	1·802	1·740
	2·000	2·084	1·963

TABLE 2. ENERGY LEVELS FOR HEPTALENE (II)

	HMO	ω-Technique	$\omega\beta$-Technique
bonding	−2·278	−2·308	−2·208
	−1·732	−1·728	−1·699
	−1·481	−1·473	−1·431
	−1·317	−1·343	−1·288
	−1·000	−0·997	−1·005
	0·000		
anti-bonding	0·311	0·096	0·093
	0·705	0·229	0·245
	1·000	0·737	0·675
	1·732	1·011	1·022
	1·891	1·741	1·719
	2·170	1·900	1·862
		2·136	2·015

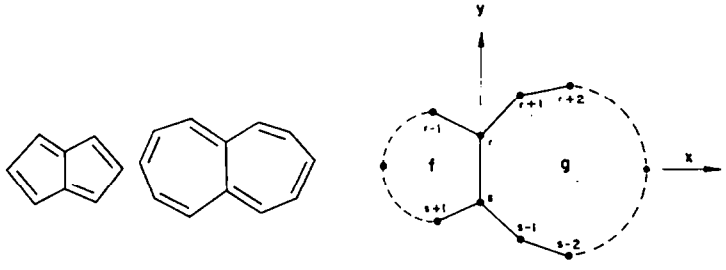
HMO calculations for pentalene (I) yield 4 bonding (B), 1 non-bonding (N), and 3 anti-bonding (AB) molecular orbitals. The 8 π-electrons can be placed in the 4 BMO's so that a closed-shell configuration with a substantial delocalization energy results, which conflicts with all the available experimental[5,6] and theoretical[7–9] evidence. However, the presence of a NBMO serves as a warning since the slightest change in the Hückel matrix will affect the energy of this orbital and drastically alter the situation. When the ω- or $\omega\beta$-technique is applied to pentalene* (Table 1) the NBMO becomes bonding, hence a consistent treatment yields an open-shell configuration and pentalene will tend to acquire two electrons, in agreement with experiment[10,11] and advanced theory.[8]

* The $\omega\beta$-technique, employing slightly different parameters, has previously been applied to pentalene[9] and heptalene.[12] The orbital energies were substantially those obtained here.

[5] C. T. Blood and R. P. Linstead, *J. Chem. Soc.* 2263 (1952).
[6] E. LeGoff, *J. Amer. Chem. Soc.* **84**, 3975 (1962).
[7] D. P. Craig, *J. Chem. Soc.* 3175 (1951).
[8] A. J. Silvestri, L. Goodman and J. A. Dixon, *Tetrahedron* **18**, 1329 (1962).
[9] P. C. den Boer-Veenendaal and D. H. W. den Boer, *Mol. Physics* **4**, 33 (1961).
[10] T. J. Katz, M. Rosenberger and R. K. O'Hara, *J. Amer. Chem. Soc.* **86**, 249 (1964).
[11] A. J. Silvestri, *Tetrahedron* **19**, 855 (1963).

The situation with regard to heptalene (II) is quite different. HMO calculations give 5 bonding, 1 non-bonding, and 6 anti-bonding MO's for the 12 π-electrons, hence Hückel heptalene does not possess a closed shell. In the di-cation 10 π-electrons occupy 5 BMO's, non-aromaticity is therefore indicated for the neutral molecule and aromaticity for the di-cation which, however, has the same delocalization energy. On applying the ω- or $\omega\beta$-method (Table 2) one finds that the NBMO becomes anti-bonding, hence a greater stability is indicated for the di-cation[8] (two fused tropylium ions) than the open-shell neutral molecule,[7,12,13] a satisfactory result.

We now use first-order perturbation theory to show that pentalene and heptalene are particular instances of two classes of non-alternant bicyclic hydrocarbons which, respectively, tend to gain or lose two electrons to achieve a closed-shell configuration. The molecules have a perimeter of $4n$ atoms and consist of two, not necessarily equal, odd rings of f and g atoms, respectively ($f + g = 4n + 2$). In the first "pentalenoid" class both rings are of the cyclopentadienide type with $f = 4h + 1$, $g = 4m + 1$; while in the second "heptalenoid" category the rings are tropylium-like ($f = 4h - 1$, $g = 4m - 1$). The HMO treatment of these molecules is considered first and this is followed by a generalization of the ω- and $\omega\beta$-techniques.



I II III

The Hückel molecular orbitals

The molecules are assumed to be planar and to possess symmetry D_{2h} for $f = g$, and C_{2v} otherwise. They all have a NBMO which is at once evident for the case $j = g$ in which the common bond lies along the twofold y-symmetry axis. In the MO's which are antisymmetric with respect to that axis the co-efficients c_r, c_s of the $2p_z$ atomic orbitals of the linked atoms r and s are both zero, and the secular equations reduce to those of the acyclic polyene radical $C_{r+1}— \cdots —C_{s-1}$, which, being alternant and odd, must possess a NBMO. To demonstrate the presence of a NBMO in the general case, in which the constituent rings may be of different size and the central bond may consequently no longer be an axis of symmetry, we use Dewar and Pettit's[14] first-order perturbation treatment, in which the energy levels of a polycyclic hydrocarbon are derived from those of the parent cyclic polyene by treating the bridging bonds as perturbations.

[12] P. C. den Boer-Veenendaal, J. A. Vliegenthart and D. H. W. den Boer, *Tetrahedron* **18**, 1325 (1962).
[13] H. J. Dauben Jr. and D. J. Bertelli, *J. Amer. Chem. Soc.* **83**, 4659 (1961).
[14] M. J. S. Dewar and R. Pettit, *J. Chem. Soc.* 1617 (1954).

The energies of the doubly degenerate MO's of the parent $4n$-cycle with quantum numbers $i = \pm 1, \pm 2, \ldots$ are given by

$$x_i = -2\cos(i\pi/2n) \tag{3}$$

The energy is measured from α, as the zero on the energy scale, in terms of β:

$$E_i = \alpha - x_i\beta \tag{4}$$

Since β is a negative quantity, the MO is bonding if x_i is negative. On linking the atoms r, s the energies of these orbitals are changed by amounts $\beta\delta x_i(\sin)$, $\beta\delta x_i(\cos)$, where

$$\delta x_i(\sin) = -A^2\{\cos[i\pi(r-s)/2n] - \cos[i\pi(r+s)/2n]\} \tag{5}$$

$$\delta x_i(\cos) = -A^2\{\cos[i\pi(r-s)/2n] + \cos[i\pi(r+s)/2n]\} \tag{6}$$

A is a normalizing factor. The phase angle[14] which should be incorporated in these equations has been caused to vanish by properly numbering the linked atoms:

$$r = \tfrac{1}{2}(g-1) \tag{7}$$

$$s = 4n - \tfrac{1}{2}(g-1) \tag{8}$$

In the $4n$ cyclic polyene, $4n-2$ π-electrons occupy the BMO's $i = 0, \pm 1, \ldots \pm(n-1)$ and the remaining two are placed in the degenerate NBMO's with quantum numbers $\pm n$, one in each. On establishing the cross-link r—s the energy changes of the NBMO's are, from Eqs (5)–(8):

$$\begin{aligned}\delta x_n(\sin) &= -A^2\{\cos[\pi(4n-g+1)/2] - \cos 2n\pi\} \\ &= -A^2\{\cos[\pi(4n-g+1)/2] - 1\}\end{aligned} \tag{9}$$

$$\delta x_n(\cos) = -A^2\{\cos[\pi(4n-g+1)/2] + 1\} \tag{10}$$

If the molecule is pentalenoid ($g = 4m+1$),

$$\left.\begin{aligned}\delta x_n(\sin) &= -A^2\{\cos[2\pi(n-m)] - 1\} \\ &= 0 \\ \delta x_n(\cos) &= -2A^2\end{aligned}\right\} \tag{11}$$

hence NBMO(sin) remains non-bonding and NBMO(cos) becomes bonding. On the other hand, in heptalenoid compounds ($g = 4m-1$)

$$\left.\begin{aligned}\delta x_n(\sin) &= -A^2\{\cos[2\pi(n-m)+\pi] - 1\} \\ &= 2A^2 \\ \delta x_n(\cos) &= 0\end{aligned}\right\} \tag{12}$$

NBMO(cos) remains non-bonding and NBMO(sin) becomes anti-bonding.

Thus, in pentalenoid molecules the highest occupied MO is the last bonding MO and the lowest unoccupied MO is non-bonding and there is a closed-shell configuration, while in heptalenoid molecules the highest filled MO is non-bonding with a resulting open-shell configuration. The results given earlier for pentalene and heptalene are therefore quite general.

The ω- and $\omega\beta$-techniques

We now discuss how a single application of the ω- or $\omega\beta$-variation affects the NBMO's in the two types of hydrocarbons. Second and further applications of these techniques are regarded as higher-order corrections and are not considered in this general treatment. The exact forms of the β- and ω-relationships (1) and (2) are not required, it is sufficient to state that each Coulomb integral α_j is changed by an amount $\delta\alpha_j$, which depends on the Hückel electron density q_j of atom j as follows:

$$\left.\begin{array}{lll} \delta\alpha_j > 0 & \text{for} & q_j < 1 \\ \delta\alpha_j = 0 & \text{for} & q_j = 1 \\ \delta\alpha_j < 0 & \text{for} & q_j > 1 \end{array}\right\} \tag{13}$$

By first-order perturbation theory, the change in the energy of the ith MO caused by changes $\delta\alpha_j$, $\delta\beta_{jk}$ in the Coulomb and resonance integrals, respectively, is given by $\beta\delta x_i$, where

$$\delta x_i = -\sum_j c_{ij}^2\delta\alpha_j - 2\sum_{\substack{\text{bonded} \\ j<k}} c_{ij}c_{ik}\delta\beta_{jk} \tag{14}$$

The co-efficients c_{ij} of the Hückel NBMO ($x_i = 0$) are readily obtained. The NBMO is antisymmetric or symmetric with respect to the x-axis (*cf.* III) for pentalenoid or heptalenoid molecules, respectively, and has a node along the common bond, so that $c_{ir} = c_{is} = 0$. A secular equation is, omitting the first suffix,

$$c_r(x \pm 1) + c_{r-1} + c_{r+1} = 0 \tag{15a}$$

Putting $c_r = 0$ gives $c_{r-1} = -c_{r+1}$. The next equation is

$$c_r + c_{r+1}x + c_{r+2} = 0 \tag{15b}$$

and since $x = 0$ and $c_r = 0$, $c_{r+2} = 0$. Next we find $c_{r+3} = -c_{r+1}$, and so on. All co-efficients c_{r+t} are zero for $t = 0$ or even, otherwise they are non-zero and equal in absolute magnitude with alternating sign as we proceed round the perimeter. When the molecule is pentalenoid $c_{r+1} = -c_{s-1}$, $c_{r+3} = -c_{s-3}, \ldots$ so that the NBMO is antisymmetric with respect to the x-axis; in the heptalenoid case $c_{r+1} = c_{s-1}$, etc. and the NBMO is symmetric with respect to this axis.

On applying Eq. (14) to the NBMO it is seen that the second sum vanishes since c_r and alternate co-efficients are zero. To a first approximation, therefore, a β-variation has no effect on the NBMO. In the first sum we need only consider the electron densities of those carbon atoms whose NBMO co-efficients do not vanish, i.e. of the atoms next, next but two, next but four, and so on, to the ring junctions. These electron densities can be estimated by Peters's perturbation method[15] and one finds that generally in pentalenoid molecules they are all less than 1, while in the heptalenoid types they are all greater than 1. It follows from (13) that in the former case δ_{x_i} is negative, the unfilled NBMO becomes bonding and the molecules will tend to gain two electrons to attain a closed-shell configuration; while in the latter case δ_{x_i} is positive, the filled NBMO becomes anti-bonding and these systems must lose two electrons to form closed-shell di-cations.

[15] D. Peters, *J. Chem. Soc.* 1039 (1958).

TABLE 3. DISTRIBUTION OF THE ENERGY LEVELS IN THE $4n$ BICYCLIC NON-ALTERNANT HYDROCARBONS

Perimeter	Size of rings	Type*	Method of calculation	Number of BMO's	Number of NBMO	Number of ABMO's	Closed shell configuration indicated for
4	3,3	H	HMO	1	1	2	+ ÷
			ω	1		3	+ ÷
			$\omega\beta$	1		3	+ ÷
8	3,7	H	HMO	3	1	4	+ +
			ω	3		5	+ +
			$\omega\beta$	3		5	+ +
	5,5	P	HMO	4	1	3	neutral
			ω	5		3	− −
			$\omega\beta$	5		3	− −
12	3,11	H	HMO	5	1	6	÷ +
			$\omega\beta$	5		7	+ +
	5,9	P	HMO	6	1	5	neutral
			ω	7		5	− −
			$\omega\beta$	7		5	− −
	7,7	H	HMO	5	1	6	+ +
			ω	5		7	+ +
			$\omega\beta$	5		7	+ ÷
16	3,15	H	HMO	7	1	8	+ +
			$\omega\beta$	7		9	+ ÷
	5,13	P	HMO	8	1	7	neutral
			$\omega\beta$	9		7	− −
	7,11	H	HMO	7	1	8	+ +
			$\omega\beta$	7		9	+ +
	9,9	P	HMO	8	1	7	neutral
			ω	9		7	− −
			$\omega\beta$	9		7	− −
20	3,19	H	HMO	9	1	10	+ +
			$\omega\beta$	9		11	+ +
	5,17	P	HMO	10	1	9	neutral
			$\omega\beta$	11		9	− −
	7,15	H	HMO	9	1	10	+ +
			$\omega\beta$	9		11	+ ÷
	9,13	P	HMO	10	1	9	neutral
			$\omega\beta$	11		9	− −
	11,11	H	HMO	9	1	10	+ +
			ω	9		11	+ +
			$\omega\beta$	9		11	+ +

* P = pentalenoid, H = heptalenoid

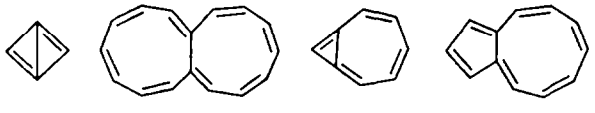
TABLE 4. ENERGY LEVELS FOR COMPOUNDS IV–VII

	HMO	ω-technique	$\omega\beta$-technique		HMO	ω-technique	$\omega\beta$-technique
IV				VI			
	−2·562	−2·697	−2·527		−2·401	−2·506	−2·382
					−1·586	−1·570	−1·524
	0·000				−1·247	−1·199	−1·173
	1·000	0·410	0·387		0·000		
	1·562	0·590	0·640				
		1·679	1·500		0·445	0·171	0·167
					1·133	0·318	0·340
					1·802	1·126	1·037
					1·854	1·752	1·665
						1·907	1·869
V	−2·253	−2·235	−2·137				
	−1·848	−1·852	−1·828				
	−1·675	−1·681	−1·643				
	−1·645	−1·638	−1·585	VII			
	−1·414	−1·419	−1·407		−2·298	−2·262	−2·156
	−0·765	−0·773	−0·788		−1·791	−1·807	−1·776
	−0·539	−0·562	−0·513		−1·576	−1·604	−1·574
	−0·233	−0·175	−0·191		−1·094	−1·085	−1·077
		−0·067	−0·065		−0·747	−0·763	−0·705
	0·000				−0·303	−0·226	−0·243
						−0·098	−0·096
	0·765	0·763	0·788		0·000		
	1·000	1·018	0·978				
	1·203	1·196	1·165		0·932	0·911	0·907
	1·414	1·413	1·399		1·197	1·200	1·169
	1·848	1·845	1·814		1·646	1·666	1·636
	1·927	1·925	1·888		1·909	1·892	1·848
	2·214	2·241	2·135		2·127	2·176	2·066

The ω- and $\omega\beta$-techniques which were shown to yield reasonable results for pentalene and heptalene are thus generally applicable to this type of compound; and it appears that the closed-shell concept may be extended to non-alternant molecules if the HMO calculations are made internally consistent.

Numerical results

The results of the perturbation methods have been verified by carrying out calculations on the fifteen bicyclic non-alternant $4n$ hydrocarbons with a perimeter of up to 20 carbon atoms. The computations were done on the London University "Atlas" computer. Iterations were continued until the matrix elements in successive cycles



IV V VI VII

differed by less than 0·001. Convergence was speeded by using averages[16] and was usually achieved after 4–5 cycles for ω- and after 7–8 cycles for $\omega\beta$-calculations. The results are summarized briefly in Table 3.* In each case the predicted pattern of the distribution of the Hückel energy levels is realized, and the predicted shift of the NBMO occurs on applying the ω- and $\omega\beta$-techniques.

Table 4 lists the energy levels of four selected hydrocarbons: bicyclobutadiene (IV), "nonalene" (V), and the mixed systems (VI) and (VII). These are all unknown but since the aromatic all-*cis* cyclononatrienide anion has been prepared[17,18] it is conceivable that the di-anions of (V) and (VII) may be sufficiently free of strain to be capable of existence.

I thank Dr. N. Singer for many stimulating discussions.

* Eigenvalues, eigenvectors, self-consistent matrix elements, electron densities and bond orders are available on request.

[16] R. Ettinger, *Tetrahedron* **20**, 1579 (1964).
[17] T. J. Katz and P. J. Garratt, *J. Amer. Chem. Soc.* **85**, 2582 (1963).
[18] E. A. LaLancette and R. E. Benson, *J. Amer. Chem. Soc.* **85**, 2583 (1963).