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SUBSTITUENT EFFECTS IN AROMATIC PROTON NMR SPECTRA—V*[1]

BENZENE-INDUCED SOLVENT SHIFTS IN MONOSUBSTITUTED (POLY)METHYLBENZENES†

Y. NOMURA and Y. TAKEUCHI

Department of Chemistry, College of General Education, University of Tokyo, Komaba,
Meguro-ku, Tokyo, Japan

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Abstract—Benzene-induced solvent shifts $\Delta(=\delta_{\text{cyclohexane}}—\delta_{\text{benzene}})$ in proton NMR spectra of 1-substituted-4-methyl-(II), -3,5-dimethyl-(III), -2,4-dimethyl-(IV), -2,6-dimethyl-(V) and -2,4,6-trimethylbenzenes (VI) have been determined. The variation of Δ values with the number and position of Me groups present was explained by assuming a 1:1 solvent-solute complex with the geometry proposed by Williams *et al.* In forming such a complex, it was shown that the steric effect is most important for protons remote from the substituent while both polar and steric effects are equally important for protons close to the substituent.

RECENT interest in solvent shifts of proton NMR spectra have prompted us to investigate the nature of the solvent-solute complex. Since the first observations of this effect,[4,5] some interesting aspects have been studied.[6,7] The cause was assumed to arise chiefly from the long-range effect of diamagnetic anisotropy of benzene coordinated with the solute. There is strong evidence[8] that benzene solvent molecules act as electron-donors to an electron-deficient region in the solute molecules. This donation induces a transient dipole in the benzene molecule, and the interaction may therefore be of the dipole-induced dipole type. In fact, the solvent shift $\Delta(=\delta_{\text{ref solvent}}—\delta_{\text{benzene}}$, ref solvent being cyclohexane or carbon tetrachloride in general) correlated excellently with the dipole moment of the solute in aliphatic molecules containing a single polar site.[9] It has been deduced from the principle of additivity of solvent shifts and dilution curves that a collision complex is formed in the ratio of 1:1[10–12] and as the solvent shifts are temperature dependent, the reversible equilibrium (benzene + solute ⇄ complex) has real significance.[2]

Concerning the general geometry of the collision complex, widely differing models have been put forward.[13] Ronayne and Williams[10] proposed the geometry 1 for benzene–N,N-dimethylaniline complex and the geometry 2 for benzene–nitrobenzene complex. The negative Δ values of ring protons of N,N-dimethylaniline and positive Δ values of those of nitrobenzene[14] appear consistent with the proposed geometry. Recently Le Fèvre *et al.*[15] studied the geometry of complexes through the solvent dependence of molar Kerr constants and proposed a similar geometry for benzene–chlorobenzene and benzene–nitrobenzene complexes in which the angle

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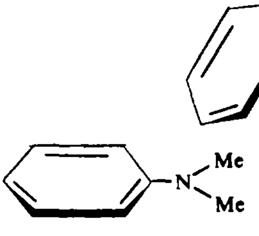
† Soon after we finished this investigation, Williams *et al.*[2] reported the polar and steric effects on toluene-induced solvent shifts of various substituted (poly)alkylbenzenes by measuring the temperature dependence of solvent shifts. Their results as well as methods differ from ours.

between the direction of dipole of the solute and the plane of the benzene molecule is about 35° for the former and less than 35° for the latter.



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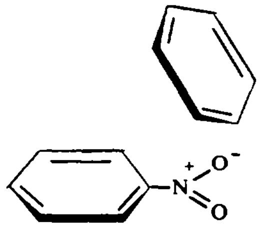

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As the observed δ values represent the "time-averaged blur" of the chemical shifts of any particular solute proton or group of protons for each of the species present, Matsuo *et al.*[16] criticized the complex model and suggested that the interaction is a general solvation rather than a specific complexing.

Recently, we compiled the proton NMR data for various monosubstituted (poly)methylbenzenes to elucidate the nature of the substituent effect which determines the substituent chemical shift (SCS).[1] The benzene-induced solvent shifts in monosubstituted benzenes (I)* would be perturbed by substituting ring proton(s) by Me group(s). As this variation may contribute to a better understanding of the solvent shifts, we determined the solvent shifts Δ of both ring and Me (and substituent, if any) protons of 1-substituted-4-methyl-(II), -3,5-dimethyl-(III), -2,4-dimethyl-(IV), -2,6-dimethyl-(V) and -2,4,6-trimethylbenzenes (VI). After comparing the benzene-induced solvent shifts of I and VI, Diehl[17] attributed the correlation to the steric effect on the non-random distribution of solvent molecules in the neighborhood of dipolar solute molecule, but his data was too limited to allow definite conclusions.

We do not claim to prove or disprove the complex model proposed,[10] but rather aim at finding the scope and limitation of this model in understanding the solvent shifts of substituted aromatic compounds.

RESULTS

Materials. As some compounds (II–VI) are commercially available, others were prepared by the established procedures. Physical constants of IV, V and VI are given in the preceding communication.[1] The purity of each sample was accertained by gas chromatography.

Measurement of NMR *spectra.* Proton NMR spectra of II–VI were determined in a cyclohexane or benzene (-d_6) solution (1–3 mol%) with TMS as an internal standard by a JNM-4H-100 spectrometer with an installed frequency counter. The chemical shifts (δ) of II–VI in cyclohexane, in benzene and the solvent shifts Δ ($\delta_{\text{cyclohexane}}$—$\delta_{\text{benzene}}$) are tabulated in Tables 1–5.

* Unfortunately most of the data for I[18] were obtained indirectly from the data for polysubstituted benzenes assuming the additivity relation of solvent shifts. Hence data for I should be regarded critically.

TABLE 1. PROTON CHEMICAL SHIFTS (δ)[a] IN CYCLOHEXANE AND IN BENZENE-d_6 AND SOLVENT SHIFTS (Δ) OF 1-SUBSTITUTED 4-METHYLBENZENES (II)

Substituent		$H_{2,6}$	$H_{3,5}$	Me'_4	Substituent
NH_2	(cyclohexane)	6·39	6·78	2·16	3·16
	(benzene)	6·32	6·88	2·14	2·63
	Δ	0·07	−0·10	0·02	0·53
NMe_2	(cyclohexane)	6·56	6·91	2·20	2·83
	(benzene)	6·61	7·03	2·21	2·55
	Δ	−0·05	−0·12	−0·01	0·28
OH	(cyclohexane)	6·61	6·89	2·20	5·94[b]
	(benzene)	6·54	6·84	2·06	4·50
	Δ	0·07	0·05	0·14	1·44
OMe	(cyclohexane)	6·66	6·93	2·19	3·62
	(benzene)	6·68	6·94	2·11	3·34
	Δ	−0·02	−0·01	0·08	0·28
Cl	(cyclohexane)	7·08	6·95	2·22	
	(benzene)	7·04	6·66	1·90	
	Δ	0·04	0·29	0·32	
Br	(cyclohexane)	7·25	6·90	2·21	
	(benzene)	7·19	6·59	1·86	
	Δ	0·06	0·31	0·35	
I	(cyclohexane)	7·47	6·78	2·21	
	(benzene)	7·36	6·46	1·84	
	Δ	0·11	0·32	0·37	
CO_2Me	(cyclohexane)	7·87	7·08	2·32	3·75
	(benzene)	8·05	6·89	1·99	3·54
	Δ	−0·18	0·19	0·33	0·21
CN	(cyclohexane)	7·36	7·14	2·32	
	(benzene)	6·97	6·53	1·79	
	Δ	0·39	0·61	0·53	
NO_2	(cyclohexane)	8·00	7·17	2·38	
	(benzene)	7·79	6·55	1·78	
	Δ	0·21	0·62	0·60	

[a] In ppm relative to TMS.

[b] δ in CCl_4.

TABLE 2. PROTON CHEMICAL SHIFTS (δ)[a] IN CYCLOHEXANE AND IN BENZENE AND SOLVENT SHIFTS (Δ) OF 1-SUBSTITUTED 3,5-DIMETHYLBENZENES (III)

Substituent		$H_{2,6}$	H_4	$Me_{3,5}$	Substituent
NH_2	(cyclohexane)	6·11	6·26	2·11	3·23
	(benzene)	6·06	6·38	2·12	2·79
	Δ	0·05	−0·12	−0·01	0·44
NMe_2	(cyclohexane)	6·27	6·27	2·21	2·83
	(benzene)	6·38	6·46	2·23	2·58
	Δ	−0·11	−0·19	−0·02	0·25
OH	(cyclohexane)	6·37	6·45	2·14	5·75
	(benzene)	6·26	6·43	2·06	4·34
	Δ	0·11	0·02	0·08	1·41
OMe	(cyclohexane)	6·43	6·47	2·22	3·63
	(benzene)	6·54	6·51	2·13	3·37
	Δ	−0·11	−0·04	0·09	0·26
Cl	(cyclohexane)	6·87	6·73	2·21	
	(benzene)	6·84	6·50	1·91	
	Δ	0·03	0·23	0·30	
Br	(cyclohexane)	7·04	6·78	2·22	
	(benzene)	7·00	6·52	1·89	
	Δ	0·04	0·26	0·33	
I	(cyclohexane)	7·27	6·82	2·20	
	(benzene)	7·22	6·54	1·86	
	Δ	0·05	0·28	0·34	
CO_2Me	(cyclohexane)	7·61	7·05	2·29	3·77
	(benzene)	7·82	6·80	2·02	3·53
	Δ	−0·21	0·25	0·27	0·24
CN	(cyclohexane)	7·11	7·07	2·28	
	(benzene)	6·71	6·58	1·78	
	Δ	0·40	0·49	0·50	
NO_2	(cyclohexane)	7·77	7·17	2·36	
	(benzene)	7·58	6·61	1·81	
	Δ	0·19	0·56	0·55	

[a] In ppm relative to TMS.

TABLE 3. PROTON CHEMICAL SHIFTS (δ)[a] IN CYCLOHEXANE AND IN BENZENE AND SOLVENT SHIFTS (Δ) OF 1-SUBSTITUTED 2,4-DIMETHYLBENZENES (IV)

Substituent		H_3	H_5	H_6	Me_2	Me_4	Substituent
NH_2	(cyclohexane)	6·70	6·68	6·33	1·94	2·08	3·04
	(benzene)	6·78	6·82	6·35	1·84	2·16	2·65
	Δ	−0·08	−0·14	−0·02	0·10	−0·08	0·39
NMe_2	(cyclohexane)	6·79	6·79	6·79	2·30	2·26	2·64
	(benzene)	6·90	6·90	6·90	2·16	2·29	2·45
	Δ	−0·11	−0·11	−0·11	0·14	−0·03	0·19
OH	(cyclohexane)	6·72	6·69	6·45	2·19	2·24	5·88
	(benzene)	6·77	6·75	6·39	2·10	2·10	4·47
	Δ	−0·05	−0·06	0·06	0·09	0·14	1·41
OMe	(cyclohexane)	6·82	6·80	6·53	2·13	2·18	3·66
	(benzene)	6·85	6·89	6·51	2·16	2·26	3·37
	Δ	−0·03	−0·09	0·02	−0·03	−0·08	0·29
Cl	(cyclohexane)	6·90	6·79	7·08	2·29	2·23	
	(benzene)	6·67	6·61	7·12	2·14	1·95	
	Δ	0·23	0·18	−0·04	0·15	0·28	
Br	(cyclohexane)	6·91	6·70	7·28	2·31	2·17	
	(benzene)	6·67	6·51	7·30	2·17	1·91	
	Δ	0·24	0·19	−0·02	0·14	0·26	
I	(cyclohexane)	6·96	6·58	7·56	2·33	2·20	
	(benzene)	6·68	6·35	7·58	2·20	1·91	
	Δ	0·28	0·23	−0·02	0·13	0·29	
CO_2Me	(cyclohexane)	6·90	6·87	7·77	2·52	2·24	3·71
	(benzene)	6·75	6·79	7·95	2·60	1·98	3·50
	Δ	0·15	0·08	−0·18	−0·08	0·26	0·21
CN	(cyclohexane)	7·00	6·95	7·30	2·42	2·29	
	(benzene)	6·49	6·46	7·02	2·12	1·82	
	Δ	0·51	0·49	0·28	0·30	0·47	
NO_2	(cyclohexane)	7·00	6·97	7·75	2·55	2·37	
	(benzene)	6·46	6·50	7·62	2·22	1·82	
	Δ	0·54	0·47	0·13	0·33	0·55	

[a] In ppm relative to TMS.

Table 4. Proton chemical shifts (δ)[a] in cyclohexane and in benzene and solvent shifts (Δ) of 1-substituted 2,6-dimethylbenzenes (V)

Substituent		$H_{3,5}$	H_4	$Me_{2,6}$	Substituent
NH_2	(cyclohexane)	6·78	6·50	2·00	3·20
	(benzene)	6·91	6·70	1·89	2·80
	Δ	−0·13	−0·20	0·11	0·40
NMe_2	(cyclohexane)	6·82	6·82	2·23	2·78
	(benzene)	6·95	6·95	2·21	2·60
	Δ	−0·13	−0·13	0·02	0·18
OH	(cyclohexane)	6·84	6·64	2·12	4·49
	(benzene)			1·94	4·03
	Δ			0·18	0·46
OMe	(cyclohexane)	6·88	6·77	2·21	3·59
	(benzene)	6·79	6·90	2·20	3·35
	Δ	0·09	−0·13	0·01	0·24
Cl	(cyclohexane)	6·89	6·89	2·30	
	(benzene)	6·78	6·78	2·20	
	Δ	0·11	0·09	0·10	
Br	(cyclohexane)	6·94	6·94	2·37	
	(benzene)	6·78	6·78	2·21	
	Δ	0·16	0·16	0·16	
I	(cyclohexane)	6·94	6·94	2·41	
	(benzene)	6·74	6·83	2·26	
	Δ	0·20	0·11	0·15	
CN	(cyclohexane)	6·97	7·17	2·46	
	(benzene)	6·55	6·80	2·14	
	Δ	0·42	0·37	0·32	
NO_2	(cyclohexane)	6·97	7·10	2·20	
	(benzene)	6·54	6·72	1·91	
	Δ	0·43	0·38	0·29	

[a] In ppm relative to TMS.

TABLE 5. PROTON CHEMICAL SHIFTS (δ)* IN CYCLOHEXANE AND IN BENZENE AND SOLVENT SHIFTS (Δ) OF 1-SUBSTITUTED 2,4,6-TRIMETHYLBENZENES (VI)

Substituent		$H_{3,5}$	$Me_{2,6}$	Me_4	Substituent
NH_2	(cyclohexane)	6·62	2·00	2·12	3·11
	(benzene)	6·72	1·92	2·20	2·68
	Δ	−0·10	0·08	−0·08	0·43
NMe_2	(cyclohexane)	6·62	2·18	2·15	2·74
	(benzene)	6·76	2·25	2·15	2·68
	Δ	−0·14	−0·07	0·00	0·06
OH	(cyclohexane)	6·62	2·10	2·14	4·23
	(benzene)	6·65	2·00	2·14	3·97
	Δ	−0·03	0·10	0·00	0·26
OMe	(cyclohexane)	6·65	2·19	2·19	3·57
	(benzene)	6·73	2·21	2·21	3·40
	Δ	−0·08	−0·02	−0·02	0·17
Cl	(cyclohexane)	6·70	2·29	2·20	
	(benzene)	6·62	2·23	2·02	
	Δ	0·08	0·06	0·18	
Br	(cyclohexane)	6·74	2·30	2·16	
	(benzene)	6·61	2·27	1·99	
	Δ	0·13	0·03	0·17	
I	(cyclohexane)	6·75	2·36	2·16	
	(benzene)	6·61	2·33	1·98	
	Δ	0·14	0·03	0·18	
CO_2Me	(cyclohexane)	6·72	2·21	2·21	3·72
	(benzene)	6·63	2·26	2·04	3·54
	Δ	0·09	−0·05	0·17	0·18
CN	(cyclohexane)	6·79	2·39	2·24	
	(benzene)	6·40	2·19	1·89	
	Δ	0·39	0·20	0·35	
NO_2	(cyclohexane)	6·79	2·17	2·22	
	(benzene)	6·36	2·00	1·87	
	Δ	0·43	0·17	0·35	

* In ppm relative to TMS

DISCUSSION

Though Williams *et al.*[2,10] used carbon tetrachloride, this reference solvent has a large van der Waals interaction with solute molecules and the magnitude of this interaction may differ in accordance with the steric requirement of the proton in question.[11] As we wished to compare the solvent shifts of protons sterically hindered in a different degree, carbon tetrachloride is not to be recommended although this solvent is nonpolar.

Actually we determined proton NMR spectra of II–VI in three solvents, i.e., carbon tetrachloride, cyclohexane and benzene. The δ values in carbon tetrachloride[1] are in general lower than those in cyclohexane and the difference, $\delta_{\text{cyclohexane}}$—$\delta_{\text{carbon tetrachloride}}$, amounts to, in not a few cases, almost 0·1 ppm. This is apparently due to the van der Waals interaction between carbon tetrachloride and the solute protons. Since this difference seems to vary with the steric effect, we prefer cyclohexane as the reference solvent. Details of this solvent shift will be published elsewhere.

Replacing hydrogen(s) of I by Me group(s) would affect the benzene-induced solvent shifts in various ways.

(i) The presence of Me groups inhibit the solvent molecules from approaching the ring proton or substituent, if any, of the solute. Consequently the sterically hindered protons will have an environment which is close to that in a gas phase, or approximately in a cyclohexane solution. In other words, Δ values will approach to zero or become even negative if the steric hindrance is severe.[2,19]

(ii) At the same time, association of solvent molecule(s) to Me group(s) must be considered since the latter is electron-deficient due to the hyperconjugative electron-donation to the ring.[20] Indeed it is accepted that for large solute molecules with more than one polar site, a benzene molecule may be associated with each site, provided they are not too closely located.[10] These two points are well demonstrated by the Δ values of (poly) methylbenzenes (Table 6). The positive Δ values for Me protons together with small negative Δ values for ring protons suggest the weak association at the Me groups together with slight steric inhibition of approach of solvent molecules to the aromatic ring protons.[2,19]

TABLE 6. SOLVENT SHIFTS (Δ) OF RING- AND METHYL-PROTONS IN (POLY)-METHYLBENZENES

	toluene	*m*-xylene	*p*-xylene	mesitylene
Ring-proton	−0·01[a]	−0·02[a]	−0·02[b]	−0·02
Methyl-proton	0·17	0·10		0·06

[a] Estimated from the δ value of the strongest peak.

[b] Data taken from rf. 19.

(iii) The presence of *ortho* Me group(s) needs particular consideration. Not only will the solvent molecule find it more difficult to approach the polar site, but the polarity of the solute may be reduced due to the steric inhibition of resonance if the substituent is bulky. Fig. 1 shows the variation of Δ values for the substituent protons. Apparently the polarity of the solute is not the only reason for the observed solvent shifts even if the H-bonding OH group is excluded.

(iv) The presence of *meta*- and *para* Me group(s) will not alter the polarity of the solute nor the stereo-chemical environment around the substituent. Therefore, for the electron-donating substituents (complex **1**), the geometry of the complex will remain unchanged, but the formation of a type **2** complex will be made difficult by the presence of Me group(s) regardless of position. Thus the change in solvent shifts due to the introduction of Me group(s) would be large for electron-withdrawing substituents and halogens.

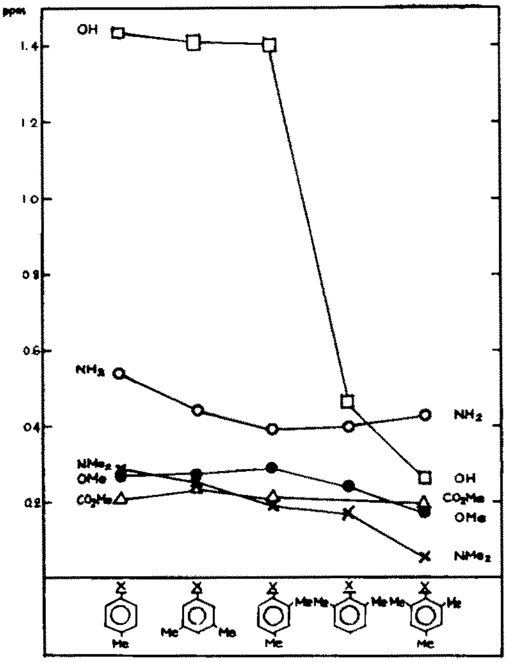

FIG. 1 Δ Values of protons in substituents.

(v) Among the electron-withdrawing substituents, the CO_2Me group must be considered. Δ Values of *ortho* ring protons and *ortho* Me protons are both negative. This indicates that the solvent associates with the carbonyl (C═O) fraction of the group. Since *ortho* positions lie in front of the "carbonyl plane"* provided the rotation about C_{Ph}—$C_{C=O}$ bond is rapid, Δ values for these protons must be negative.

We can judge whether the observed Δ values are in accordance with prediction if either geometry **1** or **2** is assumed. The variations of Δ values due to Me group(s) for *ortho*, *meta* and *para* ring protons and *ortho* and *para* Me protons are shown in Figs 2–6.

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* The "carbonyl plane rule"[21] states that Δ values will be positive for protons lying behind a plane drawn at right angles to the C═O bond and passing through the carbonyl carbon atom, but negative for protons lying in front of this plane.

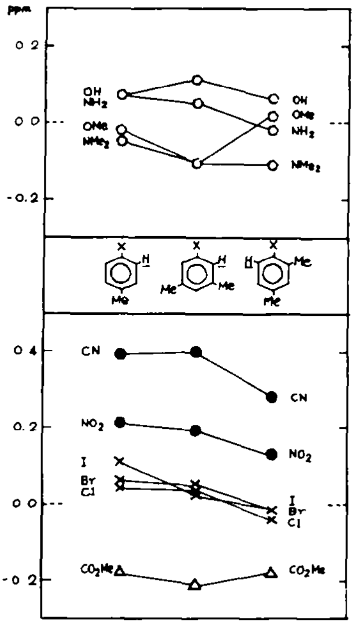


FIG. 2 Δ Values of various *o*-ring protons.

ortho *Ring proton* (Fig. 2) The Δ values (and even their signs) of four electron-donating substituents show no definite correlation with the number and position of Me group(s) present nor any indication that Δ values decrease as the steric inhibition increases. The are, however, internally consistent with the proposed geometry **1**. The presence of Me group(s) may modify slightly the stereochemistry and/or the electronic state near the polar site (hence in the geometry of complex), but complex formation itself is not made difficult.

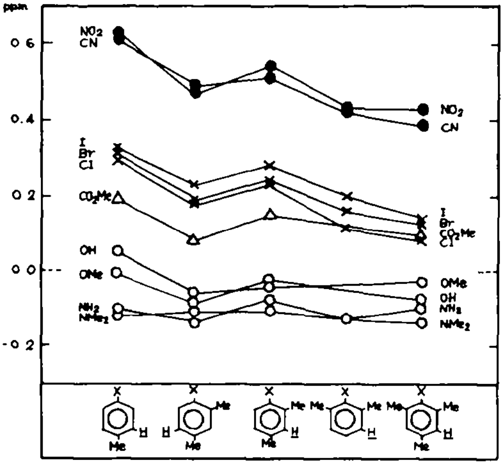


FIG. 3 Δ Values of various *m*-ring protons.

Halogens and electron-withdrawing substituents result in nearly equal Δ values for II and III. The presence of a *para* Me group or two *meta* Me groups seem of equal steric importance in complex formation, but the presence of an *ortho* Me group results in much smaller Δ values for IV as anticipated from the geometry 2.

meta *Ring proton* (Fig. 3). The variation of Δ values for *meta* ring protons is in accordance with the expected tendency, i.e., they have relatively no effect on electron-donating substituents and there is a constant decrease in the Δ values for halogens and electron-withdrawing substituents as the number of Me groups increases.

An anomaly was observed for the 3- and 5-protons of IV. The 3-proton, due to the presence of a 2-Me group, is sterically more crowded than the 5-proton and should have a smaller Δ value. Instead, the less crowded 5-proton has the smaller Δ value. One possible explanation is the asymmetric deformation of the geometry of complex caused by the steric asymmetry at the polar site of IV. The 2-Me group pushes the overlying solvent molecule aside, causing the slant of the plane of solvent molecule out of that of the solute. Provided the geometry of complex of IV is like 3 (4-Me group is not shown), the 5-proton is more deeply immersed in the paramagnetic region of the solvent than the 3-proton.

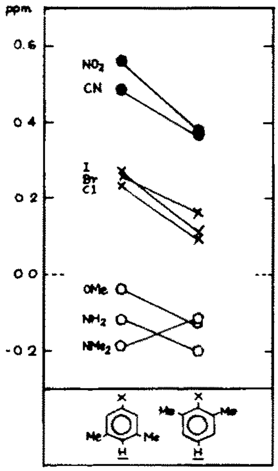
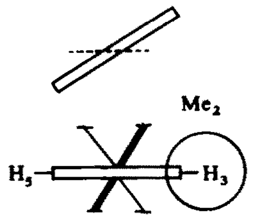


FIG. 4 Δ Values of various *p*-ring protons.

para *Ring proton* (Fig. 4). Δ Values for *para* protons seem to depend primarily on the steric factor of the polar site. For example, both III and V have two Me groups



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and Δ values of 4-proton of V, sterically less crowded without 3- or 5-Me groups, are much smaller than those of III with both 3- and 5-Me groups. It must be emphasized that linear substituents (irrelevant to the steric inhibition of resonance) as well as bulky substituents show the same decrease of Δ values from III to V. It seems that the farther the proton is from the polar site, the more important is the steric factor in the neighborhood of the substituent.

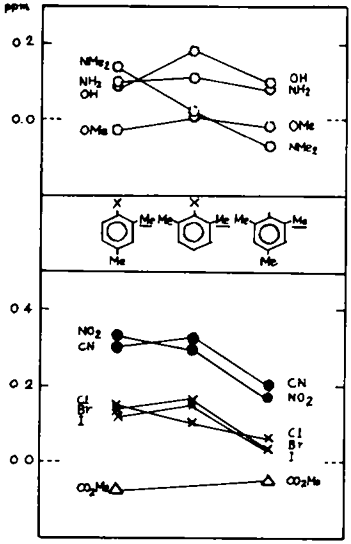

FIG. 5 Δ Values of various o-methyl protons.

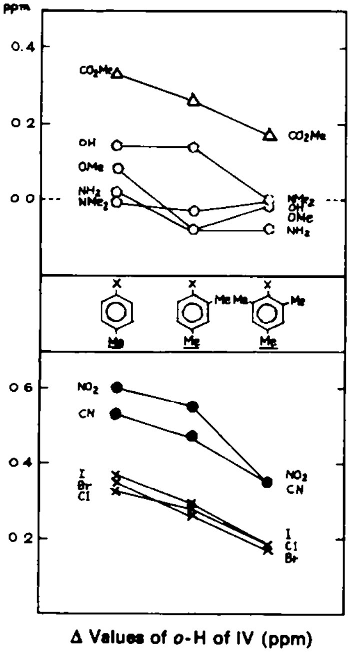

FIG. 6 Δ Values of various p-methyl protons.

ortho *and* para *Methyl protons* (Figs 5 and 6). The general tendency is similar with that for ring protons.

Δ Values of ring proton vs *Δ values of methyl protons.* In Figs 7–9, plots of Δ values of ring proton *vs* those of Me protons for *ortho*, *meta* and *para* positions are given.

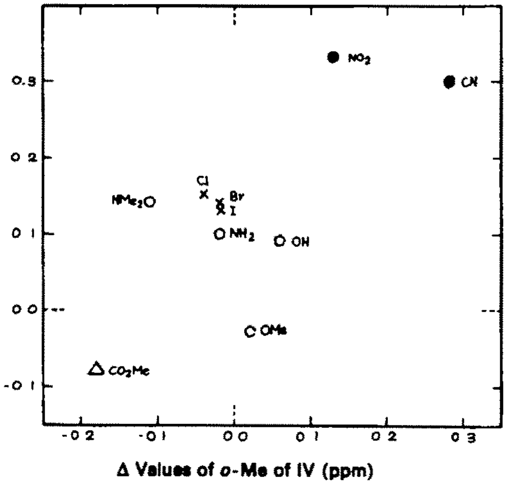

FIG. 7 Δ Values at *ortho*-position.

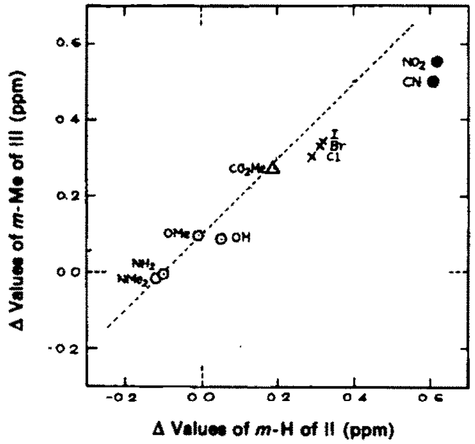

FIG. 8 Δ Values at *meta*-position.

Though the *ortho* plot shows no correlation, a linear correlation is observed for *meta* and *para* plots. If the origin of benzene-induced solvent shifts is solely due to the large diamagnetic anisotropy of benzene, a proton bonded to sp^3 hybridized carbon and a proton bonded to sp^2 hybridized one should show much the same Δ value if the geometric relation to the anisotropic solvent is identical. Then, if the difference in the distance from the associated solvent to ring proton and to Me protons is negligible, one can expect a line with a slope of unity for the plots given in the Figs 7–9 (dotted line in Figs 8 and 9). The intercepts of the dotted lines correspond accurately to the increment of Δ values of Me protons due to benzene association. (Table 6). However, the difference in the distance cannot be neglected. Generally the distance to the associated benzene is slightly larger for Me protons than for ring protons:* the difference is large when the proton in question is close to the associated benzene (as in complex 2). As the position to the associated solvent becomes closer, the ratio (Δ values of Me protons)/(Δ values of ring proton) is reduced to less than unity. More precisely the ratio varies with respect to the nature of the substituent and to the position relative to the substituent. As for the nature of the substituent, the ratio decreases in the order; electron-donating substituent > halogen > electron-withdrawing substituent. Regarding the position, (a) for electron-donating substituent; *ortho* > *meta* > *para*, and (b) for halogen and electron-withdrawing substituent; *ortho* > *meta* > ≈ *para*. For both *meta* and *para* plots, halogens and electron-withdrawing substituents deviate slightly in the expected direction, again supporting model 2.

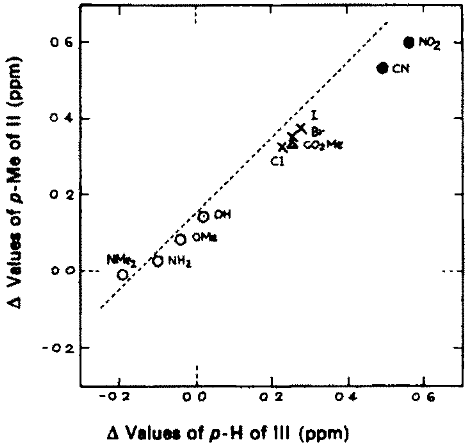

FIG. 9 Δ Values at *para*-position.

An alternative explanation for these deviations is that the approach of benzene molecules to the Me group(s) is made difficult by the overlying benzene molecule associated with the substituent. Although this explanation is simpler, we have at present no definite information on this type of steric hindrance. The effect of dilution on Δ values may provide valuable information, and this is being currently investigated, and is also consistent with the assumed geometries 1 and 2.

Another possibility is the change of the hyperconjugative interaction between the Me group(s) and the aromatic ring due to the substituent. This could alter the degree of interaction between the Me group and the benzene solvent molecules, hence, the fraction of Δ values due to this coordination. This is, however, highly unlikely since the geminal coupling constants of Me protons in a series of II are quite insensitive to the electron-withdrawing nature of the substituents.[23]

Two lines of evidences, i.e., (1) the variation of Δ values with the number and position of Me groups and (2) plots of Δ values of ring proton *vs* those of Me protons, support

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[*] For methyl protons an average position (located along the extension of C_{Ph}—C_{Me} bond) may be assumed. The error associated with this approximation is allowable if the distance between the proton and the anisotropic center is moderately remote.[22]

the general approximation of the solvent shifts of monosubstituted (poly)methylbenzenes in terms of complex 1 (with additional benzene solvent molecule(s) weakly associated with Me group(s)) for compounds with electron-donating substituents and complex 2 (with additional benzene solvent molecule(s) weakly associated with Me group(s)) for those with halogens or electron-withdrawing substituents provided that the coordination of benzene with Me group(s) is not seriously perturbed by the presence of the substituent. In forming such complexes, the steric effect is of prime importance for protons remote from the polar site, and the polar effect as well as steric factor is responsible for protons close to the polar site.

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REFERENCES

[1] Part IV. Y. Nomura and Y. Takeuchi, *Org. Mag. Resonance* **1**, in press.
[2] R. G. Wilson and D. H. Williams, *J. Chem. Soc.* (B) 1163 (1968).
[3] N. S. Bhacca and D. H. Williams, *Application of NMR Spectroscopy in Organic Chemistry* Chapter 7. Holden-Day, San Francisco (1964).
[4] A. A. Bothner-By and R. E. Glick, *J. Chem. Phys.* **26**, 1651 (1957).
[5] L. W. Reeves and W. G. Schneider, *Canad. J. Chem.* **35**, 251 (1957).
[6] T. Schaefer and W. G. Schneider, *J. Chem. Phys.* **32**, 1218, 1224 (1960).
[7] A. D. Buckingham, T. Schaefer and W. G. Schneider, *Ibid.* **32**, 1227 (1960).
[8] R. E. Klinck and J. B. Stothers, *Canad. J. Chem.* **40**, 1071, 2329 (1962); *Ibid.* **44**, 37 (1966).
[9] T. L. Brown and K. Stark, *J. Phys. Chem.* **69**, 2679 (1965).
[10] J. Ronayne and D. H. Williams, *J. Chem. Soc.* (B). 540 (1967).
[11] J. Ronayne and D. H. Williams, *Chem. Comm.* 712 (1966).
[12] J. E. Anderson, *Tetrahedron Letters* 4713 (1965).
[13] T. Ledaal, *Ibid.* 1683 (1968).
[14] W. G. Schneider, *J. Phys. Chem.* **66**, 2653 (1962).
[15] R. J. W. Le Fèvre, D. V. Radford, G. L. D. Ritchie, P. J. Stiles, *J. Chem. Soc.* (B). 148 (1968).
[16] Y. Ichikawa and T. Matsuo, *Bull. Chem. Soc. Japan* **40**, 2030 (1967).
[17] P. Diehl, *J. chim. Phys.* **61**, 199 (1964).
[18] P. Diehl, *Helv. Chim. Acta* **45**, 568 (1962).
[19] D. H. Williams, J. Ronayne and R. G. Wilson *Chem. Comm.* 1089 (1967).
[20] D. J. Barraclough, P. W. Hickmott and O. Mech-Cohn, *Tetrahedron Letters* 4289 (1967).
[21] J. D. Connolly, R. McCrindle, *Chem. & Ind.* 379 (1965).
[22] Y. Nomura and Y. Takeuchi, *Tetrahedron Letters* 5665 (1968).
[23] W. C. Ripka and D. E. Applequist, *J. Am. Chem. Soc.* **89**, 4035 (1967).