A Theoretical Relation between Bond-order and Bond-length in Conjugated Systems using Morse-type Potential Function

By Toshinobu ANNO, Mitsuo ITO,
Ryoichi SHIMADA, Akira SADÔ
and Wataru MIZUSHIMA

(Received December 12, 1955)

It has been well known that there exists a definite relation between bond-order and bond-length in conjugated systems[1]. For C-C bonds Coulson[2] derived a theoretical formula explaining the relation between bond-lengths and bond-orders calculated by MO approximation. Anno and Sado[3] showed that a similar formula applies also to C-Cl bonds in conjugated systems. In deriving their formula, they used a method originally due to Lennard-Jones[4], who used Hooke-type stretching potential functions of bonds in reference molecules. For this reason, their formulae combined with the empirical values of parameters do not explain completely the order-length relationships for C-C and C-N bonds, where the bond-orders and bond-lengths change widely from molecule to molecule. One way of removing this difficulty may be to use the Morse-type function instead of the Hooke-type one. This idea was first suggested by Lennard-Jones[4] and used by Coulson[2] in qualitative explanation of the correction to the empirical parameters for fitting the theoretical order-length curve to an empirical one. However, the quantitative study of the theoretical order-length relationship using Morse-type function has not been undertaken.

In the present communication, a theoretical equation for order-length relation will be proposed taking this idea into account. The results for applications to C-C and C-N bonds will also be given.

The energy difference between pure single and triple bonds may be considered to be mainly due to π-electrons. Then the following equation holds:

$$4\beta = E_t^0 - E_s^0 + V_t(x-x_t) - V_s(x-x_s) \qquad (1)$$

where β is the resonance integral, and E_s^0 and E_t^0 denote the bond energy in pure single and triple bonds at their equilibrium values x_s and x_t, respectively. $V_s(x-x_s)$ and $V_t(x-x_t)$ are the potential energies of single and triple bonds when the internuclear distances are x. Instead of assuming the Hooke-type function, the following forms of the Morse-type function may be assumed:

$$\begin{aligned} V_s(x-x_s) &= D_s[1-\exp\{-a_s(x-x_s)\}]^2 \\ V_t(x-x_t) &= D_t[1-\exp\{-a_t(x-x_t)\}]^2 \end{aligned} \qquad (2)$$

where D is the bond strength and a is given by

$$a = \sqrt{\frac{k}{2D}}$$

in which k is the bond stretching force constant.

On the other hand, the total bond energy F which allows for the compression of the σ-bond is given by

$$F = V_s(x-x_s) + 2p\beta \qquad (3)$$

where p is the mobile bond-order. By a method similar to that used by Coulson[2], and using Eqs. (1), (2) and (3), it follows that

$$p = \frac{2}{1 - \dfrac{a_t D_t}{a_s D_s}\left[\dfrac{\exp\{-a_t(x-x_t)\} - \exp\{-2a_t(x-x_t)\}}{\exp\{-a_s(x-x_s)\} - \exp\{-2a_s(x-x_s)\}}\right]}. \qquad (4)$$

Taking reasonable values of constants, which will be discussed in subsequent articles, curves shown in Figs. 1 and 2 are obtained. Figs. 1 and 2 refer to C-C and C-N bonds, respectively. As can be seen in these figures

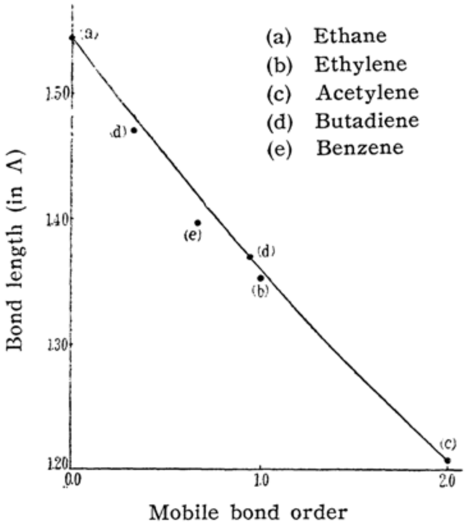

Fig. 1. The relation between bond-order and bond-length for C-C bonds

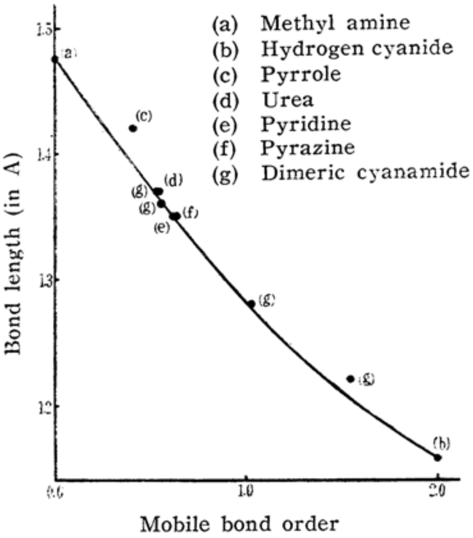

Fig. 2. The relation between bond-order and bond-length for C-N bonds.

the theoretical curves explain the empirical data in fair approximation.

The equation (4) can also be used to calculate the force canstants if it is combined with the considerations similar to those due to Coulson and Longuet-Higgins[5].

Full account of this communication will be published in the near future.

The authors express their hearty thanks to Professor S. Imanishi for his encouragement throughout this work and for reading this manuscript.

Department of Chemistry, Faculty of Science
Kyushu University, Fukuoka

---

[1] See, for example, E.G. Cox and G.A. Jeffery, *Proc. Roy. Soc.* (London), A **207**, 110 (1951).

[2] C.A. Coulson, *Proc. Roy. Soc.* (London), A **169**, 413 (1939).

[3] T. Anno and A. Sado, This Bulletin, **28**, 350 (1955).

[4] J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), A **158**, 280 (1937).

[5] C.A. Coulson and H.C. Longuet-Higgins, *Proc. Roy. Soc.* (London), A **193**, 456 (1948).