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SUBSTITUENT EFFECTS IN AROMATIC PROTON NMR SPECTRA. I. THE ROLE OF INDUCTIVE (OR FIELD) EFFECT.

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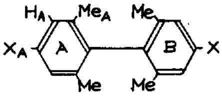
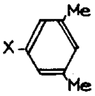
In an aromatic molecule, the change in the proton chemical shift was shown to be proportional to the change in π-electron charge density on the carbon atom to which the hydrogen is bonded(1). For monosubstituted benzenes(III), however, this proportionality seems to hold only for the para-proton shift. Thus Wu and Dailey(2) showed that the linear correlation exists between para-proton shift and π-electron charge density calculated by the Hückel LCMO method. Schug(3) proposed that the change in π-electron charge density of next-nearest-neighbor carbon atoms also have an effect on proton chemical shift and inclusion of this second term can significantly improve the correlation between theory and experiment.

One strange thing is a failure of correlating the meta-proton shift of III with Taft's inductive substituent constant σ_I, though the corresponding correlation for the meta-fluorine shift of meta-substituted fluorobenzenes(IV) is satisfactory(4). The reasonable correlation between meta-proton shift of III and Hammett's para substituent constant σ_p(5,6) seems to support the importance of π-electron density at the next-nearest-neighbor carbon atoms because π-electron density variation caused by a substituent is very small at meta position(2,3). However, other effects, such as inductive, diamagnetic anisotropy(7) and electric field(8) effects of a substituent might also be operative. Of these, the first effect needs particular consideration in connection with Hammett's constants or fluorine nmr spectra of IV.

Various 4,4'-disubstited 2,6,2',6'-tetramethylbiphenyls(I) and 1-substituted 3,5-dimethylbenzenes(II) were prepared(9) and their proton nmr spectra were measured(10). The chemical shifts(δ) of ring proton of I and ortho-proton of II(H),

TABLE I

Proton Chemical Shifts(δ) of I and II in ppm.

X	δ_I  (I)		δ_{II}  (II)		$\Delta\delta = \delta_{II} - \delta_I$	
	H	Me	H	Me	H	Me
NH_2	6.27	1.78	6.11	2.17	-0.16	0.39
NMe_2	6.36	1.78	6.22	2.23	-0.14	0.39
OH	6.47	1.82	6.32	2.22	-0.15	0.42
OMe	6.54	1.84	6.39	2.26	-0.15	0.42
Cl	7.05	1.85	6.88	2.29	-0.17	0.43
Br	7.21	1.88	7.07	2.28	-0.14	0.40
I	7.41	1.84	7.27	2.26	-0.14	0.42
H	7.01	1.87	6.85	2.29	-0.16	0.42
CN	7.41	1.90	7.22	2.35	-0.19	0.45
NO_2	7.96	2.00	7.76	2.42	-0.20	0.42

and methyl protons of I and II(Me), and the differences $\Delta\delta(= \delta_{II} - \delta_I)$ for H and Me shifts are tabulated in TABLE I. If the additivity relation of substituent effect in polysubstituted benzenes is taken for granted(5,6,11), $\Delta\delta$ can be ascribed to the substituent effect of 4'-substituted 2',6'-dimethylphenyl group(ring B) on H_A or Me_A. The two benzene rings of I are mutually orthogonal because of large steric requirement of four methyl groups and there is no mesomeric interaction between the two rings(12). Thus the substituent effect of ring B can be regarded as the sum of inductive effect of X_B and the ring current effect of ring B. The inductive effect of dimethylphenyl group itself is difficult to be separated from the ring current effect of ring B. Both diamagnetic anisotropy and electric field effects are proportional to $1/r^3$ where r is the distance from the substituent to the proton in question; therefore such a long-range effect as from X_B to H_A or Me_A can be neglected(13). If the inductive effect of X_B is transmitted by the successive polarization of intervening σ-bonds(σ-inductive effect)(14), the effect caused by

X_B will diminish during transmission to H_A or Me_A(six intervening bonds). If the inductive effect is in fact the field effect transmitted directly across space following Dewar-Wells's $\cos\theta/r$ relation(15), the effect from X_B to H_A or Me_A in I will be nearly as large as one half of that from X to meta-proton of III.

$\Delta\delta$ values in the TABLE are more or less scattered, but there is observed no distinct variation with the order of electron-donating abilities of the substituents. For electron-withdrawing substituents(X = CN or NO_2), a slightly enhanced downfield shift is observed for H_A of I relative to II. Since meta-proton shift of benzonitrile and nitrobenzene is 0.19 and 0.26ppm lower than that of benzene itself(16), a larger discrepancy is expected between I and II if the observed downfield shift in III is chiefly due to Dewar-Wells's field effect. These facts indicate that the Dewar-Wells type field effect is, unless masked by the other effect, i.e., ring current effect, not important in proton nmr of aromatic compounds. The last possibility is eliminated by the following consideration. The $\Delta\delta$ values for parent hydrocarbons(X = H), -0.16 and 0.42ppm for H and Me, can be ascribed to the ring current effect of the second aromatic ring to which the proton in question is *not* attached. In fact such values are in qualitiative agreement with Johnson and Bovey's calculation(17). According to Figeys and Flammang(18), all substituents cause a decrease of ring current in III up to 13% of that of benzene itself. Such a decrease of ring current in ring B will cause up to 0.02ppm upfield shift and 0.05ppm downfield shift for H_A and Me_A respectively. Since inaccuracy of *ca.* ±0.01ppm(1.0cps) is inevitable, the susbstituent effect on ring current predicted by Figeys and Flammang cannot be observed directly from H shifts of I and II. However, the following point can be emphasized. When the substituent is electron-donating, both field effect and ring current variation predict upfield shift for H. When it is electron-withdrawing, both effects predict downfield shift for Me(methyl protons are immersed in the diamagnetic region of ring B). In the two cases there is no cancellation of two effects and yet $\Delta\delta$ values are very close to those with that of parent hydrocarbons. Thus it seems that the role of inductive (or field) effect of X_B in determining the chemical shifts of H_A or Me_A is negligible: this might in turn support the importance of the π-electron charge density on the next-nearest-neighbor carbon atoms or π-inductive effect(19) in meta-proton shift.

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