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Molecular Orbital Interpretation of Infrared Absorption Frequencies. II.[1] α,β-Unsaturated Carbonyl, *para*- and *meta*-Substituted Aromatic Carbonyl Compounds, an Introduction of the Mutual Additive Substituent Parameter

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The infrared frequencies of α,β-unsaturated carbonyl compounds were correlated well with their π bond orders calculated by HMO method employing hetero-atomic parameters selected in the previous paper. Carbonyl frequencies of each group of *para*-substituted benzaldehydes, acetophenones and methylbenzoates were also shown to be in tolerable correlation with their π bond orders, respectively. But the regression lines of these three groups of compound run parallel separately. This phenomenon was considered to show a defect of conventional method of HMO calculation of disubstituted aromatic compounds [X-C_6H_4-Y]. As a method of improvement of this defect a series of mutual additive substituent parameter (MASP) was introduced. The MASP of substituent [X] is added to the coulomb integral of a hetero atom of substituent [Y], and *vice versa*. By use of MASP to aromatic compounds, carbonyl frequencies of not only saturated, α,β-unsaturated and *para*-, but also *meta*-substituted aromatic carbonyl compounds were all found to be linearly correlated with their π bond orders.

In the previous paper[1] a linear correlation was obtained between C=O stretching frequencies of a variety of aliphatic and a few aromatic carbonyl compounds and π bond orders of their carbonyl groups calculated by HMO method employing several selected hetero-atomic parameters.

This paper describes the results of molecular orbital interpretation of infrared (IR) absorption frequency extended to α,β-unsaturated carbonyl compounds, *para*- and *meta*-substituted benzaldehydes, acetophenones and methylbenzoates, indicates the intrinsic defect of conventional method of HMO calculation of disubstituted aromatic compounds, and presents a novel method of HMO calculation of these compounds.

Experimental

Method of Calculation——Two hetero-atomic parameters, Ö[3] and OCH_3, selected in the previous paper were revised and a few parameters were newly added. The parameters used in this paper are listed in Table I.

Mutual additive substituent parameter (MASP), shown in Table IV, of a substituent [X] of disubstituted benzene derivatives [X-C_6H_4-Y] is added arithmetically to the coulomb integral of the hetero atom of another substituent [Y], and *vice versa*. When Y is constituted of two atoms, such as C=O and -C≡N, MASP of X is added to the atom having a larger electronegativity of Y, such as O and N atoms of the above examples. In the case of $NHCH_3$ and $N(CH_3)_2$ it is added to N atom. When NO_2 is concerned, a half of MASP of X is added equally to both O atoms.

AIP technique (30%) reported in the previous paper is also introduced to the carbon next to hetero atom except the one of benzene ring.

Calculations were carried out on a FACOM 230-60 computer at the Computation Center of the Kyushu University.

Materials——Carbonyl frequencies of eleven α,β-unsaturated aliphatic carbonyl compounds, most *para*- and *meta*-substituted acetophenones and all of *meta*-substituted benzaldehydes and *meta*-substituted

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[1] Part I: Y. Ono and Y. Ueda, *Chem. Pharm. Bull.* (Tokyo), **18**, 2013 (1970).

[2] Location: *Katakasu, Fukuoka.*

[3] In the previous paper the coulomb integral of Ö was misprinted, and it should read as 2.0.

Table I. Selected Parameter Values for Hetero-atoms

Atoms	Coulomb integral	Resonance integral
$\dot{O}$	$h_{O}=1.2$	$k_{C=O}=2.0$
$\ddot{O}$	$h_{O}=2.3$	$k_{C-O}=0.6$
OCH_3	$h_{OCH_3}=2.1$	$k_{C-OCH_3}=0.6$
$\ddot{N}$	$h_{N}=1.1$	$k_{C-N}=0.6$
Cl	$h_{Cl}=3.0$	$k_{C-Cl}=0.5$
Br	$h_{Br}=2.0$	$k_{C-Br}=0.4$
NO_2	$\begin{cases} h_{N}=0.6 \\ h_{O}=1.0 \end{cases}$	$k_{N-O}=1.0$ $k_{C-N}=0.8$
CN	$\begin{cases} h_{C}=0.0 \\ h_{N}=0.5 \end{cases}$	$k_{C-C}=0.7$ $k_{C\equiv N}=1.4$
CH_3 (inductive model)	$h_{CH_3}=-0.15$	$k_{C-CH_3}=0.0$

$$\begin{cases} \alpha_X=\alpha+h_X\cdot\beta \\ \beta_{C-X}=k_{C-X}\cdot\beta \end{cases}$$

methylbenzoates were taken from the literatures[4] so as to select the ones determined in CCl_4 and at low concentrations.

para-Substituted benzaldehydes and methylbenzoates and some acetophenone derivatives were purified by either recrystallization or distillation, and their infrared spectra were measured at the concentration of 0.05 mole % (w/v) in CCl_4 by Nihon-Bunko DS-301 infrared spectrophotometer using NaCl cell with 0.1 mm optical path length.

Result and Discussion

α,β-Unsaturated Carbonyl Compounds

Since α,β-unsaturated compounds were not included in the previous paper except an enol form of acetylacetone, we extended our study to eleven compounds whose infrared absorption data are known. The results of calculation are tabulated in Table II accompanying with six π bond orders of aromatic compounds and six recalculated ones of aliphatic compounds because of the revision of hetero-atomic parameters of $\ddot{O}$ and OCH_3.[5] The plot of these α,β-unsaturated compounds on the regression line ($\nu=1651.86\ p_{C=O}+177.59$) newly obtained from the data of seventeen saturated compounds including six recalculated compounds are shown in Figure 1. This picture indicates that our method of calculation can reveal the quantum chemical aspect of aliphatic carbonyl compounds satisfactorily, regardless of saturated or α,β-unsaturated.

Carbonyl stretching frequencies of aromatic carbonyl compounds which have no other substituent than carbonyl groups are also shown to be correlated well with their π bond orders.

Disubstituted Aromatic Carbonyl Compounds

Pauling-Wheland Method——Infrared absorption frequencies and π bond orders calculated by the Pauling-Wheland method of *para*-substituted benzaldehydes, acetophenones and methylbenzoates are shown in Table III.

Although the variations of π bond order are comparatively small in every group, all groups show respective tolerable correlations between frequencies and π bond orders (Figure 2).

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[4] W.A. Seth-Paul and A. Van Duyse, *Spectrochim. Acta*, **28A**, 211 (1972); L.J. Bellamy, "Advances in Infrared Group Frequencies," Methuen & Co. Ltd., London, 1968.

[5] After the publication of the previous paper we noticed that hetero-atomic parameters of $\ddot{O}$ and OCH_3 were not adequate to calculate benzoic acid and methylbenzoate, and they were revised to give a good correlation. This revision was found to be very useful not only for aromatic compounds but also for aliphatic compounds. And both the standard deviation and the correlation coefficient calculated from seventeen saturated aliphatic compounds were remarkably improved. That is, the new standard deviation and correlation coefficient were 7.23 cm^{-1} and 0.9867, respectively, instead of 18.45 cm^{-1} and 0.9299 of the case employed previous parameters.

Table II. The Infrared Frequencies and Calculated π Bond Orders of Saturated, α,β-Unsaturated and Aromatic Carbonyl Compounds

No.	Compounds	(cm^{-1})	π Bond order
1	NH_2COOCH_3	1733	0.9402
2	CH_3COOCH_3	1756	0.9608
3	$CH_3OCOOCH_3$	1758	0.9587
4	CH_3COOH	1772	0.9656
5	$HCOOH$	1783[a]	0.9713
6	$ClCOOCH_3$	1786[b]	0.9727
7	$CH_3COCH{=}C(OH)CH_3$	1616	0.8786
8	$CH_2{=}CHCHO$	1703	0.9262
9	$CH_2{=}CHCOCH_3$	1686	0.9175
10	$CH_3CH{=}CHCHO$	1696	0.9227
11	$CH_3CH{=}CHCOCH_3$	1676	0.9142
12	$CH_2{=}C(CH_3)COCH_3$	1684	0.9182
13	$CH_2{=}C(CH_3)CHO$	1702	0.9268
14	$CH_2{=}CHCOOCH_3$	1734	0.9322
15	$CH_2{=}C(CH_3)COOCH_3$	1727	0.9325
16	$CH_3CH{=}CHCOOCH_3$	1726	0.9285
17	$(CH_3)_2C{=}CHCHO$	1697	0.9191
18	$(CH_3)_2C{=}CHCOCH_3$	1686	0.9108
19	$C_6H_5{-}CHO$	1710	0.9310
20	$C_6H_5{-}COCH_3$	1692	0.9220
21	$C_6H_5{-}COOCH_3$	1730	0.9371
22	$C_6H_5{-}COOH$	1744	0.9410
23	$C_6H_5{-}CONH_2$	1675	0.9085
24	$C_6H_5{-}CO{-}C_6H_5$	1664	0.9056

a) revised value: J.K. Wilmshurst, *J. Chem. Phys.*, **25**, 478 (1956)
b) revised value: D. Cook, *J. Am. Chem. Soc.*, **80**, 49 (1958)

Table III. The Infrared Frequencies and Calculated π Bond Orders by the Pauling–Wheland Method of Benzaldehydes, Acetophenones and Methylbenzoates

Subst.	Benzaldehyde		Acetophenone		Methylbenzoate	
	(cm^{-1})	$P_{C=O}$	(cm^{-1})	$P_{C=O}$	(cm^{-1})	$P_{C=O}$
p-$N(CH_3)_2$	1692	0.9289			1713	0.9348
p-NH_2			1680	0.9208	1717	0.9355
p-OCH_3	1699	0.9311	1684	0.9221	1722	0.9372
p-OH	1703	0.9313	1686	0.9223	1723	0.9374
p-CH_3	1708	0.9302	1690	0.9212	1727	0.9362
p-H	1710	0.9310	1692	0.9220	1730	0.9371
p-Cl	1712	0.9321	1694	0.9230	1731	0.9383
p-Br	1714	0.9316	1695	0.9226	1732	0.9378
p-CN	1715	0.9312	1701	0.9222	1736	0.9373
p-NO_2	1714	0.9322	1703	0.9236	1737	0.9380
p-CHO	1712	0.9315			1732	0.9376
p-$COCH_3$			1691	0.9224	1732	0.9376
p-COOH					1737	0.9377
p-$COOCH_3$	1713	0.9315			1731	0.9376
m-$N(CH_3)_2$					1727	0.9373
m-NH_2			1689	0.9221	1730	0.9372
m-OCH_3	1709	0.9310	1695	0.9220	1730	0.9372
m-OH			1695	0.9220	1732	0.9372
m-CH_3					1731	0.9372
m-Cl	1718	0.9310	1696	0.9220	1737	0.9372
m-Br			1695	0.9221	1736	0.9371
m-NO_2	1714	0.9311	1705	0.9221	1741	0.9372

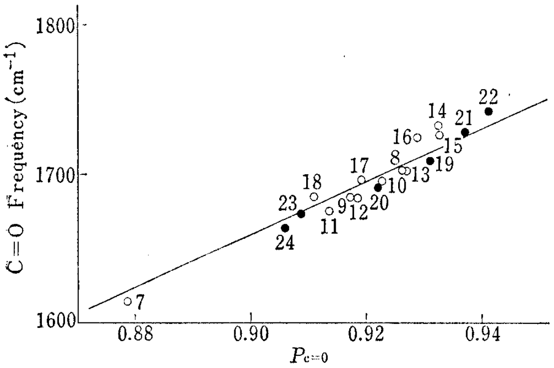

Fig. 1. α,β-Unsaturated and Aromatic Carbonyl Compounds Plotted on the Recalculated Regression Line for Saturated Compounds

The number in this figure corresponds to the one in Table II.

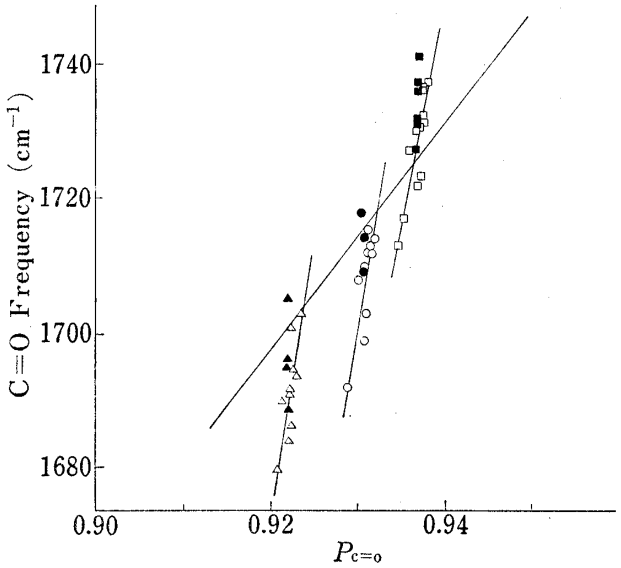

Fig. 2. Plot of Infrared Frequency against Calculated π Bond Order by the Pauling–Wheland Method

○: *para*-, ●: *meta*-substituted benzaldehydes (σ=4.54 cm^{-1}, r=0.7631)

△: *para*-, ▲: *meta*-substituted acetophenones (σ=4.75 cm^{-1}, r=0.7150)

□: *para*-, ■: *meta*-substituted methylbenzoates (σ=3.99 cm^{-1}, r=0.8251)

However, it must be noticed that three regression lines run parallel separately.

This fact means that π bond orders of each of three groups of *para*-substituted aromatic carbonyl compounds calculated by the conventional method of HMO calculation show so limited value of mutual difference, even if the value is enough to explain the variation of carbonyl absorption frequencies of compounds belonging to the same group, that compounds of different group absorbing at similar frequencies have distinctly different values of π bond order. The reason of this discrepancy is hardly explainable, because absorption frequencies of three parent compounds, benzaldehyde, acetophenone and methylbenzoate, lay on the regression line drawn by the data of aliphatic carbonyl compounds and also IR spectra of all compounds were determined at almost the same condition.

Concerning with *meta*-substituted compounds, the results of calculation were much worse, namely, π bond orders of compounds in one group were calculated to have almost equal value in spite of the observed difference of absorption frequencies.

Modifications of hetero-atomic parameters of substituents seem to make the variation of π bond orders big enough to bring a correlation between π bond orders and absorption frequencies of all compounds, but bond-atom polarizability[6,7] denied the possibility. Namely, bond-atom polarizability, given by the following equation,

$$\pi_{rs,t} = 2\sum_{i=1}^{m}\sum_{j=m+1}^{n}\frac{C_{ti}C_{tj}(C_{ri}C_{sj}+C_{si}C_{rj})}{E_i-E_j}$$

$$dp_{rs} = \pi_{rs,t}d\alpha_t$$

The first and second summation are over the occupied and over the unoccupied orbitals, respectively. C_{ri} is the LCAO coefficient of rth atom in ith molecular orbital, and E_i is the energy of ith molecular orbital. p_{rs} is π bond order of bond r-s, and α_t is the coulomb integral of tth atom.

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6) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," John Wiley and Sons, Inc., New York, **1961**.

7) C.A. Coulson and H.C. Longuet-Higgins, *Proc. Roy. Soc.* (London), **A191**, 39 (1947); K. Fukui, C. Nagata, T. Yonezawa, and A. Imamura, *Bull. Chem. Soc. Japan*, **32**, 452 (1959).

of *p*-(dimethylamino)benzaldehyde, $\pi_{CO,N}=0.00255$, indicates that if we expect to have the value of $p_{C=O}$ of around 0.92, which seems to be appropriate to its frequency, $d\alpha_t$ must be around -4β, then the coulomb integral of $N(CH_3)_2$ group must be about α-3β. This parameter is of course unacceptable. $\pi_{CO,C}=0.00518$ of the same compound, in which C means the carbon atom attached to $N(CH_3)_2$ group, also indicates that AIP of about 200% with negative sign is necessary. This is unreasonable, too.

In the case of *meta*-substituted compounds, much more illogical conditions will be required, because $\pi_{rs,t}$ has much smaller value ($\pi_{CO,N}=0.00141$, $\pi_{CO,C}=0.00046$) than the above case.

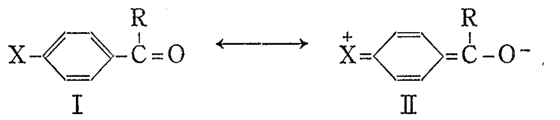
The inclusion of either ω-technique[6,8] or variable-beta technique[9] to the Pauling-Wheland method did not give any satisfactory results.

Therefore, it must be considered that the conventional method of HMO calculation has an intrinsic defect to the calculation of disubstituted aromatic compounds, that is the influence of a substituents to another one cannot be calculated to be big enough to correspond with the experimental result.

The EIP method[10] presented by Krygowski, *et al.* seemed to make up the defect. However, in this method the substituent [X] at *para* position of aromatic compound[X-C_6H_4-Y] is wholly replaced by an effective inductive parameter (EIP) added to the carbon atom where X is attached, therefore, no information of X is obtained. So its applicability to our study was not examined.

A Novel Method Employing a Mutual Additive Substituent Parameter

As indicated by the values of $\pi_{CO,O}$ and $\pi_{CO,C}$, 0.0737 and -0.0559 in *p*-(dimethylamino)benzaldehyde, even a small modification of coulomb integral of either oxygen atom or carbon atom of carbonyl function itself will influence its π bond order considerably. Therefore, if the degree of this modification is changed depending on the effect of substituent, the calculated bond orders thereby may make up the defect of HMO method mentioned above. By the way, the change of π bond order of carbonyl function depending on the substituent at *para* position is expressed by resonance theory as a change of weight of structure [II] to the resonance hybrid (1). This suggests that the substituent [X] exerts its resonance effect mainly to oxygen atom. As regards an inductive effect of *para*-substituent, its influence on carbon atom may be a little bit bigger than that on oxygen atom, so the modification of the coulomb integral of carbon atom may be requested. The latter modification may also be useful to emphasize the substituent effect of *meta* position. But it may be expected that the difference of degrees of influence of inductive effect on oxygen atom and carbon atom is comparatively small because of the fairly long distance between carbonyl group and the substituent at *para* or *meta* position. Therefore, even if the atom whose coulomb integral is to be modified is limited to oxygen there may be no significant change in the result. From these considerations the novel method presented in this paper implies only a modification of coulomb integral of oxygen atom of carbonyl group. It may be said that both this modification of disubstituted aromatic compounds



(1)

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[8] G.W. Wheland and D.E. Mann, *J. Chem. Phys.*, **17**, 264 (1949); A. Streitwieser, Jr., *J. Am. Chem. Soc.*, **82**, 4123 (1960); N. Muller, L.W. Pickett, and R.S. Mulliken, *ibid.*, **76**, 4770 (1954); N. Muller, L.W. Pickett, and R.S. Mulliken, *ibid.*, **80**, 3489 (1958); A. Streitwiser, Jr. and P.H. Nair, *Tetrahedron*, **5**, 149 (1959).

[9] G.V. Boyd and N. Singer, *Tetrahedron*, **22**, 3383 (1966); A.Y. Meyer, *ibid.*, **25**, 4449 (1969).

[10] W. Kemula and M.T. Krygowski, *Bull. Acad. Polon. Sci. Ser. Sci. Chim.*, **15** (10), 479 (1967); M.T. Krygowski and P. Tomasik, *ibid.*, **18** (5), 303 (1970); W. Kemula and M.T. Krygowski, *Tetrahedron Letters*, **1968**, 5135.

and the introduction of AIP to carbon atom of carbonyl function of aliphatic compounds depend on essentially the same idea, because in aliphatic carbonyl compounds substituent is located at the position next to carbonyl group and resonance effect is reflected fairly well to π bond order as shown by the value of $\pi_{\mathrm{CO,X}}$, for example 0.0294 of $\pi_{\mathrm{CO,N}}$ in formamide.

In order to decide the degree of modification Hammett's σ_p and σ_m were employed. This is due to the facts that (i) many kinds of substituent constant are available, and (ii) it was considered that this method of modification may be much more convenient than to modify the coulomb integral of oxygen atom by proportionating to the resonance substituent constant, *e.g.* $\Delta\sigma_R$,[11] and to introduce AIP having proportional value to the coulomb integral of the same substituent.

The employment of Hammett's σ value[11,12] had an especial advantage in this study, because the aromatic system [$X\text{-}C_6H_4COOH$] employed to derive σ values and the substituted aromatic carbonyl compounds in this study resemble each other very well.

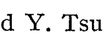
For the purpose of the decision of degree of modification *p*-(dimethylamino)benzaldehyde was chosen as a standard compound, because the value of σ_p of $N(CH_3)_2$ group is fairly big. And the coulomb integral of oxygen atom was modified by trial and error so as to give an appropriate value of π bond order for its absorption frequency. The difference between thus modified and original coulomb integrals was found to be $+1.00\beta$. This value of $N(CH_3)_2$ group at *para* position was set as one of the standard value. Another standard value was $+0.00\beta$ of H atom at *para* position of benzaldehyde, because this compound needs no modification. By assuming that the difference of degrees of modification of coulomb integral of $N(CH_3)_2$ and H group ($+1.00\beta-0.00\beta=+1.00\beta$) is proportional to the difference of their σ_P values ($-0.83-0.00=-0.83$), the degrees of modification of coulomb integrals of other substituents were calculated.

In disubstituted aromatic compound[$X\text{-}C_6H_4\text{-}Y$], X and Y must influence mutually, therefore the parameters of both substituents must be modified simultaneously. Then π bond order of carbonyl group of *p*-(dimethylamino)benzaldehyde was calculated again by the employment of modified coulomb integrals of both oxygen (due to $N(CH_3)_2$ group) and nitrogen atom (due to CHO group). The new (0.92078) and the original value (0.92086) of π bond order did not show any significant difference. Therefore, the degrees of modification calculated above were considered to be decisive, and they are shown in Table IV. These values will be called as the mutual additive substituent parameter (MASP) hereafter.

The relationship between IR absorption frequencies of benzaldehydes, acetophenones

TABLE IV. Mutual Additive Substituent Parameters

Subst.	*para* Position (β)	*meta* Position (β)	Subst.	*para* Position (β)	*meta* Position (β)
$N(CH_3)_2$	$\Delta h=0.100$	$\Delta h=0.024$	COOH	$\Delta h=-0.054$	$\Delta h=-0.042$
$NHCH_3$	$\Delta h=0.090$	$\Delta h=0.022$	COOR	$\Delta h=-0.054$	$\Delta h=-0.045$
NH_2	$\Delta h=0.080$	$\Delta h=0.019$	$COCH_3$	$\Delta h=-0.060$	$\Delta h=-0.045$
OH	$\Delta h=0.045$	$\Delta h=-0.015$	CHO	$\Delta h=-0.027$	$\Delta h=-0.042$
OCH_3	$\Delta h=0.032$	$\Delta h=-0.014$	CN	$\Delta h=-0.080$	$\Delta h=-0.067$
CH_3	$\Delta h=0.020$	$\Delta h=0.008$	NO_2	$\Delta h=-0.094$	$\Delta h=-0.086$
Cl	$\Delta h=-0.027$	$\Delta h=-0.045$	$CONH_2$		$\Delta h=-0.034$
Br	$\Delta h=-0.028$	$\Delta h=-0.047$			



$$\begin{cases} h_Y=\alpha+h_Y\cdot\beta+\Delta h_X\cdot\beta \\ h_X=\alpha+h_X\cdot\beta+\Delta h_Y\cdot\beta \end{cases}$$

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11) Y. Yukawa and Y. Tsuno, "Kagaku no Ryoiki, Zo-kan," 85, Nankodo Co., Ltd., Tokyo, Japan, 1968.
12) L.P. Hammett, "Physical Organic Chemistry," 2nd ed., McGraw-Hill Book Company, New York, 1970.

and methylbenzoates and π bond orders of their carbonyl groups (Table V) calculated by a new HMO method employing mutual additive substituent parameters (MASP) are shown in Figure 3. Each of these three groups of compounds including not only *para*- but also *meta*-substituted compounds showed a respective linear relation, and moreover, it is clear that all of them can be expressed well by the regression line which was obtained from saturated

Table V. Calculated π Bond Orders by the MASP Method of Benzaldehydes, Acetophenones and Methylbenzoates

Subst.	Benzaldehyde $P_{C=O}$	Acetophenone $P_{C=O}$	Methylbenzoate $P_{C=O}$
p-N(CH$_3$)$_2$	0.9208		0.9272
p-NH$_2$		0.9138	0.9301
p-OCH$_3$	0.9276	0.9178	0.9339
p-OH	0.9267	0.9176	0.9332
p-CH$_3$	0.9286	0.9194	0.9353
p-H	0.9310	0.9220	0.9371
p-Cl	0.9325	0.9236	0.9390
p-Br	0.9325	0.9237	0.9390
p-CN	0.9368	0.9282	0.9439
p-NO$_2$	0.9382	0.9298	0.9445
p-CHO	0.9334		0.9400
p-COCH$_3$			0.9419
p-COOH			0.9416
p-COOCH$_3$	0.9353		0.9415
m-N(CH$_3$)$_2$			0.9358
m-NH$_2$		0.9207	0.9368
m-OCH$_3$	0.9323	0.9231	0.9380
m-OH		0.9232	0.9381
m-CH$_3$			0.9374
m-Cl	0.9342	0.9255	0.9406
m-Br		0.9256	0.9407
m-NO$_2$	0.9371	0.9286	0.9431

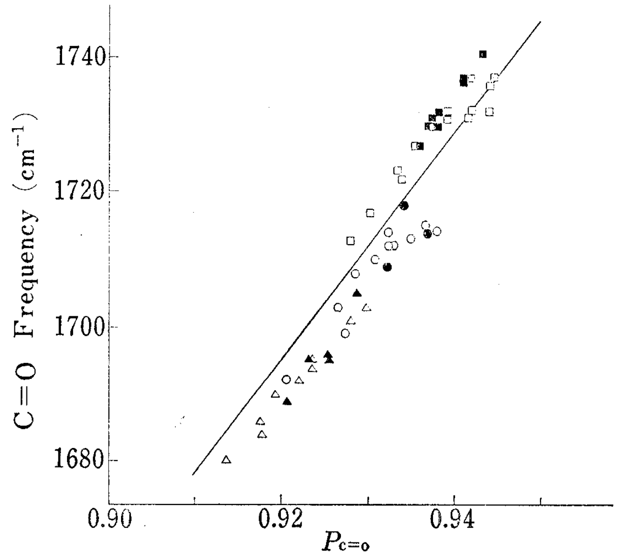

Fig. 3. Plot of Infrared Frequency against Calculated π Bond Order by the MASP Method

○: *para*-, ●: *meta*-substituted benzaldehydes (σ=2.83 cm^{-1}, r=0.9097)
△: *para*-, ▲: *meta*-substituted acetophenones (σ=1.39 cm^{-1}, r=0.9776)
□: *para*-, ■: *meta*-substituted methylbenzoates (σ=2.08 cm^{-1}, r=0. 9438)

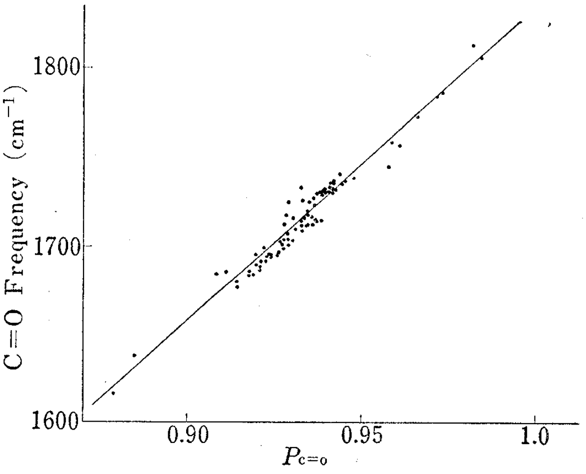

Fig. 4. Plot of Infrared Frequency against Calculated π Bond Order for all Carbonyl Compounds in this Study

(σ=6.78 cm^{-1}, r=0.9748)

compounds. This result proves the novel method is very suitable for the calculation of disubstituted aromatic compounds.

The linear correlation between carbonyl frequencies and π bond orders of all carbonyl compounds studied is shown in Figure 4, and the correlation coefficient and standard deviation were 0.9748 and 6.78 cm^{-1}, respectively.

The investigation of the usefulness of the introduction of MASP to HMO calculation is now going on, and the results will be published in near future.

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