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SUBSTITUENT EFFECTS IN AROMATIC PROTON NMR SPECTRA. II(1).
THE EFFECT OF SUBSTITUENT DIAMAGNETIC ANISOTROPY.

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Recently much attention has been paid to the bond or substituent diamagnetic anisotropy effect on proton nmr chemical shift(2). In estimating the long-range diamagnetic anisotropy effect, McConnell's equation(3), $\delta_{anis} = [\Delta\chi(1 - 3\cos^2\theta)]/3\underline{r}^3$, has frequently been used and sometimes a satisfactory agreement was reported between the predicted and observed shifts for aliphatic or alicyclic compounds containing C-C(4,5),C=C(5), C≡C(6), C≡N(6) or C-halogen(4,7) bonds. An application of this equation to nmr spectra of halobenzenes was, however, rather unsuccessful (8) though such an attempt seemed promising as to interpret the "anomalous" behavior of halogen substituents in correlating proton chemical shifts of monosubstituted benzenes(III) with reactivity parameters like Hammett's σ constants in terms of their diamagnetic anisotropy(9). It has not yet been decided, however, whether this failure is due to the absence of diamagnetic anisotropy effect or to the inadequate form of McConnell's equation, or simply this effect is masked by other substituent effects.

In the preceding communication(1) we have compared proton nmr spectra of various 4,4'-disubstituted 2,6,2',6'-tetramethylbiphenyls(I) with those of 1-substituted 3,5-dimethylbenzenes(II) and found that the inductive (or field) effect of substituent $\underline{X}_B$ on $\underline{H}_A$ or $\underline{Me}_A$ proton shifts are practically null in I. This observation prompted us to examine the related systems to clarify the above uncertainty on the diamagnetic anisotropy effect. Thus four 4,2'-disubstituted 2,6,4',6'-tetramethylbiphenyls(I') ($\underline{X}$ = Cl, Br, I and H) were prepared(10) and their proton nmr spectra were determined. δ values of $\underline{H}_A$ and $\underline{Me}_A$ protons are 7.07 and 1.91 for

X = Cl, 7.22 and 1.92 for X = Br, 7.43 and 1.82 for X = I and 7.02 and 1.90ppm for X = H, respectively.

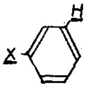
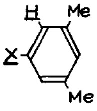
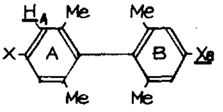
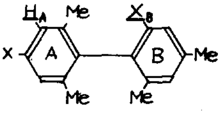
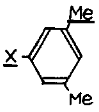
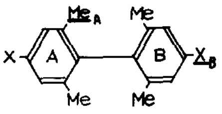
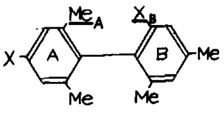
In TABLE I the geometric factor $G = (1 - 3\cos^2\theta)/3r^3$ for H_A or Me_A protons of I and I' relative to X_B, and SCS(11) for these protons are listed. Those of II and III are also included for the sake of reference. In calculating the G values the point dipole approximation was used and the dipole was assumed to locate near the center of C-halogen bond. For methyl protons an average position was taken In fact the protons rotate about the C-Me bond, so r and θ must be averaged over this rotation. The "integrated" G values for *m*-Me protons of II, -0.0038, -0.0038 and -0.0046 for Cl, Br and I, respectively(12) are essentially in the similar magnitude of the "average" G values, so the latter seems sufficient for the present purpose. The positive G values for I' means downfield shifts($\Delta\chi<0$).

As was pointed out, H_A SCS of I are nearly identical with *o*-H SCS of II. In this case the $|G|$ values are relatively small and the diamagnetic anisotropy effect of X_B might not be sufficiently transmitted to the remote H_A. To our surprize, H_A SCS of I' are also nearly identical with *o*-H SCS of II, though in this case the $|G|$ values are nearly 40% of those for *m*-H of III. It seems that halogen diamagnetic anisotropy effect on aromatic proton shifts is not important, or at least, this effect is much smaller than that predicted by McConnell's equation. A comparison of Me_A(or *m*-Me) SCS for I and I'(or II) are also suggestive. That SCS differences between I and II are small(less than 0.03ppm) again suggests the effect of X_B on Me_A shifts is negligible(13). This is supported by Me_A SCS of I' where McConnell's equation predicts a large downfield shift while the observed SCS are reverse in direction(particularly when X = I).

Recently Smith *et al.*(14)suggested that the shieldings of aromatic protpn meta to a substituent is due to a combination of "through space" and "through bond" mechanism, the first of which might be insulated if a second substituent is placed between the substituent and meta proton. Our results seem to indicate that the long-range "through space" effect of halogens are originally absent irrespective as to whether an insulating group is present or not. A comprehensive theory as for the origin of proton shifts of halobenzenes is being awaited. Study on this problem is under progress in our laboratory.

TABLE I

Geometric Factor(G) and SCS for I, I', II and III in CCl_4.

Compounds		X	G[a]	SCS(ppm)
	III	Cl	-0.0097	0.03[b]
		Br	-0.0093	0.09[b]
		I	-0.0091	0.22[b]
	II	Cl	---	-0.03[c]
		Br	---	-0.22[c]
		I	---	-0.42[c]
	I	Cl	-0.0018	-0.05
		Br	-0.0018	-0.22
		I	-0.0017	-0.42
	I'	Cl	0.0035	-0.05
		Br	0.0036	-0.20
		I	0.0037	-0.41
	II	Cl	-0.0048	0.00[c]
		Br	-0.0047	0.01[c]
		I	-0.0046	0.03[c]
	I	Cl	-0.0038	0.03
		Br	-0.0038	0.00
		I	-0.0038	0.04
	I'	Cl	0.0081	-0.01
		Br	0.0081	-0.02
		I	0.0072	-0.08

a) Values are for the indicated protons relative to the indicated substituent.

b) Data taken from K. Hayamizu and O. Yamamoto, J. Mol. Spectroscopy **25**, 422 (1968).

c) Data taken from ref. 1.

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10. Satisfactory analyses were obtained for new compounds prepared(*X* = Cl, Br and I).
11. Substituent Chemical Shift as defined by M. J. S. Dewar and A. P. Marchand, *J. Am. Chem. Soc.* **88**, 3318 (1966).
12. We owed for these values to Prof. N. Nakagawa, the University of Electro-Communications, Tokyo, Japan.
13. It is interesting to notice that, whatever is the origin of the substituent effect in general, the halogen substituent effect is reluctant to the transmission to methyl protons. Thus a plot of *m*-*H* SCS of III *vs*. *m*-*Me* SCS of II gave a linear correlation with a slope of *ca*. 0.5 for most of the standard substituents except halogens, for which the observed *m*-*Me* SCS are much smaller than those predicted by this correlation.

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