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BOND LENGTHS IN CYCLIC POLYENES $C_{2n}H_{2n}$ A RE-EXAMINATION FROM THE VALENCE-BOND POINT OF VIEW

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Abstract -- The valence-bond resonance method for predicting bond lengths in conjugated hydrocarbon molecules has been reconsidered. New values are obtained for the variation of the fundamental exchange and Coulomb integrals with bond length. Application to the cyclic polyenes $C_{2n}H_{2n}$ shows that for large n there will be substantial bond alternation. Inclusion of Dewar structures diminishes this alternation, but does not destroy it.

1. INTRODUCTION

TWENTY-TWO years ago Lloyd and Penney[1] made calculations of the bond lengths in certain small conjugated molecules (e.g. butadiene and benzene) using the valence-bond (v.b.) method of resonance. But since that time practically no further calculations have been made with this approximation, and the molecular-orbital (m.o.) method has been almost exclusively adopted. During the last few years, however, several new considerations have been proposed, leading to substantial changes in our opinion with regard to several matters previously regarded as settled. Thus (1) the influence of the compressional energy[2-5] is now recognised to be of supreme importance in determining equilibrium bond lengths; (2) in any use of an order-length relationship to link bond order with bond length, it is admitted that the covalent radius of a trigonal carbon atom is less than that of a tetrahedral carbon atom, thus leading to a displaced order-length curve, in which the C - C single bond length[6,7] is about 1·50 - 1·51 Å; (3) in long chain polyenes $C_{2n}H_{2n+2}$ and in large cyclic polyenes $C_{2n}H_{2n}$ the bonds do not tend to equality[8] as n increases, but rather there is an alternating character represented, in an exaggerated form, by the familiar bond diagram - · - · . . . . · -=. The situation of equal lengths, as originally predicted[9] by naive use of simple bond order calculations, turns out to be a saddle point and not a true minimum of the energy. For large molecules the alternation of bond length is of

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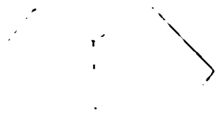
[1] E. H. Lloyd and W. G. Penney, *Trans. Faraday Soc.* **35**, 835 (1939).
[2] J. E. Lennard-Jones, *Proc. Roy. Soc.* A **158**, 280 (1937).
[3] R. S. Mulliken, C. A. Rieke and W. G. Brown, *J. Amer. Chem. Soc.* **63**, 41 (1941).
[4] C. A. Coulson, *Victor Henri Memorial Volume* p. 15. Desoer, Liège (1948).
[5] C. A. Coulson and S. L. Altmann, *Trans. Faraday Soc.* **48**, 293 (1952).
[6] H. J. Bernstein, *J. Phys. Chem.* **63**, 565 (1959).
[7] M. J. S. Dewar and H. N. Schmeising, *Tetrahedron* **5**, 166 (1959) who suggest an even shorter value 1·48 Å.
[8] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A **251**, 172 (1959) and later papers by the same authors.
[9] C. A. Coulson, *Proc. Roy. Soc.* A **169**, 413 (1939).

the order of 0·04 Å. A similar alternation is also predicted[10] though with rather larger disparity between the shorter and longer bonds, of the order of magnitude 0·09 Å—in the hypothetic bridged ring molecule pentalene C_8H_6 (see I).



I

The results in references 8 and 10 were all obtained using the m.o. method, though without configuration interaction. It would seem desirable, therefore, to see to what extent the predictions depend on using this method. We have therefore thought it worthwhile to re-examine the same problems within the v.b. approximation. For this purpose it would have been pleasant to be able to use the numerical values of exchange and Coulomb integrals obtained by Lloyd and Penney[1], but we have not done so, and have preferred to work independently, though in a very similar spirit. In the first place the calculations of Lloyd and Penney require to be corrected so as to take account of the revised C–C trigonal single-bond radius, referred to in (2) above; and in the second place Lloyd and Penney, in their anxiety to take full account of all exchange terms, appear to us (see also reference 5 where further comments are made on this work) to have taken a σ-π exchange integral equal in magnitude to π-π exchange integrals. A rough estimation of these integrals suggests that this is not very probable, and so also does an elementary consideration of the likely contributions to the exchange integral from different regions of space. When we allow for these two changes, somewhat different curves are obtained for the Coulomb integral $Q(r)$ and the exchange integral $J(r)$ as functions of the bond length r.

The first part of this paper is therefore concerned with using certain experimental molecular magnitudes to deduce empirical $Q(r)$ and $J(r)$ curves. In the second part we show that when proper allowance is made for the σ-bond compressional energy, cyclic polyenes $C_{2n}H_{2n}$ are not expected to be regular polygons except for small n (in complete agreement with the m.o. results) though the critical value of n at which alternation sets in cannot yet be predicted accurately, since the Dewar-structures and more highly-excited structures also serve partly to weaken the strong tendency of the Kekulé structures to induce bond alternation. This surprising result differs from the usual belief that resonance among Kekulé structures tends to cause equality of bonds: but a very simple calculation does in fact show that this is not necessarily the case. Finally we present some detailed calculations for the cyclic polyenes $C_{2n}H_{2n}$ in which $2n = 6, 8$ and 10. Except in the case of benzene ($2n = 6$) these calculations are only illustrative, since neither C_8H_8 nor $C_{10}H_{10}$ are planar molecules. But we believe that these calculations, all made on the assumption of planarity, are sufficient to illustrate the general conclusions obtained earlier. We have also tacitly assumed all the valence angles to be 120°. Apart from benzene, this is manifestly impossible geometrically for small values of n. But it is possible, and probably occurs, for the larger molecules which have been isolated experimentally, and which we shall discuss in Sections 3 and 4.

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[10] P. C. den Boer-Veenendaal and D. H. W. den Boer, *Molec. Phys.* 4, 33 (1961).

2. THE FUNCTIONS $Q(r)$ AND $J(r)$

Let us represent the total energy of a π-electron molecule in the form

$$E_{\text{total}}(r_1,\ldots) = E_\sigma(r_1,\ldots) + E_\pi(r_1,\ldots) + E_{\pi\sigma}(r_1,\ldots) \tag{1}$$

where

$r_1,\ldots$ are the various bond lengths
E_σ is the total σ-bond energy
E_π is the total π-electron energy
$E_{\pi\sigma}$ is the total π-σ exchange energy.

We shall now make the assumption that either $E_{\pi\sigma}$ is so small in relation to the other terms of (1) that it may be neglected, or else it varies with bond lengths in so similar a way to E_σ that it may be incorporated in this latter function. This seems very reasonable, at least for molecules such as those being considered in this paper, for the distributions of π and of σ electrons are effectively uniform. It might, however, be less valid if heteroatoms were present, such as in pyridine. Thus (1) is replaced by

$$E_{\text{total}}(r_1,\ldots) = E_\sigma(r_1,\ldots) + E_\pi(r_1,\ldots) \tag{2}$$

In order to use this formula to determine the Coulomb and exchange integrals $Q(r)$ and $J(r)$ we must choose two molecules for which E_{total} is known experimentally; and we must also know the corresponding expressions for E_π and E_σ. If we adopt the usual approximations of orthogonality of all atomic orbitals, then the method of Pauling[11] enables us to write for ethylene

$$E_\pi^{\text{ethylene}}(r) = Q(r) + J(r), \tag{3}$$

and for benzene, when all bonds are equal

$$E_\pi^{\text{benzene}}(r) = 6\{Q(r) + 0{\cdot}434\,J(r)\} \tag{4}$$

In writing (3) and (4) we have made the usual assumption that $Q(r)$ and $J(r)$ are the same functions of r for benzene and for ethylene. This implies—at very least—that we neglect direct *meta*- and *para*-interactions in the benzene ring. If we consider the two molecules at the same bond distance r, then $E_\sigma^{\text{benzene}}(r) = 6E_\sigma^{\text{ethylene}}(r)$, and so, using (3) and (4)

$$E_{\text{total}}^{\text{ethylene}}(r) - \tfrac{1}{6}E_{\text{total}}^{\text{benzene}}(r) = 0{\cdot}566\,J(r) \tag{5}$$

Empirical curves of $E_{\text{total}}(r)$ for ethylene and $\frac{1}{6}E_{\text{total}}(r)$ for benzene are drawn in Fig. 1. According to (5) their difference enables us to draw the curve of the exchange integral $J(r)$. This is also shown in the figure.

In drawing the curves for $E_{\text{total}}(r)$ we have used Morse functions of the usual form

$$W(r) = W_0\{e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}\} \tag{6}$$

where the values adopted (which, apart from r_0, are identical with those adopted by Lloyd and Penney) are as shown in Table 1. Any alteration in the latent heat of sublimation of carbon would affect the values of W. For purposes of comparison we have accepted for our own calculations precisely the same values as Lloyd and Penney. These differ very little from the best modern values, and in such a way as to make only very minute changes in the calculated bond lengths. The values of r_0 in this table are

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[11] L. Pauling, *J. Chem. Phys.* 1, 280 (1933). For a simple account see C. A. Coulson, *Valence* pp. 228–236. Oxford University Press (1952).

now firmly established, and the parameter (a) is dependent upon the fundamental breathing frequency of each molecule. It is worth reporting that in some preliminary calculations we had tried to avoid the complication of a Morse function, with its exponential terms, by using a harmonic oscillator expression $\frac{1}{2}k(r - r_0)^2$ for the energy of a σ-bond. This expression is the one most widely used in m.o. calculations. But we found that the resulting $J(r)$ curve was seriously affected by this, and its use gave absurd numerical results for the equilibrium bond lengths of cyclic molecules. We therefore abandoned it, with regret. As an indication of the serious dependence of $J(r)$ on the choice of a Morse function of $E_{total}(r)$ instead of a parabolic law, we show in Fig. 2 rough diagrams of $J(r)$ and $Q(r)$ obtained by both techniques. It will be noticed at once that the curvature of $J(r)$ is changed in sign. This implies that d^2J/dr^2 also changes sign. Now questions of stability of a given set of bond lengths depend on the sign of d^2E_{total}/dr^2. Thus, if $J(r)$ plays any significant part in fixing the equilibrium

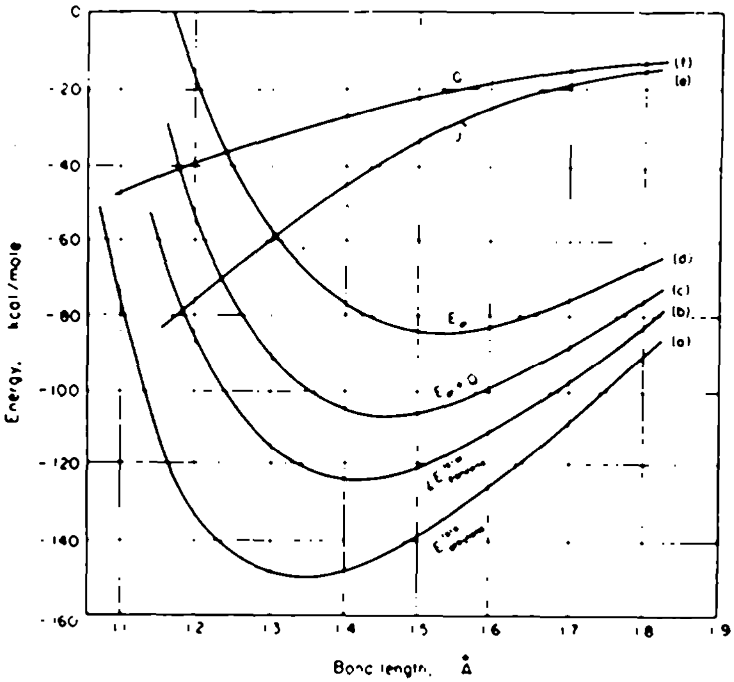

FIG. 1 (a) total energy E_{total} for ethylene (experimental), (b) one-sixth of total energy E_{total} for benzene (experimental); (c) $E_\sigma(r) + Q(r)$ deduced from (a) and (b), (d) assumed form of $E_\sigma(r)$, (e) $J(r)$ deduced from (a) and (b), (f) $Q(r)$ deduced from (c) and (d), crosses denote values of $J(r)$ calculated by Altmann[19].

TABLE 1

	W_0 (kcal mole)	a (Å^{-1})	r_0 (Å)
Ethylene	151	2·189	1·34
Benzene	124	2·093	1·40
Ethane	84	2·028	1·54

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[19] S. L. Altmann, *Proc. Roy. Soc.* A 210, 327, 343 (1951).

bond length—as it most clearly does—we can see why we may be led to unacceptable positions of stability or instability, if we abandon Morse functions in favour of the simpler parabolic ones. All our later work, therefore, will use only the Morse functions (6) and the parameters of Table 1.

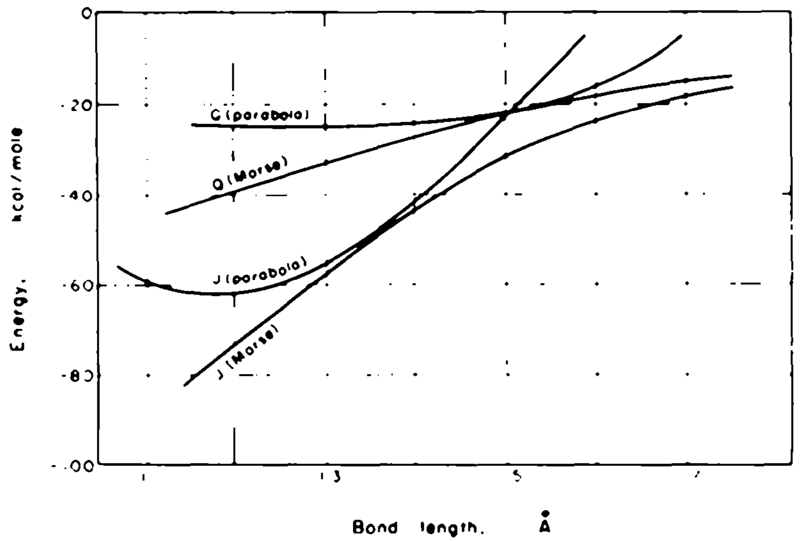

FIG. 2. Curves showing difference between exchange integral $J(r)$ and Coulomb integral $Q(r)$ with use of parabolic or Morse potential functions for ethylene and benzene.

We have still to determine $Q(r)$ and $E_\sigma(r)$ where this latter quantity is the σ-bond energy for a bond of length r, so that

$$E_\sigma(r_1, r_2 \ldots) = E_\sigma(r_1) + E_\sigma(r_2) + \ldots \tag{7}$$

Equations (2), (3), (4) and (7) allow us to write

$$E_\sigma(r) + Q(r) = 1{\cdot}767 \frac{E^{\text{benzene}}_{\text{total}}(r)}{6} - 0{\cdot}767 E^{\text{ethylene}}_{\text{total}}(r) \tag{8}$$

We have shown this quantity in Fig. 1. Since it depends only upon equations (2), (3), (4) and (6) it is independent of any assumptions that we may make about the nature of $E_\sigma(r)$, other than that the π-σ interactions are included in it.

Table 2, columns 2 and 3, shows the values of $J(r)$ and $E_\sigma(r) + Q(r)$, both in kcal/mole for various values of r, in Å. This is the table of values which we shall use in our later numerical work. At this stage it is not necessary to separate $E_\sigma(r)$ and $Q(r)$, since in all our applications we shall find that it is their sum which appears. This would not be the case if we were considering heteronuclear molecules, and then we should find that each was required separately. Simple analytical approximations to the functions in Table 2—valid to within 0·020 kcal. in the range $1{\cdot}34 < r < 1{\cdot}51$ are

$$J(r) = -41{\cdot}199 + 121{\cdot}2(r - 1{\cdot}42) + 114{\cdot}2(r - 1{\cdot}14)^2 \tag{9}$$

$$E_\sigma(r) + Q(r) = -105{\cdot}905 - 39{\cdot}6(r - 1{\cdot}42) + 526(r - 1{\cdot}42)^2$$
$$1000(r - 1{\cdot}34)(r - 1{\cdot}42)(r - 1{\cdot}51) \tag{10}$$

The last figure in these numerical values is entirely without significance in any absolute sense: but for locating stationary values of the total energy it may have some significance.

There is not very much with which we may compare the numerical entries in Table 2. But Altmann[12], in some studies of the ethylene molecule, calculated $J(r)$, using a full twelve-electron Hamiltonian. For the distances 1·34, 1·39 and 1·54 Å he found values −62·9, −52·4 and −28·6 kcal respectively. These vary in the right way as our values, and are of the right order of magnitude, though they differ by about 10 kcal for short bonds. In view of the different types of approximation involved in the two estimates of $J(r)$, this is probably as good agreement as may be expected.

TABLE 2

	Kekulé and Dewar structures		Kekulé structures only	
r	$J(r)$	$\{E_\sigma(r) + Q(r)\}$	$J(r)$	$\{E_\sigma(r) + Q(r)\}$
1·34	51·625	99·375	48·70	102·30
1·36	48·892	101·834		—
1·37	47·557	102·839	44·86	105·54
1·38	46·236	103·707	—	—
1·39	44·927	104·449	—	
1·40	43·650	105·056	41·18	107·53
1·41	42·411	105·539	40·01	107·94
1·42	41·199	105·905	38·83	108·27
1·43	39·992	106·183	—	—
1·44	38·790	106·371	36·59	108·57
1·45	37·653	106·432	—	—
1·48	34·336	106·148	32·39	108·09
1·51	31·206	105·211	29·44	106·98

If we wish to go further than this, and obtain expressions for $E_\sigma(r)$ and $Q(r)$ separately, we must use some additional data. The most natural is $E_\sigma(r)$, which we could approximate as if it were the energy of a single bond between two trigonal carbon atoms. For this purpose we use a Morse curve in which the equilibrium length is not 1·54 Å, as in ethane, but is taken to be 1·51 Å, to allow for point (2) in the Introduction. It is not quite obvious which values we should choose for W_0 and a in equation (6); but we have, somewhat arbitrarily, chosen −84 kcal/mole and 2·028 Å^{-1} respectively. With this choice we can draw the $E_\sigma(r)$ curve of Fig. 1, and so determine $Q(r)$. For obvious reasons this curve is much less reliable than $E_\sigma(r) + Q(r)$, but in the region $1{\cdot}34 < r < 1{\cdot}54$ Å, it may be represented approximately by

$$Q(r) = -25{\cdot}275 + 49{\cdot}9(r - 1{\cdot}42) - 53{\cdot}5(r - 1{\cdot}42)^2 \qquad (11)$$

The difference between (10) and (11) is, of course, a representation of $E_\sigma(r)$.

We have now obtained approximate values of $J(r)$, $Q(r)$ and $E_\sigma(r)$. These are ready for application to our cyclic molecules. But before proceeding there is a point to consider. In (4) we have used the energy expression for the π-electrons of benzene, taking into account Kekulé and Dewar structures. It is not immediately obvious that we have any right to use this formula—and the implied $J(r)$—in larger molecules, where there will also be doubly-excited and more highly excited structures. But we shall assume that this is so, and shall try, when dealing with other molecules, to write down the expression for E_π analogous to (4), neglecting all structures other than the Kekulé and first-excited ones. It is doubtful that inclusion of the more highly-excited structures would seriously affect the predicted bond lengths and stabilities, though it is known[13] that for sufficiently large conjugated molecules the more highly-excited structures dominate over the less-excited. However, we can make an alternative calculation, in which we consider only Kekulé structures. If we do this, equation (3) is unchanged, and equation (4) is replaced by

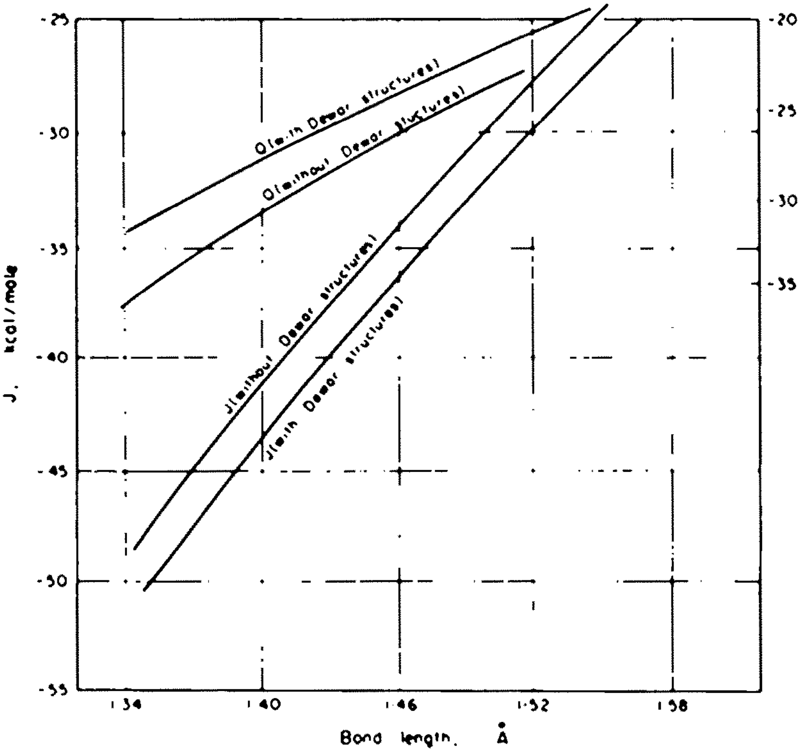

FIG. 3 Curves showing variation of exchange integral $J(r)$ and Coulomb integral $Q(r)$ when Dewar structures are included and when they are not included

$$E_\pi^{\text{benzene}}(r) = 6\{Q(r) + 0{\cdot}400\,J(r)\} \tag{12}$$

By an entirely similar process, this leads to values of $J(r)$ and $Q(r)$ which differ slightly from those previously determined (Table 2, columns 4 and 5). Fig. 3 shows, on a larger scale than Fig. 1, the variation of $J(r)$ and $Q(r)$ both with and also without inclusion of Dewar structures in benzene. The general variations are remarkably similar, leading to the view that predictions based on them would also be similar. Table 2 also allows a direct comparison of the values of $J(r)$ and $E_\pi(r) - Q(r)$ in these two approximations.

3 THE CYCLIC POLYENES $C_{2n}H_{2n}$, n LARGE

Consider the cyclic polyene $C_{2n}H_{2n}$, represented for the case of n = 4, by II. We are supposing that the molecule is planar. This is known not to be true for cyclo-octatetraene (II), but it must be more nearly true for the larger systems 2n = 18, 24

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[13] See C. A. Coulson, *Proc. Roy. Soc.* A **207**, 91 (1951).

and 30 synthesized by Sondheimer, Wolovsky and Gaoni[14,15,16]. Let us suppose also, for the moment, that we use only the Kekulé structures. There are just two of these, for all n, and they are represented by (a) and (b). We have allowed for possible bond alternation by letting the bond lengths be alternately r_1 and r_2. If $r_1 < r_2$, as in the

II

diagram, the structure (a) will be more energetically bonding than (b), and, as Coulson and Altmann[6] showed for the case of benzene (2n = 6), the resonance energy is drastically reduced as $r_2 - r_1$ increases. Thus when $r_1 = r_2 = 1{\cdot}39$ Å they found that the delocalization energy, defined as the difference in E_π between the localized bonding of a Kekulé structure and the delocalized energy of the corresponding resonance hybrid, was about 63 kcal/mole. But when $r_1 = 1{\cdot}39$ Å, $r_2 = 1{\cdot}54$ Å (they used the old value for the length of a pure trigonal carbon-carbon bond), the delocalization energy was only 9·6 kcal/mole. We shall now show that even when 2n is large, resonance of this kind contributes relatively little to the delocalization energy, and is certainly insufficient to favour a regular shape with equal bond lengths.

If we write ψ_a and ψ_b for the Kekulé structures, and if the ground state wave function is

$$\Psi = c_1\psi_a + c_2\psi_b,$$

then the secular equations to determine the π-electrons energy E_π and the coefficients c_1, c_2 take the form

$$\begin{gathered}(nQ_1 + nQ_2 - nJ_1 - \frac{n}{2}J_2 - E_\pi)c_1 + \frac{1}{2^{n-1}}(nQ_1 + nQ_2 - nJ_1 + nJ_2 - E_\pi)c_2 = 0\\ \frac{1}{2^{n-1}}(nQ_1 + nQ_2 + nJ_1 + nJ_2 - E_\pi)c_1 + (nQ_1 + nQ_2 + nJ_2 - \frac{n}{2}J_1 - E_\pi)c_2 = 0\end{gathered} \tag{13}$$

In these equations Q_1 and Q_2 are the two Coulomb integrals, appropriate to bond lengths r_1 and r_2, and J_1, J_2 are the corresponding exchange integrals. The interesting feature of these equations lies in the coefficient $1/2^{n-1}$ multiplying the off-diagonal elements in the resulting secular determinant. In the case of benzene this factor is 1/4, but for larger molecules it rapidly decreases, so that the roots of the secular determinant are given essentially by the diagonal elements. In fact, if $r_1 < r_2$ the lowest root is approximately

$$E_\pi = n\left[Q_1 + Q_2 - J_1 - \tfrac{1}{2}J_2 + \frac{3J_2^2}{2^{2n-1}(J_1 - J_2)}\right] \tag{14}$$

Thus the delocalization energy, which is given by the last term in (14) actually tends

[14] F. Sondheimer and R. Wolovsky, *Tetrahedron Letters* No. 3, 3 (1959).
[15] F. Sondheimer and R. Wolovsky, *J. Amer. Chem. Soc.* **81**, 4755 (1959).
[16] F. Sondheimer, R. Wolovsky and Y. Gaoni, *J. Amer. Chem. Soc.* **82**, 755 (1960).

to zero as $n \to \infty$. In the case where $J_1 = J_2$ the approximation (14) must be replaced by:

$$E_e = n\left[2Q + \frac{J}{2}\left(\frac{1 + (1/2^{n-3})}{1 + (1/2^{n-1})}\right)\right] \tag{15}$$

Here again it follows that for sufficiently large n, the delocalization energy tends to zero.

Thus on the basis of Kekulé structures alone, the larger cyclic polyenes would not be expected to be as stable as the smaller ones.

But we can also show that for sufficiently large n, the regular polygon with $r_1 = r_2$ is less stable than the alternating one with (say) $r_1 < r_2$. To do this we consider $E_{total}(r_1,r_2)$, which is the sum of E_e and E_σ where $E_e(r_1 r_2)$ can be found from the equations (13), and where $E_\sigma(r_1 r_2) = nE_\sigma(r_1) + nE_\sigma(r_2)$. It is obvious from symmetry considerations alone that there is a stationary value of the total energy when $r_1 = r_2$ and their common value is such that

$$\frac{d}{dr}\left[E_\sigma(r) + Q(r) + \frac{1}{4}\left(\frac{1 + (1/2^{n-3})}{1 + (1/2^{n-1})}\right)J(r)\right] = 0 \tag{16}$$

This common value differs very little from that appropriate to benzene, though it actually increases slowly with n. With $r = 1{\cdot}400$ for $n = 3$, it becomes $1{\cdot}403$ for $n = 4$ and $1{\cdot}413$ for $n = 5$.

A tedious calculation, which we shall not reproduce, but which uses the appropriate $J(r)$ and $Q(r)$ from Fig. 3, shows that, at these stationary values, E_{total} is an absolute minimum in the case of benzene, but a saddle point for $n = 4$ and $n = 5$ and all higher values of n. Thus, using Kekulé structures only, benzene is predicted to be a regular polygon, but all larger even cyclic molecules should show bond alternation.

It is not possible to give a similar general demonstration when Dewar structures are included in addition to the Kekulé structures. But (see later) detailed calculation of the energy contours for a variety of values of r_1 and r_2 shows that almost certainly precisely the same situation obtains. We conclude, therefore, that in the larger cyclic polyenes the configuration of greatest stability is one with alternating bond lengths, in agreement with the results of m.o. theory.[8] But in our v.b. theory the alternation appears to set in earlier than in the m.o. theory. In view of the approximations in both, such divergencies are not altogether surprising.

It is worth writing down the expression for the total energy, which results from solving equations (13) for E_e and then adding E_σ. It will be convenient to write $\mathscr{E}_1$ for $E_\sigma(r_1) + Q(r_1)$, and $\mathscr{E}_2$ for $E_\sigma(r_2) + Q(r_2)$. Then for benzene, where $2n = 6$, and taking the negative value of the square root,

$$E_{total}(r_1,r_2) = 3\mathscr{E}_1 + 3\mathscr{E}_2 + \tfrac{7}{10}(J_1 + J_2) - \tfrac{8}{15}\{4(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}$$

for the case where $2n = 8$,

$$E_{total}(r_1,r_2) = 4\mathscr{E}_1 + 4\mathscr{E}_2 + \tfrac{62}{63}(J_1 + J_2) + \tfrac{32}{63}\{16(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}.$$

For the case where $2n = 10$,

$$E_{total}(r_1,r_2) = 5\mathscr{E}_1 + 5\mathscr{E}_2 + \tfrac{127}{102}(J_1 + J_2) + \tfrac{128}{255}\{64(J_1 - J_2)^2 + J_1J_2\}^{\frac{1}{2}}.$$

Once again we see the growing importance of $J_1 - J_2$ as the size of the polyene increases.

4. DETAILED CALCULATIONS FOR 2n = 6, 8, 10

In more detailed calculations for the smaller molecules of this type, we have included both Dewar and Kekulé structures. In the case of benzene, with $r_1 \neq r_2$ there are five structures. The two Kekulé structures III(a)(b) will have different weights but the three Dewar structures, of which III(c) is one example, will all have the same weight. The secular determinant is a 3×3 determinant. This has already been given by Coulson and Altmann[5] in equation (3) of their paper. We have verified that this is correct. In our symbols it is

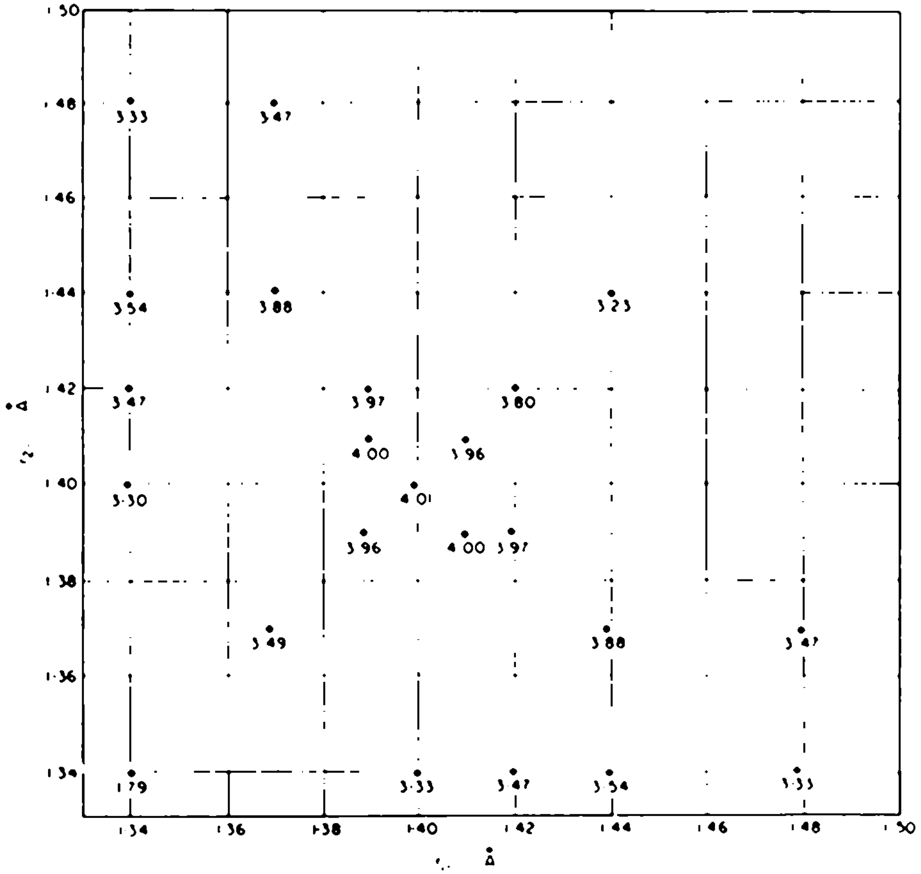


FIG. 4. Calculated values of the total energy $-E(r_1,r_2)$ for benzene, using Kekulé + Dewar structures. The zero of energy is taken at $E = -120$ kcal/mole.

$$24x^3 - 4(J_1 + J_2)x^2 - 2\{3(J_1 - J_2)^2 + 4J_1J_2\}x + (J_1 - J_2)^2(J_1 + J_2) = 0 \qquad (17)$$

where $6x = 3Q_1 + 3Q_2 - E_\pi$.

By choosing various combinations of r_1 and r_2 this equation can be solved numerically, and $E_\pi(r_1,r_2)$ obtained. By addition of $E_\sigma(r_1r_2)$ we obtain the total energy $E_{\text{total}}(r_1r_2)$. A typical set of such values is shown in Fig. 4. It is at once clear that the equilibrium value $r_1 = r_2 = 1{\cdot}40$ Å is the position of stable equilibrium, though the curve is much flatter along the line $r_1 + r_2 = 2{\cdot}80$ than along the line $r_1 = r_2$. This is just what we should expect from the known force constants of benzene in the two corresponding normal modes B_{2u} and A_{1g} respectively.


(a) (b) (c)

III

In the case of C_8H_8, there are 2 Kekulé structures and 8 Dewar structures, which divide up as in IV, where we have simplified the diagrams by only representing the π-electrons.

IV

The secular determinant is of order 4 × 4 and the equation for the energy is

$$2048x^4 - 160(J_1 + J_2)x^3 - 20\{24(J_1 - J_2)^2 + 23J_1J_2\}x^2$$
$$+ 28(J_1 + J_2)\{2(J_1 - J_2)^2 + J_1J_2\}x - J_1J_2\{7(J_1 - J_2)^2 - 20J_1J_2\} = 0 \quad (18)$$

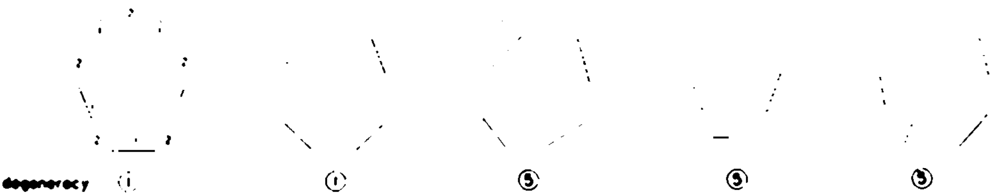
where, now

$$8x = 4Q_1 + 4Q_2 - E_\pi \quad (19)$$

A check on (18) may be found from the fact that it gives correct values when $J_1 = J_2$ and when $J_2 = 0$. The significance of $(J_1 - J_2)^2$, which depends on the degree of bond alternation, is very clear.

Fig. 5(a) shows a set of values of $E_{tot}(r_1, r_2)$ for various r_1 and r_2. Along the line $r_1 = r_2$ we have a minimum energy at $r_1 = r_2 = 1{\cdot}404$ Å. But Fig. 5(b), which shows the variation of energy along the line AB, where $r_1 + r_2 = 2{\cdot}81$ Å, suggests that the point (1·404, 1·404) is really a saddle point, and the stable configurations are at (1·375, 1·435) and (1·435, 1·375). Thus we predict a bond alternation with difference 0·06 Å. This is of the same order as that predicted by Longuet-Higgins and Salem[8], but rather larger.

In the case of $n = 5$, there are three types of Dewar structure:



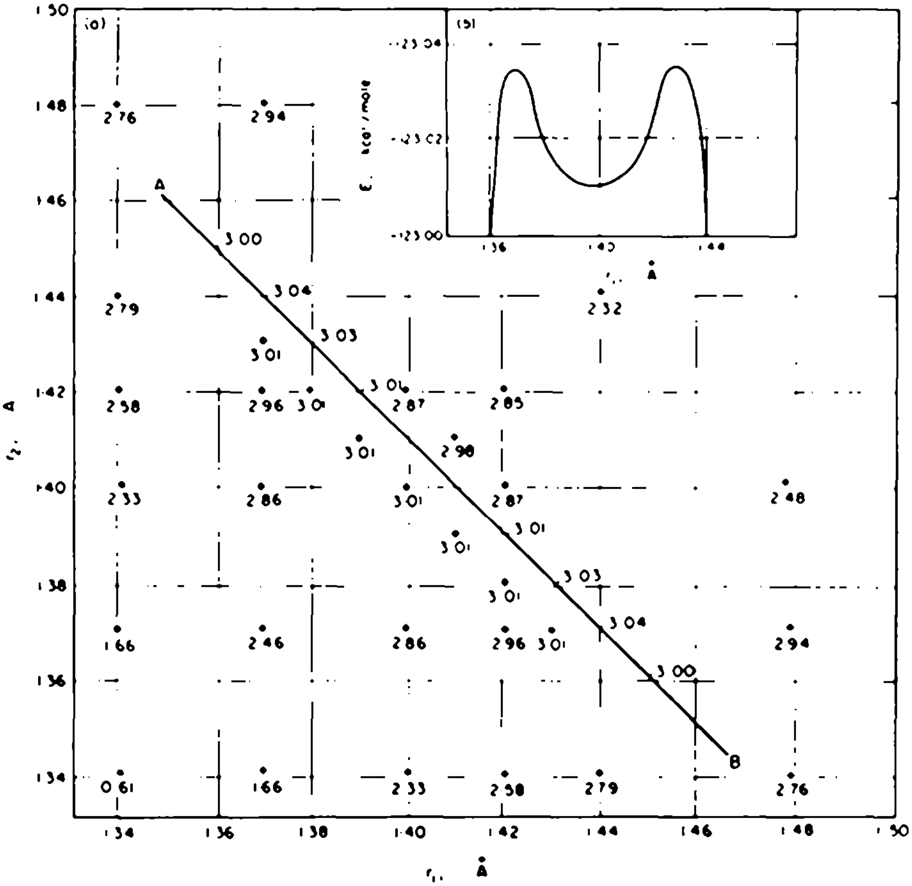


FIG. 5. Main diagram (a). Calculated values of the total energy $-E(r_1,r_2)$ for hypothetical planar C_6H_6, using Kekule + Dewar structures. The zero of energy is at $E = -120$ kcal/mole. Small inset diagram (b). Curve showing total energy along the line AB of (a), i.e. where $r_1 + r_2 = 2{\cdot}81$ Å. The minimum energy occurs at $r_1 = 1{\cdot}37$, $r_2 = 1{\cdot}44$ Å, and the equivalent position $r_1 = 1{\cdot}44$, $r_2 = 1{\cdot}37$ Å.

The secular determinant is of order 5 × 5 and the equation for the energy eventually reduces to:

$$\begin{aligned} 31x^5 - 11(J_1 + J_2)x^4 - x^3(738\{J_1^2 + J_2^2\} - 846J_1J_2) \\ + x^2(J_1 + J_2)(682\{J_1^2 + J_2^2\} - 1018J_1J_2) \\ + x[1043\{J_1^4 + J_2^4\} + J_1J_2\{7182J_1J_2 - 3302(J_1^2 + J_2^2)\}] \\ + (J_1 + J_2)[J_1J_2\{1730(J_1^2 + J_2^2) - 4470J_1J_2\} + 335(J_1^4 + J_2^4)] = 0 \end{aligned} \tag{20}$$

where

$$10x = 5Q_1 + 5Q_2 - E_\pi \tag{21}$$

This equation was checked by putting $J_1 = J_2$, when it is divisible by the equation derived *ab initio* viz.

$$31x^3 - 22Jx - 444J^2x - 560J^3 = 0 \tag{20a}$$

The quintics obtained on inserting numerical values for J_1, J_2 were solved by means of the Oxford 'Mercury' electronic computer, and the energy surface (symmetrical about $r_1 = r_2$, of course) plotted. (Fig. 6).

It turns out that there is a much more definite minimum in this case (n = 5) than in the case n = 4. This occurs at $r_1 = 1{\cdot}365$ Å, $r_2 = 1{\cdot}455$ Å leading to a difference of 0·09 Å in the two bond lengths. From this result, it would appear that bond alternation tends to increase with the size of the rings (i.e. when including singly-excited structures in the calculation). It seems to us rather unlikely that subsequent addition of doubly-excited and higher structures would materially alter this. But it should be mentioned that the inclusion of the Dewar structures has led to a distinct change in the bond lengths: for a similar calculation using only the two Kekulé structures leads to bond lengths not greatly different from the values 1·51 and 1·34 Å appropriate to non-resonating single and double bonds.

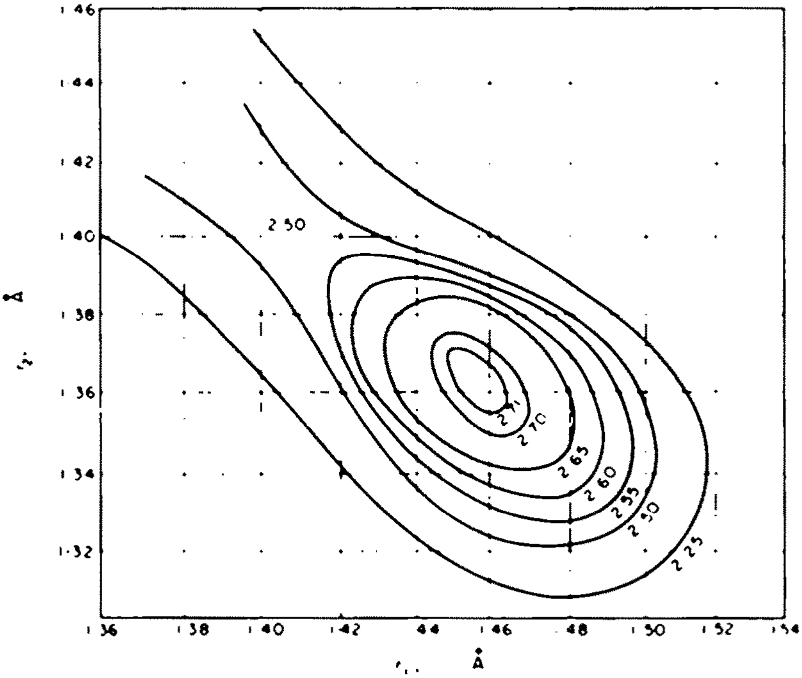


Fig. 6. Calculated values of the total energy $-E(r_1,r_2)$ for hypothetical planar $C_{10}H_{10}$, using Kekule and Dewar structures. The zero of energy is taken, as in Fig. 5, at $E = -120$ kcal/mole.

The difference in energy between the unsymmetrical and symmetrical structures can be seen, from Fig. 6, to be about 0·2 kcal. This, although quite definite, is not large, so that molecules of this kind would show rapid interconversion at room temperature. Further, since the interconversion motion would be slow at the saddle point, an X-ray diagram might easily show an apparently symmetrical appearance.

5. CONCLUSION

The discussion just given seems to us to show that in many respects the v.b. technique leads to very similar results to the m.o. technique, when applied to cyclic polyenes $C_{2n}H_{2n}$. Small members of this series will tend to have equal bond lengths, but larger ones will definitely show alternation. With Kekulé structures only it is found that beyond 2n = 8 there is very little resonance, so that one of the two structures dominates the complete wave function. Even in the symmetrical configuration the resonance (more strictly, delocalization) energy is much smaller than in benzene. Inclusion of Dewar structures tends to favour more nearly equal bond lengths, but bond alternations of the order of 0·1 Å may occur.

Note added in proof. Since the manuscript was written, we have included doubly-excited structures in the description of the eight and ten membered rings. This makes almost no difference to the calculated bond lengths in the equilibrium configurations.