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131. **Masako Ohnishi and Yutaka Kawazoe** : Nuclear Magnetic Resonance Studies. VIII. Solvent Effect of Trifluoroacetic Acid on Proton Magnetic Resonance of Substituted Benzene Derivatives.*[1]

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We have been interested in the effect of the hydrogen bond formation on the proton magnetic resonances of the proton acceptor (electron donor) molecules which act as the base in the hydrogen bonding. Very few studies were reported on this problem, whilst many have been done on the resonances of the protons themselves directly taking part in the hydrogen bonding.

Strongly acidic molecules are supposed to interact with basic molecules to produce spectral changes of the resonance of the protons neighboured by basic centers, more change being expected in increase of ability to form the hydrogen bond, in other words, in increase of basicity of the proton acceptor centers of the basic molecule. From this standpoint of view, trifluoroacetic acid was employed as a measurement solvent acting as proton donor in the previous paper,[1] where the general features of this effect were discussed with regard to the aliphatic compounds containing $-NR_2$, $-OR$, $-COOH$, $CONR_2$, $-NO_2$, halogens etc. as the basic center.

Now, in connection with the above investigation, this paper concerns the study on the π-electronic structure of substituted benzene derivatives affected by the surrounding proton donor (electron acceptor) molecules. The resonance and inductive effects of the substituent group on the ring π-electronic structure may be easily perturbed by surrounding molecules or ions. In the ionic substitution reactions, the perturbed π-electronic structure of the aromatic ring might determine very often the destination of the chemical reactions at least in their initial states. Important is, therefore, the dynamic study on the deviation of the π-electrons by the perturbation of reagents and/or reaction medium. As one of our serial studies on this problem, this paper includes what kind of effects might be brought to the magnetic resonances of the aromatic protons by the acid-base interaction (electron donor-acceptor type interaction) between ring substituents and strong acidic molecules, taking account of localization of the π-electrons. Trifluoroacetic acid was employed as proton donor reagent. The chemical shift data measured both in carbon tetrachloride and in trifluoroacetic acid were compared with each other, each mutual shift being discussed in term of the change of the π-electron densities on each ring carbon.

Experimental

Compounds——Most of the compounds examined were commercially available and some of them were prepared by authentic synthetic methods.

Spectra——NMR spectra of the compounds were obtained both in ca. 5% CCl_4 and 5% F_3CCOOH solutions at room temperature (25° to 30°) by a Varian Associates DP-60 NMR spectrometer (60 Mc.p.s.) or by a Japan Electron Optics Laboratory 3H-60 NMR spectrometer (60 Mc.p.s.). The chemical shifts were given in the τ-unit, spectrum calibrations being carried out by the side band technique using the internal $Si(CH_3)_4$.

[*1] This paper was read at the third NMR Symposium in Osaka (1963). Part Ⅶ : Yakugaku Zasshi, **83**, 523 (1963).

[*2] Tsukiji, Chuo-ku, Tokyo (大西柾子, 川添 豊).

1) Y. Kawazoe, M. Ohnishi : This Bulletin, **11**, 243 (1963).

Terms of "Solvent Effect" and "Substituent Effect"——Solvent effect is presented by the differences between the chemical shifts measured in CCl_4 and F_3CCOOH :

$$\text{Solvent Effect} = \tau_{F_3CCOOH} - \tau_{CCl_4}$$

The comparison of the chemical shifts in these two different solvents has been done by calibrating the spectra with the same referred compound ($Si(CH_3)_4$) dissolved in each solution examined. The negative sign of these values denotes that a downward shift was given in F_3CCOOH solution in comparison with the chemical shift in CCl_4 solution.

Substituent effects, on the other hand, include two kinds of them for each functional group, one in $CCl_4(S^{CCl_4})$ and one in F_3CCOOH (S^{F_3CCOOH}). They were referred to the signal position of benzene itself in the respective solvent, CCl_4 or F_3CCOOH.[*3] The positive sign means that the substituent affects the resonance position of the ring proton situated on the denoted site (*ortho*, *meta* or *para*) to shift in a higher field than before replacing a hydrogen by the substituent.

Results and Discussion

Many works have already been reported on the substituent effects on the chemical shifts of benzene ring protons in such inert solvents as carbon tetrachloride, hexane, cyclohexane, etc. since the first report by Corio and Dailey. But accurate measurements of the chemical shift of *ortho*, *meta*, and *para* protons of substituted benzenes are usually difficult to be done both because chemical shifts are considerably subjected to large solvent effects and because a complete analysis of the spectra can hardly be carried out to determine the accurate resonance positions. Moreover, the additivity of the substituent effects, which has been assumed for simpler analysis of the complex spectra, may be very unreliable for tri or more substituted benzenes and even for disubstituted derivatives since the substituents on a benzene ring are expected to interact electronically or/and sterically with each other. In spite of difficulty to estimating the substituent effect, however, many efforts have been done to interprete the chemical shift of ring protons in term of electronic effect of the substituent and to correlate them with the chemical reactivities in connection with the Hammett's σ-parameters. In the present work, the chemical shifts were determined in dilute carbon tetrachloride and trifluoroacetic acid solutions in the same way as employed by Diehl[2] and then, the substituent effects in both media were estimated. They are given in Table I to IV. It should be kept in mind, however, that beside the experimental error, a considerable error might be caused by assuming the additivity of the substituent effects (possibly up to near a half tenth of p.p.m. as a whole). In spite of this ambiguity, these values can be considered to be enough for qualitative discussion intended here. The fact that the magnitude of the substituent effects are variable depending on the nature of other substituents on the same ring might be explained in term of the mutual electronic interaction between the substituents through ring π-electrons. The detailed discussion will be reported in near future by us.

In order to interprete ring proton chemical shifts of substituted benzenes, many attempts have been made in terms of (i) π-electron density on the carbon atom to which they are bonded, (ii) electric field effect by substituents and (iii) magnetic anisotropy effect by the substituent group and by the ring carbon atom which they are bonded. The ring current effect, however, which depend on electron-withdrawing or -releasing character of the substituent might possibly take part together with the above main effects. Under careful consideration of these possibilities, we have assumed as a working

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[*3] Calibrations were made with reference to the signal of $Si(CH_3)_4$ dissolved in each solution examined, and then, the chemical shift thus obtained were compared to that of benzene.

2) P. Diehl : Helv. Chim. Acta, **44**, 94 (1961).

Table I. On Alkylbenzenes

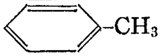
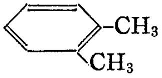
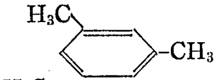
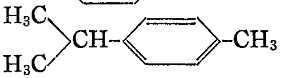
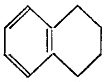
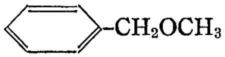
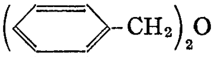
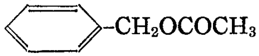
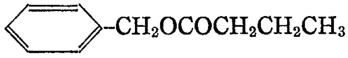
	Chemical shift (τ)		Solvent effect	Substituent effect referred to benzene (p.p.m.)	
	in CCl_4	in F_3CCOOH	$\tau_{F_3CCOOH}-\tau_{CCl_4}$	in CCl_4	in F_3CCOOH
	2.78	2.73	−0.05	0	0
	2.94	2.87	−0.07	+0.16	+0.14
	3.05	2.96	−0.09	+0.27	+0.23
	3.09	2.98	−0.11	+0.31	+0.25
	(3.13)	(3.01)	(−0.12)	(+0.35)	(+0.28)
	3.06	2.92	−0.14	+0.28	+0.19
	3.10	3.01	−0.09	+0.32	+0.28
	2.82	2.71	−0.11	+0.04	−0.02
	2.81	2.68	−0.13	+0.08	−0.05
	2.76	2.72	−0.04	−0.02	−0.01
		2.70			−0.03

Table II. On Aminobenzenes

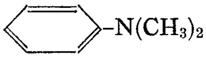
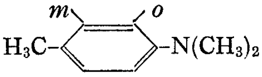
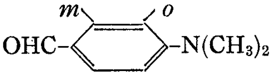
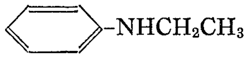
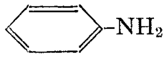
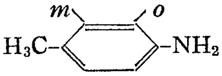
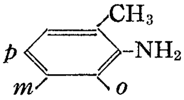
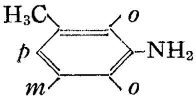
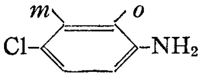
		Chemical shift (τ)		Solvent effect	Substituent effect referred to benzene (p.p.m.)	
		in CCl_4	in F_3CCOOH	$\tau_{F_3CCOOH}-\tau_{CCl_4}$	in CCl_4	in F_3CCOOH
		2.78	2.73	−0.05	0	0
	*o*	(3.41)	2.41	(−1.00)	(+0.63)	−0.32
	m	2.92	2.41	−0.51	+0.14	−0.32
	p	(3.41)	2.41	(−1.00)	(+0.63)	−0.32
	*o*	3.49	2.56	−0.93	+0.71	−0.17
	m	3.09	2.56	−0.53	+0.31	−0.17
	*o*	3.41	2.15	−1.26	+0.63	−0.58
	m	2.46	1.75	−0.71	−0.32	−0.98
	*o*		2.44			−0.29
	m	2.96	2.44	−0.52	+0.18	−0.29
	p		2.44			−0.29
	*o*		2.49			−0.24
	m	2.96	2.49	−0.47	+0.18	−0.24
	p		2.49			−0.24
	*o*	3.63	2.70	−0.93	+0.85	−0.03
	m	3.20	2.70	−0.50	+0.42	−0.03
	*o*		2.65			−0.08
	m		2.65			−0.08
	p		2.65			−0.08
	*o*	3.73			+0.95	
	m	3.15			+0.37	
	p					
	*o*	3.58			+0.75	
	m	3.03			+0.25	

TABLE III. On Halogenobenzenes

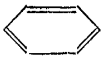
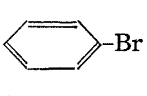
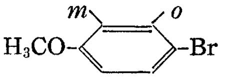
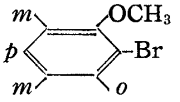
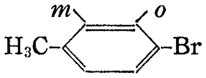
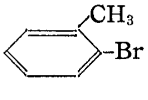
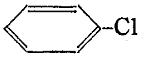
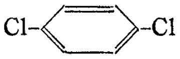
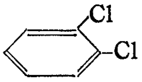
		Chemical shift (τ)		Solvent effect	Substituent effect referred to benzene (p.p.m.)	
		in CCl_4	in F_3CCOOH	$\tau_{F_3CCOOH}-\tau_{CCl_4}$	in CCl_4	in F_3CCOOH
		2.78	2.73	−0.05	0	0
	*o*	2.53	2.56	+0.03	−0.25	−0.17
	m	(2.79)	(2.75)	(−0.04)	(+0.01)	(+0.02)
	p	(2.79)	(2.75)	(−0.04)	(+0.01)	(+0.02)
	*o*	2.71	2.58	−0.13	−0.07	−0.15
	m	3.31	3.12	−0.19	+0.53	+0.39
	*o*	2.56	2.50	−0.06	−0.22	−0.23
	m	(3.20)			(+0.42)	
	p	(3.20)			(+0.42)	
	*o*	2.69	2.71	+0.02	−0.09	−0.02
	m	3.06	3.05	−0.01	+0.28	+0.32
	*o*	2.51	2.55	+0.04	−0.27	−0.18
	m	(2.88)	(2.89)	(+0.01)	(+0.10)	(+0.16)
	p	(2.88)	(2.89)	(+0.01)	(+0.10)	(+0.16)
		2.78	2.78	0	0	+0.05
		2.77	2.79	+0.02	−0.01	+0.06
		2.79	2.83	+0.04	+0.01	+0.10

TABLE IV. On Oxoderivatives

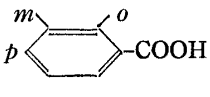
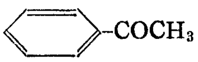
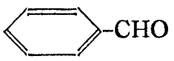
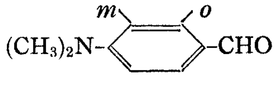
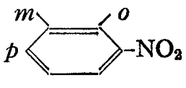
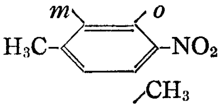
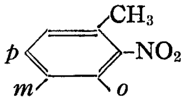
		Chemical shift (τ)		Solvent effect	Substituent effect referred to benzene (p.p.m.)	
		in CCl_4	in F_3CCOOH	$\tau_{F_3CCOOH}-\tau_{CCl_4}$	in CCl_4	in F_3CCOOH
		2.78	2.73	−0.05	0	0
	*o*	1.89	1.92	+0.03	−0.89	−0.81
	m	(2.53)	(2.46)	(−0.07)	(−0.25)	(−0.27)
	p	(2.53)	(2.46)	(−0.07)	(−0.25)	(−0.27)
	*o*	2.19	1.98	−0.21	−0.59	−0.75
	m	(2.64)	(2.49)	(−0.15)	(−0.14)	(−0.24)
	p	(2.64)	(2.49)	(−0.15)	(−0.14)	(−0.24)
	*o*	2.20	2.06	−0.14	−0.58	−0.67
	m	(2.52)	(2.43)	(−0.09)	(−0.26)	(−0.30)
	p	(2.52)	(2.43)	(−0.09)	(−0.26)	(−0.30)
	*o*	2.46	1.75	−0.71	−0.32	−0.98
	m	3.45	2.15	−1.30	+0.67	−0.58
	*o*	1.81	1.73	−0.08	−0.97	−1.00
	m	(2.40)	(2.33)	(−0.07)	(−0.38)	(−0.40)
	p	(2.40)	(2.33)	(−0.07)	(−0.38)	(−0.40)
	*o*	1.96	1.84	−0.12	−0.82	−0.89
	m	2.73	2.62	−0.11	−0.05	−0.11
	*o*	2.15	2.00	−0.15	−0.63	−0.73
	m	(2.66)	(2.57)	(−0.09)	(−0.12)	(−0.16)
	p	(2.66)	(2.57)	(−0.09)	(−0.12)	(−0.16)

Table V. Substituent Effects of Various Functional Groups on Ring Proton Resonances

	Substituent effect						Solvent effect		
	in CCl_4 (p.p.m.)			in F_3CCOOH (p.p.m.)					
	S_o	S_m	S_p	S_o	S_m	S_p	*ortho*	*meta*	*para*
H	0	0	0	0	0	0	-0.0_5	-0.0_5	-0.0_5
$N(CH_3)_2$	$+0.6$	$+0.1_5$	$+0.6$	-0.3	-0.3	-0.3	-0.9_5	-0.5	-0.9_5
NHR		$+0.2$		-0.3	-0.3	-0.3		-0.5	
NH_2	$+0.8$	$+0.2_5$	$+0.6_5$	-0.2_5	-0.2_5	-0.2_5	-1.0_5	-0.5	-0.9_5
OCH_3	$+0.4$	$+0.1_5$	$+0.4$	$+0.2_5$	0	$+0.2_5$	-0.2_5	-0.2	-0.2_5
CH_3	$+0.1_5$	$+0.1_5$	$+0.1_5$	$+0.1_5$	$+0.1_5$	$+0.1_5$	-0.0_5	-0.0_5	-0.0_5
CH_2OCH_3	$+0.0_5$	$+0.0_5$	$+0.0_5$	0	0	0	-0.1	-0.1	-0.1
$CH_2OCH_2C_6H_5$	$+0.0_5$	$+0.0_5$	$+0.0_5$	-0.0_5	-0.0_5	-0.0_5	-0.1_5	-0.1_5	-0.1_5
CH_2OCOR	0	0	0	0	0	0	-0.0_5	-0.0_5	-0.0_5
$COCH_3$	-0.6	(-0.1_5)	(-0.1_5)	-0.7_5	(-0.2_5)	(-0.2_5)	-0.2	-0.1_5	-0.1_5
CHO	-0.5	-0.2		-0.6_5	-0.3		-0.2	-0.1	
COOH	-0.9	(-0.2_5)	(-0.2_5)	-0.8	(-0.2_5)	(-0.2_5)	$+0.0_5$	-0.0_5	-0.0_5
NO_2	-0.9_5	-0.2	-0.3	-1.0	-0.2_5	(-0.2_5)	-0.0_5	-0.0_5	0
Cl	0	0	0	$+0.0_5$	$+0.0_5$	$+0.0_5$	0	0	0
Br	-0.2_5	$+0.1_5$		-0.1_5	$+0.1$		$+0.0_5$	$+0.0_5$	

hypothesis that the π-electron density might have most effective contribution to *meta*- and *para*-(and sometimes *ortho*-) proton chemical shifts.

Now, in Table V, it is shown as the general features of the substituent effects that individual substituents give characteristic effects to their *ortho*, *meta*, and *para*-posititons, respectively and that, roughly speaking, these results imply the *ortho*-*para* orientation of the substituent effects, just as that of the chemical reactivities. Trifluoroacetic acid affects the substituent in most cases to give rise to a considerable downward shift of ring proton chemical shifts, which corresponds to the fact that any of the substituents acts as a proton accepting (electron donating) center against strongly acidic molecules.

The magnitudes of the downward shifts (the solvent effect) can be qualitatively correlated with the proton accepting power (the basicity) of the substituent. Thus, a rough parallelism was shown between the basicities of the substituents and the solvent effects of the ring protons, as follows;

$$-NR_2 > -OR > -COR > -CH_2OR > -CH_3 > -NO_2 > -COOH > -H$$

It can be considered that the contribution of onium cation forms such as ammonium, oxonium, etc. causes less electron transfer from the substituent to the ring π-orbitals, followed by electron-withdrawing inductive effect of the substituent. Thus, larger positive substituent effects (S) which might be caused by mesomeric effect of electron-releasing groups ($-NR_2$ and $-OR$) are more effectively reduced by neutralizing their lone-paired electrons which take part in overlapping with π-orbital. With regard to aniline derivatives, for instance, their *ortho* and *para* protons were subjected to larger solvent effect almost twice than the *meta* proton, all of them being largest in magnitude in comparison with all other derivatives.

Now let us consider the substituent effects in trifluoroacetic acid solution. In this solvent, benzene itself showed a very little downward shift of about 0.05 p.p.m. compared with that in carbon tetrachloride. One of most interesting features is that each of anilinium cation and their N-alkyl derivatives shows a singlet peak (slightly broa-

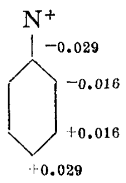


Chart 1.

dened).*[4] It is a quite unexpected phenomenon for each of the ring protons to have the same chemical shifts. According to molecular orbital calculation by Bishop, *et al.*,³⁾ charge density on each carbon atom was predicted as shown in Chart 1.

Alternatively, it is expected that positive charge localization may be induced to *ortho* and *para* carbons by increase of electronegativity of C_1 atom as shown in Chart 2.

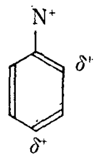
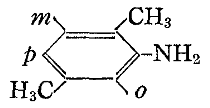
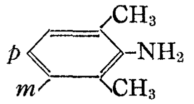
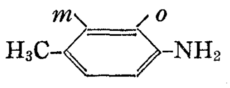
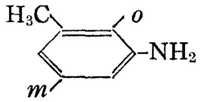
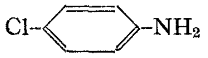
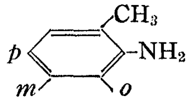
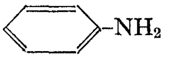
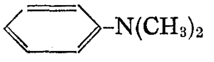


Chart 2.

By the chemical shift data, however, evener charge distribution was implied to each ring carbon atom rather than that calculated above. Now, in order to examine how much chemical shifts of ring protons depend on the sort of anions of acidic media, aqueous 3*N* hydrochloric acid was used as the measuring solvent for eight aniline derivatives, instead of trifluoroacetic acid. As shown in Table Ⅵ, no noticeable spectral differences were observed between in both acidic media, the whole ring pro tons giving a singlet signal for each compound. As a result, provided that chemical shift data reflect π-electron density at least for *meta* and *para* protons, a tentative estimation on the charge density might be possible for *meta* and *para* carbon atoms, using the equation $\delta=10\cdot\rho$ proposed by Fraenkel⁵⁾ and Spieseck, *et al.*,⁶⁾ as Chart 3.

Table Ⅵ. Chemical Shifts of Aminobenzenes in Acidic Media

	Solvent	*o*	*m*	*p*	CH_3
	CCl_4	3.73	3.25	3.67	7.97 7.82
	3*N* HCl	2.80	2.85	2.85	7.73 7.63
	F_3CCOOH	2.67	2.65	2.67	7.63 7.58
	CCl_4	—	3.25	3.55	7.93
	3*N* HCl	—	2.80	2.80	7.55
	F_3CCOOH	—	2.73	2.73	7.60
	CCl_4	3.60	3.20	—	7.82
	3*N* HCl	2.68	2.68	—	7.63
	F_3CCOOH	2.70	2.70	—	7.67
	CCl_4	3.73	3.15		7.80
	3*N* HCl	2.65			7.60
	CCl_4	3.58	3.03	—	—
	3*N* HCl	2.57	2.57	—	—
	CCl_4				7.92
	3*N* HCl	2.58	2.58	2.58	7.60
	F_3CCOOH	2.65	2.65	2.65	
	CCl_4		2.96		—
	F_3CCOOH	2.49	2.49	2.49	—
	CCl_4	(3.41)	2.92	(3.41)	—
	F_3CCOOH	2.41	2.41	2.41	—

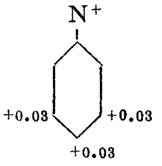


Chart 3.

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[4] The same observation was recently reported by Reynolds, *et al.*⁴⁾

3) D. M. Bishop, D. P. Craig : Mol. Phys., **6**, 139 (1963).

4) W. F. Reynolds, T. Schaefer : Can. J. Chem., **41**, 2340 (1963).

5) G. Fraenkel, R. E. Carter, A. McLachlan, J. H. Richards : J. Am. Chem. Soc., **82**, 5846 (1960).

6) H. Spiesecke, W. G. Schneider : Tetrahedron Letters, **1961**, 468.

These values can be considered to be of importance in connection with the inductive effect of ammonio group, although they are poorly coincident with those from MO calculation.

With regard to alkyl benzenes, in carbon tetrachloride, alkyl groups affect ring protons to shift to higher field as already known as shown in Table I.

As the substituent effects of a methyl groups on the benzene ring protons at *ortho*, *meta*, and *para*-positions, the following values have been given by Diehl[2]:

$$S_{ortho}^{CCl_4}+0.17\ \text{p.p.m.}$$

$$S_{meta}^{CCl_4}+0.13\ \text{p.p.m.}$$

$$S_{para}^{CCl_4}+0.17\ \text{p.p.m.}$$

Provided that the above values can be applicable in an additive way to dialkyl benzene derivatives, it can be expected that any ring protons of *ortho* and *para* disubstituted benzenes are equally affected to shift upwards by +0.30 p.p.m. due to two alkyl groups and that, therefore, the resonance signals must be only a singlet. The experimental results were proved to be consistent the above expectations. Thus, the spectra from *o*-xylene, *p*-xylene, *p*-cymene and tetraline showed a singlet peak for their ring protons, appearing in higher field by 0.27, 0.31, 0.28, and 0.32 p.p.m., respectively, than that of benzene itself. On the other hand, with regard to *meta*-dimethylbenzene (*m*-xylene) each of 2-,4- and 6-protons is related to *ortho* to one methyl and *ortho* or *para* to the other, but the 5-proton is related to *meta*-position to each of them. The substituent effect can, therefore, be estimated, as 0.34 p.p.m. (=0.17+0.17) for each 2-,4- and 6-protons, but as 0.26 p.p.m. (=0.13+0.13) for 5-proton. Then, a multiplet peak can be expected. It was proved experimentally, although spectrum was not well analyzed. As a result, as Diehl and other authors already mentioned, the effect of methyl group on the ring protons is clearly oriented more to *ortho* and *para* than *meta*-position.

Now, when trifluoroacetic acid was used as a measurement solvent, a certain effect by this acidic solvent was observed on the substituent effects of methyl group.*[5]

The following set of the substituent effect to *ortho*, *meta*, and *para* protons were conveniently chosen as to fit for all available alkylbenzene derivatives.

$$S_{ortho}^{F_3CCOOH}=+0.15\ \text{p.p.m.}$$

$$S_{meta}^{F_3CCOOH}=+0.12\ \text{p.p.m.}$$

$$S_{para}^{F_3CCOOH}=+0.15\ \text{p.p.m.}$$

These values show that the effect of alkyl groups becomes somewhat smaller than in case of CCl_4 solution. This result might be interesting in connection with hyperconjugation of methyl group.

Now, it has been generally accepted that the ring protons at the *para*-position are linearly correlated with the Hammett's σ-values. Fig. 1 represents the correlation between substituent effects and simple σ-values.[7] These values might be enough for the present discussion, although improvements for linearity would be made by using some other modified σ-values. That of $-NR_3^+$ is the only one available datum of onium

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*[5] Methyl proton resonances themselves of methyl benzenes were shown not to shift by changing the solvent from CCl_4 to F_3CCOOH as shown in the previous paper.[1]

7) H.H. Jaffe: Chem. Revs., 53, 191 (1953).

type substituents from the usual method by the ionization constant of *p*-substituted benzoic acid. The result is satisfactorily correlated with the chemical shift of aniline derivatives in trifluoroacetic acid, as shown in Fig. 1. It might, therefore, become possible that Hammett's parameters of various substituents in trifluoroacetic acid be estimated graphically using Fig. 1. Those obtained above might be related to the ionization constant of benzoic acids bearing onium type substituents (that is, the substituent groups electronically perturbed by the strong acidic medium) at *para*-position toward the carboxylic group. These estimated parameters can be obtained from the plots suffixed by parentheses in Fig. 1.

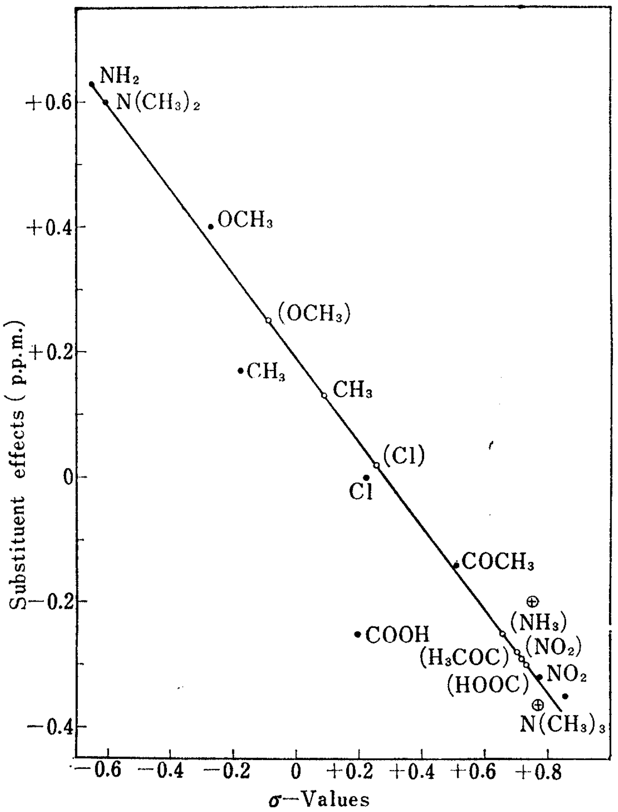

Fig. 1. Correlation of Substituent Effect with Hammett's σ

Conclusion

It might be concluded that the chemical shift data of benzene ring protons are of great use for information of the π-electron distribution on the aromatic nuclei. On the above information, it was qualitatively discussed how much the substituent would influence the ring π-electrons by a solvent of trifluoroacetic acid.

The authors are indebted to Drs. O. Yamamoto and T. Suzuki of the Government Chemical Industrial Research Institute of Tokyo for making a NMR spectrometer available for the present work.

Summary

The nuclear magnetic resonance spectra of a number of substituted benzenes were measured in carbon tetrachloride and in trifluoroacetic acid and the substituent effect of each substituent was estimated in both media. The results were discussed in connection of the π-electron densities on the ring carbon atoms.

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