A Relation between Bond-orders and Bond-lengths of C-Cl Bonds in Conjugated Systems: An Example of the Order-length Relation for Bonds other than C-C Bonds

By Tosinobu ANNO and Akira SADÔ

(Received January 20, 1955)

Introduction

By the method of molecular orbital, Coulson[1] has found a relation between bond-order and bond-length in C-C bonds in conjugated systems and derived the relation theoretically. If the order of a bond is known, this relation can be used to predict the bond distance except in special cases. However, as is mentioned by Coulson[2], such a theoretical order-length relation has not yet been derived for other bonds than C-C bonds.

It is the purpose of this paper to show that a relation similar to that for C-C bonds does exist also for C-Cl bonds. The theoretical relation which we present here is similar in form to that given by Coulson and predicts the bond-length from the bond-

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[1] C.A. Coulson, *Proc. Roy. Soc.* (London), A169, 413 (1939).

[2] C.A. Coulson, *J. Phys. Chem.*, **56**, 311 (1952).

order which agrees very well with the observed length.

Theoretical

We shall use the simple LCAO molecular orbital method. The total energy E of π-electrons is shown to be

$$E=\sum_{r=1}^{k} q_r\alpha_r+2\sum\sum_{i<j} p_{ij}\beta_{ij},$$

where α_r and β_{ij} are usual coulomb and resonance integrals and q_r and p_{ij} denote the formal charge and the mobile bond order, respectively.

Consider a hypothetical state where all π-electrons are localized at "original" atoms giving those π-electrons, i.e. where π-bonds are not formed. Then the total π-electron energy would be

$$E_0=\sum_{r=1}^{k} q_r^{*}\alpha_r,$$

where q_r^{*} denotes the number of π-electrons localized at atom r. The binding energy of π-electrons is the energy difference between the actual and the hypothetical state. Allowing for the compression of the σ-bond, minimization of the total energy (including both the σ- and π-energies) with respect to the internuclear distance at constant p_{ij}'s and q_r's gives,[1),3)]

$$\sigma_{ij}(x_{ij}-s_{ij})+2p_{ij}(\partial\beta_{ij}/\partial x_{ij})=0, \qquad (1)$$

where x_{ij} is the bond-length of bond i-j, σ_{ij} is its single bond force constant and s_{ij} is the single bond distance.

For the C-Cl bond, we cannot use as standards the single and double bonds to obtain the functional variation of β with x, since there is no double bond between carbon and chlorine atoms. Instead of the double bond, however, we can take up a C-Cl bond whose mobile order is as near to unity as possible. For this purpose we take the C-Cl bond in chloroacetylene, whose mobile order p_a is calculated at 0.661 (see below). Let us consider a C-Cl bond whose mobile order and bond-length are p_a and x, respectively. The π-electron energy of this bond can be expressed by $2p_a\beta_{\text{C-Cl}}$ where $\beta_{\text{C-Cl}}$ is the resonance integral in this C-Cl bond. On the other hand, taking the methyl chloride and chloroacetylene molecules as standards, considerations similar to the case of C-C bonds[1),3)] show that this π-electron energy is

$$E_a^0-E_s^0+(1/2)\,\kappa_a(x-d_a)^2-(1/2)\,\sigma(x-s)^2,$$

where E_a^0, E_s^0; κ_a, σ and d_a, s are the bond energies, force constants and the internuclear distances in C-Cl bonds in the chloroacetylene and methylchloride molecules, respectively. Equating this to $2p_a\beta_{\text{C-Cl}}$, differentiation with respect to x gives

$$2p_a(\partial\beta_{\text{C-Cl}}/\partial x)=\kappa_a(x-d_a)-\sigma(x-s). \qquad (2)$$

Combining Eqs. (1) and (2) it follows that

$$x=s-\frac{s-d_a}{1+\dfrac{\sigma}{\kappa_a}\left(\dfrac{1-p'}{p'}\right)}, \qquad (3)$$

where $p'=p/p_a$.

Test of the Theory

We have calculated the bond-order for the C-Cl bond in some molecules and the result is shown in Table I. In calculating the bond-order the following assumptions were made.

TABLE I

CALCULATED BOND-ORDERS AND OBSERVED BOND-LENGTHS OF SOME C-Cl BONDS

Molecule	Bond-length*(Å)	Bond-order**
Chloromethane	1.77	(1.00)
trans-Dichloroethylene	1.69	1.29
1,3,5-Trichlorobenzene	1.69	1.32
Dichloroacetylene	1.64	1.55
Chloroacetylene	1.63	1.66

* These values are taken from reference 9 in text. All values are determined by electron diffraction except for chloroacetylene. The value for chloroacetylene is determined by microwave spectroscopy.

** It should be noted that the figures given here are for total bond orders defined by $(1+p_{ij})$, where p_{ij}'s are mobile orders.

(i) The coulomb integral at an atom is proportional to its electronegativity scale[4)] given by Pauling[5)].

(ii) The resonance integral β_{ij} is zero when i and j refer to non-neighboring atoms. When i and j refer to neighboring atoms β_{ij} is proportional to the overlap integral S_{ij} between these two atoms[6)]. The overlap integral is available in the table by Mulliken et al.[7)].

(iii) The ratio of the coulomb integral α_{C} at the carbon atom in benzene to the resonance integral β_{CC} for the C-C bond in the same molecule is

$$\alpha_{\text{C}}/\beta_{\text{CC}}=3.9^{8)}.$$

[3)] J. E. Lennard-Jones, *Proc. Roy. Soc.* (London), A158, 280 (1937).

[4)] C. Sandorfy, *Bull. soc. chim. France*, **1949**, 615.

[5)] L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, (1940).

[6)] G.W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).

[7)] R.S. Mulliken, C.A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

[8)] S. Nagakura, This Bulletin, **25**, 164 (1952).

(iv) The overlap integral is negligible throughout. The empirical internuclear distances are also given in Table I.

If internuclear distances and bond-orders are plotted in a diagram we can expect a simple relation between them. In Fig. 1 the curve of Eq. (3) is drawn, accepting the following numerical values.

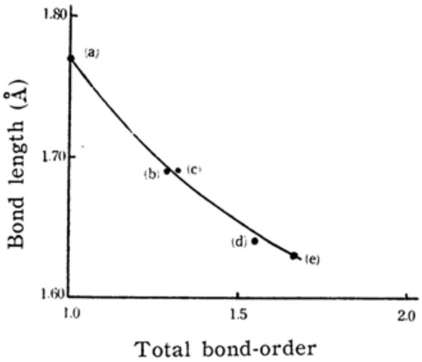

Fig. 1. Relation between bond-order and bond-length in C-Cl bonds. Points represent observed bond-lengths versus calculated bond-orders. Curve is the graphical representation of Eq. (3) (see text).

- *a*, Chloromethane;
- *b*, *trans*-Dichloroethylene;
- *c*, 1,3,5,-Trichlorobenzene;
- *d*, Dichloroacetylene;
- *e*, Chloroacetylene.

$$s=1.77\ \text{Å}^{9)} \qquad d_a=1.63\ \text{Å}^{9)}$$
$$\sigma=3.64\times10^5\ \text{dynes/cm.}^{10)}$$
$$\kappa_a=5.52\times10^5\ \text{dynes/cm.}^{11)}$$

Points in the figure represent the calculated bond-orders and the observed bond-lengths. Fig. 1 shows that these points lie on the theoretical curve within experimental error. Therefore a similar equation as the one for the C-C bond can be seen to be available also for the other bond if the suitable reference molecule is chosen (for example, for C-Cl bonds the chloroacetylene molecule).

However, the effects of hybridization, charge distribution and the repulsion of non-bonding electrons must be taken into consideration.

Hybridization effect can be considered in the same way as in the case of the C-C bond. For various C-Cl bonds, the hybridization ratio of the σ-atomic orbital of the chlorine atom can be considered as approximately constant in all cases. Only the variation in the hybridization ratio of the carbon atomic orbital needs to be considered. Accepting Coulson's result (see Fig. 2 of reference 12) which shows carbon atomic radius as the function of the hybridization ratio, a separate order-length curve should apply according to the hybridization of the carbon σ-atomic orbital. However, our insufficient knowledge concerning the geometrical structure of polyatomic molecules will invalidate such a treatment. It is to be noted that Coulson's result shows that the difference between carbon atomic radii corresponding to sp and sp^3 hybridizations is 0.035 Å.

It is true that the effect of the charge distribution must be taken into account in cases where the migration of the charge is large, but for C-Cl bonds in molecules whose bond-orders are calculated here, the effect of the charge distribution considered as described by Coulson[12] amounts only to a few thousandths of an angstrom which may be immaterial.

The effect due to the repulsion of non-bonding electrons would have to be considered in the absolute calculation of bond length. For bonds between a particular pair of atoms this type of effect can be considered as constant. Therefore in the relative calculation using the order-length curve, this effect may cancel out.

Thanks are due to Prof. S. Imanishi who read this manuscript.

Department of Chemistry, Faculty of Science, Kyushu University, Fukuoka

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[10] G. Herzberg, " Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co. Inc., New York (1945), p. 193.

[11] W. S. Richardson and J.H. Goldstein, *J. Chem. Phys.*, 18, 1314 (1950).

[12] C. A. Coulson, Contribution à l'étude de la structure moléculaire, Desoer, Liège (1948), p. 15.