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VALENCY BOND STUDIES OF SOME CONJUGATED HYDROCARBONS–IV*

BOND LENGTHS AND PENNEY–DIRAC BOND ORDERS

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Abstract—A relation between bond lengths and Penney–Dirac bond orders has been derived.

INTRODUCTION

ACCORDING to Dirac,[1] the total energy of a molecule may be written as:

$$E = E^{atoms} + \sum Q_{ij} - \sum \tfrac{1}{2}(1 + \overline{4\mathbf{s}_i \cdot \mathbf{s}_j})\, J_{ij} \qquad (1)$$

where $\overline{\mathbf{s}_i \cdot \mathbf{s}_j}$ is the quantum mechanical mean of the scalar product of electron spin vectors $\mathbf{s}_i$ and $\mathbf{s}_j$. The Q_{ij} and J_{ij} are the familar Coulomb and exchange integrals from the Valence Bond theory. So if the double bond in ethylene is treated as a sum of a π and a σ bond we find $\overline{\mathbf{s}_i \cdot \mathbf{s}_j} = -\frac{3}{4}$ for the opposed π-electron spins on both carbon atoms. A no π-bond situation is represented then by random spins for which $\overline{\mathbf{s}_i \cdot \mathbf{s}_j} = 0$.

Penney[2] defined the mobile bond order p_{ij} for these cases as $+1$ and 0 respectively. Moreover he introduced fractional bond orders by linear interpolation, thus using:

$$p_{ij} = -\tfrac{4}{3}\,\overline{\mathbf{s}_i \cdot \mathbf{s}_j} \qquad (2)$$

The expression for the π-bond energy may be written now as:

$$E^{\pi} = \sum_{ij} Q_{ij} + \sum_{ij} \tfrac{1}{2}(3p_{ij} - 1)\, J_{ij} \qquad (3)$$

which enables us to take into account differences in C—C bond lengths r if Q(r), J(r) and p(r) are known.

The dependence of exchange integrals J and Coulomb integrals Q on bond lengths r has been considered recently by Coulson and Dixon[3] in a discussion of bond alternation in cyclic polyenes. Following their arguments the total binding energy for ethylene and benzene at equal bond distances may be written as:

$$E^{total}_{ethylene}(r) = Q(r) + J(r) + E^{\sigma}(r) \qquad (4)$$

and:

$$E^{total}_{benzene}(r) = 6[Q(r) + 0{\cdot}434\, J(r) + E^{\sigma}(r)] \qquad (5)$$

* Part III: *Rec. Trav. Chim.* in press. Part II: *Tetrahedron* **19**, 2163 (1963).

[1] P. A. M. Dirac, *Principles of Quantum Mechanics* Chap. 12. Oxford University Press (1947).
[2] W. G. Penney, *Proc. Roy. Soc.* **158**, 306 (1937).
[3] C. A. Coulson and W. T. Dixon, *Tetrahedron* **17**, 215 (1962).

where $E^{\sigma}(r)$ represents the σ energy of a bond of length r. Combining (4) and (5) gives:

$$J(r) = \frac{1}{0{\cdot}566}\left[E^{\text{total}}_{\text{ethylene}}(r) - \tfrac{1}{6}E^{\text{total}}_{\text{benzene}}(r)\right] \tag{6}$$

For the dependence of E^{total} on r, Morse functions were chosen:

$$E(r) = E_0[e^{-2a(r-r_0)} - 2e^{-a(r-r_0)}] \tag{7}$$

After insertion of appropriate values for the parameters a relation between J and r is obtained that can be approximated in the range $1{\cdot}34 < r < 1{\cdot}51$ Å by:

$$J(r) = -41{\cdot}199 + 121{\cdot}2(r - 1{\cdot}42) - 114{\cdot}2(r - 1{\cdot}42)^2 \tag{8}$$

Along similar lines an expression for $E^{\sigma}(r) + Q(r)$ can be derived from (4) and (5) by elimination of J. The relevant analytical expression now becomes:

$$E^{\sigma}(r) + Q(r) = -105{\cdot}905 - 39{\cdot}6(r - 1{\cdot}42) + 526(r - 1{\cdot}42)^2 + \\ -1000(r - 1{\cdot}34)(r - 1{\cdot}42)(r - 1{\cdot}51) \tag{9}$$

The use of the expressions (8) and (9) obviously lies in application to other molecules but in doing so one should realize the basic assumptions in their derivation.

Clarkson *et al.*[4] outlined a procedure to obtain fractional bond orders from the molecular wave function. In the VB approximation, the molecular wave function Ψ is obtained as a linear combination of the individual wave functions for the "resonating" structures φ_r:

$$\Psi = c_1\varphi_1 + c_2\varphi_2 + \ldots c_r\varphi_r + \ldots \tag{10}$$

The coefficients c_r and the π-electronic energy of the molecule are required to satisfy the secular equations.

$$c_1(H_{11} - E^{\pi}S_{11}) + c_2(H_{12} - E^{\pi}S_{12}) + \ldots c_r(H_{1r} - E^{\pi}S_{1r}) = 0 \tag{11}$$

etc.

where $H_{rs} = \int \varphi_r H \varphi_s \, d\tau$ and $S_{rs} = \int \varphi_r \varphi_s \, d\tau$ if we take the wave functions to be real. Hence the coefficients in (10) have to be chosen so as to minimize the molecular electronic energy E and this may be expressed as:

$$E^{\pi} = \frac{\int \Psi H \Psi \, d\tau}{\int \Psi^2 \, d\tau} = \frac{\sum\limits_{rs} c_r c_s \int \varphi_r H \varphi_s \, d\tau}{\sum\limits_{rs} c_r c_s \int \varphi_r \varphi_{rs} \, d\tau} = \frac{\sum\limits_{rs} c_r c_s H_{rs}}{\sum\limits_{rs} c_r c_s S_{rs}} \tag{12}$$

The integrals H_{rs} and S_{rs} can be written down easily with the aid of superposition diagrams.[5] In the simplest and most common applications of this method to e.g. π-electron systems of planar conjugated hydrocarbons the exchange integrals J_{ij} and Coulomb integrals Q_{ij} are assumed to be constants. If one desires however to distinguish between individual carbon-carbon bonds then the matrix elements H_{rs} must be written:

$$H_{rs} = \sum_{ij} Q_{ij}S_{rs} + \sum_{ij} a_{rs,ij}J_{ij} \tag{13}$$

[4] D. Clarkson, C. A. Coulson and T. H. Goodwin, *Tetrahedron* **19**, 2153 (1963).
[5] L. Pauling, L. O. Brockway and J. Y. Beach, *J. Amer. Chem. Soc.* **57**, 2705 (1935).

In (13) the summations Σ_{ij} must be taken over all bonds, the $a_{rs,ij}$ appear as multiples of S_{rs}, so that

$$E^{\pi} = \sum_{ij} Q_{ij} + \frac{\sum_{rsij} c_r c_s a_{rs,ij} J_{ij}}{\sum_{rs} c_r c_s S_{rs}} \tag{14}$$

A comparison of (3) and (14) shows that:

$$p_{ij} = \tfrac{1}{3}\left[1 + \frac{2\sum_{rs} c_r c_s a_{rs,ij}}{\sum_{rs} c_r c_s S_{rs}}\right] \tag{15}$$

which reduces to

$$p_{ij} = \tfrac{1}{3}[1 + 2\sum_{rs} c_r c_s a_{rs,ij}] \tag{16}$$

when the wave function Ψ is normalized.

Clarkson *et al.*[4] suggested that the bond orders obtained through (15) for a chosen set of bond lengths could be used in an iterative process leading ultimately to self-consistent lengths and bond orders. It may be emphasized that it is possible to calculate fractional bond orders for any molecular conformation but in fact a bond order only characterizes the length of a bond if obtained for the equilibrium conformation. Bond orders pertaining to this situation will be indicated here by p^0.

A BOND ORDER-BOND LENGTH CURVE

It will be shown now that for given equilibrium bond length the Penney–Dirac bond orders can be calculated directly from (8) and (9). Combination of the σ- and π-electron energy enables us to write the total molecular electron energy $E^{total}_{(r)}$ for any set of bond lengths r_{ij} as:

$$E^{total}(r) = \sum_{ij} E^{\sigma}(r_{ij}) + \sum_{ij} Q_{ij}(r_{ij}) + \sum_{ij} \tfrac{1}{2}(3p_{ij} - 1) J_{ij} \tag{17}$$

The equilibrium condition requires

$$\frac{\partial E^{total}}{\partial r_{ij}} = 0$$

for every bond; hence if we consider the variation of E^{total} in the equilibrium situation with one particular bond say r_{kl} and keep all other r_{ij}^0 fixed it appears that

$$0 = \left(\frac{\partial E^{total}}{\partial r_{kl}}\right)_{r_{ij}^0} = \left(\frac{\partial E^{\sigma}}{\partial r_{kl}}\right)_{r_{ij}^0} + \left(\frac{\partial Q_{kl}}{\partial r_{kl}}\right)_{r_{ij}^0} + \tfrac{1}{2}(3p_{kl}^0 - 1)\left(\frac{\partial J_{kl}}{\partial r_{kl}}\right)_{r_{ij}^0}$$
$$+ \sum_{ij} \tfrac{3}{2} J_{ij} \left(\frac{\partial p_{ij}^0}{\partial r_{kl}}\right)_{r_{ij}^0} \tag{18}$$

Let us analyse first the last term in this expression i.e. a summation representing changes in the bond orders caused by variations of r. The bond orders are merely combinations of coefficients indicating the weight of the valency bond structures

in the wave equation (10). For *fixed distances* these coefficients are obtained from the secular equations i.e. by minimizing the energy with respect to *all* coefficients c_s, so that:

$$0 = \frac{\partial E^{\pi}(r)}{\partial c_s} = \frac{\partial \sum_{ij} Q_{ij}(r)}{\partial c_s} + \sum_{ij} \tfrac{1}{2}(3p_{ij} - 1)\frac{\partial J_{ij}(r)}{\partial c_s} + \tfrac{3}{2}\sum_{ij} J_{ij}(r)\frac{\partial p_{ij}}{\partial c_s} \tag{19}$$

But for a chosen set of lengths r_{ij}—not necessarily being the equilibrium set—the Q_{ij} and the J_{ij} are constants with respect to the coefficients, thus reducing (19) to:

$$0 = \sum_{ij} J_{ij}(r_{ij})\frac{\partial p_{ij}}{\partial c_s} \tag{20}$$

Allowing now for small variations of one of the r_{ij} say r_{kl}, we find

$$0 = \sum_{ij} J_{ij}(r)\frac{\partial p_{ij}/\partial r_{kl}}{\partial c_s/\partial r_{kl}} \tag{21}$$

from which

$$0 = \sum_{ij} J_{ij}(r)\frac{\partial p_{ij}}{\partial r_{kl}} \tag{22}$$

This expression obviously applies to the equilibrium situation as well. Rearrangement of (18) leads to:

$$\tfrac{1}{2}(3p_{kl}^{0} - 1) = -\frac{\dfrac{d(E_{kl}^{\sigma} + Q_{kl})}{dr_{kl}}}{\dfrac{dJ_{kl}}{dr_{kl}}} \tag{23}$$

With the aid of expression (23) and the relations (8) and (9) bond orders corresponding to given (equilibrium) lengths r^0 can be calculated. The resulting bond length–bond order curve is presented in Fig. 1. The p values obtained in this manner must be identical with those found ultimately with the self-consistent procedure outlined by Clarkson *et al.*[4]. Both methods are based on the same r-dependency of J and $(E^{\sigma} + Q)$.

The determination of molecular conformations of minimum energy through the iterative procedure can be guided now because one is able to adapt new trial lengths to the bond orders obtained from a former cycle.

It should be remarked that the Penney–Dirac order length curve comes very near to corresponding relations[6,7] obtained in the molecular orbital theory viz. $r = 1{\cdot}51 - 0{\cdot}16\,p$ or $r = 1{\cdot}53 - 0{\cdot}18\,p$. A simple analytical approximation to the valence bond curve is

$$r = +1{\cdot}53 - 0{\cdot}25\,p + 0{\cdot}06\,p^2 \tag{24}$$

It appears that a bond length of about 1·53 Å corresponds to a bond order zero. At first sight one expects here 1·51 Å because this is the length chosen for a pure single σ bond formed from two sp^2 hybridized carbon atoms. However, a bond

[6] H. C. Longuet-Higgins and L. Salem, *Proc. Roy. Soc.* **A251**, 172 (1959).
[7] D. A. Morton Blake, *Ph.D. Thesis, University of Glasgow*, 1964.

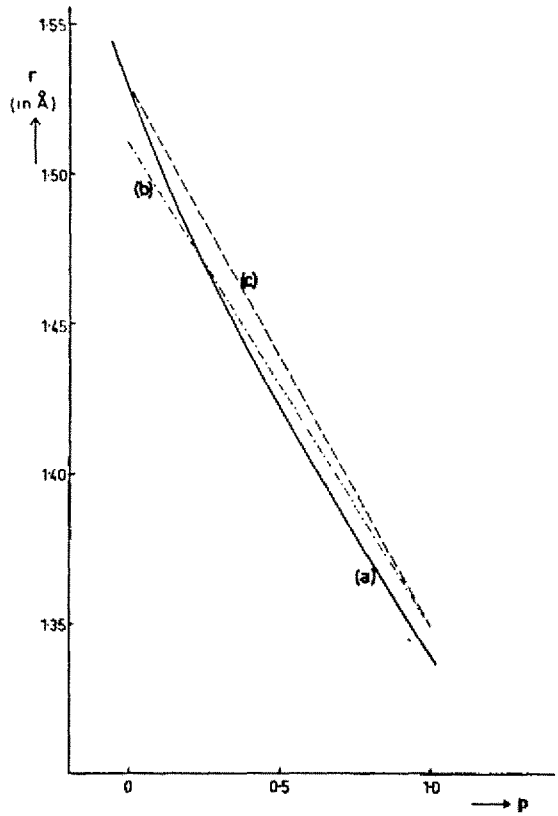

FIG. 1. Full curve (a) Penney–Dirac bond orders versus bond lengths; dotted lines show empirical relations used in molecular orbital theory (b): $r = 1{\cdot}51 - 0{\cdot}16\,p$, (c): $r = 1{\cdot}53 - 0{\cdot}18\,p$.

order zero must be assigned to the C—C bond in a hypothetical "molecule" C_2H_4 where the two π-electron spins are oriented at random. So it is plausible that a combination of (8), (9) and (23) leads to $r = 1{\cdot}523$ Å at zero bond order. In the region where very small or negative Penney–Dirac orders occur the relation can not be very accurate because rather large extrapolations from the basic data (properties of ethylene and benzene) are involved then. The applicability of the curve can be tested if more calculated bond lengths and bond orders become available for molecules such as naphthalene for which accurate structure determinations are available.

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