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A Bond Length — Bond Order Relation Derived from a Morse Type Sigma Electron Energy Curve

P. C. den Boer-Veenendaal and D. H. W. den Boer

Organisch Chemisch Laboratorium, Rijksuniversiteit, Utrecht, The Netherlands

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1. Introduction

It is customary to write the total electron energy of conjugated hydrocarbons as a sum of σ- and π-electron energies:

$$E^{\text{total}} = E^{\sigma} + E^{\pi} . \tag{1}$$

Consider a molecule in its equilibrium conformation, then for every bond kl the condition for equilibrium is:

$$\frac{\partial E^{\text{total}}}{\partial r_{kl}} = 0 . \tag{2}$$

From (1) and (2) it follows that:

$$\frac{\partial E^{\sigma}}{\partial r_{kl}} = - \frac{\partial E^{\pi}}{\partial r_{kl}} . \tag{3}$$

In simple LCAO–MO theory the mobile bond order for a bond kl may be written as:

$$p_{kl} = \tfrac{1}{2} \frac{\partial E^{\pi}}{\partial \beta_{kl}} . \tag{4}$$

Allowing for a variation of the bond length r_{kl} the right hand side of (4) becomes:

$$\frac{\partial E^{\pi}}{\partial \beta_{kl}} = \frac{\partial E^{\pi} / \partial r_{kl}}{\partial \beta_{kl} / \partial r_{kl}} . \tag{5}$$

A combination of (3), (4) and (5) leads to

$$p_{kl} = - \tfrac{1}{2} \frac{d\, E^{\sigma} / d\, r_{kl}}{d\, \beta_{kl} / d\, r_{kl}} \tag{6}$$

because the total σ-electron energy is the sum of all individual σ-bond energies. This clearly demonstrates that the choice of a linear p-r relation combined with an exponential β-r curve involves a particular function $E^{\sigma}_{kl}(r_{kl})$.

2. Bond Order and Sigma Electron Energy

Length-order relations derived from a chosen $E^{\sigma}(r)$ function and exponential β-r curves will be considered. For reasons of comparison with recent valence bond work [2] it was decided to accept for $E^{\sigma}(r)$ a Morse curve based upon the experimental force constant for the C–C stretching vibration in ethane and a length of

1.51 Å for a pure σ-bond between sp^2 hybridized carbon atoms [4]. The latter assumption is open to questions.

Coulson [3] and Mulliken [9] attribute the difference in the C–H bond lengths in methane and ethylene to a change in s-character of the bonds. A similar correction of the C–C distance in ethane leads these authors to a value of 1.51 Å for the hypothetical bond. Dewar et al. [6] among other arguments extrapolate a linear order-length curve (bond orders calculated without the usual neglect of overlap) and so deduce 1.48 Å.

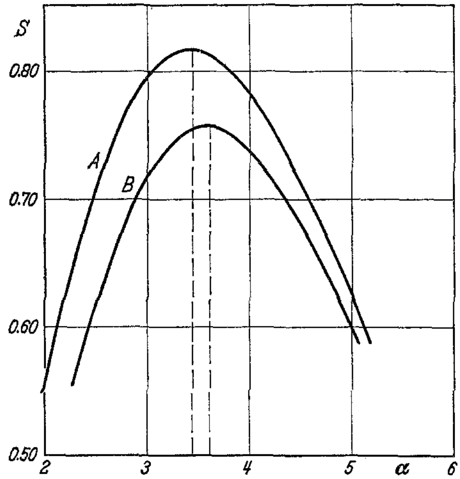

Fig. 1. Overlap integrals for σ C-C bonds versus $\alpha = ZR/2a_0$; curve A sp^2-sp^2 hybrids, curve B sp^3-sp^3 hybrids

In Fig. 1 the results are given of a calculation of overlap integrals for sp^3-sp^3 and sp^2-sp^2 hybridized C atoms as a function of $\alpha = \frac{Z}{2}\frac{R}{a_0}$ (Z = effective nuclear charge, R = interatomic distance and a_0 = Bohr radius). The maximum overlap for sp^2 hybrids is found at a smaller α-value then for the sp^3 hybrids. The uncertainty in the value to be taken for the effective nuclear charge obviously carries over in the deduced lengths. However, if it is accepted that the overlap integrals

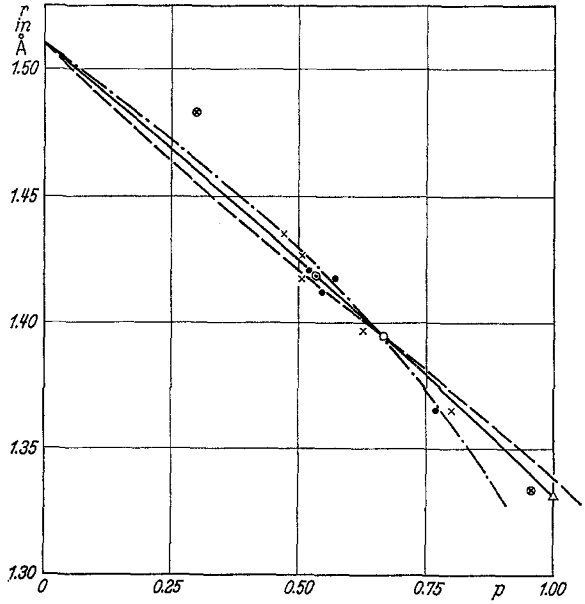

Fig. 2. Calculated bond order-bond length curves (—·—·— $a = 0.20$ Å^{-1}, ——— $a = 0.30$ Å^{-1}, — — — $a = 0.40$ Å^{-1}). Measured bond lengths are indicated for graphite ⊙, benzene o, ethylene △ versus symmetry-determined Hückel bond orders; for butadiene ⊗, naphthalene ● and anthracene × versus bond orders calculated with $a = 0.30$ Å^{-1}

considered are maximal for the equilibrium bond lengths a shortening of a few hundredths of an Å to 1.51 Å for the sp^2-sp^2 bond relative to the sp^3-sp^3 bond of 1.54 Å is reasonable. Recently, SCHAEFER and WHEATLEY [12] found by X-ray analysis of tetra-acetylethane a length of 1.508 Å for the central C–C bond and suggest this to be a single σ-bond of pure sp^2-sp^2 type.

Using the expression $\beta_{kl} = \beta_0 \exp\left(\frac{1.40 - r_{kl}}{a}\right)$ as introduced by LONGUET-HIGGINS and SALEM [8] and the Morse curve for E^σ as discussed, bond order bond length curves were calculated from (6) for three different values of a viz. 0.20, 0.30 and 0.40 Å^{-1}. The parameter β_0 was fixed in such a way that a bond order of 0.667 was obtained for the C–C bonds in benzene (1.397 Å). The graphs of Fig. 2 indicate that for $a = 0.30$ Å^{-1} and $\beta_0 = -24.7$ kcal/mole a curve approximated by the linear function $r = 1.51 - 0.17\,p$ (or by the quadratic function $r = 1.510 - 0.160\,p - 0.015\,p^2$) is found. The calculated line goes almost exactly through the three points obtained by plotting the measured bond lengths in ethylene, benzene and graphite versus their bond orders which are determined by symmetry in the simple Hückel theory [10]. The calculations on the basis of $a = 0.20$ Å^{-1} and $a = 0.40$ Å^{-1} with $\beta_0 = -16.4$ and -33.1 kcal/mole respectively, clearly show a less satisfactory behaviour.

Discussion

By using the accurately known structural data for butadiene [1], naphthalene [7] and anthracene [5], it is possible to perform an independent check on the validity of the relation derived in section 2. For these conjugated hydrocarbons Hückel type calculations were performed in which the parameters β_{kl} had been adapted to the measured bond lengths with the aid of the (three) above mentioned exponential functions. This procedure also permits a discrimination between the values taken for a because for a "selfconsistent" situation the bond orders calculated via the secular determinants should fit the corresponding curve. As can be seen from Fig. 2 this criterion is fulfilled adequately if a is chosen to be 0.30 Å^{-1}. It should be mentioned that LONGUET-HIGGINS and SALEM [8] derive $a = 0.3106$ Å^{-1} from measured vibrational frequencies of benzene.

The central bond of butadiene does not fit in any of the three curves. This anomalous result for butadiene may indicate that calculations of bond length alternation [11] for which the parameters are based only upon this compound are open to discussion.

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Professor Dr. D. H. W. den Boer
Organisch-Chemisch Laboratorium
der Rijksuniversiteit
Utrecht, The Netherlands