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The Hybridization Effect on the Equilibrium Distance. III[1]

Tomoo Miyazaki, Tsunehisa Shigetani, and Hiroyuki Shinoda
Department of Applied Chemistry, Faculty of Science and Engineering, Waseda University, Nishi-Ohkubo, Shinjuku-ku, Tokyo

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In order to re-examine the unexpected conclusion previously reported that the hybridization effect is unimportant in determining the C–C single bond length, a more reliable calculation involving the configuration interaction treatment and more elabolate calculations by the NDDO and unrestricted INDO methods have been performed. The results of the INDO-CI and unrestricted INDO calculations were in good agreement with those which were obtained by the previous calculations. According to the NDDO calculations, however, the equilibrium distances of different kinds of C–C single bonds were found to increase with the decreased *s* character in hybrids, although this effect was not very significant. The effect of interaction between non-adjacent atomic orbitals in determining the bond length has been discussed in full detail.

The object of the present paper is to explore the relative importance of the pi electron resonance and hybridization in the shortening of the single-bond length of conjugated hydrocarbons. During the past several years, many discussions have been presented concerning this problem.[4–6] Mulliken commented on this situation that it was rather necessary, and proper, to place considerable reliance on a theory, provided it was a reliable theory, since it was difficult to decide experimentally between hybridization and electron delocalization as causes of bond shortening.[7] In those days, however, there was no appropriate and direct method for calculating the equilibrium distance. At the present time, though, the interatomic distance can be calculated by such semi-empirical, self-consistent molecular orbital methods as the CNDO/2,[8–10] INDO,[11] NDDO[8] and MINDO[12] methods, in all of which all the valence electrons are taken into account. They have been developed mainly with the object of calculating the ground-state properties of molecules.

In a previous paper,[2] the CNDO/2 method was used to calculate the C–C and C–H equilibrium distances of the saturated and unsaturated simple hydrocarbons and those molecules which have broken pi bonds. The equilibrium distances of different types of C–C single and double bonds which are usually considered tri-tri, di-di single and di-di double bonds

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[1] The previous paper[2] (1969) and communication[3] (1970) are regarded as Part I and Part II of this series respectively.
[2] T. Miyazaki and H. Ohbayashi, This Bulletin, **42**, 2767 (1969).
[3] T. Miyazaki, *Tetrahedron Lett.*, **16**, 1363 (1970).
[4] M. J. S. Dewar and A. N. Schmeising, *Tetrahedron*, **5**, 166 (1959).
[5] R. S. Mulliken, *ibid.*, **6**, 68 (1959).
[6] "An Epistologue on Carbon Bonds," *ibid.*, **17**, 123—266 (1962).
[7] R. S. Mulliken, *ibid.*, **17**, 247 (1962).
[8] J. A. Pople, D. P. Santry, and G. A. Segal, *J. Chem. Phys.*, **43**, S 129 (1965).
[9] J. A. Pople and G. A. Segal, *ibid.*, **43**, S 136 (1965).
[10] J. A. Pople and G. A. Segal, *ibid.*, **44**, 3289 (1966).
[11] J. A. Pople, D. L. Beveridge, and P. A. Dobosh, *ibid.*, **47**, 2027 (1967).
[12] M. J. S. Dewar and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

were not much different from the te-te single and tri-tri double bond distances respectively. Moreover, it was found that the equilibrium distances are dependent upon the interaction between non-adjacent atomic orbitals.

In a previous communication,[3)] the INDO method was used to determine the effect of the introduction of the one-center exchange integrals into the calculation of the C–C equilibrium distance. Both the INDO and CNDO/2 methods seemed to indicate that the hybridization effect is unimportant in the shortening of the C–C single bond length.

In view of the above results, a more reliable calculation involving configuration interaction (CI) treatment and more elabolate calculations by the NDDO and unrestricted INDO methods will be used in this paper to determine the normal and hypothetical C–C equilibrium distances. The effect of interaction between non-adjacent atomic orbitals in determining the bond length has been discussed in full detail. This is because these electronic interactions are appreciably effective in determining the C–C equilibrium distance.

Methods of Calculation

Calculation of the sp^2-sp^2 Single Bond Length. The calculation is illustrated schematically in the energy curve of Fig. 1. The equilibrium distance of the sp^2-sp^2 C–C single bond was estimated by minimizing an energy (E^+) with respect to the interatomic distance considered. The energy (E^+) was defined by the following equation:

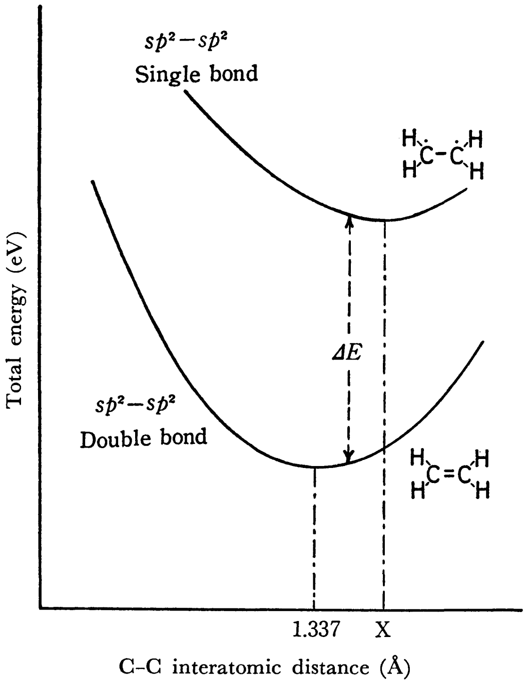

Fig. 1. Total energy as a function of C–C bond length. X is the equilibrium distance of sp^2-sp^2 single bond.

$$E^+ = E_{\text{total}} - \Delta E \tag{1}$$

$$E_{\text{total}} = E_{\text{elec}} + E_{\text{repul}} \tag{2}$$

$$\begin{aligned}\Delta E &= \frac{1}{4}\sum_{\mu}{}^{\pi}(P^{\pi}{}_{\mu\mu})^2\gamma_{\mu\mu} + \frac{1}{2}\sum_{\substack{\mu,\nu\\(\mu\neq\nu)}}{}^{\pi}P^{\pi}{}_{\mu\nu}(H_{\mu\nu}{}^{\pi}+F^{\pi}{}_{\mu\nu})\\ &= \frac{1}{4}\sum_{\mu}{}^{\pi}(P^{\pi}{}_{\mu\mu})^2\gamma_{\mu\mu} + 2P^{\pi}{}_{\mu\nu}\beta^{\pi}{}_{\mu\nu} - \frac{1}{2}(P^{\pi}{}_{\mu\nu})^2\gamma_{\mu\nu}\end{aligned} \tag{3}$$

where E_{elec} is the total electronic energy of ethylene as determined by the molecular orbital calculation, where E_{repul} is the sum of the repulsion energy between cores, which is approximated by a point charge model, where $\sum^{\pi}$ describes the summation over the pi system, where $P^{\pi}{}_{\mu\mu}$ is the pi orbital charge density, where $P^{\pi}{}_{\mu\nu}$ is the pi bond order, where $\gamma_{\mu\mu}$ and $\gamma_{\mu\nu}$ are one-center and two-center electron-electron repulsion integrals respectively, and where $\beta_{\mu\nu}$ is the resonance integral between the atomic orbitals, χ_{μ} and χ_{ν}. The equilibrium distance was calculated by the variation of the interatomic distance, while the other bonds in the molecule were held fixed at their observed equilibrium distances.

The equilibrium distances of the *sp-sp* single and double bonds can be estimated in the same manner as has been described above.

The INDO and Other Methods. The intermediate neglect of the differential overlap (INDO) method employed in the present calculation is based upon an SCF treatment of all the valence electrons and is regarded as an improvement over the CNDO/2 method used to determine the equilibrium distance of the C–C bond in the previous investigation. In the INDO method, all two-electron integrals involving differential overlap are neglected except for one-center integrals of $(\mu\nu/\mu\nu)$ type; the other one-center integrals involving orbital overlap vanish through symmetry. The one-center repulsion integrals are written in terms of the Slater-Condon parameters, which are known from analyses of the multiplet energy splitting for the free atoms. The values of these terms used in the INDO method has been listed by Pople *et al.*[11)] The monatomic core integrals differ somewhat from those of the CNDO/2 method because of the introduction of these parameters.

The molecular orbitals and their energies can be obtained by solving the set of secular equations and the corresponding secular matrix consisting of the Fock elements. The expressions for the Fock matrix elements and the details of the method can be found in Pople's original paper.[8-11)]

The NDDO method disregards differential overlap only for atomic orbitals on different atoms. At this level of approximation, $(\mu_A\nu_A/\lambda_B\sigma_B)$ type integrals are taken into account. All the electronic repulsions are theoretically evaluated according to the formulas listed by Roothaan,[13)] and the approximation where all the electron repulsion integrals are calculated as Coulomb integrals involving a valence *s* function is avoided.

A more reliable method of calculation for determining the equilibrium distance uses a configuration interaction (CI) treatment. The hypothetical bond length of a molecule, including the broken pi bonds,

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13) C. C. J. Roothaan, *J. Chem. Phys.*, **19**, 1445 (1951).

can be calculated by the corrected total energy considering the interaction of the ground state with doubly-excited configurations (^1A_g) for the sigma system. All the doubly-excited configurations were taken into account for ethylene and acetylene, but the CI calculation was restricted to the 30 doubly-excited states for ethane.

The configurations of the molecules including the broken pi bonds are all open-shell. In applying the unrestricted INDO method to the calculation of these molecules, calculations for different types of spin multiplicity are possible. However, the spin multiplicity of the hypothetical molecule discussed in this work may be considered to be a singlet state.

In order to investigate the effect of electronic interaction between non-adjacent atomic orbitals in determining the bond length, the equilibrium distance has been determined from the total energy, neglecting some interactions between atomic orbitals. The invariance property of the INDO method under a simple transformation, such as the replacement of the *s* and *p* orbitals by hybrids, is effective for this investigation.

Through the similarity transformation by some appropriate matrix, the energy ($H'_{\mu\nu}$ and $F'_{\mu\nu}$) and population ($P'_{\mu\nu}$) matrices, with reference to the carbon hybrids, can be obtained from the results of the INDO calculation. The interactions (E^*) between non-adjacent hybrids are given by:

$$E^*_{\mu\nu} = P'_{\mu\nu}(H'_{\mu\nu}+F'_{\mu\nu})\,. \tag{4}$$

Results and Discussion

The C–H equilibrium distances of ethane, ethylene, and acetylene calculated by both the CNDO/2 and INDO methods are shown in Table 1. In Table 2, the C–C equilibrium distances of C_2-hydrocarbons calculated by a variety of methods are collected. The distances obtained by the INDO-CI treatment of the present work are in complete agreement with those obtained by the CNDO/2 and INDO methods of the previous paper. Generally, the equilibrium distances calculated by the INDO and INDO-CI methods are slightly longer than those obtained by the CNDO/2 calculation. The C–C equilibrium distances calculated by the NDDO method were shorter than those obtained by the INDO and CNDO/2 calculations. The calculated interatomic distances of the tri-tri, di-di single, and di-di double bonds by the INDO-CI treatment are substantially in agreement with the results of the CNDO/2 calculation, the simplest form of calculation. The results of the unrestricted INDO calculations for the equilibrium distances in different types of spin states are listed in Table 3. They did not differ from one another in the calculated equilibrium distance.

Table 1. Carbon-hydrogen equilibrium distances

Molecule	C-H Equilibrium distance (Å)		
	CNDO/2[a]	INDO	Obsd[b]
Ethane	1.117	1.120	1.093
Ethylene	1.106	1.113	1.086
Acetylene	1.088	1.095	1.058

a) The result of the CNDO/2 method was published in the previous paper.[2]

b) "Interatomic Distances," Supplement, Special Publication, No. 18, The Chemical Society (London).

However, a tendency for the bond length to decrease with an increased *s* character of the hybrid was found in the results of the NDDO calculations for the hypothetical tri-tri and di-di single and di-di double bond lengths. This is a noteworthy fact, but the difference between the te-te and tri-tri single bonds is negligible. The result obtained by the NDDO method must be due to the fact that all the electronic repulsions are theoretically calculated; that is, the usual approximation, in which they are assumed to depend only on the atoms and not on the actual type of orbital, is unnecessary in this calculation.

From the results of the NDDO calculation, it follows that the C–C single bond length is certainly affected by the types of the hybridization of the carbon atom, but this hybridization effect is not so large as has previously been believed.

The problem in this paper should be re-examined by the modified CNDO/2[14] and MINDO[15] methods, in which the off-diagonal bonding parameters are given by the different types of approximation. This is true because the off-diagonal bonding parameter

Table 2. Carbon-carbon equilibrium distances

Type of C-C bond	C-C Equilibrium distance (Å)				
	CNDO/2[a]	INDO[a]	INDO-CI	NDDO	Obsd[b]
te-te single	1.471	1.472	1.472	1.460	1.534
tri-tri single	1.475	1.479	1.480	1.456	
di-di single	1.476	1.479	1.480	1.447	
tri-tri double	1.317	1.319	1.328	1.305	1.337
di-di double	1.323	1.325		1.301	
di-di triple	1.198	1.200	1.210	1.181	1.205

a) The results of the CNDO/2 and INDO methods were published in the previous paper[2] and communication.[3]

b) "Interatomic Distances," Supplement, Special Publication, No. 18, The Chemical Society (London).

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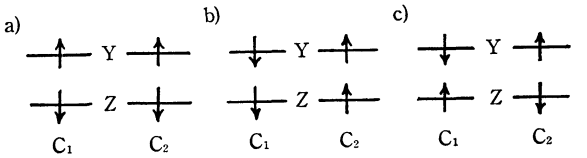
[14] J. D. Bene and H. H. Jaffé, *J. Chem. Phys.*, **48**, 1807 (1968).

[15] For example, M. J. S. Dewar, and E. Haselbach, *J. Amer. Chem. Soc.*, **92**, 590 (1970).

Table 3. Carbon-carbon equilibrium distances by the unrestricted INDO calculation

Type of C-C bond	C-C Equilibrium distance (Å)		
	Singlet	Triplet	Quintet
te-te single	(1.472)		
tri-tri single	1.483	1.479	
di-di single	1.479[a)]		1.483
di-di single	1.485[b)]		
di-di single	1.482[c)]		

Electron spins are assigned as illustrated below.



$(\beta_A{}^0)$ is given the same value for resonance integrals between sigma orbitals and those between pi orbitals in the CNDO/2 and INDO methods. In the modified CNDO/2 method proposed by Bene and Jaffé, the $\beta^\sigma_{\mu\nu}$, where μ and ν are sigma orbitals, is distinguished from the $\beta^\pi_{\mu\nu}$, where μ and ν are pi orbitals, by introducing a empirical parameter, k, as follows:

$$\beta^\sigma_{\mu\nu} = \frac{1}{2} S_{\mu\nu}(\beta_A{}^0+\beta_B{}^0) \tag{5}$$

$$\beta^\pi_{\mu\nu} = \frac{1}{2} kS_{\mu\nu}(\beta_A{}^0+\beta_B{}^0) \tag{6}$$

Also, in the MINDO method proposed by Dewar *et al.*, the resonance integrals are approximated by the following equation:

$$\beta_{\mu\nu} = \frac{1}{2} k'S_{\mu\nu}(I_\mu+I_\nu) \tag{7}$$

where k' is a constant and where I_μ and I_ν are valence-state ionization potentials for the atomic orbitals, χ_μ and χ_ν respectively. However, the energies and orbitals obtained using the approximation (Eq. (7)) will not be invariant to hybridization of the atomic-orbital basis set.

The results of the NDDO calculation indicate the hybridization effect on the equilibrium distance should be discussed by the use of the calculations presented above.

The effect of the interaction between non-adjacent atomic orbitals for determining the interatomic distance can be made clear by the use of Tables 4—6. The magnitude of the absolute value of Δr in Tables 4—6 proves the extent of the effect of non-adjacent atomic orbital interaction (E^*) in determining the equilibrium distance. It should be emphasized that the most effective factor in determining the interatomic distance is the gradient of the variation of the interaction energy (E^*) with the change in the interatomic distance rather than the magnitude of its absolute value.

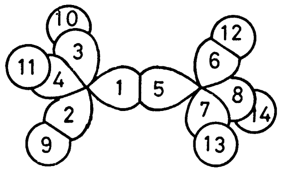


Fig. 2. The numbering of atomic orbital. (Ethane)

Table 4. The effect of interaction between non-adjacent atomic orbitals[a)] for determining the equilibrium distances

Neglected atomic orbital interaction[b)]	Ethane, C-H (1.120 Å), C-C (1.472 Å)[a)]	
	Δr (Å)[c,d)]	
	C-H	C-C tri-tri single
(9—10), (9—11), (10—11), (12—13), (12—14), (13—14)	+0.001	−0.003
(9—12), (9—13), (9—14), (10—12), (10—13), (10—14), (11—12), (11—13), (11—14)	−0.001	+0.001
(2—12), (2—13), (2—14), (3—12), (3—13), (3—14), (4—12), (4—13), (4—14), (6—9), (6—10), (6—11), (7—9), (7—10), (7—11), (8—9), (8—10), (8—11)	−0.001	+0.008
(2—10), (2—11), (3—9), (3—11), (4—9), (4—10), (6—13), (6—14), (7—12), (7—14), (8—12), (8—13)	0	+0.010
(1—9), (1—10), (1—11), (5—12), (5—13), (5—14)	+0.003	−0.028
(1—12), (1—13), (1—14), (5—9), (5—10), (5—11)	+0.007	+0.034
(1—2), (1—3), (1—4), (2—3), (2—4), (3—4), (5—6), (5—7), (5—8), (6—7), (6—8), (7—8)	−0.007	−0.024
(1—6), (1—7), (1—8), (5—2), (5—3), (5—4)	−0.007	+0.058
(2—6), (2—7), (2—8), (3—6), (3—7), (3—8), (4—6), (4—7), (4—8)	−0.007	+0.123

a) The equilibrium distances were calculated by the INDO method.
b) The orbital numbers are indicated in Fig. 2.
c) The Δr is difference between the equilibrium distance and the bond length calculated from the total energy neglecting the non-adjacent atomic orbital interaction.
d) The plus and minus signs refer to the lengthening and shortening of distance, respectively.

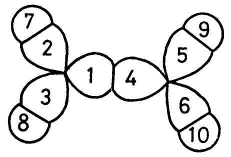


Fig. 3. The numbering of atomic orbital. (Ethylene sigma system)

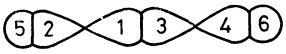


Fig. 4. The numbering of atomic orbital. (Acetylene sigma system)

Conclusion

The unexpected conclusion reported previously that the C-C bond length is little affected by the types of the hybridization of the carbon atom has been re-examined by the INDO-CI, NDDO and unrestricted INDO methods.

The conclusion from the INDO-CI and unrestricted INDO calculations has agreed with that obtained previously by the CNDO/2 calculation. However, a tendency for the bond length to decrease with an increase in the *s* character in hybrids was found in the results of the NDDO calculations for the hypothetical tri-tri and di-di single, and the di-di double bond

TABLE 5. THE EFFECT OF INTERACTION BETWEEN NON-ADJACENT ATOMIC ORBITALS FOR DETERMINING[a] THE EQUILIBRIUM DISTANCE

Neglected atomic orbital interaction[b]	Ethylene, C-H (1.113 Å), C=C (1.319 Å), C-C (1.479 Å)[a]		
	Δr (Å)[c,d]		
	C-H	C=C tri-tri double	C-C tri-tri single
(7—8), (9—10)	−0.001	0	0
(7—9), (8—10)	−0.001	−0.003	−0.004
(7—10), (8—9)	0	+0.010	+0.005
(1—2), (1—3), (2—3), (4—5), (4—6), (5—6)	−0.019	−0.019	−0.031
(1—5), (1—6), (4—2), (4—3)	−0.009	+0.052	+0.036
(2—5), (3—6)	−0.003	+0.028	+0.025
(2—6), (3—5)	−0.006	+0.043	+0.040
(1—7), (1—8), (2—8), (3—7), (4—9), (4—10), (5—10), (6—9)	0	−0.007	−0.011
(1—9), (1—10), (4—7), (4—8)	+0.008	+0.012	+0.009
(2—9), (3—10), (5—7), (6—8)	−0.001	+0.003	+0.002
(2—10), (3—9), (5—8), (6—7)	0	+0.001	−0.011

a) The equilibrium distances were calculated by the INDO method.
b) The orbital numbers are indicated in Fig. 3.
c) The Δr is difference between the equilibrium distance and the bond length calculated from the total energy neglecting the non-adjacent atomic orbital interaction.
d) The plus and minus signs refer to the lengthening and shortening of distance, respectively.

TABLE 6. THE EFFECT OF INTERACTION BETWEEN NON-ADJACENT ATOMIC ORBITALS FOR DETERMINING THE EQUILIBRIUM DISTANCE

Neglected atomic orbital interaction[b]	Acetylene, C-H (1.095 Å), C≡C (1.200 Å), C=C (1.325 Å), C-C (1.479 Å)[a]			
	Δr (Å)[c,d]			
	C-H	C≡C di-di triple	C=C di-di double	C-C di-di single
(5—6)	0	+0.001	−0.003	+0.001
(1—4), (3—2)	−0.006	+0.023	+0.008	−0.001
(2—4)	−0.002	+0.009	+0.002	+0.004
(1—2), (3—4)	−0.019	−0.013	−0.023	−0.032
(1—5), (3—6)	+0.004	0	−0.005	−0.003
(1—6), (3—5)	+0.001	−0.001	−0.005	−0.005
(2—6), (4—5)	0	0	−0.003	0

a) The equilibrium distances were calculated by the INDO method.
b) The orbital numbers are indicated in Fig. 4.
c) The Δr is difference between the equilibrium distance and the bond length calculated from the total energy neglecting the non-adjacent atomic orbital interaction.
d) The plus and minus signs refer to the lengthening and shortening of distance, respectively.

lengths. The tendency was, however, very small in comparison with those generally found.

It has been noted that the equilibrium distances are largely dependent on some electronic interactions between non-adjacent atomic orbitals.

A more extensive study of this problem by methods using different types of approximation for estimating the resonance integral will be the subject of a subsequent paper.

Our thanks are offered to Professor K. Higasi for his continuous interest and encouragement. The calculations were carried out on the IBM-7040 computer at the Computation Center of Waseda University. We would like to thank I.B.M. Japan, Ltd., for lending this computer to the university.