[Chem. Pharm. Bull. 22(4) 871—876 (1974)]

UDC 547.546.03 : 547.239.2.03 : 543.422.4

Molecular Orbital Interpretation of Infrared Absorption Frequencies. III.[1] Nitrobenzene Derivatives, Cyano Compounds and an Application of Mutual Additive Substituent Parameters to Benzophenone Derivatives

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(Received August 10, 1973)

The frequencies of the asymmetric stretching vibrations of NO_2 groups of *para*- and *meta*-substituted nitrobenzenes and of the stretching vibrations of C≡N groups of aliphatic and aromatic cyano compounds were satisfactorily correlated with their respective π bond orders calculated by the HMO method employing the MASP technique.

The usefulness of the application of this technique to the HMO calculation of such aromatic systems as benzophenone derivatives is also described.

The establishment of a satisfactory linear correlation between the stretching frequencies and the π bond orders of a wide variety of carbonyl compounds[1] encouraged us to carry out similar investigations on other groups of organic compounds. Furthermore, as the introduction of mutual additive substituent parameters (MASP) to the HMO calculation proved to be useful to achieve the proper π bond orders of carbonyl groups receiving considerable electronic effects of substituents at their *para* or *meta* position,[1] we were brought along to examine the usefulness of the application of the MASP technique to other types of compounds than disubstituted benzene derivatives.

This paper deals with the correlations of the infrared absorption frequencies of nitrobenzene derivatives, and aliphatic and aromatic cyano compounds with their π bond orders calculated by the HMO method including MASP technique, hereafter abbreviated as the HMO–MASP method, and emphasizes the usefulness of this method for benzophenone derivatives.

Experimental

Method of Calculation——Both the hetero-atomic parameters and the mutual additive substituent parameters already presented in our previous paper were employed throughout the work.

In the case of *p,p'*-disubstituted benzophenone derivatives [X–C_6H_4–CO–C_6H_4–Y], the MASP values of both substituents [X and Y] were added arithmetically to the coulomb integral of the O atom of the carbonyl group, and the MASP value of the carbonyl group was also added to the coulomb integrals of both substituents [X and Y].

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

Materials——The C≡N stretching frequencies of three saturated and five unsaturated aliphatic cyano compounds and the C=O stretching frequencies of thirteen mono- and di-substituted benzophenone derivatives were taken from the literature[3] in order to obtain the data determined in dilute CCl_4 solution.

Fourteen *para*- and *meta*-substituted benzonitriles and twenty *para*- and *meta*-substituted nitrobenzenes were purified by either recrystallization or distillation, and their infrared absorption spectra were measured at the concentration of 0.05 mole% (w/v) in CCl_4 on a Nihon-Bunko DS-701G infrared spectrophotometer using NaCl cell with 0.1 mm optical path length.

1) Part II: Y. Ono and Y. Ueda, *Chem. Pharm. Bull.* (Tokyo), **22**, 390 (1974).
2) Location: *Katakasu, Fukuoka.*
3) *a*) L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen & Co., Ltd., London, 1968; *b*) N. Fuson, M.L. Josien and E.M. Shelton, *J. Am. Chem. Soc.*, **76**, 2526 (1954); *c*) R.E. Kitson and N.E. Griffith, *Anal. Chem.*, **24**, 334 (1952).

The C≡N stretching frequencies of benzonitriles were determined on the spectral charts enlarged four times for 2800—2000 cm^{-1} regions, and were corrected by the known frequencies of 1,2,4-trichlorobenzene.

Result and Discussion

Among all these groups showing characteristic group frequencies except the C=O group formerly investigated, only the C-NO_2 and C≡N groups were expected to be worth examining, because firstly hydrogen atoms are not included in the HMO calculation, secondly the stretching vibration to be examined should not couple, approximately at least, with any other type of vibration of the molecule, and thirdly the group to be investigated should be able to conjugate with the remaining part of the molecule.

The C-NO_2 group has two stretching modes of vibration, asymmetric and symmetric, and it is known that the former vibration does not practically couple with the C-N stretching vibration, but the latter vibration receives the coupling effect.[3a,4] Therefore, only the former type of vibration was considered in this work.

Shlyapochnikov, *et al.*[5] calculated by the extended Hückel method the bond populations of N-O bonds of nine nitro compounds, seven of them being nitromethanes and their anions, and showed that the orders of their magnitudes were in agreement with those of force constants. However, no quantum chemical approach to the substituent effects on nitro group has been reported yet.

Since only a few data on C-NO_2 compounds measured in dilute CCl_4 solution were available, absorption frequencies of twenty *para*- or *meta*-substituted nitrobenzenes were determined carefully in our laboratory. At first 2-methyl-1-nitro-propylene was considered to be suitable for this study, because the asymmetric stretching frequency of its nitro group was reported to be 1515 cm^{-1} in the same condition,[6] but later on it was cancelled from this study because of the following reason: although its π bond order was expected to be about 0.65 due to the resemblance of its frequency to that of *p*-methoxy-nitrobenzene (1514 cm^{-1}) which has π bond order of 0.6513, the HMO calculation, using the hetero-atomic parameters selected in our previous paper, gave a much smaller value (0.6349). The origin of this discrepancy could not be caused by the selection of hetero-atomic parameters of the nitro group, because the magnitudes of the values of bond-atom and bond-bond polarizabilities of 2-methyl-1-nitro-propylene and *p*-methoxy-nitrobenzene which are respectively——$\pi_{NO,N}$: 0.01986 and 0.02300; $\pi_{NO,O}$: −0.22740 and −0.23019; $\pi_{NO,NO}$: 0.37660 and 0.37076; $\pi_{NO,CN}$: −0.14309 and −0.11078 —— were so similar that it was not expected that any modification of either the coulomb integral of nitrogen and/or oxygen atom or the resonance integral of N-O and/or C-N bond could reduce the difference of their π bond orders. Therefore, it was assumed that the NO_2 stretching vibration of this compound may receive considerable influences other than the electronic one.

The asymmetric stretching frequencies and π bond orders of nitrobenzene derivatives calculated by both the Pauling–Wheland and the HMO–MASP method are listed in Table I, and plots of absorption frequencies against π bond orders are shown in Figure 1.

The results indicate that although the Pauling–Wheland method, giving a rather poor linear correlation (r=0.8093) between the absorption frequencies and the π bond orders, could not show any distinct difference of the π bond orders of *meta*-substituted compounds, notwithstanding the obvious difference of their absorption frequencies, the HMO–MASP method

4) *a*) J.F. Brown, Jr., *J. Am. Chem. Soc.*, **77**, 6341 (1955); *b*) R.D. Kross and V.A. Fassel, *ibid.*, **78**, 4225 (1956).
5) V.A. Shlyapochnikov and S.G. Gagarin, *Bull. Acad. Sci. USSR, Div. Chem. Sci.*, **20**, 1024 (1971).
6) M. Kotake, "Series of Comprehensive Organic Chemistry. ——Constants of Organic Compounds——," The Asakura Publishing Company, Ltd., Tokyo, Japan, 1963.

Table I. Asymmetric Vibration Frequencies and π Bond Orders of Nitrobenzenes Calculated by the Pauling–Wheland and the HMO–MASP Methods

Substituents	cm^{-1}	P_{NO}	
		Pauling–Wheland	HMO–MASP
p-$N(CH_3)_2$	1487	0.6490	0.6430
p-NH_2	1505	0.6514	0.6465
p-OCH_3	1514	0.6552	0.6513
p-OH	1517	0.6556	0.6511
p-CH_3	1520	0.6534	0.6513
p-Cl	1522	0.6573	0.6546
p-H	1526	0.6552	0.6549
p-Br	1527	0.6563	0.6546
p-COOH	1528	0.6560	0.6573
p-$COOCH_3$	1531	0.6560	0.6573
p-CHO	1533	0.6560	0.6565
p-$COCH_3$	1535	0.6560	0.6574
p-CN	1536	0.6552	0.6572
m-OCH_3	1526	0.6552	0.6554
m-Cl	1527	0.6552	0.6563
m-OH	1529	0.6552	0.6555
m-CH_3	1531	0.6552	0.6518
m-Br	1532	0.6552	0.6564
m-$COOCH_3$	1532	0.6553	0.6564
m-CN	1538	0.6553	0.6571

gave not only distinct differences of the π bond orders of *meta*-substituted compounds, but also a very satisfactory linear correlation (r=0.9356).

As regards the cyano groups, only one paper[7] described a correlation, but not a linear one, between the π bond orders calculated by the HMO method and the absorption frequencies of four heterocyclic nitriles. Ofcourse, a triply-bonded cyano group has two π bond orders to be considered, however as we made an approximation in this investigation, only one of them was considered to be able to receive the substituent effects, because this π orbital is formed by a linear combination of $2p_z$ atomic orbitals of all the atoms available in the molecule, the other π orbital being localized on the region of the cyano group is orthogonal to the above orbital. Therefore, it may be assumed that the latter π bond order is kept to be constant in all the compounds examined just as in the case of the σ bond order of the cyano group. From this consideration the frequency shifts due to the difference of substituents were correlated with the former π bond orders.

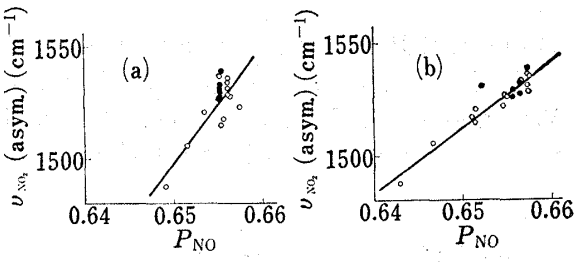


Fig. 1. Plot of Infrared Frequencies against π Bond Orders of Nitrobenzenes Calculated by the Pauling–Wheland Method(a) and the HMO–MASP Method(b)

—: regression lines; ●: *meta*- and ○: *para*-substituents
(a): ν=5304.76 P_{NO}−1949.60; σ=6.85 cm^{-1}; r=0.8093
(b): ν=2881.53 P_{NO}−359.99; σ=4.12 cm^{-1}; r=0.9356

The absorption frequencies and π bond orders of eight aliphatic and fourteen aromatic cyano compounds calculated by both the Pauling–Wheland method and the HMO–MASP method are listed in Table II, and the plots of absorption frequencies against π bond orders are shown in Figure 2. The results indicate that, just as in the case of carbonyl groups,[1] the

7) A. Ide, K. Matsumori, K. Ishizu, and H. Watanabe, *Nippon Kagaku Zasshi*, **92**, 83 (1971).

Table II. Infrared Frequencies and π Bond Orders of Aliphatic and Aromatic Cyano Compounds Calculated by the Pauling–Wheland and the HMO–MASP Methods

Compounds	cm^{-1}	P_{CN}	
		Pauling–Wheland	HMO–MASP
$C(CH_3)_2$=CH–CN	2216	0.9341	
CH_2=CH–CH=CH–CN	2217	0.9330	
$(CH_3)_2$N–CN	2222	0.9358	
CH(CH_3)=CH–CN	2223	0.9381	
CH_2=C(CH_3)–CN	2229	0.9422	
CH_2=CH–CN	2230	0.9417	
CH_3NH–CN	2237	0.9475	
CH_3–CN	2255	0.9741	
p-N(CH_3)$_2$–C_6H_4–CN	2220	0.9460	0.9372
p-NH_2–C_6H_4–CN	2225	0.9470	0.9400
p-OH–C_6H_4–CN	2228	0.9489	0.9443
p-OCH_3–C_6H_4–CN	2229	0.9487	0.9451
p-CH_3–C_6H_4–CN	2229	0.9478	0.9459
p-H–C_6H_4–CN	2230	0.9487	0.9487
p-Cl–C_6H_4–CN	2232	0.9497	0.9499
p-Br–C_6H_4–CN	2233	0.9492	0.9500
p-CHO–C_6H_4–CN	2233	0.9490	0.9507
p-COOH–C_6H_4–CN	2234	0.9490	0.9524
p-$COCH_3$–C_6H_4–CN	2234	0.9490	0.9528
p-NO_2–C_6H_4–CN	2238	0.9494	0.9547
m-CH_3–C_6H_4–CN	2229	0.9487	0.9481
m-NO_2–C_6H_4–CN	2240	0.9488	0.9542

HMO-MASP method gave a reasonable linear correlation (r=0.9647) for all the compounds including not only the aromatic but also the aliphatic derivatives, but that the Pauling-Wheland method gave two correlation lines corresponding to aromatic and aliphatic compounds and an overall correlation coefficient of r=0.8796.

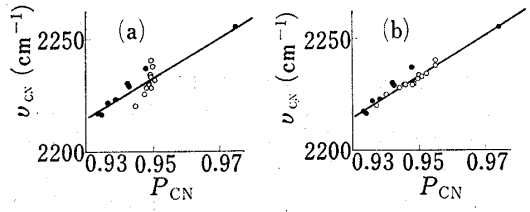


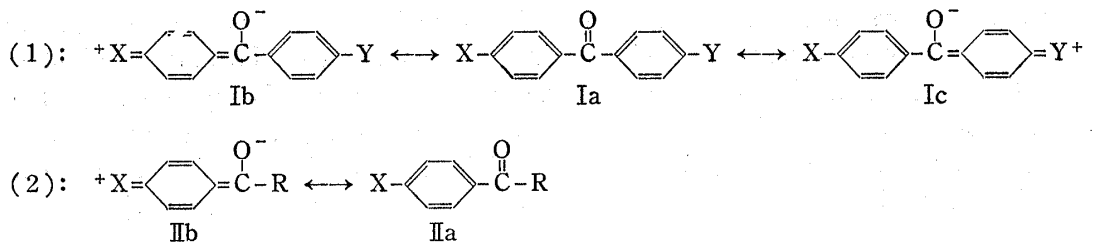
Fig. 2. Plot of Infrared Frequencies against π Bond Orders of Aliphatic (●) and Aromatic (○) Cyano Compounds Calculated by the Pauling–Wheland Method(a) and the HMO–MASP Method(b)

——: regression lines
(a): ν=912.16 P_{CN}+1366.64; σ=3.93 cm^{-1}; r=0.8796
(b): ν=904.08 P_{CN}+1374.53; σ=2.18 cm^{-1}; r=0.9674

The favourable results given by the HMO-MASP method in the calculation of nitrobenzene derivatives and cyano compounds may be accepted as an indicator of the reliability and the usefulness of its application to the disubstituted benzene derivatives.

As a first example, in order to prove the usefulness of the application of the MASP technique to aromatic systems other than disubstituted benzene derivatives, a correlation between the frequency shifts of carbonyl stretching vibrations of benzophenone derivatives, having substituents on both aromatic rings, and their π bond orders was studied. Concerning this correlation it was already reported that a simple summation of Hammett's σ values of X and Y correlates well with the carbonyl absorption frequency shifts.[3b,8] However, if the electronic state of benzophenone derivatives (Ia) is expressed as a resonance hybrid (1) by the resonance theory, each weight of Ib and Ic may probably be smaller than the weight of IIb in a similar hybrid (2) expressing disubstituted benzene derivatives (IIa). The reduc-

8) L.P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Company, New York, 1970.



tions of both the MASP values of X and Y groups to be added to the coulomb integral of the oxygen atom of the carbonyl group and that of the carbonyl group to be added to the coulomb integrals of X and Y groups may be expected to reveal this circumstance. In order to decide the extent of these reductions the π bond orders of six *p*,*p*′-disubstituted benzophenones were calculated twice by the HMO-MASP method employing different sets of MASP values of these three groups, namely 100% and 50% of their original values. And the correlations between the carbonyl absorption frequencies of these compounds and two sets of π bond orders obtained were analyzed.

The correlation coefficients and the standard deviations obtained were $r=0.9930$ and $\sigma=1.33$ cm^{-1} for the calculation with 100% MASP values, and $r=0.9895$ and $\sigma=1.62$ cm^{-1} for 50% MASP values. This result indicates that the former calculation gives a somewhat

Table III. Infrared Frequencies and π Bond Orders of Benzophenone Derivatives Calculated by the Pauling–Wheland and the HMO–MASP Methods

Substituents	cm^{-1}	P_{CO}	
		Pauling–Wheland	HMO–MASP
p-N(CH$_3$)$_2$–*p*′-N(CH$_3$)$_2$	1639	0.9016	0.8835
p-NH$_2$–*p*′-H	1651	0.9038	0.8972
p-OCH$_3$–*p*′-OCH$_3$	1655	0.9026	0.8973
p-OCH$_3$–*p*′-H	1658	0.9057	0.9021
p-CH$_3$–*p*′-CH$_3$	1659	0.9041	0.9009
p-CH$_3$–*p*′-H	1661	0.9030	0.9031
p-H–*p*′-H	1664	0.9056	0.9056
p-Br–*p*′-H	1665	0.9052	0.9074
p-Cl–*p*′-H	1666	0.9052	0.9073
p-Cl–*p*′-CH$_3$	1667	0.9059	0.9050
m-Br–*m*′-H	1669	0.9057	0.9093
p-Cl–*p*′-Cl	1670	0.9047	0.9089
m-Br–*m*′-Br	1672	0.9057	0.9128

better correlation than the latter one does. Therefore, the reduction of the original MASP values was considered to be unnecessary.

Concerning the mutual circumstances of substituents X and Y, no important influences could be expected between them, therefore the MASP technique was not applied to them.

The absorption frequencies and π bond orders calculated by both the Pauling–Wheland method and the HMO–MASP method of thirteen benzophenone derivatives are listed in Table III and the plots of absorption frequencies against π bond orders are shown in Figure 3.

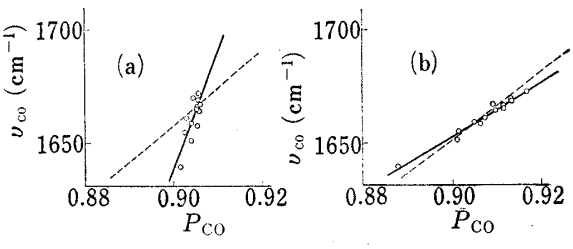


Fig. 3. Plot of Infrared Frequencies against π Bond Orders of Benzophenones calculated by the Pauling–Wheland Method(a) and the HMO–MASP Method(b)

——: regression lines in this study; ·····: regression line in our previous paper

(a): $\nu=5205.58\ P_{CO}-3047.34$; $\sigma=5.19$ cm^{-1}; $r=0.8030$

(b): $\nu=1189.93\ P_{CO}+586.60$; $\sigma=1.64$ cm^{-1}; $r=0.9822$

This figure shows clearly that the carbonyl absorption frequencies of benzophenone derivatives can be correlated very well with their π bond orders calculated by the HMO–MASP method without any reduction of MASP values, and the correlation is expressed clearly enough by the regression line drawn for a wide variety of carbonyl compounds in our previous paper. Therefore, these results can be considered as a sufficient proof of the usefulness of the application of MASP technique to such aromatic systems as benzophenone derivatives.