The Electronic Structures and Spectra of Pentalene and Heptalene

By Takeshi NAKAJIMA, Yoshiko YAGUCHI, Ryoji KAERIYAMA* and Yuzo NEMOTO**

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Recently Dauben and Bertelli[1] have reported the synthesis of the bicyclic nonbenzenoid aromatic hydrocarbon, heptalene (II), and discussed its physical and chemical properties. From the viewpoint of the molecular orbital theory, pentalene (I) is closely related to the hydrocarbon; pentalene has, however, so far defied synthesis, although the molecule has long been of interest since it was first postulated as a possible aromatic system by Armit and Robinson.[2] It should be noted that if the bridged bonds are disregarded, both these molecules are very similar to the planar cyclic polyenes with the general formula $C_{4n}H_{4n}$.

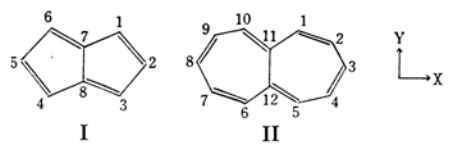

Fig. 1. Carbon skeleton, choice of axes, and numbering of pentalene and heptalene.

Early theoretical investigators,[3] presuming the molecular symmetry D_{2h} and using the simple MO and VB methods, have predicted appreciable π-electron delocalization energies for I and II and, on this basis, have suggested that the molecules may have a more or less

* Present address: Laboratory of Polymer Science, Tokyo Institute of Technology, Meguro-ku, Tokyo.
** Present address: Hitachi Chemical Co., Ltd., Chiyoda-ku, Tokyo.

1) H. J. Dauben, Jr. and D. J. Bertelli, *J. Am. Chem. Soc.*, **83**, 4659 (1961).

2) J. W. Armit and R. Robinson, *J. Chem. Soc.*, **121**, 827 (1922).

3) Reviewed by E. D. Bergmann, "Non-Benzenoid Aromatic Compounds," Ed. by D. Ginsburg, Interscience Publishers, New York (1959), p. 141. See also (a) B. Pullman and A. Pullman, "Les Théories Electroniques de la Chimie Organique," Masson, Paris (1952); and (b) C. A. Coulson and R. Daudel, "Dictionary of Values of Molecular Constants," Vol. III, D. N. R. S., Paris (1955).

pronounced aromatic character. Craig and Maccoll[4] have, on the other hand, pointed out that the two methods are discordant, even as regards such a fundamental property as the symmetry of the ground state, and in a latter paper Craig[5] has classified molecules like I and II as pseudo aromatics. In addition, Longuet-Higgins[6] has suggested that pentalene may tend to be distorted in an asymmetrical (C_{2h}) manner and to undergo, at the limit, spontaneous decomposition to give two molecules of acetylene and one of butadiyne. Boer et al.[7,8] and Snyder,[9] on the basis of a modified MO theory, have recently shown that in I and II an asymmetrical (C_{2h}) structure is more favorable energetically than the symmetrical (D_{2h}) one. A more elaborate treatment, one which explicitly includes electron repulsion, has been proposed by Silvestri et al.,[10] who have examined the ground-state electronic properties of molecules I and II by a semiempirical self-consistent field method. These authors have, however, presumed molecular symmetry D_{2h} and have not been concerned with the electronic spectra.

It is the purpose of this paper to deepen our understanding of the aromatic characteristics of I and II through an attempt to examine the ground-state electronic properties and the electronic spectra in particular by means of a semiempirical SCF method. Calculations have been carried out for the two molecular symmetry models, D_{2h} and C_{2h}, of both I and II.

Method and Procedure

The SCF technique of Roothaan[11] was employed in conjunction with the Pariser-Parr approximations,[12] with slight modifications. In computing interaction terms for adjacent atoms, the internuclear distances at each step of the iterative process are predicted from the π-bond orders, p, with the aid of the formula;[13]

$$r(\text{in Å}) = 1.520 - ap \tag{1}$$

with

$$a = 0.186 \tag{2}$$

Nonneighbor internuclear distances are calculated assuming the rings to be regular, with the bond lengths taken to be 1.397Å. The Coulomb penetration and nonneighbor resonance integrals are all disregarded. The one-center electronic repulsion integral, (pp/pp), given in the Pariser-Parr theory as $I_c - A_c$ was taken to be $11.54 - 0.46 = 11.08$ eV.,[14] while the two-center repulsion integrals, (pp/qq), were determined by the extrapolation procedure of Pariser and Parr.

In addition, the resonance integral $\beta(r)$ is supposed to vary exponentially with r according to the relation:

$$\beta(r) = -2.38 \exp[b(1.397 - r)] \text{ eV.} \tag{3}$$

with

$$b = 2.5802 \text{ Å}^{-1} \tag{4}$$

This value of b is considerably smaller than that, 5.6864 $Å^{-1}$, obtained by Pariser and Parr. The b value of Pariser and Parr was determined from $\beta(r)$ values so adjusted as to reproduce the experimental spectral data for ethylene and benzene, the bond lengths of which were taken to be 1.35 and 1.39Å respectively. The present b value was obtained by the use of the same spectral data, but using the recently observed value, 1.333Å, for the bond length of ethylene[15] and 1.397Å for that of benzene.

It is perhaps interesting to note in this connection that the applicability of the Pariser-Parr parameterization to the calculation of ground-state electronic properties has not been clearly established. In fact, Pariser-Parr's formulation, with its original parameterization, if applied to benzene in conjunction with the SCF technique, gives the unexpected result that self-consistency is achieved for two symmetry types, D_{6h} and D_{3h}, and there is good reason for believing that in such a case the skew structure (D_{3h}) is more favorable energetically than the symmetrical one (D_{6h}).[16] This absurd result is undoubtedly due to too large a value of b having been assigned by Pariser and Parr. According to the present parameterization, the symmetrical structure turns out to be most stable.

The starting molecular orbitals employed were the Hückel-type ones obtained with $\beta_{\text{single}}/\beta_{\text{double}} = 1$ for the D_{2h} model and those obtained with $\beta_{\text{single}}/\beta_{\text{double}} = 0.55$ for the C_{2h} model. In general, some ten iterative procedures were followed to achieve four-place self-consistency.

Results and Discussion

Charge Densities, Bond Orders and Free Valences. — The calculated charge densities,

4) D. P. Craig and A. Maccoll, *J. Chem. Soc.*, **1949**, 964.
5) D. P. Craig, ibid., **1951**, 3175.
6) H. C. Longuet-Higgins, "Theoretical Organic Chemistry; Kekulé Symposium," Butterworths, London (1959), p. 19.
7) P. C. den Boer-Veenendaal and D. H. W. den Boer, *Mol. Phys.*, **4**, 33 (1961).
8) P. C. den Boer-Veenendaal, J. A. Vliegenthart and D. H. W. den Boer, *Tetrahedron*, **18**, 1325 (1962).
9) L. C. Snyder, *J. Phys. Chem.*, **66**, 2299 (1962).
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13) T. Nakajima and S. Katagiri, *Mol. Phys.*, **6**, (1963) in press.
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TABLE I. CHARGE DENSITIES, BOND ORDERS AND FREE VALENCES

Molecule	Molecular symmetry	Atom	Charge density	Free valence	Bond	Bond order
Pentalene	D_{2h}	1	0.797	0.558	1— 2	0.657
		2	1.176	0.417	1— 7	0.517
		7	1.230	0.173	7— 8	0.525
	C_{2h}	1	0.975	0.581	1— 2	0.923
		2	1.048	0.506	1— 7	0.229
		3	0.917	0.550	2— 3	0.303
		7	1.060	0.321	3— 8	0.879
					7— 8	0.303
Heptalene	D_{2h}	1	1.158	0.527	1— 2	0.676
		2	0.851	0.435	1—11	0.529
		3	1.153	0.489	2— 3	0.621
		11	0.829	0.186	11—12	0.487
	C_{2h}	1	1.002	0.546	1— 2	0.919
		2	0.983	0.513	1—11	0.267
		3	1.017	0.524	2— 3	0.301
		4	0.979	0.509	3— 4	0.908
		5	1.042	0.540	4— 5	0.315
		11	0.977	0.310	5—12	0.878
					11—12	0.278

bond orders, and free valences for the two molecular symmetry types are summarized in Table I. In both I and II, the charge distributions for the asymmetrical models are remarkably smoothed out as compared with those for the symmetrical models. In contrast to this, the distributions of bond orders for the asymmetrical models are significantly uneven. The predicted bond lengths are 1.35 to 1.36Å for the double bonds and 1.46 to 1.48Å for the single bonds, the extent of bond length alternation being comparable to those in such chain polyenes as butadiene. From the viewpoint of the chemical reactivity, of particular notice is the fact that the free valences of the peripheral (secondary) carbon atoms of I and II, particularly for the asymmetrical models, are considerably larger than those for classical aromatic molecules (e. g., benzene, 0.40). Both of these molecules are thus expected to be highly susceptible to homolytic reactions. This is in agreement with the available experimental facts. Heptalene has been known readly to undergo polymerization by oxygen or mild warming.[1] In addition, the free valence numbers indicate that in I and II the highest reactivity should be expected at the ortho-positions. As regards II, this has also been confirmed experimentally.

The Total Electron Energy. — Now let us enquire which of the symmetrical and asymmetrical models is more favorable energetically. It has been emphasized[17,18] that a conclusion regarding the stability or the equilibrium configuration of a conjugated molecule cannot be based on π-electron calculations only; allowance for the effects of the σ-bond compression must also be made. Obviously the total electron energy should be considered in comparing the energetic stabilities of the two models. Using the assumptions of Longuet-Higgins and Salem,[17] the total binding energy of a conjugated molecule, taken to be the sum of π-bond energy and σ-bond energy, is given by

$$V=E_\pi+E_\sigma=(2/ab)\sum_{p<q}\overline{\beta}_{pq}+\sum_p q_p\overline{\alpha}_p+\text{const.} \tag{5}$$

in which we assume

$$\overline{\beta}(r)=\overline{\beta}_0\exp[\overline{b}(1.397-r)] \tag{6}$$

$$\overline{\alpha}_p=\overline{\alpha}_0+\omega(1-q_p)\overline{\beta}_0 \tag{7}$$

where ω is a proportionality coefficient here taken to be unity. Equation 6 differs from Eq. 3. $\beta(r)$ is the core resonance integral. On the other hand, $\overline{\beta}(r)$ should be interpreted as an effective resonance integral which includes an electron interaction term;* the value 4.5988

17) H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.*, **A251**, 172 (1959).
18) C. A. Coulson and W. T. Dixon, *Tetrahedron*, **17**, 215 (1962).

* Explicitly, β_{pq} may be expressed as $(\beta_{pq}+\beta^F_{pq})/2$, where $\beta^F_{pq}=\beta_{pq}-\frac{1}{2}p_{pq}(pp/qq)$.[16]

TABLE II. PREDICTED AND OBSERVED SINGLET TRANSITIONS

Molecule	Molecular symmetry	Transition type	Excitation energy, eV.		f, c. g. s.	
			Calcd.	Obs.	Theor.*	Obs.
Pentalene	D_{2h}	$B_{1g}\leftarrow A_{1g}$	0.75		Forb.	
		$B_{3u}\leftarrow A_{1g}$	3.73		0.75 (x)	
		$B_{2u}\leftarrow A_{1g}$	4.99		0.52 (y)	
	C_{2h}	$A_g\leftarrow A_g$	2.43		Forb.	
		$B_u\leftarrow A_g$	4.54		0.64	
		$B_u\leftarrow A_g$	5.64		0.51	
Heptalene	D_{2h}	$B_{1g}\leftarrow A_{1g}$	0.67		Forb.	
		$B_{3u}\leftarrow A_{1g}$	3.18		1.29 (x)	
		$B_{2u}\leftarrow A_{1g}$	4.06		0.64 (y)	
	C_{2h}	$A_g\leftarrow A_g$	2.72	Tail	Forb.	Tail
		$B_u\leftarrow A_g$	4.10	3.52	0.76	0.15
		$B_u\leftarrow A_g$	4.93	4.84	0.44	?

* Theoretical f values for pentalene were calculated using the predicted transition energies (in cm^{-1}) for ν in Eq. 8.

$Å^{-1}$ is taken for the parameter, $\bar{b}$.[13] The total energy values thus calculated indicate that in both I and II the asymmetrical structures are more favorable energetically than the symmetrical ones, the deformation energies which favor the structures being, respectively, -0.52 and $-0.58\bar{\beta}_0$, about 10 kcal./mol., if we take $\bar{\beta}_0=-16.5$ kcal./mol.[19] These figures are appreciable, and it is now clear that in I and II there exists a significant bond length distortion, one comparable in extent to those in linear chain polyenes. Such alternating bond lengths, if molecules I and II are treated as slightly perturbed hypothetical planar cyclooctatetraene and cyclodoecahexaene respectively, may be understood to be due to a pseudo Jahn-Teller effect.[20]

Electronic Spectra.—The calculated energies and oscillator strengths, f, for the lower singlet electronic transitions in I and II are summarized in Table II. No configuration interactions were allowed for (see below), and the theoretical f values were all obtained by the use of the well-known formula;

$$f_{th}=1.085\times10^{11}\nu Q^2 \qquad (8)$$

It may be noted that the f_{th} values calculated using Eq. 8 are usually about three times as large as the f_{obs} values.

It may be seen that, in both I and II, in passing from the symmetrical (D_{2h}) to the asymmetrical model (C_{2h}), the transition energies (particularly for the lowest (forbidden) transitions) increase, while the f_{th} values decrease, and in heptalene the C_{2h} model leads to numerical results in good agreement with experimental data. In this molecule the longest wavelength maximum is assigned to an electronic transition, $B_u\leftarrow A_g$, polarized approximately along the long axis (x), whereas the next maximum is assigned to a transition of the same type but with a moment roughly parallel to the short axis (y). The longest wavelength maximum is accompanied by an almost linearly decreasing absorption tail throughout the visible region. Such a tail may arise from a forbidden transition becoming partially allowed by molecular vibrations or twisting, and from transitions which take place according to the Franck-Condon process between a ground and an excited state having potential energy curves appreciably different in shape from each other. It has been shown[19] that in heptalene the potential energy curve for the lowest excited state differs considerably in shape from that for the ground state, the former having a single potential energy minimum, whereas the latter has a double minimum.

Recently hexaphenyl pentalene has been synthesized by Le Goff.[21] The absorption spectrum of this molecule shows a weak maximum at 13900 cm^{-1} (1.72 eV.) with $\log\varepsilon=1.95$ and followed by a long tail. This maximum may perhaps be assigned to the predicted forbidden transition, $A_g\leftarrow A_g$, in pentalene, which is allowed and shifted toward the red by the substitution.

In molecules I and II, if they are distorted in an asymmetrical mannar, a configuration interaction is possible between the ground and the lowest excited state, as the symmetry

19) T. Nakajima, "Molecular Orbitals in Chemistry, Physics and Biology," Ed. by P. O. Löwdin and B. Pullman, Academic Press, New York (1963), in press.
20) C. A. Coulson, *Chem. Soc. (London) Spec. Publ.*, No. 12, 85 (1958).
21) E. Le Goff, *J. Am. Chem. Soc.*, **84**, 3975 (1962).

groups of the two states are both A_g in distorted structures. Insofar as the distortion remains slight, this interaction may be of primary importance, and heavy mixing of the two states will occur, the ground state being substantially depressed in energy (pseudo Jahn-Teller effect).[6] However, in the asymmetrical structures here achieved, the interaction is of little importance, for the two states are well separated in energy from each other. In fact, in heptalene the lowering of the ground state energy caused by the interaction is calculated to be only about 0.1 eV. The SCF technique considerably reduces the effects of the configuration interaction.

Ionization Potentials. — In Roothaan's SCF formulation the ionization potentials are approximated by the orbital energies (Koopmans' theorem). Although this approximation has recently been criticized,[22-24] the orbital energies may still give at least an indication of the relative magnitude of ionization potentials. The orbital energies, $\varepsilon - W_{2p}$ (where W_{2p} is the ionization potential of the $2p\pi$-electron of the carbon atom) for the top occupied orbitals of I and II are calculated to be 1.55 (D_{2h}) and 0.84 (C_{2h}), and 3.20 (D_{2h}) 2.17 eV. (C_{2h}) respectively. It should be noted that, while in general $\varepsilon - W_{2p}$ values are negative for the top occupied orbitals (and for all other occupied orbitals), the values turn out to be positive in I and II. This indicates that the ionization potentials of these molecules are exceptionally small; in this sense they are unstable, the symmetrical structures being less stable than the asymmetrical ones.

22) R. D. Brown and A. Heffernan, *Trans. Faraday Soc.*, 54, 757 (1958).
23) J. R. Hoyland and L. Goodman, *J. Chem. Phys.*, 33, 946 (1960).
24) Y. I'Haya, *Mol. Phys.*, 3, 513 (1960).

Summary and Conclusion

The semiempirical SCF technique has been applied to pentalene and heptalene. Self-consistency has been achieved for the two symmetry types, D_{2h} and C_{2h}, and the total binding energy examination indicates that in both the molecules the asymmetrical structure (C_{2h}) is more favorable energetically than the symmetrical one (D_{2h}). The calculated uneven charge distributions, the high free valence values, and the low ionization potentials supply the reasons for the instability of these molecules. The theoretical spectral calculations for the asymmetrical structures are in good agreement with the available experimental data. It may be concluded that, in these molecules, there exists a remarkable bond length alternation, and that in this sense they cannot be considered aromatic. They show, rather, characteristics of cyclic polyolefins.

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Department of Chemistry
Ibaraki University
Watarai-cho, Mito