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126. Masako Ohtsuru, Kazuo Tori, and Haruyuki Watanabe: Correlation of the Methyl Substitution Effect upon the Chemical Shifts of *ortho*-Protons with π-Bond Orders in Aromatic Molecules.*1

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From a number of collected proton magnetic resonance data on various aromatic molecules and their methyl derivatives, it was derived a hypothesis that the methyl substitution effect upon the signal position of an ***ortho***-proton transmits through the aromatic C=C bond having more double bond character (the larger value of π-bond order) more strongly than through the C=C bond having less double bond character (the smaller value of π-bond order). This rule might be useful in inferring the double bond character of a C=C bond in an aromatic molecule.

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Effects of a methyl group substituted in an aromatic molecule upon changes in the chemical shifts of its ring protons have been frequently discussed in recent years.[1~5] Introduction of a methyl group generally shifts ring proton signals upfield in its proton magnetic resonance spectrum. This fact has been explained in terms of the electron transfer from the methyl group to the aromatic ring by its inductive and mesomeric effect, but not yet quantitatively been explained so far as we are aware. In a previous paper,[6] we made comparisons between the methyl substitution effects on the chemical shifts of *ortho*-protons at the both sides of the substituted methyl group, and examined the correlation between the relative magnitudes of the changes in the proton chemical shifts and those of the π-bond orders of the carbon-carbon bonds through which the effects are transmitted. From the results was deduced a hypothesis that the carbon-carbon bond having a larger double bond character transmits the effect to the *ortho* carbon more profoundly than that having a smaller double bond character and the resulting effect on the *ortho* carbon is reflected upon the proton chemical shift. This hypothesis is based on the observations that the methyl signal in propane appears at a higher field by 0.04 p.p.m. than that in ethane, whereas the changes of signal positions of the β-protons produced by a methyl substitution in ethylene are 0.41 p.p.m. for a *trans* and 0.32 p.p.m. for a *cis* proton.[7] These illustrate two extreme cases on the effect through a single and a double bond. In benzene, which is considered as a typical aromatic ring with a π-bond order of 0.66, the methyl effect upon the two *ortho*-protons is the same and about 0.25 p.p.m. upfield-shift.[8] In order to confirm this hypothesis, we have collected a number of data on the methyl substitution effects

*1 NMR Studies of Heteroaromatic Molecules, Part IX. For Part VIII, see K. Tori, M. Ohtsuru, K. Aono: Ann. Rept. Shionogi Res. Lab., **16**, 68 (1966).

*2 Fukushima-ku, Osaka (大鶴真佐子, 通 和夫, 渡辺春幸).

1) *a*) G. S. Reddy, J. H. Goldstein: J. Am. Chem. Soc., **83**, 5020 (1961); *b*) G. S. Reddy, R. T. Hobgood, Jr., J. H. Goldstein: *Ibid.*, **84**, 336 (1962), and references cited therein.
2) S. Gronowitz, G. Sörlin, B. Gestblom, R. A. Hoffman: Arkiv Kemi, **19**, 483 (1963), and references cited therein.
3) K. Tori, M. Ogata, H. Kano: This Bulletin, **11**, 235 (1963).
4) K. Tori, M. Ogata: *Ibid.*, **12**, 272 (1964).
5) S. Matsuura, T. Goto: J. Chem. Soc., **1963**, 1773, and references cited therein.
6) Y. Makisumi, H. Watanabe, K. Tori: This Bulletin, **12**, 204 (1964).
7) G. S. Reddy, J. H. Goldstein: J. Am. Chem. Soc., **83**, 2045 (1961).
8) J. A. Pople, W. G. Schneider, H. J. Bernstein: "High-resolution Nuclear Magnetic Resonance," 263 (1959). McGraw-Hill Book Co., Inc., New York.

TABLE I. Chemical Shifts of Relevant Protons, Effects on Them Due to Introduction of a Methyl Group, and Calculated π-Bond Orders in Various Compounds containing π-Systems

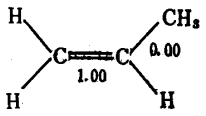
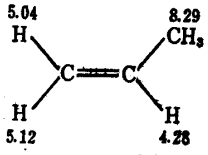
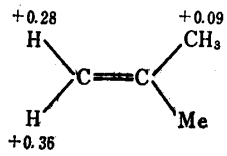
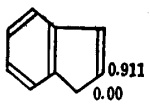
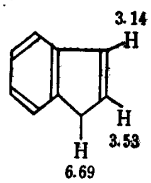
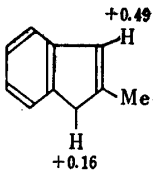
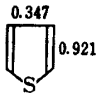
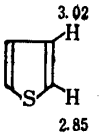
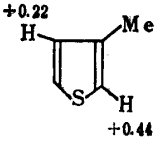
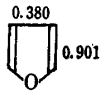
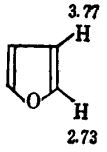
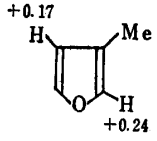
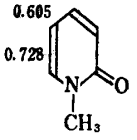
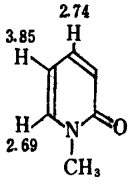
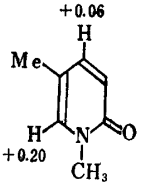
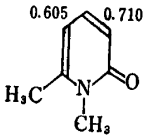
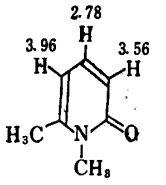
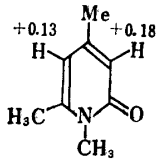
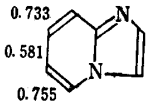
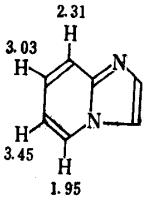
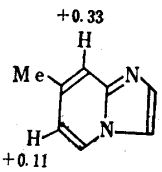
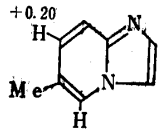
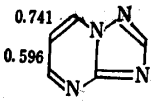
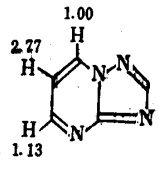
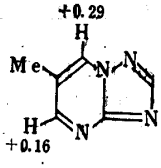
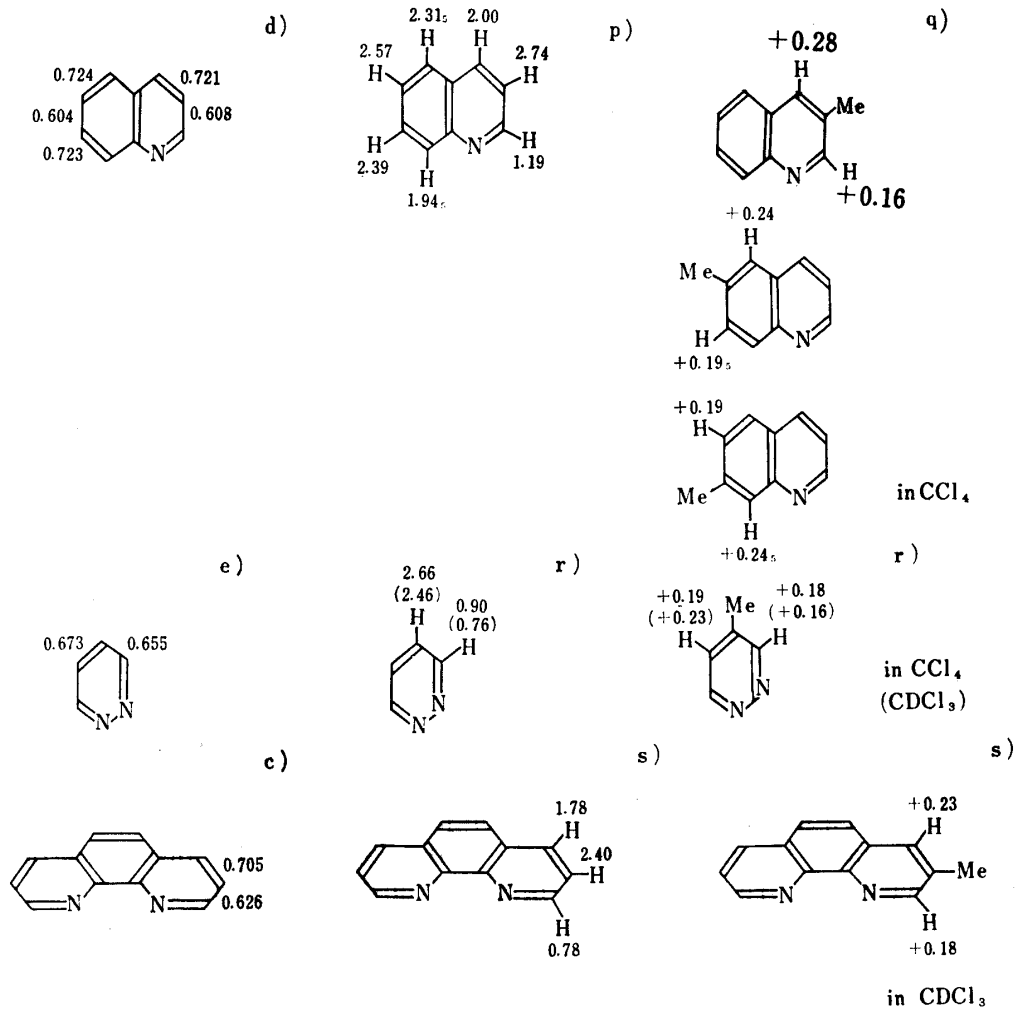
Compound and π-bond orders calculated	Chemical shifts of relevant protons (τ)	Effects on chemical shifts due to the methyl group (Me) in p.p.m. and solvent used
Group I		
	h) 	i)  in CCl_4
a) 	 j)	 j) in CCl_4
b) 	 k)	 k) in TMS
b) 	 l)	 l) in cyclohexane
c) 	 m)	 m) in $CDCl_3$
c) 	 m)	 m) in $CDCl_3$
c) 	 n)	 n)
		 in $CDCl_3$
c) 	 o)	 e) in $CDCl_3$

Table I. (continued)

Group II

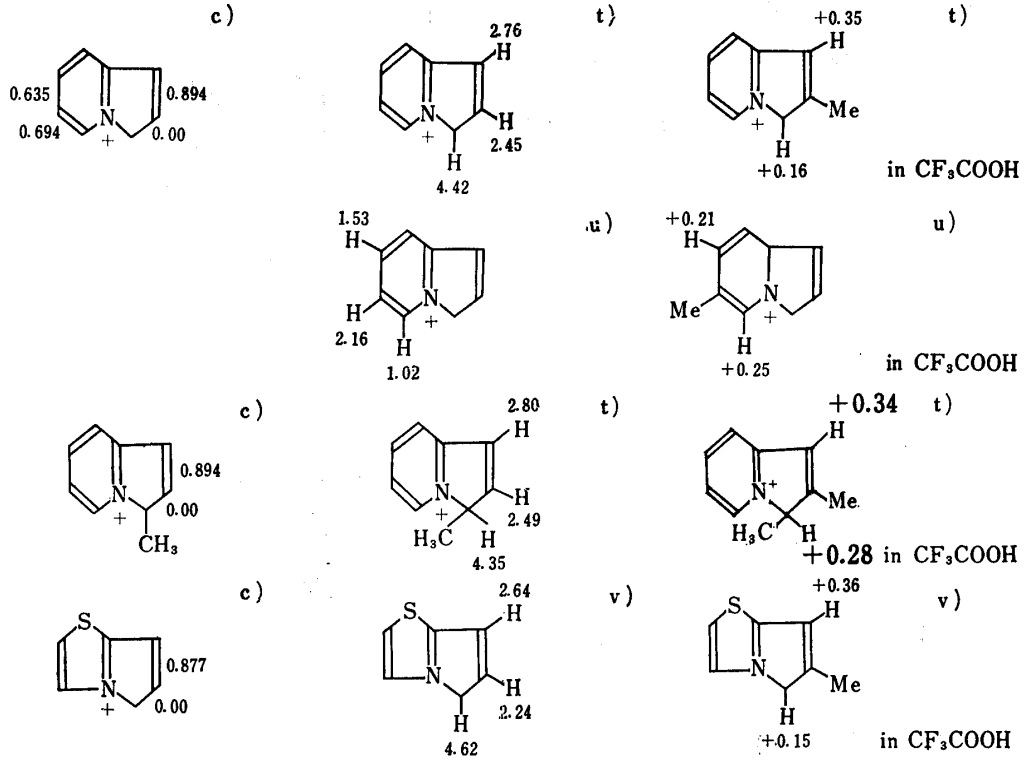


in various aromatic compounds. Although the atom-atom polarizability, π_{rs}, should be correlated to the change in the *ortho* proton chemical shift which reflects the electron density on the *ortho* carbon, we adopted the π-bond order calculated by using the molecular orbital method because the concept of the π-bond order seems familiar to most of organic chemists. In Table I are listed the collected data. Each comparison should be made within a pair of molecules to eliminate various effects except the shielding due to the electron density change on the carbon atom to which the proton in question is attached. Solvent effects can be excluded by comparing two molecules methyl-substituted and non-substituted in the same solvent unless the solvent used heavily interacts the molecules examined. Values of the anisotropic shielding effects of a substituted methyl group on the *ortho*-protons at the both sides should almost be the same and are small as +0.01 p.p.m. or less, if calculated by the bond-anisotropy theory.[9] Similarly, the van der Waals interaction[10] and electric field effects[11] of the methyl gruop on the *ortho*-protons can be expected to be almost the same.

9) L. M. Jackman: "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Chapter 7 (1959). Pergamon Press, New York.
10) W. Nagata, T. Terasawa, K. Tori: J. Am. Chem. Soc., **86**, 3746 (1964); S. Winstein, P. Carter, F. A. L. Anet, A. J. R. Bourn: *Ibid.*, **87**, 5247 (1965); and references cited therein.
11) A. D. Buckingham: Can. J. Chem., **38**, 300 (1960).

TABLE I. (continued)

Group III



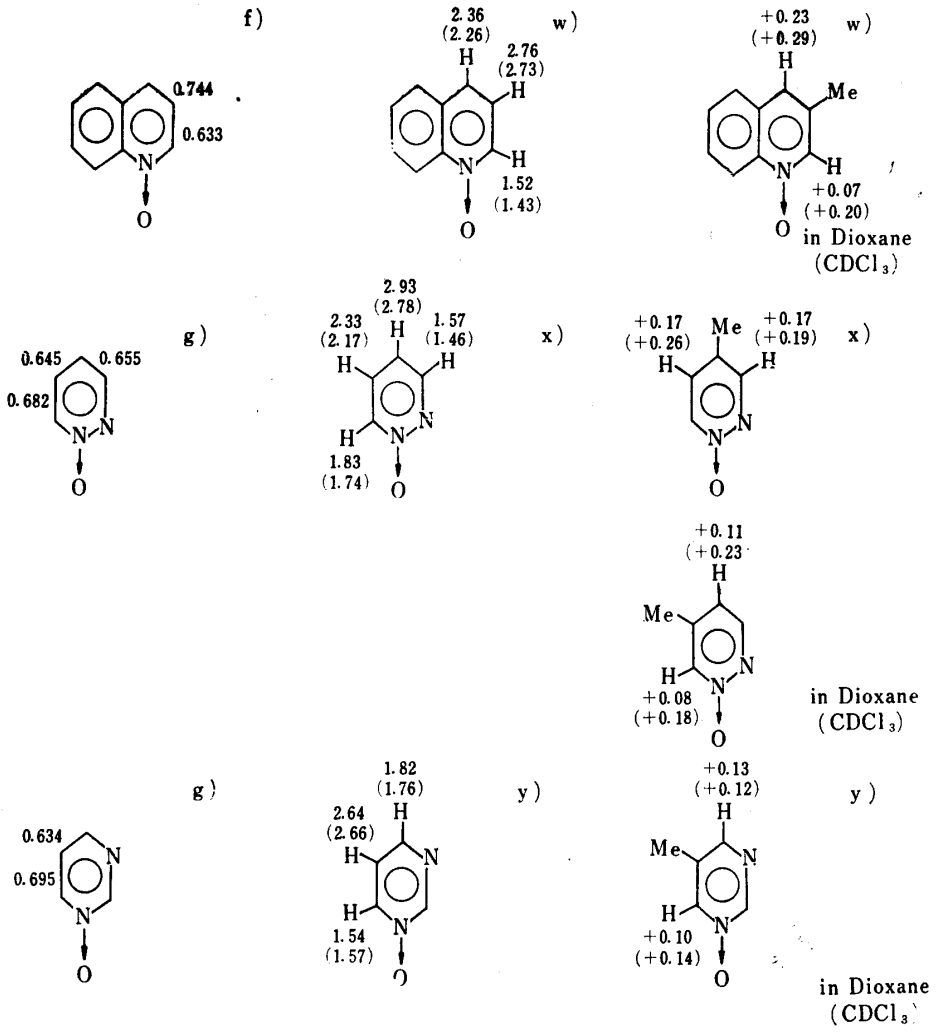
In Group I of Table I are classified compounds having a relatively localized π-system. In this case, the differences in the shifts between the protons *ortho* to the introduced methyl group are fairly large because those in π-bond orders between the two aromatic C=C bonds concerned are large. In Group II, we classified the compounds having somewhat delocalized π-character, but the double bonds in the structural formulas are shown in bonds having larger π-bond orders. In this case, the differences in the proton chemical shifts are comparatively small because of the small differences in the π-bond orders. In Group III are listed some aromatic compounds having ionic character. Here also, our hypothesis can be seen to be realized. In Group IV, we exhibits aromatic N-oxides. Aromatic N-oxides, as is well known, show an interesting feature in its electronic structure.[12] Their π-bond orders calculated are not always alternant. Also it is pointed out that the total methyl substitution effect is fairly weak when the methyl group is introduced into the *ortho* position to an N→O group.[3,13] However, as can be seen in Table I, the hypothesis also appears true in these molecules. In this case, the solvent should be selected to exclude its protonation effect because the protonation usually changes the electronic structures of aromatic N-oxides.[12,14]

The present result might be very useful in inferring the double bond character in an aromatic molecule. Further, this proposal might be extended to effects of other substituents upon their *ortho*-proton chemical shifts in proton magnetic resonance spectra of aromatic molecules, as exemplified by several 3-substituted furans and thiophens reported by a Swedish research group.[2]

12) T. Kubota: Bull. Chem Soc. Japan, **35**, 946 (1962).
13) M. Ogata, H. Watanabe, K. Tori, H. Kano: Tetrahedron Letters, No. 1, 19 (1964).
14) M. Ohnishi, M. Tsuda, Y. Kawazoe, T. Okamoto: "The International NMR Symposium," Tokyo (1965). Abstract, M-2-18.

TABLE I. (continued)

Group IV



a) A. Streitwieser: "Molecular Orbital Theory for Organic Chemists," 107 (1961). John Wiley & Sons, Inc., New York.
b) N. Solony, F.W. Birss, J.B. Greenshields: Can. J. Chem., **43**, 1569 (1965).
c) These π-bond orders were calculated with the Hückel MO method using the parameter values for heteroatoms recommended by Streitwieser (see, p. 135 in ref. a)). The changes of the Coulomb integral α and the bond integral β of heteroatom X are expressed in units of those for benzene, α_0 and β_0, by the use of the definitions $\alpha_X=\alpha_0+h_X\beta_0$ and $\beta_{CX}=k_{CX}\beta_0$. Here the following values were adopted for the parameters h_X and k_{CX}.
$h_{\dot{N}}=0.5$ $h_{\ddot{N}}=1.5$ $h_{\dot{O}}=1.0$ (ketone) $h_{\ddot{O}}=2.0$ (ether) $\beta_0=\beta_{CO}=\beta_{CN}$ $\beta_{NO}=0.7\beta_0$ $\beta_{SC}=0.8\beta_0$
Auxiliary inductive effect parameter was taken as $0.1\,h_X$ for the carbon atoms directly bonded to the atom X. Two orbitals model was used for sulfur atom.
d) C.A. Coulson, A. Streitwieser, Jr.: "Dictionary of π-Electron Calculations," 297 (1965). Pergamon Press Inc., New York.
e) *Idem*: *Ibid.*, p. 251.
f) T. Kubota: Nippon Kagaku Zasshi, **80**, 578 (1959).
g) T. Kubota, H. Watanabe: Bull. Chem. Soc. Japan, **36**, 1093 (1963).
h) A.A. Bothner-By, C. Naar-Colin: J. Am. Chem. Soc., **83**, 232 (1961).
i) G.V.D. Tiers, "Characteristic nuclear magnetic resonance *shielding values* for hydrogen in organic structures" (1958). Minnesota Mining and Manufacturing Co., St. Paul, Minn.
j) J.A. Elvidge, R.G. Foster: J. Chem. Soc., **1963**, 590.
k) See ref. 1a).
l) See ref. 2).
m) J.A. Elvidge, L.M. Jackman: J. Chem. Soc., **1961**, 859.
n) W.W. Paudler, H.L. Blewitt: Tetrahedron, **21**, 353 (1965).
o) See ref. 6).
p) P.J. Black, M.L. Heffernan: Austral. J. Chem., **17**, 558 (1964).
q) This work.
r) (CCl_4) This work; ($CDCl_3$) see ref. 4).
s) R.M. Carman, J.R. Hall: Austral. J. Chem., **17**, 1354 (1964).
t) M. Fraser, S. McKenzie, D.H. Reid: J. Chem. Soc. (B), **1966**, 44.
u) M. Fraser, A. Melera, B.B. Molloy, D.H. Reid: J. Chem. Soc., **1962**, 3288.
v) B.B. Molloy, D.H. Reid, S. McKenzie: J. Chem. Soc., **1965**, 4368.
w) (Dioxane) This work; ($CDCl_3$) K. Tori, M. Ogata, H. Kano: This Bulletin, **11**, 681 (1963).
x) (Dioxane) This work; ($CDCl_3$), see ref. 3).
y) (Dioxane) This work; ($CDCl_3$), see ref. 13).

Experimental

Proton magnetic resonance spectra were taken with a Varian A-60 spectrometer, the calibration of which was checked by the usual side-band method, by using about 5% (w/v) solutions of samples. Accuracies of chemical shifts are about $\pm 0.02\,\tau$.

We are indebted to Drs. Y. Makisumi and M. Ogata for supplying us with samples used.