Tetrahedron, 1963, Vol. 19, pp. 2153 to 2161. Pergamon Press Ltd. Printed in Northern Ireland

VALENCY-BOND STUDIES OF SOME CONJUGATED HYDROCARBONS—I

PENNEY-DIRAC BOND ORDERS; GENERAL THEORY AND APPLICATIONS TO 1,3-BUTADIENE AND FULVENE

D. CLARKSON, C. A. COULSON and T. H. GOODWIN
Chemistry Dept., The University, Glasgow
and Mathematical Institute, Oxford

(*Received* 3 *June* 1963)

Abstract—The Penney-Dirac calculation of bond orders in conjugated hydrocarbons is reconsidered, and a method of computing them, which does not involve perturbation theory, is developed. This method is general, in that it permits the exchange and Coulomb integrals for the various bonds to have values appropriate to their lengths, and not necessarily all equal. Detailed application to 1,3-butadiene and fulvene leads to results in close correspondence with molecular-orbital calculations.

VALENCY-BOND studies of aromatic and other conjugated hydrocarbons were developed by Pauling[1–3] quite early in the applications of wave mechanics to chemical problems. One of the many assumptions inevitably made in those early days was that all the bonds were equal, so that the bond Coulomb and exchange integrals (Q and J respectively) did not vary from bond to bond. In recent years, however, the alternation of bond lengths in large cyclic polyenes has been demonstrated theoretically[4] using the molecular-orbital approach; also, a re-examination of the same problem from the valency-bond point of view by Coulson and Dixon[5] has confirmed this result. Such calculations require both a knowledge of the variation of Q and J with bond length L, and also specific inclusion of the σ-bond energy, in computing the total energy of the molecule. Now complete minimization of the energy with respect to variations of all bond lengths is clearly impracticable except for small molecules. We have therefore re-examined the bond-order method for estimating bond lengths, for this method can easily be applied to larger molecules. There are serious theoretical difficulties (see later) in the simple Pauling superposition calculation of bond orders. However, as long ago as 1937 Penney[6] had given a definition of fractional bond order that avoided these difficulties by relating bond order to the degree of coupling of the spins of the electrons in the atomic orbitals at each end of the bond. This method has not been much used. In the present paper, therefore, we show that it may be adapted to the case of varying Q and J without difficulty. We then illustrate the general theory by specific application to benzene, butadiene and the non-alternant molecule fulvene. Subsequent papers will discuss naphthalene, pentalene, azulene, heptalene etc., and develop a correlation curve between Penney–Dirac bond orders and bond length.

[1] L. Pauling, *J. Chem. Phys.* **1**, 280 (1933).
[2] L. Pauling and G. W. Wheland, *J. Chem. Phys.* 362 (1933).
[3] L. Pauling and J. Sherman, *J. Chem. Phys.* 606 (1933).
[4] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* A, **251**, 172 (1959), **255**, 435 (1960).
[5] C. A. Coulson and W. T. Dixon, *Tetrahedron* **17**, 215 (1962).
[6] W. G. Penney, *Proc. Roy. Soc.* 158, 306 (1957).

First, however, a brief recapitulation of Penney's argument is desirable.*

General considerations. In a two-electron system let us denote the spins of the electrons by $\mathbf{s}_1$ and $\mathbf{s}_2$, and their sum by S, so that $\mathbf{S} = \mathbf{s}_1 + \mathbf{s}_2$. Then since the total spin is 0 or 1, in conventional units, and the magnitude of any vector S^2 is $\mathrm{S}(\mathrm{S} + 1)$, we can use the relation

$$\mathrm{S}^2 = (\mathbf{s}_1 + \mathbf{s}_2)\cdot(\mathbf{s}_1 + \mathbf{s}_2) = \mathbf{s}_1{}^2 + 2\mathbf{s}_1\cdot\mathbf{s}_2 + \mathbf{s}_2{}^2$$

to show that

$$\begin{aligned}\mathbf{s}_1\cdot\mathbf{s}_2 = \tfrac{1}{2}(\mathrm{S}^2 - \mathbf{s}_1{}^2 - \mathbf{s}_2{}^2) &= -\tfrac{3}{4} \quad \text{if} \quad \mathrm{S} = 0 \quad \text{(antiparallel spins)}\\ &= +\tfrac{1}{4} \quad \text{if} \quad \mathrm{S} = 1 \quad \text{(parallel spins)}\end{aligned} \tag{1}$$

But we also know that in a Heitler-London type of wave function, on the assumption that the two atomic orbitals are mutually orthogonal, the total energy E is given by

$$E = E_{\text{atoms}} + Q \pm J, \tag{2}$$

where the + sign applies for antiparallel spins, and the − sign for parallel spins. Combining (1) and (2)

$$E = E_{\text{atoms}} + Q - \tfrac{1}{2}(1 + 4\,\mathbf{s}_1\cdot\mathbf{s}_2)J \tag{3}$$

With more than two electrons, all the separate scalar products $\mathbf{s}_1\cdot\mathbf{s}_2$ cannot be simultaneously quantised. But Dirac[7] showed that on a similar assumption of mutual orthogonality of all atomic orbitals, (3) becomes

$$E = E_{\text{atoms}} + \Sigma Q_{ij} - \Sigma\tfrac{1}{2}(1 + \overline{4\mathbf{s}_i\cdot\mathbf{s}_j})J_{ij} \tag{4}$$

where the summation is over all pairs of orbitals, and the bar above $\overline{\mathbf{s}_i\cdot\mathbf{s}_j}$ denotes that now the quantum-mechanical mean value is to be taken. In practice we usually neglect all Q_{ij} and J_{ij} other than those between nearest neighbour atoms, and then the summation in (4) becomes a summation over all the bonds in the molecule.

Definition of bond order. Since bond order is not an observable, it must be defined. We follow Penney[6] in taking $p_{ij} = 1$ (mobile, or π−, bond order unity) if the spins on the two atoms are antiparallel, as in the pure double bond of ethylene; and $p_{ij} = 0$ (no bond) if the spins are mutually random. In the first case $\overline{\mathbf{s}_i\cdot\mathbf{s}_j} = -\tfrac{3}{4}$, and in the second $\overline{\mathbf{s}_i\cdot\mathbf{s}_j} = 0$. This latter result follows from the fact that if the two spins are randomly oriented with respect to each other, and we think in terms of a vector model, the angle between the vectors representing $\mathbf{s}_i$ and $\mathbf{s}_j$ is equally likely to be above or below 90°, and hence the mean value of the cosine of this angle must vanish. Thus the mean value of scalar product $\mathbf{s}_i\cdot\mathbf{s}_j$ will vanish.

The definition of bond order just given applies strictly only when $p_{ij} = 0$ or 1. But Penney defined intermediate (fractional) bond orders by linear interpolation. Thus

$$p_{ij} = -\tfrac{4}{3}\,\overline{\mathbf{s}_i\cdot\mathbf{s}_j} \tag{5}$$

It should perhaps be added that for the triplet state, where according to (1), $\mathbf{s}_i\cdot\mathbf{s}_j = \tfrac{1}{4}$, formula (5) leads to a π-bond order $-\tfrac{1}{3}$. At first sight one might have expected that

---

* A short (but not wholly accurate) account of the simpler form of this analysis is given by B. and A. Pullman, *Les Théories Electroniques de la Chimie Organique* pp. 337–339 Masson, Paris (1952).

[7] P. A. M. Dirac, *Principles of Quantum Mechanics* Chap. 12. Oxford University Press, Oxford (1947).

the formula should have led to $p = -1$ not $p = -\frac{1}{3}$. But this value is actually a very reasonable one, if we realize that the triplet state is represented on a molecular-orbital model by a combination of a bonding orbital and the corresponding anti-bonding one. It is known that the anti-bonding orbital is slightly more antibonding than the bonding orbital is bonding. Thus a total bond order of $-\frac{1}{3}$ is not unreasonable. It is probably true, however, that (5) is more useful when $p > 0$ than in those rare situations when $p < 0$.

Energy and bond order. Combining (4) and (5) we are led to our fundamental energy-bond order relationship:

$$E = E_{\text{atoms}} + \Sigma Q_{ij} + \Sigma\tfrac{1}{2}(3p_{ij} - 1)J_{ij} \tag{6}$$

An advantage of this formula is that we do not need to suppose that each Q_{ij} and J_{ij} are the same, so that the way is open to allow directly for differences in bond length.

Moffitt[8] noticed that (6) has a close resemblance to the fundamental molecular-orbital formula

$$E_{\pi} = \Sigma q_r \alpha_r + 2\Sigma p_{rs}\beta_{rs} \tag{7}$$

Both (6) and (7) show linear dependence on p, and lead to similar differential relationships

$$\frac{\partial E}{\partial J_{ij}} = \tfrac{1}{2}(3p_{ij} - 1), \qquad \frac{\partial E_{\pi}}{\partial \beta_{rs}} = 2p_{rs} \tag{8}$$

From our present point of view, however, the real importance of (8) is that if, by any means, we can find a way of writing the energy in the form

$$E = E_{\text{atoms}} + \Sigma Q_{ij} + \Sigma t_{ij}J_{ij} \tag{9}$$

then the bond orders are given by

$$p_{ij} = \tfrac{1}{3}(2t_{ij} + 1) \tag{10}$$

Bond orders calculated in this way will be called Penney-Dirac bond orders. A trivial illustration of (10) is found from the two electron case, for which the energy E is given by (2). Thus $t_{ij} = \pm 1$, leading to $p_{ij} = 1$ for the singlet ground state, and $p_{ij} = -\frac{1}{3}$ for the triplet excited state.

Another simple illustration of (10) is found in the ground state of benzene. Here all six J_{ij} are equal (to J, say) and also all six Q_{ij} (to Q say). If we consider merely the two Kekulé structures then

$$E = E_{\text{atoms}} + 6Q + 2{\cdot}4J$$

Comparison with (9) leads to $t = 0{\cdot}4$, and so $p = 0{\cdot}6$. But if we improve the wave function by also incorporating the Dewar structures, then

$$E = E_{\text{atoms}} + 6Q + 2{\cdot}606J,$$

leading to $t = 0{\cdot}434, p = 0{\cdot}623$. Penney had already observed that, by relating bond order to energy, as in (6), we insured that an increase of binding energy as a result of including more resonance structures would lead to an increase in bond orders. A

---

[8] W. E. Moffitt, *Proc. Roy. Soc.* **A, 199,** 487 (1949).

serious theoretical drawback to the Pauling superposition definition of bond orders[9] is that increasing the resonance energy in this way leads to a decrease in bond orders.

General technique. We can now make this analysis more general. If $A, B, \ldots R, \ldots$ are the resonating structures, with wave functions $\psi_a, \psi_b, \ldots \psi_r, \ldots$ then the molecular wave function Ψ may be written as

$$\Psi = c_a\psi_a + c_b\psi_b + \cdots + c_r\psi_r + \cdots$$

The corresponding energy is (taking Ψ and each ψ_r to be real):

$$E = \frac{\int \Psi \mathscr{H} \Psi \, d\tau}{\int \Psi^2 \, d\tau} = \frac{\sum\limits_{rs} c_r c_s H_{rs}}{\sum\limits_{rs} c_r c_s S_{rs}} \tag{11}$$

where $H_{rs} = \int \psi_r \mathscr{H} \psi_s \, d\tau$, and $S_{rs} = \int \psi_r \psi_s \, d\tau$.

The matrix elements H_{rs} and S_{rs} may be obtained by standard methods (e.g. the superposition diagram method of Pauling, or the closed cycle method described by Eyring, *et al.*[10] but care must be taken to keep all the J_{ij} distinct, even if, by symmetry, two or more of them are numerically equal.

If we exclude the term E_{atoms}, which is of no interest each H_{rs} is of the form,

$$H_{rs} = \sum_{i,j} Q_{ij} S_{rs} + \sum_{i,j} a_{rs,ij} J_{ij}, \tag{12}$$

where the coefficients $a_{rs,ij}$ are simple multiples of S_{rs} and the summations are over all bonds *ij*,

$$E = E_{\text{atoms}} + \sum_{i,j} Q_{ij} + \frac{\sum\limits_{r,s,i,j} c_r c_s a_{rs,ij} J_{ij}}{\sum\limits_{r,s} c_r c_s S_{rs}} \tag{13}$$

Identification of (13) and (6) shows that

$$p_{ij} = \frac{1}{3}\left\{1 + \frac{2\sum\limits_{r,s} c_r c_s a_{rs,ij}}{\sum\limits_{r,s} c_r c_s S_{rs}}\right\} \tag{14}$$

This means that, once the molecular wave-function Ψ has been obtained, the Penney-Dirac bond orders are almost as easy to compute as are the Pauling superposition bond orders. They require merely the linear expansion coefficients c_r and the geometrical factors a_{rs} and S_{rs}. The exchange integrals J_{ij} themselves do not appear in (14); but they are implicit through the coefficients c_r, which are found from the secular equations. In these equations the J_{ij} do appear explicitly. If the wave function Ψ is already normalized, then $\sum\limits_{r,s} c_r c_s S_{rs} = 1$, and (14) takes the simpler form

$$p_{ij} = \tfrac{1}{3}\{1 + 2\sum_{r,s} c_r c_s a_{rs,ij}\} \tag{15}$$

In an actual problem, the J_{ij} are functions of the bond lengths. It is clearly desirable that these lengths should be self-consistent in the sense that (a) the lengths determine the J_{ij}, (b) the J_{ij} determine the c_r from the secular equations, (c) the c_r

---

[9] L. Pauling, L. O. Brockway, J. Y. Beach, *J. Amer. Chem. Soc.* **57**, 2705 (1935).

[10] H. Eyring, J. Walter and G. E. Kimball, *Quantum Chemistry* Chap. 13. Wiley, New York (1960).

determine the p_{ij} from (14), and (d) the p_{ij} are consistent with the orginal assumed values of the bond lengths. This process evidently lends itself to an iterative procedure, as in the molecular-orbital method. However, if we do not wish to carry through this iteration to the end, we may often be content with a first level of approximation. Here we start with all J_{ij} equal, as has usually been assumed in the past, and calculate the p_{ij} with the c_r-values that follow from this assumption. The bond orders so calculated are the valency-bond analogues of the molecular-orbital bond orders obtained with simple Huckel molecular orbitals.

As an alternative to iterating till self-consistence is obtained we may choose the following different procedure for getting the c_r. In (13) the energy E appears to depend on both the c_r and the J_{ij}. In fact the c_r follow from the secular equations, so that E really depends only on the J_{ij}. We are therefore to choose the bond lengths so that, when the corresponding J_{ij} are used in (13) the energy is minimum. This is essentially the process used by Coulson and Dixon.[5] When adopting it, it is necessary to include the σ-electron energy E_σ as well as the π-electron energy given by (13).

Butadiene $\quad \underset{a}{1 = 2 - 3 = 4} \qquad \underset{b}{1 - 2 = 3 - 4}$

In butadiene there are two resonance structures a and b. The matrix components are

$$\begin{aligned} H_{aa} &= Q_{12} + Q_{23} + Q_{34} + J_{12} - \tfrac{1}{2}J_{23} + J_{34}, & S_{aa} &= 1 \\ H_{ab} &= \tfrac{1}{2}\{Q_{12} + Q_{23} + Q_{34} + J_{12} + J_{23} + J_{34}\}, & S_{ab} &= \tfrac{1}{2} \\ H_{bb} &= Q_{12} + Q_{23} + Q_{34} - \tfrac{1}{2}J_{12} + J_{23} - \tfrac{1}{2}J_{34}, & S_{bb} &= 1 \end{aligned} \tag{16}$$

The secular equations are

$$\begin{aligned} c_a\{H_{aa} - ES_{aa}\} + c_b\{H_{ab} - ES_{ab}\} &= 0 \\ c_a\{H_{ab} - ES_{ab}\} + c_b\{H_{bb} - ES_{bb}\} &= 0 \end{aligned} \tag{17}$$

In the first level of approximation, where all J_{ij} are equal to J, this gives (e.g. Pullmann and Pullman, p. 142)

$$\begin{gathered} E = 3Q + \sqrt{3}\,J \\ c_a = \sqrt{2/3} = 0{\cdot}817; \qquad c_b = \sqrt{\frac{2-\sqrt{3}}{3}} = 0{\cdot}299 \end{gathered} \tag{18}$$

To obtain individual bond orders we must from now on distinguish between the bonds.

$$E_{\text{exchange}} = \Sigma\, c_r c_s H_{rs} - \Sigma\, Q_{ij} \tag{19}$$

$$= (c_a^2 + c_a c_b - \tfrac{1}{2}c_b^2)(J_{12} + J_{34}) + (c_a c_b - \tfrac{1}{2}c_a^2 + c_b^2)J_{23} \tag{20}$$

by substitution of (16) in (19). Hence from (6), (10), (18) and (20)

$$\begin{aligned} p_{12} = p_{34} &= \tfrac{1}{3}\{2c_a^2 + 2c_a c_b - c_b^2 + 1\} \\ &= 0{\cdot}911 \end{aligned} \tag{21}$$

$$\begin{aligned} p_{23} &= \tfrac{1}{3}\{2c_a c_b - c_a^2 + 2c_b^2 + 1\} \\ &= 0{\cdot}333 \end{aligned} \tag{22}$$

These are not very different from the molecular orbital values 0·894 and 0·447 respectively.

In the second level of approximation we admit general inequality of the J_{ij}. (19), (20), (21) and (22) are unaltered in form but in order to get the c_r we shall, in this case of butadiene, use the known bond lengths to evaluate the J_{ij} and Q_{ij} and hence from (17) c_a and c_b. The experimental lengths as determined by electron diffraction by Almenningen, Bastiansen and Traetteberg[11] are $L_{12} = L_{34} = 1{\cdot}337\text{A}$, $L_{23} = 1{\cdot}483\text{A}$. The formulae of Coulson and Dixon[5] now give $J_{12} = J_{34} = -52{\cdot}046$, $J_{23} = -34{\cdot}014$, $(Q + E_\sigma)_{12} = (Q + E_\sigma)_{34} = -99{\cdot}041$, $(Q + E_\sigma)_{23} = -106{\cdot}080$ all in kg.cal/mole and the secular determinant becomes

$$\begin{vmatrix} -391{\cdot}245 - E & \tfrac{1}{2}(-442{\cdot}269 - E) \\ \tfrac{1}{2}(-442{\cdot}269 - E) & -286{\cdot}130 - E \end{vmatrix} = 0.$$

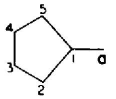
For the ground state this gives

$$E = -396{\cdot}094 \text{ kg.cal./mole}, \quad c_a = 0{\cdot}893, \quad c_b = 0{\cdot}188.$$

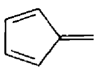
Substituting in (19)

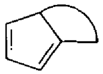
$$p_{12} = p_{34} = 0{\cdot}965, \quad p_{23} = 0{\cdot}203. \tag{23}$$

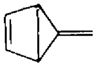
Comparison of (21), (22) and (23) shows that allowing for variations in bond length increases high bond orders, and decreases low ones. Exactly the same situation occurs in the molecular-orbital method.

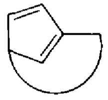


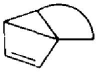
Fulvene C_6H_6. Fulvene has six π-electrons, and so, as in benzene, there will be five independent covalent structures. Those derived from the Rumer diagram[12] in which the atomic orbitals are arranged in the cyclic order α,1,2,3,4,5 are A,B,F,D,G. These, however, are not chemically very satisfying, and, if used in the simple Pauling superposition model they lead to mobile bond order zero in the bond 1–5. (This, incidentally, shows how dangerous this superposition is with non-alternant molecules).

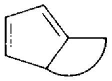

A

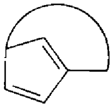

B


F


D


G


C


E

We therefore chose A,B,C,D,E. This group has the advantage of being symmetrical, and every bond except 1-α appears *double* in at least two structures. In addition only singly-excited structures appear. They are not, however, canonical in the sense

---

[11] A. Almenningen, O. Bastiansen and M. Traetteberg, *Acta Chem. Scand.* **12**, 1221 (1958).

[12] G. Rumer, *Göttingen Natchr.* p. 337 (1932).

of being derivable from a single Rumer diagram without including crossed bonds. As a result greater care is needed to be sure that the correct powers of -1 are used in the matrix components. To avoid these difficulties we found it safer, though much slower, to calculate these by the method described by Eyring *et al.*[10] instead of by the Pauling superposition method.

In the first level of approximation, with all $J_{ij} = J$, we obtained the value for the energy already found by others (see below) *viz.* $E = 6Q + 2J$. This leads to a normalised wave-function in which

$$c_A = 0{\cdot}632, \quad c_B = -c_C = c_D = -c_E = 0{\cdot}211$$

Straightforward analysis similar to that already described now leads to

$$\begin{aligned} p_{\alpha 1} = p_{23} = p_{45} &= 0{\cdot}911; \\ p_{12} = p_{34} = p_{51} &= 0{\cdot}200. \end{aligned} \tag{24}$$

Evidently the single structure A dominates this molecule. The bond orders (21) may be compared with those calculated by the simple molecular orbital method by Coulson *et al.*[13]

$$\begin{aligned} p_{\alpha 1} = 0{\cdot}76; \quad p_{23} = p_{45} = 0{\cdot}78 \\ p_{12} = p_{51} = 0{\cdot}45; \quad p_{34} = 0{\cdot}52 \end{aligned} \tag{25}$$

and with a molecular-orbital calculation by Nakajima and Katagiri[14] who take our structure A but with $L_{\alpha 1} = L_{23} = L_{34} = 1{\cdot}34\text{A}$, $L_{12} = L_{34} = L_{51} = 1{\cdot}48\text{A}$ and introduce a bond alternation parameter to correlate the resonance integrals in the formal single and double bonds. They then obtain bond orders

$$\begin{aligned} p_{\alpha 1} = 0{\cdot}925, \quad p_{23} = p_{45} = 0{\cdot}926 \\ p_{12} = p_{15} = 0{\cdot}266, \quad p_{34} = 0.284 \end{aligned} \tag{26}$$

The general pattern of our results (24) is quite similar to (25) and closely similar to (26).

Coulson *et al.* also applied the Penney–Dirac technique to find the bond orders in fulvene and, selecting the structures A,D,E,H,J obtained (of course) the same energy $E = 6Q + 2J$, but the bond orders

$$\begin{aligned} p_{\alpha 1} = 0{\cdot}94; \quad p_{23} = p_{45} = 0{\cdot}50 \\ p_{12} = p_{51} = 0{\cdot}60; \quad p_{34} = 0{\cdot}20 \end{aligned} \tag{27}$$

Unfortunately an error has recently been detected in this latter calculation and these authors now recognise the validity of the present work.

To get a higher approximation for fulvene we shall use the Coulson–Dixon minimum energy method. The true bond lengths are not known experimentally, so we take the length of α—1 to be L_1, those of 2—3 and 4—5 to be L_3, and those of 1—2, 3—4, 5—1 (the three formally single bonds in the dominant structure A) to be L_2. It is of course, not necessary to suppose that 1—2 and 3—4 are identical but (21) shows that it is not likely to be far wrong, and the assumption considerably reduces the amount of computation.

[13] C. A. Coulson, D. P. Craig and A. Maccoll, *Proc. Phys. Soc.* **61**, 22 (1948).

[14] T. Nakajima and S. Katagiri, *Bull. Chem. Soc., Japan* **35**, 910 (1962).

We have to determine the values of L_1, L_2, L_3 for which the total energy E, including both σ- and π-electron contributions, is least. A mesh of $5 \times 5 \times 5 = 125$ values of the three lengths was chosen, and a programme was written to find the eigenvalues of the matrix $\|H_{rs} - ES_{rs}\|$ on the Glasgow University DEUCE computer. It is possible that a method of steepest descents might have reduced the time needed. The final result was that the minimum energy was associated with

$$L_1 = 1{\cdot}35, \quad L_2 = 1{\cdot}49, \quad L_3 = 1{\cdot}35, \quad \text{all in A} \tag{28}$$

and $E_{\text{ground}} = -732{\cdot}282$ kg.cal./mole
These optimum bond lengths lead to a normalized wave function in which

$$c_A = 0{\cdot}7453, \quad c_B = -c_C = c_D = -c_E = 0{\cdot}1522 \tag{29}$$

Thus the classical structure is approximately 25 times as significant as any other structure, and quite accurately represents the ground state.

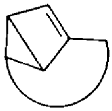
By the method described earlier it is found that

$$p_{\alpha 1} = p_{23} = p_{45} = 0{\cdot}954, \quad p_{12} = p_{34} = p_{51} = 0{\cdot}148 \tag{30}$$

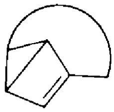
Comparison of (30) and (24) shows once more that allowing for variations in the exchange integrals increases big p_{ij} and decreases small p_{ij}.

If we accept the value of E_{ground} in (28) we obtain a resonance energy of 11·8 kg.cal./mole. This is much less than with benzene, in accordance with our conclusion in (30) that structure A is dominant.

In addition to the work of Coulson *et al.* referred to earlier, Sklar[15] had determined the energy levels in fulvene also using the structures A,D,E,H,J which are a canonical set if based on a Rumer diagram with the atomic orbitals in the cyclic order 1,2,3,α,4,5.



H



J

He, too, gave the energy of the ground state as $6Q + 2J$ (all $J_{ij} = J$) but did not calculate the bond orders.

We have applied the superposition technique to this set of structures (in which no confusion can arise over powers of -1 in the matrix elements) for the lengths L_1, L_2, L_3 in (24) thereby confirming $E_{\text{ground}} = -732{\cdot}282$ kg.cal./mole, deriving the normalized coefficients

$$c_A = 0{\cdot}7453; \quad c_D = c_E = -0{\cdot}1522; \quad c_H = c_J = 0{\cdot}3044 \tag{31}$$

and confirming exactly the bond orders in (30).

Discussion

The following conclusions seem to follow from this work.

(1) The calculation of Penney–Dirac bond orders is scarcely any more complicated

---

[15] A. L. Sklar, *J. Chem. Phys.* **5**, 669 (1937).

than the usual superposition method; and for non-alternant molecules it is much more significant chemically.

(2) A good first approximation can be obtained on the assumption that all exchange (and Coulomb) integrals are equal. This tends, however, to underestimate high bond orders, and overestimate small ones.

(3) Allowance can easily be made for variations in exchange and Coulomb integrals, and the use of formulae such as those of Coulson and Dixon are well suited to this purpose.

(4) In the case of butadiene and fulvene, chemically reasonable results are obtained. For each molecule the amount of conjugation in the ground state is quite small.

(5) The analysis which we have used considers only covalent resonance structures. It is therefore suitable only for hydrocarbon molecules; even then there will be difficulty with non-alternants. The inclusion of polar (i.e. ionic) structures is beset with many difficulties, and does not seem worthwhile in work of this kind.