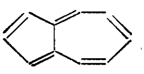
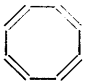
207. *The Non-benzenoid Aromatic Hydrocarbon Pentalene. A Theoretical Discussion.*

By D. P. Craig and Allan Maccoll.

Pentalene is an unknown hydrocarbon with two fused five-membered rings and four double bonds. Reported attempts to prepare it have failed. A quantum-mechanical study by the valence-bond and the molecular orbital method is given. This shows, on both views, that a considerable resonance energy ought to be associated with the molecule (comparable with benzene). But in the valence-bond method this large resonance energy is developed in a state which lacks the full symmetry of the carbon framework. Bond orders for the molecule are reported in both approximations, and the energies of the lowest triplet and excited singlet states are calculated.

A NUMBER of non-benzenoid aromatic hydrocarbons, such as azulene (I) and *cyclo*octatetraene (II) are now well known (see Baker, *J.*, 1945, 258) but there are still some apparently simple molecules in this class which have not been prepared. This paper will be primarily concerned with pentalene (III), although heptalene (IV) is in some ways similar. *cyclo*Butadiene (V) has been considered by Penney (*Proc. Roy. Soc.*, 1934, **146**, *A*, 233) and recently by Coulson and Moffitt. The latter have shown that its stability is marginal (private communication, and see also *J. Chem. Physics*, 1947, **15**, 151). Both pentalene and heptalene have resisted attempts at preparation. Barrett and Linstead (*J.*, 1936, 612) sought to prepare the former, and Horn, Nunn, and Rapson (*Nature*, 1947, **160**, 830) the latter. Neither attempt was successful. It is striking, too, that no derivatives of these molecules have been reported as occurring naturally, yet those of azulene are well known. Further, the considerations which assist the organic chemist in assessing the chances of preparing a given molecule do not afford any very convincing grounds for believing that either pentalene or heptalene should be specially set apart from azulene.


(I.)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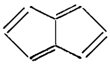
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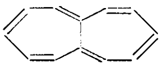
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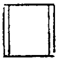

(V.)

A theoretical study of pentalene is now given. It is found that in the valence-bond approximation, pentalene (and this applies equally to heptalene) has a feature which distinguishes it from azulene, and from the usual six-membered ring hydrocarbons. The difference lies in the symmetry properties of the wave function which describes the ground state of the aromatic (π) electrons : in azulene and all the benzenoid hydrocarbons this wave function has the full symmetry of the carbon " skeleton ", but in pentalene and heptalene this is no longer true and the ground state wave functions show properties of anti-symmetry which in other molecules are associated only with *excited* molecular states. That this should make pentalene and heptalene difficult to prepare must be admitted to be intuitive rather than logical.

The Quantal Treatment.—The quantal treatment of conjugated molecules depends upon the classification of the valency electrons. Carbon in its quadrivalent state has the structure $1s^2 2s 2p^3$. The $2s$, $2p_x$, $2p_y$ orbitals are hybridised to form the so-called trigonal or σ orbitals (see Coulson, *Quart. Reviews*, 1947, **1**, 144), while the $2p_z$ or π orbitals retain their individuality. The σ orbitals are used to form the framework C–C and C–H bonds, and the π orbitals, one for each carbon atom, give the conjugation properties. The usual quantal approximation to conjugated systems treats only the π electrons. Two methods of attack are in common use. In the first, the valence-bond (V.B.) method, account is taken of the fact that the π electrons may be paired in a number of different ways. Each of these ways of pairing corresponds with a structure, no single one being an adequate representation of the state of the molecule. A better representation is given by a combination of the structures, and quantum theory shows how to obtain the combination with the lowest energy. This process of minimising the energy gives rise to the quantum-mechanical secular equation, the roots of which are approximations to the energy levels of the molecule.

In the second method, the method of molecular orbitals (M.O.), the energy levels of a single π electron are found in the combined potential field of the nuclei and of the other electrons. The energy is determined with the use of molecular orbitals formed by linear combination of atomic orbitals, one for each carbon atom. Minimising the energy leads to another secular equation, the roots of which are the energies of the single-electron m.o.s. The electrons are fed, two at a time, into the orbitals of lowest energy, and the molecular energy is found by adding the energies of the occupied orbitals.

Both methods have been much used to calculate the resonance energies of molecules. In each case the resonance energy is the energy difference between the calculated ground state and a hypothetical structure in which the π electrons are localised in specified bonds. In the V.B. method results are obtained in terms of α, the quantum-mechanical exchange integral, and in the M.O. they are obtained in terms of γ, the resonance integral. No attempt is made to compute these integrals : they are evaluated empirically. Wheland (*J. Amer. Chem. Soc.*, 1941, **63**, 2025) has shown that for a large number of molecules the two methods are in agreement, provided γ is set equal to $0{\cdot}55\alpha$. However, Coulson and Rushbrooke (*Proc. Camb. Phil. Soc.*, 1940, **36**, 193) have put forward reasons for supposing that the M.O. method may not be reliable in the case of pentalene, and indeed a discrepancy between the two methods has been noticed by Syrkin and Diatkina (*Acta Physicochim. U.R.S.S.*, 1946, **21**, 641).

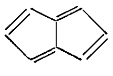
The energy difference between the ground and the first excited molecular level is called the transition energy, and corresponds with the long-wave-length absorption frequency of the molecule. The V.B. method has been very successful in accounting for the light absorption of conjugated systems (Maccoll, *Quart. Reviews*, 1947, **1**, 16); but the M.O. method suffers from the fact that in it the first excited state has both singlet and triplet components, and the separation of these is left out of consideration; consequently, transition energies are not so accurately calculable as in the V.B. treatment.

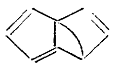
The methods have been used for a calculation of the bond distances of molecules (Penney, *Proc. Roy. Soc.*, 1937, **158**, *A*, 306; Coulson, *ibid.*, 1939, **169**, *A*, 413). The results are expressed in terms of the bond order, which is empirically related to the bond distance. The agreement between the two methods is good for the majority of molecules.

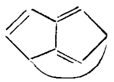
Most molecules have a singlet ground state, that is, the π electron spins are coupled to give zero resultant spin. In pentalene it seemed possible that the ground state might be a triplet, *i.e.*, that it might have two of its electrons unpaired. The V.B. method, with its explicit account of electron spin, is the more suitable to test this possibility.

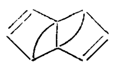
In the present paper the two methods are used to calculate the resonance energy, light absorption, and bond orders for pentalene. In addition, for the reason that has been explained, the V.B. method is used for a calculation of the lowest triplet level.

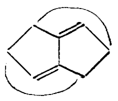
The Valence-bond Method.—Singlet states. This method starts with a canonical set of structures (Rumer, *Göttingen Nachr.*, 1932, 337), in terms of which any structure may be represented by appropriate linear combination. There are 14 canonical structures for pentalene, two with all " effective " bonds (*A*), eight with one " ineffective " bond (*B* and *C*), and four with two " ineffective " bonds (*D* and *E*). Typical structures are :


A_1 (2).

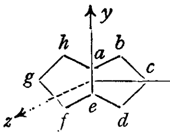

B_1 (4).


C_1 (4).


D_1 (2).


E_1 (2).

The complete secular equation is then of the fourteenth degree. However, symmetry may be used to reduce it to two fifth-degree equations and two quadratics. Pentalene has the symmetry D_{2h}. Each of the structures of the canonical set is associated with a bond eigen-function, and to reduce the secular equation transformation properties of these bond eigen-functions have to be found under the characteristic symmetry operations of the group. These operations are in Table I, with the axes shown in (VI).



(VI.)

TABLE I.

Symmetry type.	Rotn. about $x(C_2^x)$.	Rotn. about $y(C_2^y)$.	Rotn. about $z(C_2^z)$.
A	+	+	+
B_{1g}	—	—	+
B_{2u}	—	+	—
B_{3u}	+	—	—

The transformation properties of the bond eigen-functions are shown in Table II.

TABLE II.

	Eigen-function.				
Operation.	A_1	B_1	C_1	D_1	E_1
C_2^x	$-A_2$	$-B_2$	$-C_2$	$-D_2$	$-E_2$
C_2^y	$-A_2$	$-B_3$	$-C_3$	$-D_2$	$-E_2$
C_2^z	A_1	B_4	C_4	D_1	E_1

The group representation afforded by the bond eigen-functions can now be broken up into its irreducible representations. This gives

$$\Gamma = 5A_g + 5B_{1g} + 2B_{2u} + 2B_{3u}$$

Tables II allows linear combinations of the bond eigen-functions of the correct symmetry types to be formed. The advantage of using these linear combinations is that matrix elements between two of different symmetry types are zero. Only the B_{1g} and A_g representations are required, as these contain respectively the ground and the first excited states. The proper linear combinations are

$$B_{1g} : \Psi_{Gd} = N_A(\psi_{A_1} + \psi_{A_2}) + N_B(\psi_{B_1} + \psi_{B_2} + \psi_{B_3} + \psi_{B_4}) + \\ N_C(\psi_{C_1} + \psi_{C_2} + \psi_{C_3} + \psi_{C_4}) + N_D(\psi_{D_1} + \psi_{D_2}) + N_E(\psi_{E_1} + \psi_{E_2})$$

$$A_g : \Psi_{Ex} = N_A'(\psi_{A_1} - \psi_{A_2}) + N_B'(\psi_{B_1} - \psi_{B_2} - \psi_{B_3} + \psi_{B_4}) + \\ N_C'(\psi_{C_1} - \psi_{C_2} - \psi_{C_3} + \psi_{C_4}) + N_D'(\psi_{D_1} - \psi_{D_2}) + N_E'(\psi_{E_1} - \psi_{E_2})$$

The matrix elements between the bond eigen-functions have been found by Pauling's method (*J. Chem. Physics*, **1933**, **1**, 280). The following secular equations were obtained for the B_{1g} and the A_g states :

$$\mathrm{B}_{1g} : \begin{vmatrix} 3/6 & 4/12 & 4/14 & 2/3 & 2/5 \\ 4/12 & 10/10 & 6/18 & 4/8 & 4/10 \\ 4/14 & 6/18 & 10/14 & 2/8 & 4/10 \\ 2/3 & 4/8 & 2/8 & 3/-2 & 1/2 \\ 2/5 & 4/10 & 4/10 & 1/2 & 3/-2 \end{vmatrix} = 0$$

$$A_g : \begin{vmatrix} 7/6 & 4/12 & 4/6 & 2/-9 & 2/-3 \\ 4/12 & 10/6 & -2/6 & -4/0 & 2/6 \\ 4/6 & -2/6 & 10/-6 & 2/0 & -4/6 \\ 2/-9 & -4/0 & 2/0 & 7/-18 & 1/-6 \\ 2/-3 & 2/6 & -4/6 & 1/-6 & 7/-18 \end{vmatrix} = 0$$

where x/y stands for $x(Q - W) + y\alpha$, W being the energy of the system, Q the Coulomb, and α the exchange integral. Four methods of solution were used : (I) Only the two structures *A* considered. (II) Structures *A* and *B* used, the latter all being given the same coefficient. (III) Structures *A* and *B* used, the latter being considered in two groups. (IV) The complete set used. The results are shown in Table III. The transition energy ($B_{1g} \longrightarrow A_g$) has been calculated, using the same approximation for the excited as for the ground state.

Table III.

Assumption.	$\frac{E-Q}{a}$.	Resonance energy.	Transition energy.	Ground-state wave function.				
				N_a.	N_b.	N_c.	N_d.	N_e.
(I)	2·000	0·50	1·143	0·5773	0	0	0	0
(II)	2·529	1·05	1·102	0·3189	0·0878	0·0878	0	0
(III)	2·559	1·06	0·976	0·3692	0·0655	0·1364	0	0
(IV)	2·597	1·10	0·867	0·3557	0·0704	0·1047	0·0685	0·0276

The best value for the resonance energy is thus 1·10α, and the ground-state wave function has the symmetry properties of B_{1g}.

The bond orders given in Table IV have been found from the calculated energies according to Penney's definition of bond order (*loc. cit.*). The definition depends on a theorem of Dirac, which shows that the energy effects between two electrons due to the quantum-mechanical exchange phenomenon can be dealt with as if they came from a cosine coupling between the electron spins. By dividing the electrons in a complex system into pairs, the electronic energy can be written :

$$W = \text{const.} - \tfrac{1}{2} \sum_{i \neq j} \alpha_{ij}(1 + 4\,\overline{\mathbf{s}_i \,.\, \mathbf{s}_j})$$

In this expression, α_{ij} is the exchange integral between the orbitals i and j, and the quantity $\overline{\mathbf{s}_i \,.\, \mathbf{s}_j}$ is the scalar product of the spin vectors of the electrons in these orbitals. Binding is greatest when the spins are antiparallel; the spin product then has the value $-3/4$, corresponding with a bond between the orbitals. If there is no bond, the value is zero. Penney therefore defined the bond order, p_{ij}, as

$$p_{ij} = -4/3\,\overline{\mathbf{s}_i \,.\, \mathbf{s}_j}$$

In dealing with π-electron bonds in unsaturated molecules, the π-bond order is therefore 0 for a single bond, 1 for a double bond, and has intermediate values for bonds with partial double-bond character. The meaning of a negative bond order in this scheme is as follows. When the bond order is zero, there is still a repulsive interaction between the electrons, due to the appearance of a constant term in the bracketed part of the energy expression, which is left over when the spin term vanishes. Thus a negative bond order means that there is a repulsion between the electrons greater than given by this constant term. The greatest negative bond order is $-1/3$, when the system of two electrons is in its triplet state, with spins parallel.

To find the bond orders, the energy of the molecule is determined in terms of the α_{ij}'s, and the $\overline{\mathbf{s}_i \cdot \mathbf{s}_j}$ values obtained. For example, from the fourth entry in Table III,

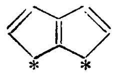
$$W_{gd.} = \text{const.} + 1{\cdot}7809\alpha_{ab} + 1{\cdot}3790\alpha_{bc} - 0{\cdot}5833\alpha_{ae}$$

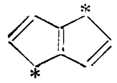
where α_{ij} is the exchange integral between atoms i and j. This leads to the bond order $p_{ab} = 0{\cdot}630$, $p_{bc} = 0{\cdot}566$, and $p_{ae} = -0{\cdot}056$. The results to the various approximations are shown in Table IV. The results for the ground state as calculated by the M.O. method are given for comparison. It is shown later, however, that the two methods actually describe *different* states as the ground state, so that no agreement between the last entries in each column and the others is to be looked for.

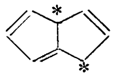
TABLE IV.

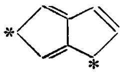
Approximation.	p_{ab}.	p_{bc}.	p_{ae}.
(I)	0·556	0·556	−0·117
(II)	0·607	0·607	−0·170
(III)	0·627	0·582	−0·130
(IV)	0·630	0·566	−0·056
M.O.	0·524	0·650	0·530

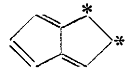
The triplet levels. In order to explore the possibility that the ground state of pentalene might be one having two unpaired electrons, the triplet levels were calculated using the following structures:

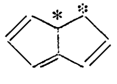

A_1 (2).


B_1 (2).


C_1 (4).


D_1 (4).


E_1 (4).


F_1 (4).

The asterisks indicate the unpaired electrons. The other structures in the set are obtained by rotations around the symmetry axes as shown in Table V. Not all these structures are members of a canonical set. Such a set as is used here has been used for the treatment of naphthalene (Craig, XIth International Congress of Pure and Applied Chemistry, London, 1947), and has the advantage over a canonical set in that there are many equalities among the matrix elements and so the labour of computation is reduced. It is, of course, important to verify that the structures selected are independent. This has been done. All long-bonded structures have been neglected. Structures E and F roughly correspond to the long-bonded structures of the singlet state calculations in that they are destabilised compared with the others by the adjacent electrons with parallel spins.

The transformation properties of the structures are shown in Table V.

TABLE V.

	Eigen-function.					
Operation.	A_1	B_1	C_1	D_1	E_1	F_1
C_2^z	$-A_2$	$-B_1$	C_4	D_4	E_4	F_4
C_2^y	$-A_1$	B_2	C_3	D_3	E_3	F_3
C_2^x	A_2	$-B_2$	C_2	D_2	E_2	F_2

With the aid of the transformation table it can be shown that the reducible representation of the structures breaks up as follows:

$$\Gamma = 4A_g + 5B_{1g} + 5B_{2u} + 6B_{3u}$$

The secular equation thus factors into a sixth-, two fifth-, and one fourth-degree equation. The lowest root is found in the B_{1g} set, and the variation function is

$$\Psi = \mathrm{F}(\psi_{A_1} + \psi_{A_2}) + \mathrm{G}(\psi_{C_1} - \psi_{C_2} - \psi_{C_3} + \psi_{C_4}) + \mathrm{H}(\psi_{D_1} - \psi_{D_2} - \psi_{D_3} + \psi_{D_4}) + \mathrm{I}(\psi_{E_1} - \psi_{E_2} - \psi_{E_3} + \psi_{E_4}) + \mathrm{J}(\psi_{F_1} - \psi_{F_2} - \psi_{F_3} + \psi_{F_4})$$

This leads to the secular equation

$$\begin{vmatrix} 3/-3 & 3/5 & -3/-7 & 2/6 & 0/4 \\ 3/5 & 14/15 & -9/-21 & 6/14 & 8/12 \\ -3/-7 & -9/-21 & 14/15 & 8/16 & 6/9 \\ 2/6 & 6/14 & 8/16 & 10/2 & 2/14 \\ 0/4 & 8/12 & 6/9 & 2/14 & 10/-2 \end{vmatrix} = 0$$

This equation has been solved under the following approximations: (I) Structures E and F excluded: (i) all structures given equal weight (and taken with proper sign); (ii) the full cubic solved. (II) All structures considered: (i) all given equal weight; (ii) structures E and F and the remainder grouped, and the quadratic solved. The results are shown in Table VI.

TABLE VI.

Assumption.	$(E - Q)/a$.	F.	G.	**H.**	I.	J.
I (i)	1·525	0·1280	0·1280	−0·1280	0	0
I (ii)	1·583	0·0464	0·1377	−0·1445	0	0
II (i)	1·676	0·0830	0·0830	−0·0830	0·0830	0·0830
II (ii)	1·677	0·0872	0·0872	−0·0872	0·0760	0·0760

The lowest triplet level lies above the lowest singlet level by $0{\cdot}920\alpha$.

The Molecular-orbital Treatment.—A molecular orbital is built up from atomic orbitals, one for each carbon atom. This function is used as a basis for a variational treatment. The secular equation will be of the eighth degree, but symmetry may be used to simplify it. The atomic orbitals form a representation of the group D_{2h}, and this may be broken up into its irreducible representations, giving

$$\left.\begin{aligned}\phi_1 &= \psi_a + \psi_e\\ \phi_2 &= \psi_b + \psi_d + \psi_f + \psi_h\\ \phi_3 &= \psi_c + \psi_g\end{aligned}\right\} B_{1u} \qquad \left.\begin{aligned}\phi_4 &= \psi_a - \psi_e\\ \phi_5 &= \psi_b - \psi_d - \psi_f + \psi_h\end{aligned}\right\} B_{3g}$$

$$\left.\begin{aligned}\phi_6 &= \psi_c - \psi_g\\ \phi_7 &= \psi_b + \psi_d - \psi_f - \psi_h\end{aligned}\right\} B_{2g} \qquad \phi_8 = \psi_b - \psi_d + \psi_f - \psi_h \; \} \; A_u$$

The secular equation thus factors into a cubic, two quadratics, and a linear equation. The cubic equation, for example, is

$$\begin{vmatrix} x & 2 & 2 \\ 2 & 2(x+1) & 0 \\ 2 & 0 & 2x \end{vmatrix} = 0$$

where $x = (q - e)/\gamma$, q being the Coulomb and γ the resonance integral. The usual neglect of resonance integrals involving non-adjacent atoms and of non-orthogonality of atomic orbitals on different nuclei has been made. Mulliken (*J. Amer. Chem. Soc.*, 1941, **63**, 41) and Wheland (*ibid.*, p. 2025) have shown how this neglect may be avoided. Below are given the four lowest orbitals together with the energies by both the simple (e) and the Mulliken–Wheland (e') treatment:

$$B_{1u}\ \psi_1 = 0{\cdot}4735(\psi_a + \psi_e) + 0{\cdot}3179(\psi_b + \psi_d + \psi_f + \psi_h) + 0{\cdot}2714(\psi_c + \psi_g)$$
$$e_1 = q + 2{\cdot}343\gamma \qquad e_1' = q' + 1{\cdot}480\beta$$

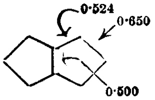
$$B_{2g}\ \psi_2 = 0{\cdot}5000(\psi_c - \psi_g) + 0{\cdot}3535(\psi_b + \psi_d - \psi_f - \psi_h)$$
$$e_2 = q + 1{\cdot}414\gamma \qquad e_2' = q' + 1{\cdot}041\beta$$

$$B_{3g}\ \psi_3 = 0{\cdot}5774(\psi_a - \psi_e) - 0{\cdot}4082(\psi_b - \psi_d - \psi_f + \psi_h)$$
$$e_3 = q + 1{\cdot}000\gamma \qquad e_3' = q' + 0{\cdot}800\beta$$

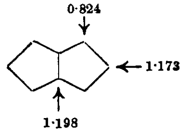
$$B_{1u}\ \psi_4 = -0{\cdot}4560(\psi_a + \psi_e) - 0{\cdot}1207(\psi_b + \psi_d + \psi_f + \psi_h) - 0{\cdot}5125(\psi_c + \psi_g)$$
$$e_4 = q + 0{\cdot}471\gamma \qquad e_4' = q' + 0{\cdot}421\beta$$

The total energy of the molecule in its ground state is thus $8q + 10{\cdot}456\gamma$, or $8q' + 7{\cdot}484\beta$, the resonance energy being $2{\cdot}456\gamma$ or $1{\cdot}084\beta$. The M.O. method, of course, describes as totally symmetrical the state of lowest energy, for in that state all the orbitals are doubly filled, and all therefore contribute a totally symmetrical part to the molecular wave function.

Coulson and Rushbrooke (*loc. cit.*) have examined pentalene in the molecular-orbital approximation, and the bond orders which come from their results are shown in the diagram below. They point out, however, that the molecular-orbital treatment cannot be carried through in a satisfactory way for any of the molecules pentalene, azulene, or heptalene, for in all these cases the method finds that the π electrons are not uniformly distributed over the carbon atoms, but tend to accumulate at certain points at the expense of others. The distribution found for pentalene by Coulson and Rushbrooke is shown in the diagram below. Such a difficulty can only arise in the valence-bond method when polar structures are taken into account;



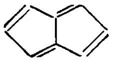
Bond orders.



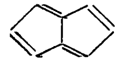
π electron density.

otherwise all the states must have exactly one π electron per carbon atom. In other words the valence-bond method encounters no difficulty of procedure to match that encountered here by the M.O. method.

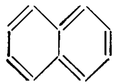
Discussion of the Results.—The most striking difference between the two methods is the predicted symmetry of the ground and the first excited state. The non-totally symmetrical ground state for pentalene in the valence-bond method arises from the fact that under the conditions which give the ground state as a sum of canonical structures, structure A_1, for example, is transformed into $-A_2$ by rotation about the x and y axes. This is to be compared



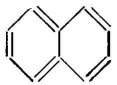
(A_1.)



(A_2.)



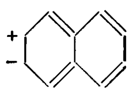
(P.)

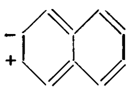


(Q.)

with the case of naphthalene, which is typical of all hydrocarbons built up from six-membered rings and for which (P) goes into (Q) under the second of these operations. The same discrepancy between the two methods of treatment is met with in *cyclo*butadiene and the planar model of *cyclo*octatetraene. In the M.O. treatment it is readily seen that this method *must* lead to a totally symmetrical ground state, except in those cases where orbital degeneracy occurs. This is the case, for example, in *cyclo*butadiene (Wheland, *Proc. Roy. Soc.*, 1938, **164**, *A*, 397), in which the orbital of lowest energy is of symmetry A_{2u}, and then there is a pair of degenerate orbitals of symmetry E_g. The lowest state thus has the symmetry $(A_{2u})^2(E_g)^2$, so that if the orbital degeneracy were removed the four states would have the symmetries A_{1g}, A_{2g}, B_{1g}, and B_{2g}. A more complete treatment, *i.e.*, the inclusion of electron repulsion, would remove the degeneracy and separate the above four levels.

Another aspect of the same problem is the lack of self-consistency in the M.O. treatment, which is brought to light by the appearance of charge separation. The reason for this is readily understood by a consideration of what in the V.B. method would be called polar structures. For a molecule like naphthalene the structures shown below have equal coefficients in the M.O. wave function :

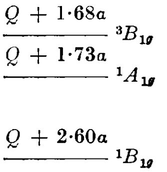


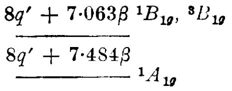


However, for pentalene the corresponding two structures come into the molecular wave function with unequal coefficients, giving a net charge drift. The difficulty then arises because of the over-emphasis placed on structures involving charge separation by the M.O. method. The V.B. method, with its neglect of polar structures, does not lead to any inconsistency. In view of the different symmetries of the ground states predicted by the two methods there is no point in carrying the comparison between the states further.

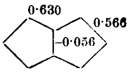
The same symmetry difficulty is found with heptalene : again the ground and first excited states in the V.B. approximation have the symmetries B_{1g} and A_g, respectively. In azulene, there is only a single axis of symmetry and the ground state of this molecule is symmetric to rotation around the axis. Thus *cyclo*butadiene, pentalene, and heptalene are singled out from naphthalene and azulene in that their ground states are not totally symmetrical. In speaking of a non-totally symmetrical ground state it is, of course, not implied that the electron distribution is unsymmetrical, for the V.B. method cannot give that result. The difference between pentalene and naphthalene in their ground states is that the wave function for the first changes sign under certain symmetry operations, whereas for naphthalene it is invariant.

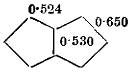
The energy levels and bond orders are summarised below.





V.B. M.O.





The small negative bond order obtained by the Penney method for the bond between the atoms common to the two rings indicates that there is a weak repulsive interaction exerted by the π electrons across this bond. However, the magnitude of the resonance energy ($1{\cdot}10\alpha$) shows that the interaction of the π electrons as a whole is quite strongly stabilising—not much less, per electron, than in benzene. The resonance splitting between the ground and the first excited state is such as to suggest a long wave-length absorption band at about 6600 A., so that the molecule would be deeply coloured according to the V.B. theory.

The M.O. treatment of pentalene and heptalene is inconsistent. There is, however, no evident difficulty with the V.B. method, which can be carried through just as for an " ordinary " molecule. If therefore it can be concluded that the V.B. is here the more reliable account, pentalene should have a considerable resonance energy, about the same, per π electon, as azulene and a little less than benzene. The symmetry of the ground state is a qualitative feature which distinguishes pentalene and heptalene from known hydrocarbons, but it is not clear what connection this has with the fact that these molecules have neither been found in Nature nor prepared chemically.

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