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VALENCY-BOND STUDIES OF SOME CONJUGATED HYDROCARBONS—II

PENTALENE, AND SOME PRELIMINARY RESULTS ON HEPTALENE

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Abstract—Valency-bond studies of the still unknown molecule pentalene C_8H_6 in which the molecular symmetry may be either D_{2h} or C_{2h} show that a more stable molecule (lower ground state energy) is found for the lower symmetry, and that marked alternation of bond lengths occurs. The corresponding Penney-Dirac bond orders have been determined. Preliminary results for heptalene forecast a similar conclusion.

INTRODUCTION

CRAIG and Maccoll,[1] assuming that the molecular symmetry of pentalene is D_{2h} (Fig. 1a of the present communication), showed that application of valency-bond and molecular-orbital methods to this still unknown molecule led to different symmetries for its ground state. Using molecular-orbital theory den Boer-Veenendaal and den Boer[2] and den Boer-Veenendall *et al.*[3] have found that this molecule and heptalene $C_{12}H_{10}$ (Figs. 2a, b) should possess bonds of alternating lengths along their perimeters. In other words, structures exhibiting molecular symmetry C_{2h} (Figs. 2b, c) appeared to be energetically favoured as compared with those of the higher D_{2h} symmetry.

Coulson and Dixon, developing the approach of Lloyd and Penney[4] to the study of small conjugated molecules, have recently[5] examined the bond lengths in the cyclic polyenes $C_{2n}H_{2n}$ from the valency bond point of view and Clarkson *et al.*[6] in Part I of the present series of papers, have extended the range of this investigation to include fulvene and the calculation of Penney–Dirac bond orders. The work described now was intended to find out whether the molecular-orbital results on pentalene and heptalene could be verified by the valency-bond approach. This has been done for pentalene by calculating and comparing the total electronic energies for structures of symmetries D_{2h}

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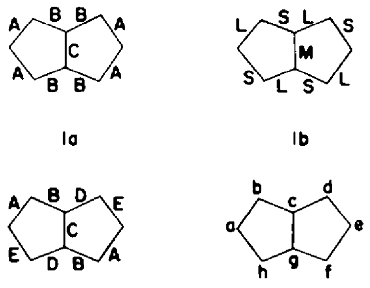
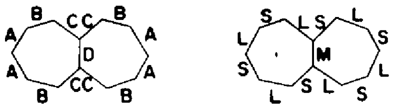
[1] D. P. Craig and A. Maccoll, *J. Chem. Soc.* 964 (1949).
[2] P. C. den Boer-Veenendaal and D. H. W. den Boer, *Molecular Physics* **1**, 33 (1961).
[3] P. C. den Boer-Veenendaal, J. A. Vliegenthart and D. H. W. den Boer, *Tetrahedron* **18**, 1325 (1962).
[4] E. H. Lloyd and W. G. Penney, *Trans. Faraday Soc.* **35**, 835 (1939).
[5] C. A. Coulson and W. T. Dixon, *Tetrahedron* **17**, 215 (1962).
[6] D. Clarkson, C. A. Coulson and T. H. Goodwin, *Tetrahedron* **19**, 2153 (1963) (previous paper).



Ia Ib

Ic Id

Fig. 1



2a 2b

Fig. 2

and C_{2h} in which bonds of three different lengths were distinguished, and even, for C_{2h} symmetry, for structures in which five bond lengths (Fig. 1c) were varied independently.

For heptalene preliminary results based on the inclusion of only the Kekulé type structures are given. These recognize four bond lengths for the D_{2h} symmetry and three only for C_{2h} (Figs. 2a, b).

Pentalene

Kekulé structures only. If pentalene has the molecular symmetry D_{2h} (Fig. 1a) one may, at most, distinguish three chemically different bonds, A, B, C. In a valency-bond treatment in which only the two Kekulé structures are taken into account the matrix elements* required for the variational treatment are

$$H_{11} - ES_{11} = H_{22} - ES_{22} = 4R_A + 4R_B + R_C + J_A + J_B - \tfrac{1}{2}J_C - E$$

$$H_{12} - ES_{12} = H_{21} - ES_{21} = \tfrac{1}{8}(4R_A + 4R_B + R_C + 4J_A + 4J_B - 2J_C - E)$$

where $E = E_\pi + E_\sigma$, $R(r) = Q(r) + E_\sigma(r)$ and the subscripts to R and J refer to the bonds A, B, C of lengths $r = L_A, L_B, L_C$. E is then given by

$$E = 4(R_A + R_B) + R_C + \tfrac{4}{3}(J_A + J_B) - \tfrac{2}{3}J_C.$$

From an inspection of this expression, bearing in mind the form of $R(r)$ and $J(r)$ as given by Coulson and Dixon,[5] it is easily seen that E has a minimum for any value of L_C when $L_A = L_B$. As to L_C one may expect here a single $sp^2 - sp^2$ σ-bond since the Kekulé structures do not contain a central double bond. The actual minimum energy is found with $L_A = L_B = 1{\cdot}41$ Å, $L_C = 1{\cdot}56$ Å, and has the mean value, E_m per bond of $-115{\cdot}8$ kcal/mole.

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* In writing down the matrix elements, there are good reasons not to rely on the recipes given in textbooks but to consult Pauling's original paper.[7]

[7] L. Pauling, *J. Chem. Phys.* **1**, 280 (1933).

If, however, one wishes to investigate bond alternation round the molecule structures of the lower symmetry C_{2h} must be chosen (e.g. Fig. 1b). For this case the matrix elements are

$$H_{11} - ES_{11} = 4R_L + 4R_S + R_M - 2J_L + 4J_S - \tfrac{1}{2}J_M - E$$

$$H_{12} - ES_{12} = H_{21} - ES_{21} = \tfrac{1}{8}(4R_L + 4R_S + R_M + 4J_L + 4J_S - 2J_M - E)$$

$$H_{22} - ES_{22} = 4R_L + 4R_S + R_M + 4J_L - 2J_S - \tfrac{1}{2}J_M - E$$

Whence

$$E = 4(R_L + R_S) + R_M + \tfrac{10}{21}(2J_L + 2J_S - J_M)$$
$$+ \tfrac{16}{21}\{16(J_L - J_S)^2 + J_LJ_S + \tfrac{1}{4}J_M(\tfrac{1}{4}J_M - J_L - J_S)\}^{\frac{1}{2}}$$

This expression provides a convenient way to compare the energies of a great number of slightly different structures. The perimeter bonds were varied independently from 1·32 to 1·56 Å at intervals of 0·02 Å, the central bond being simultaneously varied over the range 1·39 (0·04) 1·55 Å. The values of $R(r)$ and $J(r)$ were taken from the Table in Coulson and Dixon's paper[5] or calculated by their formulae. For all the L_M values used the minimum energy emerges at the same combination of L_L and L_S, *viz.* 1·52 and 1·34 Å; Fig. 3 presents these results as a contour diagram for the case where $L_M = 1{\cdot}51$ Å. To show the dependence of the mean bond energy E_m on the length L_M Fig. 4 has been plotted; it leads to the conclusion that the "absolute minimum" of energy occurs with $L_M = 1{\cdot}54$ Å and has the mean value per bond E_m of $-117{\cdot}2$ kcal/mole. This may be compared with the value of $-115{\cdot}8$ kcal/mole for the D_{2h} structure and shows conclusively that, within the limits of this approximation the C_{2h} structure is more stable by ca. 13 kcal/mole and that rather extreme alternation of bond lengths prevails.

Pentalene

Full canonical set. Craig and Maccoll's earlier treatment[1] of pentalene was based on all fourteen structures of the full canonical set, and on the deliberate simplifying assumption that all Q_{ij} and J_{ij} between atomic orbitals at atoms i and j could be taken as equal when ij is a chemical bond but zero otherwise. The 14 × 14 secular determinant was reduced by group theory so that to obtain the energy of the ground state of the D_{2h} molecule only a fifth degree equation had to be solved. (Incidentally in their paper the matrix elements 2,5 and 5,2 of the B_{1g} matrix should read 2/10 not 4/10.) For the ground state of the C_{2h} molecule a seventh degree equation had to be solved. We have recognised the sets of bond lengths portrayed in Figs. 1a, b, c as applied to the full canonical set of structures, the Rumer diagram being based on enumeration of the atomic orbitals as in Fig. 1d. We have carried through the following studies.

I. *Symmetry group D_{2h}, ground state class B_{1g}, bonds as Fig. 1a*

(a) With all nine bonds equal in length the mean bond energy E_m was as follows

L	$-E_m$	L	$-E_m$
1·35 Å	115·18 kcal/mole	1·43 Å	117·72 kcal/mole
1·37	116·56	1·45	117·30
1·39	117·41	1·47	116·50
1·41	117·77	1·49	115·50
1·42	117·79	1·51	114·21

indicating a minimum value of $E_m = -117{\cdot}79$ kcal/mole at 1·42 Å. This figure is 2·1 kcal/mole lower than the best (with variable L_A, L_B, L_C) obtainable with only the Kekulé structures contributing, although here we have artificially equated all bond lengths.

(b) All peripheral bonds equal but independent of the bridge bond. All bonds were varied over the range 1·36 (0·03) 1·48 Å leading to the minimum $E_m = -118{\cdot}42$ kcal/mole with $L_A = L_B = 1{\cdot}40$, $L_C = 1{\cdot}48$ Å.

(c) L_A, L_B, L_C all varied independently. This was effected by a "self-consistent" technique in which each of L_A, L_B, L_C was varied in turn over a suitable range (L_A and L_B 1·38 (0·01) 1·43 Å and L_C 1·48 (0·01) 1·60 Å) while the others were held constant. The eventual minimum mean bond energy was found to be $-118{\cdot}61$ kcal/mole with $L_A = L_B = 1{\cdot}40$, $L_C = 1{\cdot}57$ Å.

II. *Symmetry Group C_{2h}, ground state class A_u*

(a) L_L, L_S, L_M (Fig. 1b) varied independently as in 1c. L_L and L_S 1·36 (0·03) 1·48, L_M 1·44 (0·02) 1·50 Å gave minimum $E_m = -118{\cdot}92$ kcal/mole with $L_L = 1{\cdot}48$, $L_S = 1{\cdot}36$, $L_M = 1{\cdot}50$ Å. This E_m is 1·7 kcal/mole lower than that derived by use of the Kekulé structures only.

(b) Five independently varied bond lengths (Fig. 1c). L_A 1·47 (0·01) 1·51, LB 1·34 (0·01) 1·39, L_C 1·50 (0·01) 1·56, L_D 1·43 (0·01) 1·49, L_E 1·31 (0·01) 1·37 Å. This study gave, as each bond was varied and the others held constant, to the third decimal place exactly the same minimum $E_m = -118{\cdot}941$ kcal/mole each time. Graphical interpolation of each series of calculations led to $E_m = -118{\cdot}942$ kcal/mole with $L_A = 1{\cdot}478$, $L_B = 1{\cdot}353$, $L_C = 1{\cdot}520$, $L_D = 1{\cdot}475$, $L_E = 1{\cdot}352$ Å.

Penney-Dirac bond orders. Using the results from 2b we have calculated the Penney-Dirac bond orders for C_{2h} pentalene. The set of canonical structures used in this work may be conveniently described by reference to Fig. 1d as

A	ab	cd	ef	gh	*B*	ah	bc	de	fg
C	ab	ch	de	fg	*D*	ah	bc	dg	ef
E	ah	bg	cd	ef	*F*	ab	cf	de	gh
G	af	bc	de	gh	*H*	ah	be	cd	fg
I	ab	cd	eh	fg	*J*	ad	bc	ef	gh
K	ab	ch	dg	ef	*L*	ah	bg	cf	de
M	ad	dc	eh	fg	*N*	af	be	cd	gh

where ij signifies a π-bond (effective or formal) between $2p_z$ atomic orbitals at carbon atoms i and j. The ground state wave function is then found to be

$$\begin{aligned}\psi = {} & 0{\cdot}6916\phi_A + 0{\cdot}0691\phi_B + 0161(\phi_C + \phi_D) + 0{\cdot}1200(\phi_E + \phi_F) \\ & + 0{\cdot}0487(\phi_G + \phi_H) + 0{\cdot}1227(\phi_I + \phi_J) - 0{\cdot}0994\phi_K \\ & + 0{\cdot}0081\phi_L + 0{\cdot}0234\phi_M + 0{\cdot}0152\phi_N\end{aligned}$$

Applying then the technique described by Clarkson *et al.*[6] we have obtained the following bond-orders $p_A = 0{\cdot}2109$, $p_B = 0{\cdot}9265$, $p_C = 0{\cdot}0349$, $p_D = 0{\cdot}2107$, $p_E = 0{\cdot}9169$.

DISCUSSION

1. The most stable D_{2h} and C_{2h} conformations may, then be compared, as follows

$$D_{2h}\ E_m = -118{\cdot}61 \text{ kcal/mole with } L_A = L_B = 1{\cdot}40,\ L_C = 1{\cdot}57\ \text{Å}$$

$$C_{2h}\ E_m = -118{\cdot}94 \text{ kcal/mole with } L_L = 1{\cdot}477,\ L_S = 1{\cdot}353,\ L_M = 1{\cdot}520\ \text{Å}$$

The difference ΔE_m in the mean bond energies is small, being only 0·33 kcal/mole but the difference in the molar energies, $\Delta E = 3$ kcal/mole is approximately 5RT at room temperature. Thus the proportion of D_{2h} molecules in an equilibrium mixture would be decidedly low and their interconversion not very rapid, though in the absence of information about the transition state between C_{2h} and D_{2h} one cannot be absolutely confident about this. The simultaneous great changes in so many bond lengths is certainly going to have a low probability. Even if the D_{2h} conformation is regarded as the transition state between the two C_{2h} conformations with alternate short and long bonds the same comments apply though since conversion of D_{2h} molecules would be slow it is not quite impossible that an X-ray photograph might show this symmetry. We feel, therefore, that energy considerations definitely, if not perhaps exclusively, favour the form with alternation of bonds round the perimeter.

Moreover the great length of 1·57 Å for the central bond in the form of higher symmetry is experimentally unprecedented among hydrocarbons except in work where no claim is made to high accuracy. In lithium oxalate and ammonium oxamate C—C bonds of 1·561 ± 0·004 Å have been observed by Beagley and Small[8] but here the situation is clearly quite different. The length of the bridge bond in C_{2h} pentalene, on the other hand, does have experimental precedents, e.g. Shrivastava and Speakman's measurements on quaterrylene[9] where bond lengths of 1·52 and 1·53 Å were noted with an error of ±0·01 Å. Coulson and Dixon[5] and Longuet-Higgins and Salem[10] consider 1·51 Å to be the length of a pure σ-bond between two sp^2-hybridized carbon atoms. A slight lengthening of the central bond in pentalene would certainly be expected to relieve strain in the five-membered rings. This argument, however, cannot be advanced to support the result of the present calculations because our theoretical treatment ignores energy changes attributable to all sources except compression and extension of bond lengths. We conclude that the C_{2h} structure is slightly more favourable energetically and has a much more reasonable length for the bridge bond.

2. It is doubtful whether the third decimal place has any great numerical significance in either the energy or the bond lengths, so that within the limits of the method

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[8] B. Beagley and R. W. H. Small, *Nature* **198**, 1297 (1963).

[9] H. N. Shrivastava and J. C. Speakman, *Proc. Roy. Soc.* **A257**, 477 (1960).

[10] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **A251**, 172 (1959).

the final, graphically interpolated results suggest that $L_A = L_D$, $L_B = L_E$. Hence accurate alternation of bond lengths round the perimeter of the molecule, not noticeably interrupted by the central bond, should occur. Thus, the conclusion reached from a molecular orbital study[2] of pentalene agrees qualitatively with the valency-bond investigation presented here. Obviously these approaches are too widely different to expect quantitative agreement between the final bond lengths obtained.

3. The C_{2h} results may be compared with Coulson and Dixon's calculations on the hypothetical planar model of cyclo-octatetraene, for which, using a wavefunction restricted to contributions from the two Kekulé forms and the eight possessing only one long bond, they found the minimum mean energy per bond to be $-123{\cdot}035$ kcal/mole obtained with alternating bonds of lengths 1·435 and 1·375 Å. Inclusion of the four remaining canonical structures can only lower E_m still further and increase the remarkable difference between these two molecules. Thus the central bond seems to weaken, not to strengthen the structure.

The energy of the structure A of our canonical set is $-1048{\cdot}59$ kcal/mole and so pentalene has a resonance energy of approximately 22 kcal/mole, which is much less than the value obtained for the rather smaller molecule of benzene. This figure is in accord with the predominance of the structure A (see 6 below) and may be interpreted as a support for the apparent instability of pentalene.

4. Our calculated bond lengths should also be compared with the measured C—C distances in nonplanar cyclo-octatetraene[11] 1·462 and 1·334 Å. One would expect the central bond, by drawing π-electrons out of the perimeter, to reduce the bond orders and so increase the lengths of all peripheral bonds. Further, since the short bonds of cyclo-octatetraene have a very high electron density, one would expect these to make the greater contribution, and if a linear relation exists between order and length, it is the short bonds which should be increased most. This is just what is suggested by our calculations though the restricted conjugation in the nonplanar polyene is not allowed for here.

5. While this work was in progress Le Goff published[12] syntheses of hexaphenylpentalene. No physical examination of the structure of this molecule has yet been reported but it is reasonably certain that the phenyl groups will lie perpendicular to the plane of the five-membered rings; they will not therefore, greatly influence the geometry of the central part. Thus, in a sense pentalene has been synthesised. We await the structure determination with interest.

6. Craig and Maccoll estimated[1] Penney–Dirac bond-orders for the D_{2h} molecule in which all coulomb and exchange integrals were considered to be the same. They found

$$p_A = 0{\cdot}566, \quad p_B = 0{\cdot}630, \quad p_C = -0{\cdot}056 \text{ (see Fig. 1a)}$$

We have not made any calculation of bond orders for the D_{2h} molecule but for the C_{2h} our results have been given earlier. The most interesting point about them is that a small, but positive, bond order is found for the central bond.

It is not surprising that the orders of the short bonds are so very high: the molecular wavefunction is dominated almost completely by that of structure A in which these are double bonds. The differences between the orders of bond A and D, B and E are

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[11] O. Bastiansen, L. Hedberg and K. Hedberg, *J. Chem. Phys.* **27**, 1311 (1957).

[12] E. Le Goff, *J. Amer. Chem. Soc.* **84**, 3975 (1962).

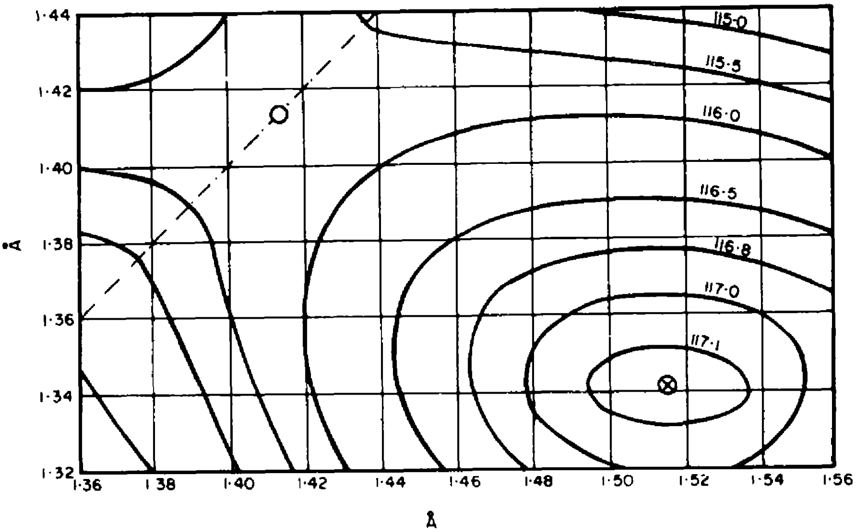

FIG. 3. Mean bond energies ($-E_m$ in kcal/mole) for pentalene (Kekulé structures only) as a function of L_L (1·36 to 1·56 Å) and L_S (1·32 to 1·44 Å) with L_M constant at 1·51 Å.

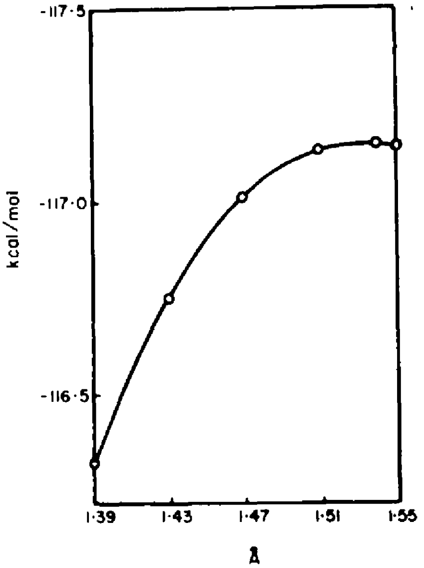

FIG. 4. Minimum mean bond energy ($-E_m$ in kcal/mole) for pentalene (Kekulé structures only) as a function of L_M.

very small. Differences would be expected because of the neighbourhood of the bridge bond to B and D but cannot be regarded as significant in view of the slight uncertainty in the method of derivation and the close agreement of the pairs of bond lengths involved.

Heptalene

Kekulé structures only. For this compound we present only the results obtained when the structures contributing to the molecular wave function are restricted to the Kekulé forms. For the D_{2h} model (Fig. 2a) the total energy is

$$E = 4(R_A + R_B - R_C) + R_D + \tfrac{12}{11}(J_A + J_B + J_C) - \tfrac{6}{11}J_D$$

and leads to a minimum mean bond energy $E_m - 114\cdot9$ kcal/mole with $L_A = L_B = 1\cdot42$ Å, $L_D = 1\cdot54$ Å.

For the C_{2h} model (Fig. 2b)

$$E = 6(R_L + R_S) + R_M + \tfrac{170}{341}(3J_L + 3J_S - J_M) + \tfrac{96}{341}\{256(J_L - J_S)^2 + J_LJ_S + \tfrac{1}{6}J_M(\tfrac{1}{6}J_M - J_L - J_S)\}^{\frac{1}{2}}$$

leading to $E_M = -118\cdot0$ kcal/mole with $L_L = 1\cdot52$, $L_S = 1\cdot34$, $L_M = 1\cdot54$ Å.

These results are following the same trend as those for pentalene and will be considered later on completion of calculations taking into account many more structures. The complete set numbers 132!

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