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Molecular Orbital Interpretation of Infrared Absorption Frequencies. I. Selection of HMO Hetero-atomic Parameters

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The π-bond orders calculated by HMO method and infrared frequencies of aliphatic carbonyl compound were successfully correlated. Each parameter of hetero-atoms in this calculation was selected as applicable to the treatments of a variety of infrared spectra. Auxiliary inductive parameter was found to be necessary.

Generally, in the theoretical treatment of physical properties or reactivities of organic compounds the resonance theory still possesses very significant situation. Although the molecular orbital method is well known to give many quantitative basis to them, very few molecular orbital interpretations of infrared absorption frequencies have hitherto been presented. This circumstance stimulated us to investigate infrared absorption frequencies by the molecular orbital method.

Various methods have been developed for molecular orbital calculations, but the Hückel LCAO-MO (HMO) method is thought to be the most approachable procedure of calculation for organic chemists. And this method is also known to give fairly good results in spite of its simplicity. For instance, physical properties such as polarographic redox potentials,[2] ultraviolet spectra,[3] infrared spectra,[4] nuclear magnetic resonance spectra,[5] and electron spin resonance spectra,[6] are well correlated with molecular indices calculated by the HMO method.

For the HMO calculation of molecular orbitals of organic compounds, which contain hetero-atoms, various kinds of parameters of every hetero-atom have been suggested.[7] And these parameters are presented to be selected as the case may give the best results. This selection is thought for organic chemists to be somewhat troublesome and to obstruct common treatments.

From these points of view our first major purpose has been directed to looking for general parameters, if any, at least for the same kind of physical phenomenon.

In this paper several parameters are presented from the results of infrared spectra of aliphatic carbonyl compounds and their general usefulness will be checked in the forthcoming papers.

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[1] Location: *Katakasu, Fukuoka.*

[2] R.W. Schmid and E. Heilbronner, *Helv. Chim. Acta*, **37**, 1453 (1954); G.J. Hojitink, *Rec. Trav. Chim.*, **77**, 555 (1958).

[3] S.F. Mason, *J. Chem. Soc.*, **1959**, 1253; *idem, ibid.*, **1960**, 219

[4] G. Berthier, B. Pullman and J. Pontis, *J. Chim. Phys.*, **49**, 367 (1952); G.M. Badger and A.G. Moritz, *Spectrochim. Acta*, **1959**, 672; S.F. Mason, *J. Chem. Soc.*, **1958**, 3619.

[5] R.W. Taft, E. Price, I.R. Fox, I.C. Lewis, K.K. Andersen and G.T. Davis, *J. Am. Chem. Soc.*, **85**, 3146 (1963); J.E. Bloor and D.L. Breen, *J. Phys. Chem.*, **72**, 716 (1968); B.M. Lynch, *Tetrahedron*, **17**, 1357 (1969); T.K. Wu and B.P. Daily, *J. Chem. Phys.*, **41**, 2796 (1964).

[6] G. Vincow and G.K. Frankel, *J. Chem. Phys.*, **34**, 1333 (1961); H.M. McConnell, *J. Chem. Phys.*, **24**, 632 (1956); A. Kuboyama, *Bull. Chem. Soc. Japan*, **32**, 1226 (1959).

[7] A. Streitwieser Jr, "Molecular Orbital Theory for Organic Chemists," John Wiley & Sons, Inc., New York, 1961.

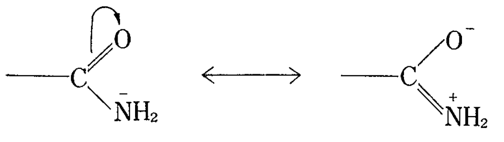
Experimental

Samples were chosen to include every variety of aliphatic carbonyl functions. Ten kinds of them, whose reported carbonyl frequencies were neither measured in CCl_4 nor coincided with each other within experimental error among several papers,[8] were purified by general procedures.

Infrared spectra of these compounds were measured at the concentration of 0.05 mole% in CCl_4 by Nihon–Bunko DS-301 infrared spectrophotometer using NaCl cell with 0.5 mm optical path length.

Result and Discussion

The stretching vibration of infrared absorption spectra has widely been interpreted by the resonance theory. For example, the low frequency shift of carbonyl group in amide is attributed to the decrease of double bond character (π-bond order) due to the existence of resonance form Ib. But, the resonance theory can not predict any degree of diminution of π-bond order of carbonyl group.



1a 1b

For double bond systems such as carbonyl group the vibrational energy might be considered to consist of σ- and π-components, and the π-component might be expected to be a function of π-bond order.

A detailed analysis by Coulson, *et al.*[9] indicated that to a first approximation, the force constant for a bond is a function of only the bond order, and to a second approximation, of both the bond order and the mutual bond polarizability. And Berthier, *et al.* showed that for a family of systems such as carbonyl groups of a few open–chain and several aromatic quinones, merely the bond order gave a satisfactory linear correlation with the infrared absorption frequency.[10]

Our first approach is to examine whether there are any appropriate parameters, which may give a clear correlation between the infrared frequencies of every variety of simple aliphatic carbonyl compounds and their calculated bond orders, or not.

The Pariser-Parr-Pople method(semiempirical)[11] has been proved to give the wave function of much higher approximation than the HMO method for π-electron system. Therefore,

Table I. Selection of Carbonyl Parameter

$h_{\dot{O}}$	$k_{C=O}$	HCHO		CH_3CHO		CH_3COCH_3	
		C_1[a]	C_2[a]	C_1[a]	C_2[a]	C_1[a]	C_2[a]
1.2	2.0	0.8022	0.5969	0.8123	0.5832	0.8073	0.5901
2.0	1.0	0.8694	0.4940	0.8710	0.4914	0.8817	0.4719
1.0	1.1	0.9135	0.4068	0.9227	0.3855	0.9216	0.3882
2.0	$\sqrt{2}$	0.8766	0.4812	0.8959	0.4443	0.9030	0.4296
1.3	1.2	0.8303	0.5574	0.8554	0.5180	0.8685	0.4956
1.0	0.8	0.8632	0.5049	0.8898	0.4563	0.9029	0.4298
P–P–P method		0.7596	0.6504	0.7976	0.6032	0.8194	0.5732

a) C_1 and C_2 are the coefficients of molecular orbital function;
$\phi_1 = C_1\chi_O + C_2\chi_C \qquad \phi_2 = C_2\chi_O - C_1\chi_C$

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[8] L.J. Bellamy, "Advances in Infrared Group Frequencies," Methuen & Co. Ltd., London, 1968; D. Cook, *J. Am. Chem. Soc.*, **80**, 49 (1958); M. Kotake, "Series of Comprehensive Organic Chemistry. -Constants of Organic Compounds-," The Asakura Publishing Company, Ltd., Tokyo, Japan, 1963.

[9] C.A. Coulson and H.C. Longuet-Higgins, *Proc. Roy. Soc.*, **A 193**, 456 (1948); H.C. Longuet-Higgins and F.H. Burkitt, *Trans. Faraday Soc.*, **48**, 1077 (1952).

[10] G. Berthier, B. Pullman and J. Pontis, *J. Chim. Phys.*, **49**, 367 (1952).

[11] J.A. Pople, *Proc. Phys. Soc.* (London), **A 68**, 81 (1955).

the wave functions of formaldehyde, acetaldehyde and acetone obtained by this method[12] were adopted as standard ones for the selection of parameters of the oxygen atom of carbonyl group.

Table I shows that parameters $h_{\dot{O}}=1.2$ and $k_{C=O}=2.0$, suggested by Pullman,[13] give the most analogous wave functions to the corresponding standard ones, and consequently, these values should be selected as the general parameters of the oxygen atom of carbonyl functions.

Parameters of other hetero-atom were determined to afford as good linear relationships as possible between infrared frequencies and calculated bond orders. Hetero-atomic parameters which gave the best results are shown in Table II. The availability of these parameters for

Table II. Selected Parameter Values for Hetero-atoms

Atoms	Coulomb integral	Resonance integral
$\dot{O}$	$h_{\dot{O}}=1.2$	$k_{C=O}=2.0$
$\ddot{O}$	$h_{\ddot{O}}=2.8$	$k_{C-O}=0.7$
$\ddot{N}$	$h_{\ddot{N}}=1.1$	$k_{C-N}=0.6$
Cl	$h_{Cl}=3.0$	$k_{C-Cl}=0.5$
OCH_3	$h_{OCH_3}=1.8$	$k_{C-OCH_3}=0.7$
CH_3 (Inductive model)	$h_{CH_3}=-0.15$	$k_{C-CH_3}=0.0$
$\dot{O}$[a] (OH……**O**=C)	$h_{\dot{O}}=1.4$	$k_{C=O}=2.0$
$\ddot{O}$[a] (**O**H……O=C)	$h_{\ddot{O}}=1.8$	$k_{C-O}=0.7$

$\left\{\begin{array}{l}\alpha_X=\alpha+h_X\cdot\beta\\ \beta_{C-X}=k_{C-X}\cdot\beta\end{array}\right.$

[a] This modification was suggested by Pullman[13] and was proved to afford good results in the calculation of enol form of acetylacetone.

Table III. The Infrared Frequencies and Calculated Bond Orders

Compounds	(cm^{-1})	AIP				
		0.0%	20%	30%	40%	50%
(1) $CH_3COCH{=}C(OH)CH_3$	1616	0.8503	0.8551	0.8730	0.8801	0.8866
(2) $(CH_3)_2NCON(CH_3)_2$	1640	0.8685	0.8801	0.8843	0.8872	0.9023
(3) NH_2CONH_2	1686	0.8832	0.9018	0.9078	0.9184	0.9137
(4) $HCON(CH_3)_2$	1687	0.9095	0.9174	0.9209	0.9250	0.9270
(5) $CH_3CONHCH_3$	1700	0.9055	0.9164	0.9213	0.9258	0.9299
(6) CH_3CONH_2	1718	0.9092	0.9221	0.9279	0.9337	0.9378
(7) CH_3COCH_3	1723	0.9363	0.9363	0.9363	0.9363	0.9363
(8) $HCONH_2$	1726	0.9261	0.9298	0.9349	0.9394	0.9433
(9) NH_2COOCH_3	1733	0.8862	0.9116	0.9190	0.9263	0.9163
(10) $HCOCH_3$	1738	0.9475	0.9475	0.9475	0.9475	0.9475
(11) $HCOOCH_3$	1742	0.9218	0.9417	0.9496	0.9560	0.9607
(12) HCHO	1740	0.9578	0.9578	0.9578	0.9578	0.9578
(13) HCOOH	1744	0.9251	0.9473	0.9558	0.9625	0.9670
(14) CH_3COOCH_3	1756	0.9121	0.9340	0.9431	0.9508	0.9569
(15) $CH_3OCOOCH_3$	1758	0.8890	0.9079	0.9305	0.9331	0.9295
(16) CH_3COOH	1772	0.9152	0.9397	0.9496	0.9577	0.9638
(17) $ClCOOCH_3$	1806	0.9115	0.9528	0.9571	0.9826	0.9308
(18) CH_3COCl	1806	0.9561	0.9722	0.9836	0.9900	0.9912
(19) ClCOCl	1813	0.9356	0.9825	0.9766	0.9513	0.9109

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[12] S. Bratoz and S. Besnainou, *J. Chem. Phys.*, 34, 1142 (1961).

[13] A. Pullman and B. Pullman, "Quantum Biochemistry," John Wiley & Sons, Inc., New York, N.Y., 1963.

other types of organic compound was simply demonstrated by an application to aromatic carbonyl compounds as shown in Fig. 3.

In the treatment of hetero-atoms, the auxiliary inductive parameter (AIP)[14] which supplements an "inductive effect" of a hetero-atom on an attached carbon of the substituents has also been known to be very helpful. Electronegative atoms have been considered to polarize the σ-bond and to increase the effective electronegativity of the attached carbon. In the molecular orbital calculations, this effect can be included by assigning an AIP to the attached carbon.

The AIP concept was theoretically criticized by McWeeny,[15] but in many approximate calculations good interpretations have been reported to be obtained by the introduction of this concept.

We estimated the AIP as 0%, 20%, 30%, 40% and 50% of each parameter of coulomb integrals of hetero-atoms, and considered it only on the carbon next to a hetero-atom.

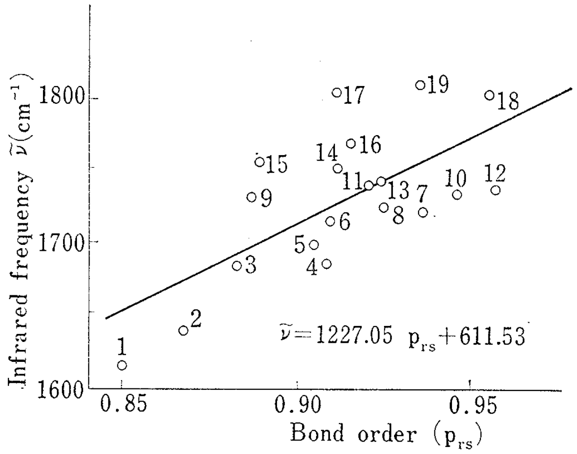

Fig. 1. Calculated Bond Orders (AIP: 0.0%) and Infrared Absorption Frequencies

Numbers in Fig. 1, 2, 3, 4, and 5 correspond to the number of compounds in Table III.

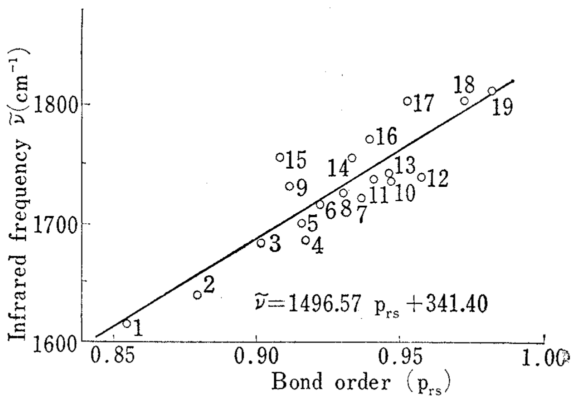

Fig. 2. Calculated Bond Orders (AIP: 20%) and Infrared Absorption Frequencies

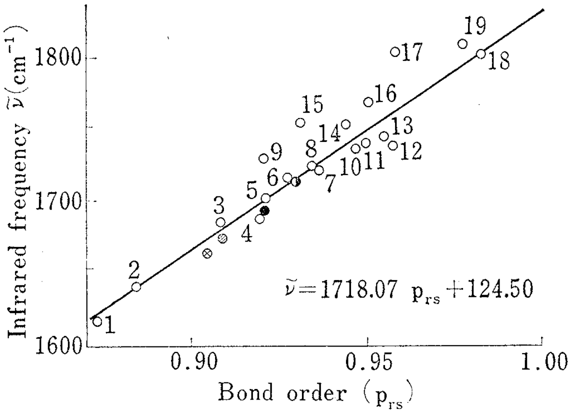

Fig. 3. Calculated Bond Orders (AIP: 30%) and Infrared Absorption Frequencies

◑: benzaldehyde ●: acetophenone
▨: benzamide ⊗: benzophenone

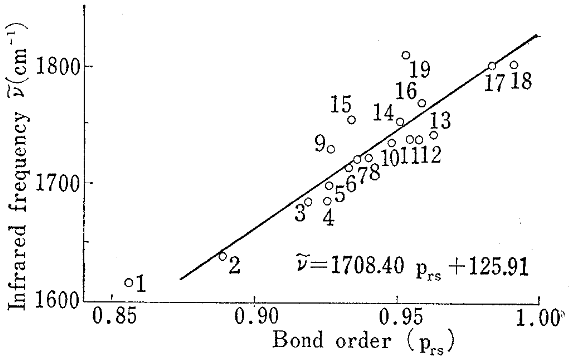

Fig. 4. Calculated Bond Orders (AIP: 40%) and Infrared Absorption Frequencies

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14) G.W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942); S.L. Matlow and G.W. Wheland, *J. Am. Chem. Soc.*, **77**, 3653 (1955); C. Sandorfy, *Can. J. Chem.*, **36**, 1739 (1958).

15) R. McWeeny, *Proc. Roy. Soc.*, **A 237**, 355 (1956); *cf.* G. Del Re, *Tetrahedron*, **10**, 81 (1960); R.D. Brown, *Quart. Revs.*, **6**, 63 (1952).

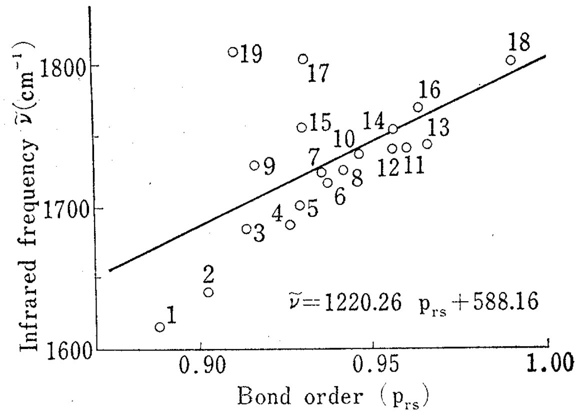

Fig. 5. Calculated Bond Orders (AIP: 50%) and Infrared Absorption Frequencies

The relations between the infrared frequencies and calculated bond orders thus obtained are tabulated in Table III, and are shown in Fig. 1, 2, 3, 4 and 5. Oblique lines in figures are their statistical regression lines. Standard deviations of each case were also calculated as shown in Table IV.

As shown in Fig. 1 a disregard of AIP gave very poor linear correlation. We might ignore the introduction of AIP and select different kinds of parameters to give a better linear correlation than that of Fig. 1, but trials indicated us that those parameters were neither usual ones nor suitable for other types of compounds. Therefore the AIP technique was proved to be significant in this case.

Figures 2, 3, 4 and 5 show that 20% and 50% give rather poor and 30% and 40% give fairly good linearity. From a comparison of Fig. 3 with Fig. 4, it might be thought that the latter has better linear correlation than the former, but the standard deviation of the case of 30% was smaller than that of 40%. This discrepancy should come from the digression of two compounds, phosgen and dimethyl carbonate, from the regression line. AIP 30% has also been used by Jaffé in his extensive calculation related to Hammett's $\rho\sigma$ relation.[16]

Table IV. Comparison of Standard Deviation between AIP Rates

AIP (%)	Standard deviation (cm^{-1})	AIP (%)	Standard deviation (cm^{-1})
0.0	37.12	40.0	20.95
20.0	23.19	50.0	40.03
30.0	18.45		

As our conclusion the parameters presented in this paper may successfully be applied for the interpretation of infrared stretching frequencies by the HMO calculation with an introduction of AIP 30% on the carbon next to hetero-atoms.

This paper also suggests that the HMO calculation would give the theoretical background to organic chemists for the assignments of vibrational frequencies of infrared spectrum.

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[16] H.H. Jaffé, *J. Chem. Phys.*, **21**, 415 (1953); H.H. Jaffé, *J. Am. Chem. Soc.*, **76**, 5843 (1954); H.H. Jaffé, *J. Am. Chem. Soc.*, 77, 274 (1955).

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