Relations among Bond Order, Force Constant and Bond Length for the C—C and the C—N Bond in Conjugated Molecules

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Introduction

In a recent communication[1], the present authors derived following relation between bond length x and bond order p calculated by molecular orbital (MO) approximation:

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

where x_s and x_t are the bond length of pure single and triple bonds, respectively. D denotes the bond strength and a is a constant given by

$$a=\sqrt{\frac{k}{2D}}\ , \quad (2)$$

where k is the bond-stretching force constant. It has also been shown briefly for C—C and C—N bonds in the previous communication that the order-length relations calculated from Eq. (1) are in good agreement with the empirical ones. On the other hand, several empirical relations between force constant and bond length have been proposed by many workers[2]. Among these Badger's relation[3] is the best known and has been accepted most widely. However, the theoretical relations between these quantities have not been derived.

In the present paper we shall propose a full account of the previous communication and a theoretical equation correlating the force constant with the bond length will be proposed, confining ourselves to C—C and C—N bonds.

For C—C bonds, there exist many accurate experimental values of bond lengths and the force constants on the one hand and the calculated values of bond orders on the other. Moreover, the empirical values of parameters necessary in the theoretical equations are known for these molecules better than for the other types of conjugated molecules. Thus the test of the theoretical equations are most feasible for C—C bonds.

For C—N bonds the single and the triple bonds are familiar in chemistry and the physical natures of these bonds are fairly well known. However, for the C—N double bond we have only a few experimental data. Therefore it may be interesting to be able to infer the nature of the C—N double bond from reasonably established relations among bond orders, force constant and bond length.

Derivation of a General Equation Correlating Bond Order and Bond Length

Although Eq. (1) is useful for explaining the relation between bond order and bond length for C—C and C—N bonds, it involves the pure single and triple bonds as references. For C—C bonds, pure single and triple bonds exist in nature as far as the effects of the hyperconjugation or the configuration interaction are neglected. This is also true for C—N single bond, but the pure C—N triple bond does not exist even in the ordinary sense as far as we stand upon the MO viewpoint. Therefore a more general equation which involves Eq. (1) as a special case will be derived first.

Let us take two bonds A_{ij} and B_{ij} whose mobile orders are p_{Aij} and p_{Bij} ($p_{Aij}>p_{Bij}$), respectively, for each bond i—j in a molecule. Other notations used in the following discussion will be easily understood

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1) T. Anno, M. Ito, R. Shimada, A. Sadô, and W. Mizushima, This Bulletin, **29**, 440 (1956).

2) A brief summary of the empirical equations has been given by (a) C. K. Wu and Chang-Tsing Yang, *J. Phys. Chem.*, **48**, 295 (1944) and (b) G. Herzberg, "Spectra of Diatomic Molecules" (D. van Nostrand Company, Inc., New York, 1950) p. 453f.

3) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934); **3**, 710 (1935).

by analogy with those described above. The total bond energy of a molecule can be expressed as follows, taking a suitable energy zero:

$$F=\sum_{i<j}D_{\mathrm{B}ij}[1-\exp\{-a_{\mathrm{B}ij}(x_{ij}-x_{\mathrm{B}ij})\}]^2 +2\sum_{i<j}(p_{ij}-p_{\mathrm{B}ij})\beta_{ij} +\sum_{i<j}\left\{\left(\frac{q_i\alpha_i}{n_i}-\frac{q_{\mathrm{B}i}\alpha_{\mathrm{B}i}}{n_{\mathrm{B}i}}\right)+\left(\frac{q_j\alpha_j}{n_j}-\frac{q_{\mathrm{B}j}\alpha_{\mathrm{B}j}}{n_{\mathrm{B}j}}\right)\right\}, \tag{3}$$

where q denotes charge density. Subscripts i and j represent atoms making ends of the bond i—j, n_i and $n_{\mathrm{B}i}$ being the numbers of bonds[4] which start from atom i in the molecule under consideration and the molecule which contains the reference bond B_{ij}, respectively. α and β are the usual coulomb and resonance integral, respectively[5]. We assume here that the terms due to the charge density can be distributed equally among various bonds[4] which start from the atom referring to the term. Then, the total energy of a particular bond is

$$F_{ij}=D_{\mathrm{B}ij}[1-\exp\{-a_{\mathrm{B}ij}(x_{ij}-x_{\mathrm{B}ij})\}]^2 +2(p_{ij}-p_{\mathrm{B}ij})\beta_{ij} +\left(\frac{q_i\alpha_i}{n_i}-\frac{q_{\mathrm{B}i}\alpha_{\mathrm{B}i}}{n_{\mathrm{B}i}}\right)+\left(\frac{q_j\alpha_j}{n_j}-\frac{q_{\mathrm{B}j}\alpha_{\mathrm{B}j}}{n_{\mathrm{B}j}}\right). \tag{4}$$

The energy difference between two bonds whose mobile orders are p_{A} and p_{B} and the internuclear distances are equally x is represented by

$$\left(\frac{q_{\mathrm{A}i}\alpha_{\mathrm{A}i}}{n_{\mathrm{A}i}}-\frac{q_{\mathrm{B}i}\alpha_{\mathrm{B}i}}{n_{\mathrm{B}i}}\right)+\left(\frac{q_{\mathrm{A}j}\alpha_{\mathrm{A}j}}{n_{\mathrm{A}j}}-\frac{q_{\mathrm{B}j}\alpha_{\mathrm{B}j}}{n_{\mathrm{B}j}}\right) +2(p_{\mathrm{A}ij}-p_{\mathrm{B}ij})\beta_{ij} =\text{const.}+D_{\mathrm{A}ij}[1-\exp\{-a_{\mathrm{A}ij}(x_{ij}-x_{\mathrm{A}ij})\}]^2 -D_{\mathrm{B}ij}[1-\exp\{-a_{\mathrm{B}ij}(x_{ij}-x_{\mathrm{B}ij})\}]^2. \tag{5}$$

From the equilibrium condition that $\frac{\partial F}{\partial x_{ij}}=0$ and from Eqs. (3) and (5) the following equation is obtained:

$$p=\frac{p_{\mathrm{A}}-p_{\mathrm{B}}}{1-\frac{D_{\mathrm{A}}a_{\mathrm{A}}}{D_{\mathrm{B}}a_{\mathrm{B}}}\left[\frac{\exp\{-a_{\mathrm{A}}(x-x_{\mathrm{A}})\}-\exp\{-2a_{\mathrm{A}}(x-x_{\mathrm{A}})\}}{\exp\{-a_{\mathrm{B}}(x-x_{\mathrm{B}})\}-\exp\{-2a_{\mathrm{B}}(x-x_{\mathrm{B}})\}}\right]}+p_{\mathrm{B}}. \tag{6}$$

4) These bonds should be restricted to those which participate in the conjugation.

5) It should be noted that β_{ij} is assumed to depend only upon the kinds of atom i and j and the distance between these atoms.

It is clear that Eq. (6) reduces to Eq. (1) when the C—C bonds in ethane and acetylene are taken as standards and the effects of hyperconjugation and configuration interaction are neglected. From the meanings of Eqs. (3), (4) and (5) it is clear that D's and a's (equivalently, D's and k's) must refer to hypothetical change where p's and q's do not change from their values in the reference molecules in equilibrium. Let us consider how to derive these constants from those obtained from the "experiment".

When we consider the reference bond B_{ij} at its equilibrium position, Eq. (4) becomes

$$F(x_{\mathrm{B}ij})=0. \tag{7}$$

Let the internuclear distance of the reference bond B_{ij} go to infinity leaving $q_i=q_{\mathrm{B}i}$ and $p_{ij}=p_{\mathrm{B}ij}$, Eq. (4) becomes

$$F(\infty)_{\text{hypothetical}}=D_{\mathrm{B}ij}. \tag{8}$$

Actually, p_{ij} does not necessarily remain equal to $p_{\mathrm{B}ij}$ and $q_i\to m_{\mathrm{B}i}$ ($m_{\mathrm{B}i}$ denotes the number of π-electrons of free atom i in its valence state) when $x_{ij}\to\infty$, so that Eq. (4) becomes

$$F(\infty)_{\text{actual}}=D_{\mathrm{B}ij}+\frac{1}{n_{\mathrm{B}i}}(m_{\mathrm{B}i}\alpha^{\infty}{}_{\mathrm{B}i}-q_{\mathrm{B}i}\alpha_{\mathrm{B}i}) +\frac{1}{n_{\mathrm{B}j}}(m_{\mathrm{B}j}\alpha^{\infty}{}_{\mathrm{B}j}-q_{\mathrm{B}j}\alpha_{\mathrm{B}j}), \tag{9}$$

considering the fact that $\beta_{ij}\to 0$ when $x_{ij}\to\infty$. $\alpha^{\infty}{}_{\mathrm{B}i}$ and $\alpha^{\infty}{}_{\mathrm{B}j}$ denote the limiting values to which $\alpha_{\mathrm{B}i}$ and $\alpha_{\mathrm{B}j}$ approach when $x_{ij}\to\infty$. It is the difference between the left hand sides of Eqs. (7) and (9) that represents the actual $D_{\mathrm{B}ij}$ value (denoted by $D'_{\mathrm{B}ij}$). Thus,

$$D_{\mathrm{B}ij}=D'_{\mathrm{B}ij}-\frac{1}{n_{\mathrm{B}i}}(m_{\mathrm{B}i}\alpha^{\infty}{}_{\mathrm{B}i}-q_{\mathrm{B}i}\alpha_{\mathrm{B}i}) -\frac{1}{n_{\mathrm{B}j}}(m_{\mathrm{B}j}\alpha^{\infty}{}_{\mathrm{B}j}-q_{\mathrm{B}j}\alpha_{\mathrm{A}j}). \tag{10}$$

Similarly,

$$D_{\mathrm{A}ij}=D'_{\mathrm{A}ij}-\frac{1}{n_{\mathrm{A}i}}(m_{\mathrm{A}i}\alpha^{\infty}{}_{\mathrm{A}i}-q_{\mathrm{A}i}\alpha_{\mathrm{A}i}) -\frac{1}{n_{\mathrm{A}j}}(m_{\mathrm{A}j}\alpha^{\infty}{}_{\mathrm{A}j}-q_{\mathrm{A}j}\alpha_{\mathrm{A}j}). \tag{11}$$

Thus, $D_{\mathrm{A}ij}$ and $D_{\mathrm{B}ij}$ values corresponding to the hypothetical changes described above may be obtained from actual $D'_{\mathrm{A}ij}$ and $D'_{\mathrm{B}ij}$ values using Eqs. (10) and (11).

Differentiating twice Eq. (3) with respect to x_{ij} and inserting the expressions for

$\frac{\partial \beta_{ij}}{\partial x_{ij}}$ and $\frac{\partial^2 \beta_{ij}}{\partial x_{ij}^2}$ obtained from Eq. (5), it follows that[5a]

$$\begin{aligned}\frac{\partial^2 F}{\partial x^2} &= 2a_B D_B[-a_B \exp\{-a_B(x-x_B)\} \\ &\quad +2a_B \exp\{-2a_B(x-x_B)\}] \\ &+\frac{2\pi}{(p_A-p_B)^2}[a_A D_A[\exp\{-a_A(x-x_A)\} \\ &\quad -\exp\{-2a_A(x-x_A)\}] \\ &\quad -a_B D_B[\exp\{-a_B(x-x_B)\} \\ &\quad -\exp\{-2a_B(x-x_B)\}]]^2 \\ &+\left(\frac{p-p_B}{p_A-p_B}\right)[2a_A D_A[-a_A \exp\{-a_A(x-x_A)\} \\ &\quad +2a_A \exp\{-2a_A(x-x_A)\}] \\ &\quad -2a_B D_B[-a_B \exp\{-a_B(x-x_B)\} \\ &\quad +2a_B \exp\{-2a_B(x-x_B)\}]], \qquad (12)\end{aligned}$$

where π is the self-polarizability of the bond under consideration. At the equilibrium position of the reference bond B, Eq. (12) becomes

$$\begin{aligned}\left(\frac{\partial^2 F}{\partial x^2}\right)_B &\equiv k'_B = k_B \\ &+\frac{2\pi_B}{(p_A-p_B)^2}(a_A D_A)^2[\exp\{-a_A(x_B-x_A)\} \\ &-\exp\{-2a_A(x_B-x_A)\}]^2, \qquad (13)\end{aligned}$$

and at the equilibrium position of the reference bond A, it becomes

$$\begin{aligned}\left(\frac{\partial^2 F}{\partial x^2}\right)_A &\equiv k'_A = k_A \\ &+\frac{2\pi_A}{(p_A-p_B)^2}(a_B D_B)^2[\exp\{-a_B(x_A-x_B)\} \\ &-\exp\{-2a_B(x_A-x_B)\}]^2, \qquad (14)\end{aligned}$$

using Eq. (2). Since D_A and D_B values can be obtained in the above-described manner and a's are expressible with D's and k's through Eq. (2), Eqs. (13) and (14) give k_A and k_B corresponding to the hypothetical change from the actual force constants k'_A and k'_B through the iterative process.

Similarly, if the Hooke-type potential functions are used the following formula for order-length relation can be obtained:

$$x = x_B - \frac{x_B - x_A}{1+\frac{k_B}{k_A}\left(\frac{1-p'}{p'}\right)}, \qquad (15)$$

where $p' = (p-p_B)/(p_A-p_B)$ and k_A and k_B may be obtained using

$$k'_B = k_B + \frac{\pi_B}{2(p_A-p_B)^2}\{k_A(x_B-x_A)\}^2, \qquad (16)$$

and

$$k'_A = k_A + \frac{\pi_A}{2(p_A-p_B)^2}\{k_B(x_B-x_A)\}^2, \qquad (17)$$

from the actual force constants k'_A and k'_B. Equation (15) is the general equation which involves those obtained previously[6-8].

Numerical Values of Parameters

As can be seen in the derivation of Eq. (6), this equation is based upon the Morse-type bond-stretching potential function which contains D's and k's as parameters. These parameters may be obtained from the actual D' and k' values as described previously. Although in diatomic molecules D''s and k''s can be obtained from experimental data, for polyatomic molecules circumstances are somewhat different.

Let us first seek for the appropriate values of k''s. As is well known, the force constants take different values depending upon the assumed force fields. However, from the derivation of Eq. (6), if the interactions among the non-bonded atoms can be neglected, it is clear that the appropriate value of k' to be used must correspond to the bond stretching, the bond angles and bond lengths, except the bond length in question, having to remain the same as in the equilibrium. This is the bond-stretching force constant in the most general quadratic potential function which contains all cross terms. Normal coordinate treatment has been carried out for ethane and acetylene, which will be taken as reference molecules in the following discussion for C—C bonds, taking all or almost all the cross terms into consideration. Thus, the following values for C—C bond force constants were taken:

$k'_B = 4.57$[9] and $k'_A = 15.79 \times 10^5$ dynes/cm.[10]

For C—N bonds, the methylamine and

5a) In Eq. (12) subscripts i and j are omitted for brevity.

6) C. A. Coulson, *Proc. Roy. Soc.* (London) **A169**, 413 (1939).
7) T. Anno and A. Sadô, This Bulletin, **28**, 350 (1955).
8) T. Anno and A. Sadô, *J. Chem. Phys.*, **25**, 176 (1956).
9) G. E. Hansen and D. M. Dennison, ibid. **20**, 313 (1952).
10) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules" (D. van Nostrand Co., Inc., New York, 1945), pp. 188—9. This value is the average of the values listed by Herzberg for C_2H_2 and C_2D_2.

hydrogen cyanide molecules may be taken as the reference molecules. While the normal coordinate treatment including the cross terms for the latter molecule gives $k'_A = 18.58 \times 10^5$ dynes/cm.[11], the C—N force constant of the methylamine is not found in the literature. We took the C—N force constant 4.68×10^5 dynes/cm. of the trimethylamine molecule[12] instead.

The most serious difficulty in applying Eq. (6) is concerned with the value of D'. The necessary value of D' must be the energy needed in the process of the rupture of the bond, leaving the other bond lengths or the bond angles unchanged. Thus, the so-called bond-dissociation energy values are not to be used, since the actual dissociation process involves the reorganization of the dissociation products. The adequate value of D' is the bond energy if the "near-atom-effect", in the sense of Glockler[13], can be neglected. As is mentioned previously this type of effect is also neglected in taking the value of k'.

Moreover, in order to calculate the bond energy of the organic compounds from the thermochemical experimental data, it is necessary to know the latent heat of sublimation of carbon (L(C)). Unfortunately, however, the precise value of this quantity is still under discussion[14]. Glockler[15] calculated the bond energies in ethane and acetylene for three conflicting values of L(C). In that paper he recommended L(C)=169.75 kcal as the best value for this quantity. The bond-energy values calculated by Glockler based on L(C)=169.75 kcal will be used in the present paper, since L(C)≈170 kcal seems to be the best[16]. The C—C bond energies taken are

$$D'_B = 85.063 \text{ and } D'_A = 182.948 \text{ kcal/mole.}$$

For C—N bonds in methylamine and hydrogen cyanide the calculation of the bond energy requires the dissociation energy of the nitrogen molecule ($D(N_2)$) as well as L(C). The precise value of $D(N_2)$ has also been under discussion[14]. Gaydon[17] has given discussion which supports $D(N_2)=9.765$ ev, reviewing the previous literatures. Since later works[18–20] seem to support this value of $D(N_2)$, we used this value of $D(N_2)$ in the calculation of the bond energy. Thus the Glockler-type calculation[15,21] yields 64.3 and 201.4 kcal/mole as the C—N bond energies in methylamine and hydrogen cyanide, respectively. Therefore we took

$$D'_B = 64.3 \text{ and } D'_A = 201.4 \text{ kcal/mole.}$$

The C—C or C—N bond lengths in the reference molecules are known with sufficient accuracy. Bond lengths of C—C bonds in ethane[9] and acetylene[22] have been derived from the analyses of rotation-vibration spectra of these molecules. From these we took

$$x_B = 1.543 \text{ and } x_A = 1.207 \text{ Å.}$$

For C—N bonds in methylamine and hydrogen cyanide, recent spectroscopic investigations have given

$$x_B = 1.474^{23} \text{ and } x_A = 1.157 \text{ Å}^{24,25}.$$

Calculation of Bond Order

In order to test the theoretical relation derived above, calculated values of bond orders are necessary. Although for C—C bonds there exist many calculated values of bond order in the literature, the calculated values of C—N bond orders are scarce in the literature, so that calculations of the C—N bond orders have been made for several molecules by MO method using the following assumptions:

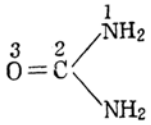
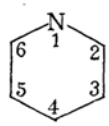
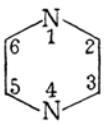
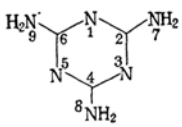
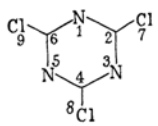
(a) All the resonance integrals between non-adjacent atoms and all the overlap integrals can be neglected.

(b) The ratio of the coulomb integral to the resonance integral in benzene is 4.1; i. e., $\alpha = 4.1\,\beta$[26].

(c) The coulomb integral of each atom, α_r, is proportional to its electronegativity.

11) A. E. Douglas and D. Sharma, *J. Chem. Phys.*, **21**, 448 (1953).
12) V. H. Siebert, *Z. anorg. allgem. Chem.*, **273**, 161 (1953).
13) G. Glockler, *J. Phys. Chem.*, **56**, 289 (1952).
14) G. Glockler, *Ann. Rev. Phys. Chem.*, **3**, 151 (1952).
15) G. Glockler, *J. Chem. Phys.*, **21**, 1242 (1953).
16) M. Hock, P. E. Blackburn, D. P. Dingledy and H. L. Johnston, *J. Phys. Chem.*, **59**, 97 (1955); W. A. Chupka and M. G. Inghram, ibid., **59**, 100 (1955).
17) A. G. Gaydon, "Dissociation Energies and Spectra of Diatomic Molecules". (Dover Publications, Inc., New York, 1950) Chapter IX.
18) J. M. Hendrie, *J. Chem. Phys.*, **22**, 1503 (1954).
19) W. Groth, *Z. physik. Chem.* (Frankfurt), **1**, 300 (1954); *Z. Elektrochem.*, **58**, 752 (1954).
20) D. C, Frost and C. A. McDowell, *Proc. Roy. Soc.* (London), **A236**, 278 (1956).
21) G. Glockler, *J. Chem. Phys.*, **19**, 124 (1951).
22) Reference 10, p. 398.
23) T. Nishikawa, T. Itoh and K. Shimoda, ibid. **23**, 1735 (1955).
24) J. W. Simmons, W. E. Anderson and W. Gordy, *Phys. Rev.*, **77**, 77 (1950).
25) I. R. Dagg and H. W. Thompson, *Trans. Faraday Soc.*, **53**, 455 (1956).
26) C. Sandorfy, *Bull. soc. chim. France*, 615 (1949).

TABLE I

Molecules	r	α_r (β unit)	β_{rs} (β unit)	π-electron densities	Orbital energies (β unit)	
Urea	1	5.276		1.783	B_1	6.335
			0.757		B_1	5.415
	2	4.346		0.654	A_2	5.276
			0.861		B_1	3.390
	3	5.518		1.780		
Pyridine	1	4.927		1.341	B_2	6.178
			0.839		B_2	5.335
	2	4.180		0.888	A_2	5.131
			0.984		B_2	3.542
	3	4.113		0.982	A_2	3.162
			0.984		B_2	2.322
	4	4.158		0.918		
Pyrazine	1	4.987		1.258	B_{1u}	6.290
			0.859		B_{3g}	5.607
	2	4.192		0.871	B_{2g}	5.158
			0.966		B_{1u}	3.854
	3	4.192		0.871	A_u	3.226
					B_{3g}	2.606
Melamine	1	4.862		1.433	A''_2	6.557
			0.879		E''	5.914
	2	4.277		0.751	A''_2	5.191
			0.767		E''	5.065
	7	5.260		1.816	E''	3.421
					A''_2	2.652
Cyanuric chloride	1	4.883		1.404	A''_2	6.502
			0.896		E''	5.737
	2	4.270		0.761	A''_2	5.000
			0.622		E''	4.965
	7	5.010		1.836	E''	3.458
					A''_2	2.658
Hydrogen cyanide	1	4.333		1.347	Π	5.497
			0.876		Π	3.644
$HC\equiv N$ (1 2)	2	4.938		2.653		

The values of the electronegativity used were those listed in Kurita and Kubo[27] for B, C, N and O, while for S and Cl Pauling's values[28] were used.

(d) The resonance integral between adjacent atoms, β_{rs}, is given by $\beta_{rs}=(S_{rs}/S)\beta$[29], where S_{rs} is the overlap integral, which may be evaluated according to Mulliken's Tables[30]. S and β are the overlap and resonance integrals in benzene, respectively.

(e) Inductive effects can be neglected.

(f) α_r and β_{rs} are to be corrected for the formal charge obtained from the calculated electron density according to the way suggested by Nagakura[31,32].

Under the above assumptions the usual MO calculation is repeated until the final results are self-consistent. In the case of the hydrogen cyanide molecule two π-bonds exist, nodal planes of which are perpendicular to each other. These π-bonds will be referred to as π_x and π_y bonds, z direction being taken along the line connecting

27) Y. Kurita and M. Kubo, This Bulletin, **24**, 13(1951).
28) L. Pauling, "The Nature of the Chemical Bond", Cornell University Press, Ithaca, New York, (1940) p. 64.
29) G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
30) R. S. Mulliken, C. A. Rieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).
31) S. Nagakura, This Bulletin, **25**, 164 (1952).
32) S. Nagakura and T. Hosoya, ibid. **25**, 179 (1952).

TABLE II

THE CALCULATED VALUES OF BOND ORDER AND THE EXPERIMENTAL VALUES OF BOND LENGTH FOR SOME C—N BONDS

Molecules	Mobile bond orders		Bond lengths* (in Å)	
	Present calc.	Other methods		
Pyrrole	0.41[b]	0.45[d] 0.50[e]	1.385±0.015	M. W.[h]
Urea	0.540		1.37	X.[i]
Pyridine	0.620	0.534[d),f] 0.64[e] 0.652[g]	1.35	M. W.[j]
Pyrazine	0.639	0.63[e] 0.660[g]	1.35±0.02	E. D.[k]
Melamine C—N (ring) C—N (outer)	 0.474 0.749	 0.449[a] 0.576[a]	 1.37±0.03 1.34±0.01	 E. D.[a]
Cyanuric chloride	0.584	0.622[a]	1.33±0.02	E. D.[a]
Amide group	0.660[c]		1.32±0.02	E. D.[l]
Hydrogen cyanide	1.890		1.157	M. W.[m]

* E. D.: Electron diffraction. X.: X-ray. M. W.: Microwave.

a) Y. Akimoto, This Bulletin, **28**, 1 (1955).

b) S. Nagakura and T. Hosoya, This Bulletin, **25**, 179 (1952). The method of calculation is the same as that used in the present paper, but slightly different values of electronegativity are used.

c) S. Nagakura, This Bulletin, **25**, 164 (1952). The value of bond order listed in this table is calculated using the final values of α's and β's listed in this paper.

d) H. C. Longuet-Higgins and C. A. Coulson, *Trans. Faraday Soc.*, **43**, 87 (1947).

e) L. E. Orgel, T. L. Cottrell, W. Dick and L. E. Sutton, *Trans. Faraday Soc.*, **47**, 113 (1951).

f) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A193**, 447 (1948).

g) D. W. Davies, *Trans. Faraday Soc.*, **51**, 449 (1955).

h) B. Bak, D. Christensen, L. Hansen and J. Rastrup-Andersen, *J. Chem. Phys.*, **24**, 720 (1956).

i) R. W. G. Wyckoff and R. B. Corey, *Z. Krist.*, **89**, 462 (1934).

j) K. E. McCuloh and G. F. Pollow, *J. Chem. Phys.*, **22**, 681 (1954).

k) V. Schomaker and L. Pauling, *J. Am. Chem. Soc.*, **61**, 1769 (1937).

l) R. B. Corey and J. Donohue, *J. Am. Chem. Soc.*, **72**, 2899 (1950).

m) reference 24.

the nuclei. For this molecule the self-consistent result is not to be obtained if the formal charges resulting from both the π_x and π_y bonds are taken into account in the next cycle of calculation concerning π_x or π_y bonds. However, if only the formal charges resulting from the π_x bond are taken into account in the next cycle of calculation concerning the same π_x bond, the self-consistent results are obtained. The same is true also for π_y bond. Therefore calculation of the hydrogen cyanide molecule was made using the additional assumption: only the formal charge resulting from π_x (or π_y) bond should be taken into account for the second cycle of calculation for π_x (or π_y) bond. The final values of α_r, β_{rs} and orbital energies are listed in Table I. Table II contains the bond orders calculated using these parameters. Bond orders calculated with other methods by several workers are also given in Table II.

Bond Order-Bond Length Relation: Test of the Theory

C—C Bonds. — In applying Eq. (6) to C—C bonds, numerical values of parameter derived directly from experiments which have been discussed in a previous section may be used when we use C—C bonds in the ethane and the acetylene molecules as standards and the effects of the hyperconjugation and the configuration interaction are neglected. Fig. 1 contains the theoretical curve thus obtained. In this figure the calculated values of bond order found in the literature for some C—C bonds are also plotted against the experimental values of bond lengths.

It can be seen that the theoretical curve explains fairly well the empirical trend. Deviation of the empirical points from the theoretical curve may be avoided if we take into account the hybridization of the carbon σ-atomic orbital in the same manner as that used by Coulson[33].

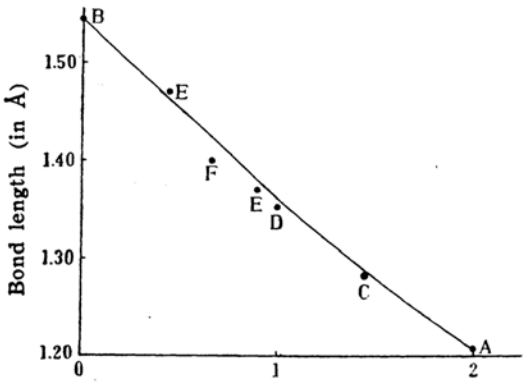


Fig. 1. The relation between bond order and bond length for C—C bonds.
A, Acetylene (a, b)*; B, Ethane (c, b); C, Butatriene (d, e); D, Ethylene (f, b); E, Butadiene (g, b); F, Benzene (g, b).
* (a, b) for example denotes that the bond length and bond order of the acetylene are taken from references a and b, respectively, cited below.
a) reference 22.
b) reference 6.
c) reference 9.
d) B. P. Soicheff, Symposium on Molecular Structure and Spectroscopy, Ohio State University, June 1956.
e) H. C. Longuet-Higgins and F. H. Burkitt, *Trans. Faraday Soc.*, **48**, 1077 (1952).
f) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).
g) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).

C—N Bonds. — For C—N bonds, bond energies and force constants of the reference molecules obtained in a previous section should be corrected as described above. If we use the C—N bonds in methylamine and hydrogen cyanide as standards and make the usual approximation, the π-electron densities (q_C, q_N), α_C, α^{∞}_C, α_N and α^{∞}_N, the self-polarizability ($\pi_{CN,CN}$), and the bond order (p_{CN}) of the C—N bond in the hydrogen cyanide molecule are sufficient to make this correction.

Using the assumptions described above it follows that

$$\left.\begin{aligned} &q_C=1.3472,\ q_N=2.6528,\\ &\quad \text{in electron unit,}\\ &\pi_{CN,CN}=0.2300/\beta \end{aligned}\right\} \quad (18)$$

and $p_{CN}=1.890$,

where β is the resonance integral of the C—C bond in benzene the value of which is determined to be 23,000 cm.$^{-1}$ by Platt[34]. The numerical values in (18) are based on

$$\alpha_C=4.33\beta \quad \text{and} \quad \alpha_N=4.94\beta.$$

On the other hand it may be considered that

$$\alpha^{\infty}_C=4.1\beta \quad \text{and} \quad \alpha^{\infty}_N=5.17\beta,$$

from the assumptions on which the MO calculation is based. Therefore, from Eqs. (10), (11), (13) and (14) and using D'_A, D'_B, k'_A, k'_B, x_A and x_B, the values of D_A, D_B, k_A and k_B can be obtained as follows:

$$\left.\begin{aligned} D_A&=175.5\ \text{kcal/mole}\\ D_B&=\ 64.3\ \text{kcal/mole}\\ k_A&=\ 20.01\times10^5\ \text{dynes/cm.}\\ k_B&=\ 4.68\times10^5\ \text{dynes/cm.} \end{aligned}\right\}. \quad (19)$$

It is to be noted in the present case that in Eq. (10)

$$m_{Bi}=m_{Bj}=q_{Bi}=q_{Bj}=0,$$

and in Eq. (11)

$$m_{Ai}=m_{Aj}=2, \text{ and } n_{Ai}=n_{Aj}=1.$$

Using the values in (19), Eq. (6) yields a curve shown in Fig. 2.

Plotting the calculated values of bond orders against the experimental data of bond lengths, as is also shown in Fig. 2, it is seen that all the points lie on the theoretical curve within the experimental errors of bond lengths.

Naturally, the numerical value of the bond order is a little affected by the method of calculation as shown in Table

33) C. A. Coulson, *J. Phys. Chem.*, **56**, 311 (1952).

34) J. R. Platt, *J. Chem. Phys.*, **18**, 1168 (1950).

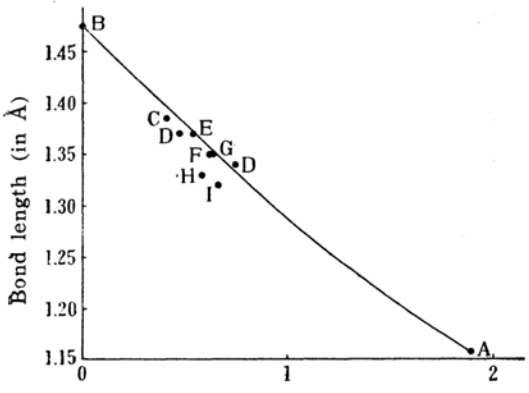


Fig. 2. The relation between bond order and bond length for C—N bonds.
A, Hydrogen cyanide; B, Methylamine; C, Pyrrole; D, Melamine; E, Urea; F, Pyridine; G, Pyrazine; H, Cyanuric chloride; I, Amide group.
In contrast with the corresponding figure in the previous communication (ref. 1) the points for dimeric cyanide are omitted in this figure since the calculation of the bond order of this molecule have been found to be in error.

II. However, the variation is less than 0.10 for most molecules, which may be taken as the measure of reliability of the calculation. According to the theoretical curve, it corresponds to the accuracy of 0.02 Å for bond length, which is nearly the same as the error in the electron-diffraction measurements. We may therefore predict the C—N bond length from the calculated bond order and using the theoretical curve within the experimental errors in the electron diffraction[35].

In concluding this section it is to be noted that the CN "double bond length" can be estimated as follows from the order-length relation obtained above. In the valence bond language the double bond has the "π-bond order" of one half of that of the triple bond which is realized by the CN bond in the hydrogen cyanide molecule if we neglect the homopolar-ionic resonance. Therefore we may consider the "double bond" as a bond whose mobile bond order is one half of that of the CN bond order of the hydrogen cyanide molecule in the molecular orbital language as well. Thus we obtain as the value of mobile bond order of the "double bond" 0.950. This value yields 1.295 Å as the value of "double bond length" from the order-length curve. This is in good agreement with the value of 1.28 Å evaluated as a sum of the covalent radii given by Pauling[36].

Relation between Force Constant and Bond Length

Substituting x, obtainable from Eq. (6), Eq. (12) would give the bond-stretching force constant as a function of p and π and the resulting equation would be analogous to that obtained by Coulson and Longuet-Higgins[37] assuming the Hooke-type potential function. However, since the contribution from the term containing π is relatively unimportant in the right hand side of Eq. (12) we can obtain a relation between force constant and bond length for bonds between a particular pair of atoms if the term containing π is neglected and p is replaced by the right hand side of Eq. (6). The resulting equation is

$$\frac{\partial^2 F}{\partial x^2} \equiv k = k_B g(2g-1) + \frac{k_A h(2h-1) - k_B(2g-1)}{1 - \dfrac{k_A a_B h(1-h)}{k_B a_A g(1-g)}} \tag{20}$$

where $g = \exp\{-a_B(x - x_B)\}$

$h = \exp\{-a_A(x - x_A)\}$,

and use has been made of Eq. (2).

Taking the same molecules as those taken in obtaining order-length relationship as references and using the same value of numerical parameters as used there[38], we obtain a curve showing relation between bond length and force constant for bonds of each pair of atoms. They are full lines in Figs. 3 and 4 for C—C and C—N bond, respectively. Available data of force constants are plotted in the same figures against experimental values of bond lengths. For comparison, curves based on Badger's equation[3] are also drawn in the figures (dotted curves)[39].

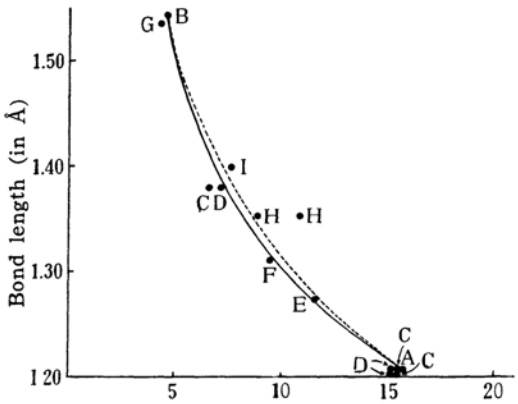
35) Since the CN bond order of the reference HCN molecule and the corrections to D_A and k_A depend upon the assumptions used in the MO calculation, the order-length curve itself depends upon such assumptions. Although this would cause a small additional error in the calculated value of bond length in the region of $p=1\sim2$, it would produce practically no error in the region of $p=0\sim1$ into which the numerical values of the CN bond order of the most interesting molecules fall.

36) Reference 28, p. 164.

37) C. A. Coulson and H. C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A193**, 456 (1948).

38) For k_A of the CN bonds, the uncorrected value was used in order that the curve may pass through the point for the HCN molecule.

39) In drawing the curve based on the Badger's equation the values of parameters in this equation (C and d) were determined from two empirical points for bonds "A" and "B".

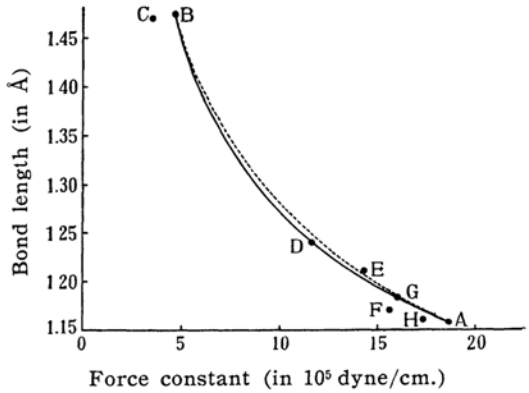


Force constant (in 10^5 dyne/cm.)

Fig. 3. The relation between force constant and bond length for C—C bonds.
A, Acetylene (a, b)*; B, Ethane (c, c); C, Diacetylene (d, e); D, Diacetylene (d, f); E, C_2(c, $^1\Pi_g$) (g, g); F, C_2(X, $^3\Pi_u$) (g, g); G, C_2(B, $^3\Pi_g$) (g, g); H, Ethylene (h, i); I, Benzene (j, k).
* (a, b) for example denotes that the bond length and force constant of the acetylene are taken from references a and b, respectively, cited below.
a) reference 22.
b) reference 10.
c) reference 9.
d) G. D. Graine and H. W. Thompson, *Trans. Faraday Soc.*, **49**, 1273 (1953).
e) S. M. Ferigle, F. F. Cleveland and A. G. Meister, *J. Chem. Phys.*, **20**, 526 (1952).
f) A. V. Jones, *Proc. Roy. Soc.* (London), **A211**, 285 (1952).
g) reference 2b, p. 513.
h) W. S. Gallaway and E. F. Barker, *J. Chem. Phys.*, **10**, 88 (1942).
i) B. L. Crawford, Jr., J. E. Lancaster and R. G. Inskeep, *J. Chem. Phys.*, **21**, 678 (1953).
j) P. W. Allen and L. E. Sutton, *Acta Cryst.*, **3**, 46 (1950).
k) F. M. Garforth, C. K. Ingold and H. G. Poole, *J. Chem. Soc.*, **1948**, 491.

Comparing our theoretical curve with the curve based on Badger's relation, it is seen that both curves coincide fairly well with each other over the whole region of bond length.

It is mentioned in the preceding section that the bond length of the C—N double bond may be predicted to be 1.295 Å from the theoretical orderlength relation. Combining this value with Eq. (20), we can obtain the force constant of the C—N double bond as 9.1×10^5 dynes/cm.



Force constant (in 10^5 dyne/cm.)

Fig. 4. The relation between force constant and bond length for C—N bonds.
A, Hydrogen cyanide (a, b)*; B, Methylamine (c, d); C, Ethylamine (e, f); D, C=N radical (g, g); E, Thiocyanate ion (h, h); F, C≡N radical (g, g); G, Methyl carbylamine (i, h); H, Ethane nitril (e, h).
* (a, b) for example denotes that the bond length and force constant of the hydrogen cyanide are taken from references a and b, respectively, cited below.
a) reference 24.
b) reference 11.
c) reference 23.
d) reference 12. The precise values of force constants of methylamine are not found in the literature, so we assume that the CN force constant in methylamine is equal to that in trimethylamine.
e) Landolt-Börnstein, "Zahlenwerte und Funktionen" (Springer, Berlin, 1951), Vol. 1, Part 2, Molekeln I, p. 17.
f) ibid., p. 234.
g) ibid., p. 228.
h) ibid., p. 230.
i) ibid., p. 18.

Summary

A general equation correlating bond orders with bond lengths of bonds between any particular pair of atoms in the conjugated systems are proposed. To test this equation applications have been made for C—C and C—N bonds. Because of the scarcity of the calculated values of bond orders for C—N bonds in the literature, bond orders of several molecules containing C—N bonds have been calculated, It is shown that the order-length relation is in good agreement with experiments. A theoretical, although approximate, equation correlating bond lengths with force constants has also been proposed and applied to C—C and C—N bonds. From these relations the length and the stretching force constant of C—N double bond

are estimated to be 1.295 Å and 9.1×10^5 dynes/cm, respectively, the former being in agreement with the value calculated from the covalent radii given by Pauling.

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