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SUBSTITUENT EFFECTS IN AROMATIC PROTON NMR SPECTRA. III(1)
SUBSTITUENT EFFECTS CAUSED BY HALOGENS.

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Regardless the large number of papers treating the subject, the nature of the substituent effect in proton nmr chemical shifts of monosubstituted benzenes (I) is not yet fully understood(2). Especially the anomolous shifts of halobenzenes remains enigmatic. Very recently we have pointed out that the well accepted McConnell's equation is not necessarily adequate as a tool for the quantitative estimation of the effect due to the diamagnetic anisotropy of halogens which is always related to the anomolous shifts of halobenzenes(1). In the present investigation we wish to cast further light on this problem by comparing ring-proton substituent chemical shift(H SCS) with methyl-proton SCS(Me SCS) of appropriately substituted benzenes at ortho-, meta- and para-positions(3). In Fig. 1, a plot of *o*-H SCS and *o*-Me SCS of 1-substituted 2,4-dimethylbenzenes(II) is given. Since effects due to steric hindrance is necessarily involved in the ortho-position, the comparison was made between similarly inhibited protons. Fig. 2 gives a plot of *m*-H SCS of I(4) vs. *m*-Me SCS of 1-substituted 3,5-dimethylbenzenes(III). Fig. 3 is a plot of *p*-H SCS of I(4) vs. *p*-Me SCS of 1-substituted 4-methylbenzenes(IV).

In common with all three plots, a somewhat linear correlation can be observed if halogens are excluded. The slope, which is to reflect the transmission coefficient of the substituent effect to the methyl-protons relative to the ring-proton, is ca. 0.34, 0.45 and 0.25, respectively. The slope for the para-

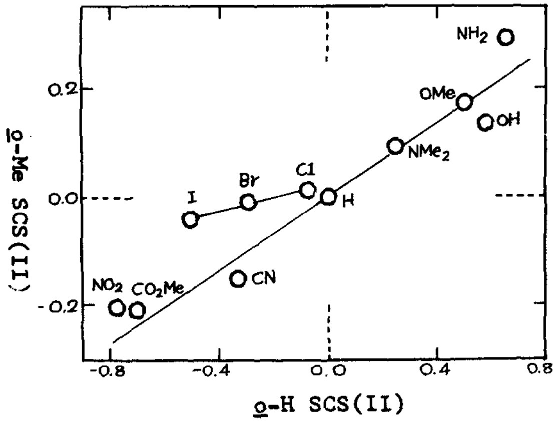

Fig.1 o-H SCS(II) vs. o-Me SCS(II).

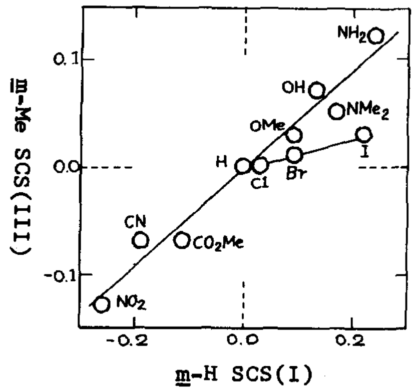

Fig.2 m-H SCS(I) vs. m-Me SCS(III).

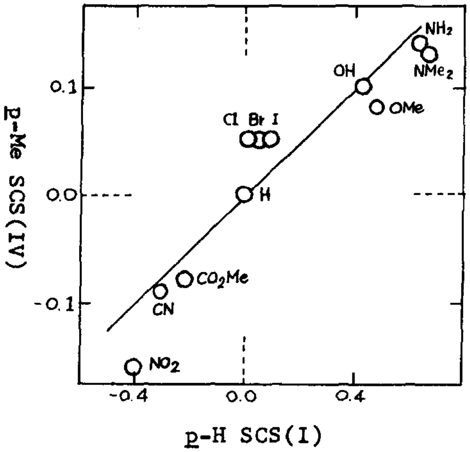

Fig.3 p-H SCS(I) vs. p-Me SCS(IV).

plot is readily understandable: first *p*-H SCS of I is known to depend primarily on the π-electron charge density on para-carbon atoms(5); secondly, according to Schug's calculation(6), the π-charge on the next-nearest-neighbor carbon atom also have an effect on proton shieldings. Hence, the π-charge on para-carbon atom influences the para-methyl proton shieldings, the transmission coefficient being ca. 0.25(6). The deviation of electron-withdrawing substituents(CN, NO_2) is not unexpected considering the enhanced hyperconjugation of methyl groups conjugated with these substituents. Such was in fact observed for 19-F SCS of para-substituted fluorobenzenes(7). For ortho- and meta-plots, effect(s) other than π-charge density might be involved. If the involved effect is multiple, a linear correlation is not necessarily expected since the transmission coefficient might differ from substituents to substituents. The observed correlation indicates, if not a mere coincidence, that either one particular effect is predominant or the transmission coefficients associated with a certain effect are essentially identical for all the substituents. We cannot, however, draw any solid conclusion on this point from the present result alone.

The "odd" SCS values of halobenzenes in the general correlations can be generalized in three points: i.e., (i) negative SCS for ortho-position and positive SCS for meta- and para-positions; (ii) very small slope for ortho- and meta-plots(Figs. 1 and 2) indicating the insensitivity of methyl protons to the substituent effect; (iii) very close SCS values for para-position(both ring- and methyl-protons). If the McConnell's equation(8) is assumed, point i can, at least qualitatively, be explained if the dipole of halogen is to locate near the center of C-halogen bond. The points ii and iii are hard to explain on this basis alone: first, the ratio of geometric factor for the ring-proton to that for the methyl-protons(if an average position is assumed) is close to 0.5 regardless the position; secondly, a fairly large and positive SCS are predicted by the McConnell's equation for the para-proton.

These discrepancies suggest a contribution of some hitherto unknown effect which is feasible to transmission to ortho- and meta-protons but reluctant to transmission to para- and methyl-protons(regardless the position). A possible explanation might be found in the "spin-polarization" shift(*LS* shift)* proposed by one of the present authors(9). The *LS* shift is caused by a large spin orbit interaction(*LS* coupling) characteristic of heavy atoms like iodine(10). Since this shift is not caused by the direct shieldings due to the induced current, but by Fermi contact interaction of a nucleus with electrons, the mechanism of

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*) The *LS* shift(σ_{LS}) is a chemical shift due to the energy term(ΔE_{LS}) which is related to a third-order perturbation term containing the coupling of the external field *H* with the electron orbit *L* ,of *L* with the electron spin *S* , and of *S* with the nuclear spin *I* where

$$\sigma_{LS} = \frac{\partial}{\partial H_0}\,\frac{\partial E_{LS}}{\partial \mu_n}, \qquad E_{LS} = \sum_{\substack{\alpha,\beta,\gamma\\=1,2,3}}\sum_{n\neq 0}\sum_{m\neq 0}\frac{\langle 0|\mathcal{H}_\alpha|m\rangle\langle m|\mathcal{H}_\beta|n\rangle\langle n|\mathcal{H}_\gamma|0\rangle}{(E_0-E_m)(E_0-E_n)}$$

$$\mathcal{H}_1 = \frac{-ie\hbar}{2mc}H_0\sum_i\left(x_i\frac{\partial}{\partial y_i}-y_i\frac{\partial}{\partial x_i}\right) \quad (LH\ \text{coupling}),$$

$$\mathcal{H}_2 = \sum_i \lambda_i\{1/2\,(l_+S_- + l_-S_+) + l_zS_z\} \quad (LS\ \text{coupling}) \quad \text{and}$$

$$\mathcal{H}_3 = \frac{\gamma_e\gamma_n\hbar^2}{r^3}\left[\left\{\frac{3(\mathbf{I}\cdot\mathbf{r})(\mathbf{S}\cdot\mathbf{r})}{r^2}\right\} - \mathbf{IS}\right] + \frac{8}{3}\pi\gamma_e\gamma_n\hbar^2\,\mathbf{IS}\delta r \quad (IS\ \text{coupling}).$$

transmission of this effect is much the same as that of the indirect spin spin interaction between nuclei(the origin of spin spin coupling constant, J). J values for ortho-, meta- and para-ring protons in benzene are +7.7~9.0, +2~3 and +0.5~1.0cps, respectively(11). J values between the side chain methyl protons and ortho-, meta- and para-ring proton are 0.63, 0.36 and 0.63 cps(signs unkown), respectively(12). The LS shift would be relatively large for ortho- and meta-protons of halobenzenes which is to increase in the order $Cl < Br < I$ since the larger is the nuclear charge(atomic number), the larger is the constant of coupling of atoms. In order to explain the observed *o*- and *m*-H SCS of halobenzenes in terms of LS shift, the sign of it is necessarily negative for ortho-proton and positive for meta-proton. Since the sign of J for ortho- and meta-protons are both positive, this assignment is not fully justified unless another line of evidence is supplied. The LS shift for para- and side chain methyl-protons is small and negligible as is the case with J.

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