HYBRIDIZATION EFFECT ON C-C BOND LENGTH

Tomoo Miyazaki

Department of Applied Chemistry, Waseda University, Shinjuku-ku, Tokyo, Japan

The relative importance of pi electron resonance and hybridization in the shortening effect for single bond length of conjugated hydrocarbon such as the C_2-C_3 bond of butadiene has been a subject of heated discussions over past years (1-3).   Mulliken (4) commented on this situation that the whole hybridization contributes somewhat more than electron delocalization to the observed shortenings, but the two causes are of the same order of magnitude.   Since it is difficult to decide experimentally between hybridization and electron delocalization as causes of bond shortening, he reached a conclusion that it becomes rather necessary, and proper, to place considerable reliance on theory, provided it is reliable theory.

Among the approximate theories now being used the CNDO/2 (5-7) and INDO (8) methods, approximate self-consistent molecular orbital methods for all valence electrons, appear to be most reliable to investigate the bond length problem, because these methods have led to good agreement with experimental values for bond lengths and bond angles of simple molecules.   And these methods satisfy the requirement that the molecular wavefunction and the orbital energy are invariant under transformations of the atomic orbital basis set such as the replacement of s, p orbitals by hybrids.   This feature of these methods seems to be useful in discussing the accuracy of the local bond approximation by comparision with the molecular orbital calculations.

In calculating the tri-tri, di-di C-C single and di-di double bond distances by the CNDO/2 and INDO methods, it was assumed that the bond distances of molecules including the broken pi bonds could be calculated by setting the pi overlap integrals equal to zero.   Using this simple assumption, the INDO calculation which includes the one-center exchange integrals were performed to

determine the equilibrium distances of different types of C-C single and double

bonds.   Table 1 records the equilibrium distances of C-C bonds calculated by

the INDO and CNDO/2 methods, the latter results being published in the previous

paper (9).   The equilibrium distances of the tri-tri and di-di C-C single

bonds are not much different from the te-te single bond distance.   Also the

di-di double bond distance is almost of the same magnitude as the tri-tri double

bond distance.   From these results, it follows that the C-C bond length of the

sigma system is little affected by the types of hybridization of carbon atoms.

The above unexpected conclusion, although it is dependent upon the validity

of the INDO and CNDO/2 methods, might be explained in the following way.

Through the similarity transformation by some appropriate matrix, the energy and

population matrices referring to the carbon hybrids can be obtained from the

results of the INDO and CNDO/2 calculations.   With the new matrix elements of

the sigma system, we can investigate the precision of the local bond approxi-

mation for ethane, ethylene and acetylene.   The total electronic energies (α)

which are neglected in the local bond approximation are shown graphically in

Fig. 2, this interaction energy being calculated from the off-diagonal elements

TABLE 1

Equilibrium Distances for Different Types of Carbon-Carbon Bonds.

Type of C-C Bond	Equilibrium Distance (A) [a]							Force Constant (dyn/cm$\times 10^5$)	
	INDO	CNDO/2	INDO[b]	CNDO/2[b]	INDO[c]	CNDO/2[c]	Obs[d]	INDO	Obs[e]
te-te single	1.472	1.471	1.627	1.621	1.600	1.562	1.535	15.7	4.5
tri-tri "	1.479	1.475	1.567	1.569	1.538	1.540		16.1	
di-di "	1.479	1.476	1.470	1.479	1.458	1.452		16.8	
tri-tri double	1.319	1.317					1.337	24.7	9.6
di-di "	1.325	1.323						25.2	
di-di triple	1.200	1.198					1.205	35.4	15.8

a) In these calculations, the C-H bond lengths were held fixed at their observed
equilibrium distances.
b) This calculation neglects the interaction energies between non-adjacent atomic
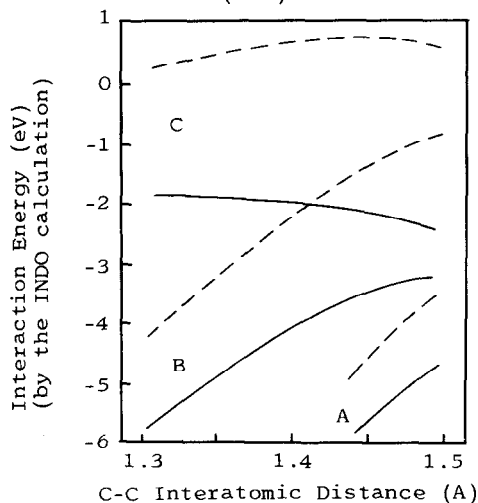orbitals except the intra-atomic interaction energies between carbon hybrids.
c) This calculation neglects the interaction energies between non-adjacent atomic
orbitals.
d) Tables of Interatomic Distances (Supplement), The Chemical Society (London)
e) G. Herzberg, Infrared and Raman Spectra,(D. Van Norstrand Co.,Inc., Princeton)

referring to the non-bonding atomic orbitals.   The interaction energies between non-adjacent carbon hybrids are shown in Fig. 3.   The energies largely contribute to the interaction energy (α).   The local bond approximation becomes less accurate with the decreased s character in hybrids. The interaction energies between adjacent carbon hybrids are shown in Fig. 1. The stabilization effects of these energies naturally increase with the increased s character in hybrids. In determining the C-C equilibrium distances, when the electronic interaction energies (α) were neglected,

FIG. 1
Variation of Electronic Interaction Energy between Adjacent Carbon Hybrids against Interatomic (C-C) Distance.

C-C Interatomic Distance (A)

FIG. 2 (a,b)
Variation of Total Electronic Interaction Energy between Non-adjacent Atomic Orbitals against Interatomic (C-C) Distance.

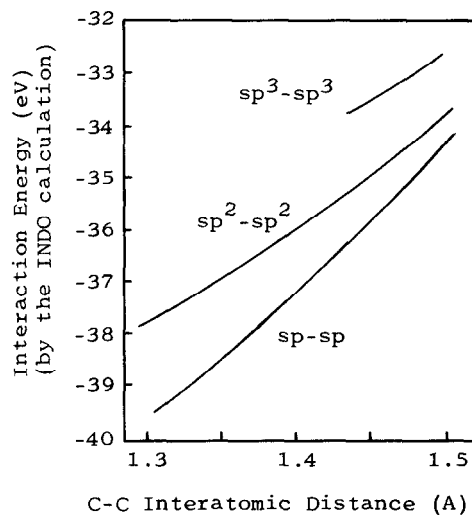C-C Interatomic Distance (A)

FIG. 3 (a,b)
Variation of Electronic Interaction Energy between Non-adjacent Carbon Hybrids against Interatomic (C-C) Distance.

C-C Interatomic Distance (A)

a) A: ethane, B: ethylene, C: acetylene.
b) In Fig. 2 and Fig. 3, the broken line indicates the variation of the interaction energy without the intra-atomic interaction energy between carbon hybrids.
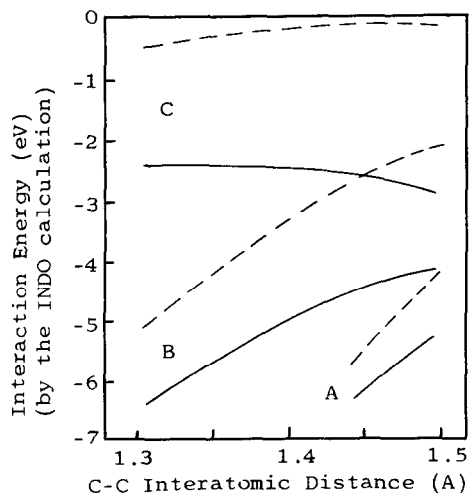
the equilibrium distances of different kinds of C-C single bonds were lengthened with the decreased s character in hybrids as shown in Table 1.   So, it should be pointed out that the electronic energies between non-adjacent atomic orbitals largely contribute to the determination of C-C bond length.

If the interaction energies between non-adjacent atomic orbitals are small or if they have values invariant with the change of the interatomic distance, one would expect the equilibrium distance to be dependent upon the hybridization state.   Indeed, this is the case for the C-H bond in which the previous calculation (9) gave the following values: _viz_. methane 1.114 A, ethane 1.117 A, ethylene 1.106 A and acetylene 1.088 A.

The stretching force constants of carbon-carbon bonds were calculated by fitting the total energy to a cubic function with respect to distance and taking the second derivative at the equilibrium distance.   The calculated force constants were found to be independent of the hybridization state, although they were much larger than the observed values as shown in Table 1.   This may also imply that the different types of C-C single bonds are equal in bond strength.

In view of the above, the conclusion to be drawn from results presented in Table 1 indicates that the shortening of C-C single bond in conjugated hydro-carbon is mainly dependent upon the effect of pi electron delocalization.

ACKNOWLEDGEMENT

REFERENCES

1. M.J.S. Dewar and A.N. Schmeising, _Tetrahedron_, 5, 166 (1959)

2. R.S. Mulliken, _Tetrahedron_, 6, 68 (1959)

3. An Epistologue on Carbon Bonds, _Tetrahedron_, 17, 123-266 (1962)

4. R.S. Mulliken, _Tetrahedron_, 17, 247 (1962)

5. J.A. Pople, D.P. Santry and G.A. Segal, _J. Chem. Phys._, 43, S 129 (1965)

6. J.A. Pople and G.A. Segal, _J. Chem. Phys._, 43, S 136 (1965)

7. J.A. Pople and G.A. Segal, _J. Chem. Phys._, 44, 3289 (1966)

8. J.A. Pople, D.L. Beveridge and P.A. Dobosh, _J. Chem. Phys._, 47, 2026 (1967)

9. T. Miyazaki and H. Ohbayashi, _Bull. Chem. Soc. Japan_, 42, 2767 (1969)