Aromatic Solvent-induced Shifts (ASIS). II. Interpretation of Benzene and Hexafluorobenzene Induced Shifts by Means of the Electrostatic Interaction Model

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The relationships between the ASIS in proton magnetic resonance and charge distribution in the solute and solvent molecules were studied. The results obtained are as follows. Protons lying in the positive charge-region of the solute dipole showed an up-field shift in C_6H_6 and a down-field shift in C_6F_6, while protons lying in the negative charge-region showed a down-field shift in C_6H_6 and an up-field shift in C_6F_6. There exists a linear relationship between the ASIS and the solute dipole moments of monosubstituted methanes, *t*-butyl derivatives, and para substituted toluenes. Shifts of para substituted toluenes and 4-methyl-4′-nitrobiphenyl are in good agreement with those expected from the electrostatic interaction model.

Aromatic solvent-induced shifts (ASIS) in ^1H NMR spectroscopy have been well investigated.[1,2] The benzene-induced shifts observed for carbonyl compounds are conveniently explained by an empirical rule, the so-called "Carbonyl plane rule."[3]

In the earlier models of ASIS, *i.e.*, the dipole-induced dipole interaction model, the quadrupole-induced quadrupole interaction model,[4] and in the H-bond interaction model,[5] the nature of intermolecular interactions was discussed without much success.

Since then, two models have been proposed to explain ASIS. One is the solute–solvent specific 1:1 complex model and the other is the time-averaged cluster model. In the former model Williams *et al.* assumed the existence of solvent molecules with favorable distances and orientations to the solute molecules; these would show the feature of ASIS.[1] Laszlo *et al.* pointed out in the latter model that the solute dipole should be the cause of clustering.[2] They did not discuss, however, the nature of the solute-solvent interaction.

In our previous paper,[6] benzene-induced shifts of methyl protons on *d*-camphor were discussed in terms of the electrostatic dipole(*d*-camphor)-quadrupole-(benzene) interaction. The results were in good agreement with the experimental ASIS values. If the main interaction between solute molecule and solvent mole cules is assumed as the electrostatic interaction, the flat surface of benzene molecules near the positive charge end of the dipole are likely to face to the positive end. Thus, benzene molecules induce up-field shifts due to their magnetic anisotropy for the protron near the positive end. On the other hand, the periphery part of benzene molecules near the negative charge end of the dipole are likely to face to the negative end. Thus, they induce down-field shifts for the proton near the negative end. These favorable orientations are similar to those proposed by Williams[1] and Ledaal.[7]

Recently, it was shown that a different solvent effect was induced by hexafluorobenzene, which generally shows shifts opposite to those induced by benzene.[8–17] The carbonyl plane rule for that solvent was also proposed,[16] but the nature of the intermolecular interaction was not discussed.

The main purpose in this paper is to clarify the mechanism of ASIS: these shifts are caused by the orientation of solvent molecules around the dipole due to intermolecular electrostatic interactions. Furthermore, it will be shown that the hexafluorobenzene(which has a different charge distribution than benzene)-induced shifts were also caused mainly by the electrostatic interaction, as in the case of benzene-induced shifts.

Thus the aromatic solvent-induced shifts (ASIS) in benzene and hexafluorobenzene of monosubstituted methanes, *t*-butyl derivatives, para substituted toluenes, and 4-methyl-4′-nitrobiphenyl were determined. Besides these determinations, the observed ASIS values of para substituted toluenes and 4-methyl-4′-nitrobiphenyl were calculated on the basis of the electrostatic interaction between solute and solvent molecules.

Experimental

ASIS(C_6H_6) and ASIS(C_6F_6) of the compounds given in Table 1 were measured with a Hitachi R-20B spectometer operating at 60 MHz as 1 mol % solutions, with cyclohexane as the internal reference. Carbon tetrachloride was assumed to be inert. The ASISs were defined by

$$\mathrm{ASIS}(C_6H_6) = \delta_{C_6D_6} - \delta_{CCl_4},$$

$$\mathrm{ASIS}(C_6F_6) = \delta_{C_6F_6} - \delta_{CCl_4},$$

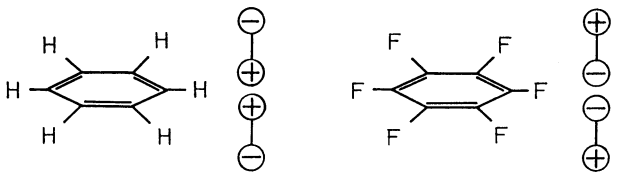
where $\delta_{C_6D_6}$, δ_{CCl_4}, and $\delta_{C_6F_6}$ are the chemical shifts in benzene-d_6, carbon tetrachloride, and hexafluorobenzene from the internal reference of cyclohexane, respectively. The chemical shifts were determined by the sideband method with the aid of a frequency counter. The standard deviation in all cases was less than ± 0.01 ppm.

Calculation

The electric charge distributions in benzene and hexafluorobenzene molecules were approximately

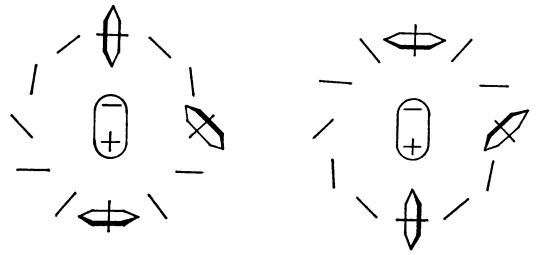
TABLE 1. SOLUTE MOLECULES

	Compound	Substituent
(I)	CH_3-X	X=NO_2, CN, CCl, I, SCN
(II)	$(CH_3)_3C$-X	X=CN, Cl, Br, NH_2, OCH_3, OH
(III)	*para*-$CH_3C_6H_4$-X	X=$\begin{cases}NO_2, CN, CHO, Br, Cl, I\\OCH_3\ NH_2,\ N(CH_3)_2\end{cases}$
(III′)	$CH_3C_5H_4N$(4-methyl pyridine)	
(IV)	$CH_3C_6H_4C_6H_4NO_2$(4-methyl-4′-nitrobiphenyl)	



a) C_6H_6 b) C_6F_6

Fig. 1. Benzene molecule(a) and hexafluorobenzene molecule(b) are approximately expressed by electric bar-quadrupoles.



C_6H_6 C_6F_6

Fig. 2. The most stabel orientation of solvent molecules around a solute molecules due to the dipole (solute)-quadrupole(solvent) interaction ($U \propto \mu Q/r^4$).

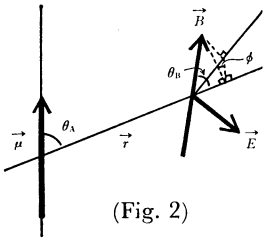
represented by electric bar-quadrupoles (see Fig. 1). The principal values of the quadrupole moment tensor, with the Z-principal axis along with the six-fold molecular axis, and the anisotropy of the magnetic susceptibility ($\Delta\chi = \chi_{\parallel} - \chi_{\perp}$; the subscripts $\parallel$ and $\perp$ here mean parallel and perpendicular to the highest axis of symmetry of the molecule) are given in Table 2. Then the ASIS value of a polar solute molecule induced by these solvents can be calculated if the orientation of these quadrupoles (solvent) around the solute dipole is assumed.

The most stable orientation of benzene molecules and hexafluorobenzene molecules around a dipole is shown in Fig. 2. The calculation of ASIS based on the electrostatic dipole(solute)-quadrupole(solvent) interaction was reported in detail in the previous paper of this series.†,[6]

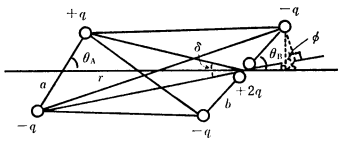
The calculations were performed by computer with the HITAC 8300 at the University of Tokyo.

† We found some errors in Figs. 2 and 4 in the previous paper.[6]

The expressions of the dihedral angle (ϕ) between the plane containing $\vec{\mu}$ and $\vec{r}$ and that containing $\vec{r}$ and $\vec{B}$ in Figs. 2 and 4 should be corrected as follows:



(Fig. 2)



(Fig. 4)

Fig. 3. Errata (Fig. 2): A benzene molecule in a permanent dipole field of a solute molecule.
(Fig. 4): Electrostatic interaction between bar-dipole and bar-quadrupole.

Table 2. Quadrupole moments and magnetic anisotropies of solvent molecules

Solvent	Quadrupole moment[18] (10^{-26} esu) Obsd	Quadrupole moment[18] (10^{-26} esu) Calcd	Magnetic anisotropies[19] (10^{-30} emu)
C_6H_6	Q_{XX} +2.8±1.4	+3.3	89±4
	Q_{YY} +2.8±1.4	+3.3	
	Q_{ZZ} −5.6±2.8	−6.6	
C_6F_6	Q_{XX} ——	−8.6	53±2
	Q_{YY} ——	−8.6	
	Q_{ZZ} ——	+17.2	

Results and Discussion

The ASIS of methyl protons *versus* dipole moments of monosubstituted methanes(I) and *t*-butyl derivatives(II) are plotted in Fig. 4. The ASIS values *versus* their dipole moments for methyl-protons and *ortho*-protons of para substituted toluenes(III) are plotted in Fig. 5. The experimental values and the calculated ones of these ASIS are summarized, together with those of the dipole moments, in Tables 3(a)—(b).

There exists a linear relationship between the ASIS and the solute dipole moments in benzene solutions. Of the protons in question, those on solute molecules lying in the positive-charge region of the solute dipole exhibit up-field shifts, while the protons lying in the negative-region exhibit down-field shifts or only minor up-field shifts.

For the convenience of further discussion, the substituted molecules can be classified into two groups according to the directions of their dipole moments. (see Table 4.) In the proposed classification, group (A) consists of protons of the methyl group and those on the aromatic ring of p-$CH_3C_6H_4X_A$ which are lying in the positive-region of the solute dipole and show up-field shifts, while group (B) consists of those which show down-field shifts or only slight up-field shifts.

ASIS(C_6H_6) values of molecules of (III), (III'), and (IV) expressed as a function of the distance between the proton in question and the carbon on the base of the substituent are plotted in Fig. 6. The "sense" of the shifts is quite different for group (A) and group (B) molecules. In order to express this difference, the "Carbonyl plane rule" is conveniently extended to other polar substituents, and renamed as the "Dipole plane rule." A dipole plane can be assumed on the polar substituents, as illustrated in Fig. 7(a). Protons lying in the positive region of the dipole are assumed to show up-field shifts. However, the dipole planes of 4-methylpyridine (III') and 4-methyl-4'-nitrobiphenyl(IV) are located near the center of these molecules.

Conversely, in hexafluorobenzene solutions, sensor protons lying in the positive-region of the solute dipole showed down-field shifts while the protons in the negative-region showed up-field shifts. Therefore, a dipole plane can be illustrated as in Fig. 7(b). Here the protons lying in the positive-region of the dipole are assumed to show down-field shifts.

The experimental "Dipole plane rule" can, though

Table 3(a). ASIS(C_6H_6) and ASIS(C_6F_6) values and dipole moments of molecules of (I) and (II)

Substituent(X)	δ_{CCl_4}	ASIS(C_6H_6)	ASIS(C_6F_6)	Dipole moment[20]
(I) CH_3-X				
CN	0.52 ppm	+1.18 ppm	−0.17 ppm	3.92 D
NO_2	2.83	+1.18	−0.17	3.46
SCN	1.17	+1.26	−0.20	3.34
I	0.71	+0.67	−0.07	1.64
CCl_3	1.29	+0.59	−0.07	1.66
(II) $(CH_3)_3C$-X				
CN	−0.07 ppm	+0.53 ppm	−0.13 ppm	3.65 D
Cl	+0.17	+0.22	−0.03	2.15
Br	+0.35	+0.26	−0.04	2.21
SH	−0.01	+0.18	−0.00	—
OH	−0.23	+0.10	+0.02	1.67
OCH_3	−0.31	+0.02	+0.03	1.23
NH_2	−0.34	+0.07	+0.03	1.32

Table 3(b). ASIS values (ppm) and dipole moments of molecules (III), (III′), and (IV)

X	CH_3			*ortho*-H			*meta*-H			μ^{20} (D)
	δ_{CCl_4}	C_6H_6	C_6F_6	δ_{CCl_4}	C_6H_6	C_6F_6	δ_{CCl_4}	C_6H_6	C_6F_6	
CN	1.00	+0.60 (+0.36)	−0.17 (−0.28)	5.80	+0.66 (+0.41)	−0.18 (−0.30)	6.05	+0.47 (+0.09)	+0.07 (+0.07)	4.40
NO_2	1.04	+0.63 (+0.35)	−0.21 (−0.28)	5.85	+0.69 (+0.41)	−0.17 (−0.30)	6.65	+0.26 (+0.10)	+0.11 (+0.06)	4.47
CHO	1.00	+0.47	−0.13	5.84	+0.41	−0.08	6.28	+0.17	+0.13	3.24
Br	0.87	+0.40	−0.12	5.23	+0.37	−0.10	6.33	+0.07	+0.22	1.98
Cl	0.88	+0.38 (+0.16)	−0.11 (−0.16)	5.60	+0.33 (+0.19)	−0.01 (−0.18)	5.72	+0.05 (+0.04)	+0.12 (+0.03)	1.96
I	0.86	+0.40	−0.13	5.43	+0.35	−0.05	6.07	+0.07	+0.17	1.73
OCH_3	0.83	+0.10	+0.01	5.23	−0.15	+0.05	5.52	−0.03	−0.03	1.21
$N(CH_3)_2$	0.79	−0.04	+0.06	5.45	−0.20	+0.16	5.10	−0.12	+0.24	1.29
NH_2	0.76	+0.02 (−0.11)	+0.04 (+0.19)	5.39	−0.11 (−0.12)	+0.12 (+0.22)	4.99	+0.05 (+0.01)	+0.15 (+0.05)	1.61
(III′)	0.88	+0.12	−0.12	5.55	+0.38	−0.04	6.92	−0.14	+0.26	2.60

	CH_3			3-H			2-H			2′-H			3′-H		
	δ_{CCl_4}	C_6H_6	C_6F_6	δ_{CCl_4}	C_6H_6	C_6F_6	δ_{CCl_4}	C_6H_6	C_6F_6	δ_{CCl_4}	C_6H_6	C_6F_6	δ_{CCl_4}	C_6H_6	C_6F_6
(IV)	0.98	+0.26 (+0.29)	−0.09 (−0.25)	6.22	+0.55 (+0.42)	−0.14 (−0.33)	6.79	+0.30 (+0.26)	−0.01 (−0.12)	6.00	+0.27 (+0.13)	+0.09 (+0.03)	5.90	−0.06 (+0.21)	+0.02 (−0.12)

( ): represent calculated values.

Table 4. Classification of solute molecules

Group (A)			Group (B)		
Positive-charge region		Negative-charge region	Negative-charge region		Positive-charge region
CH_3	—	X_A			
$(CH_3)_3$	—	X_A			
$CH_3C_6H_4$	—	X_A	$CH_3C_6H_4$	—	X_B
X_A=CN		large	X_B=OCH_3		
NO_2		↑	NH_2		
CHO		|	$N(CH_3)_2$		
Br		|			
Cl		|			
I		μ[a)]			

a) μ represents a dipole moment.

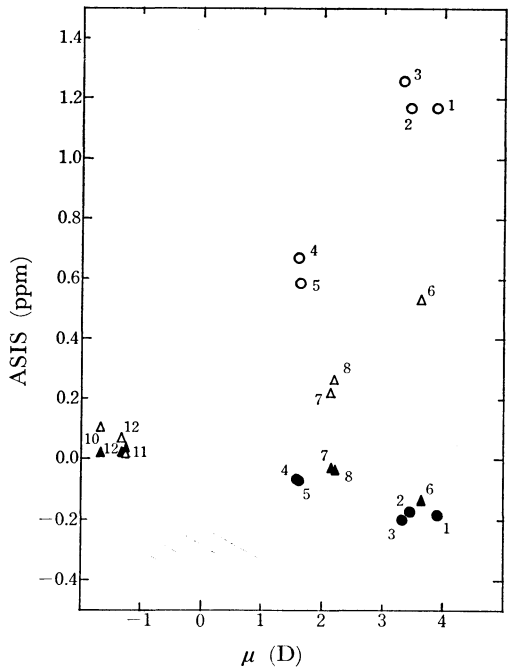


Fig. 4. ASIS values of methyl-protons *vs.* dipole moments(μ) of monosubstituted methanes (○: in C_6H_6, ●: in C_6F_6, and substituent; 1: CN, 2: NO_2, 3: SCN, 4: I, 5: CCl_3) and *t*-butyl derivatives (△: in C_6H_6, ▲: in C_6F_6, and substituent; 6: CN, 7: Cl, 8: Br, 9:SH, 10: OH, 11: OCH_3, 12: NH_2).

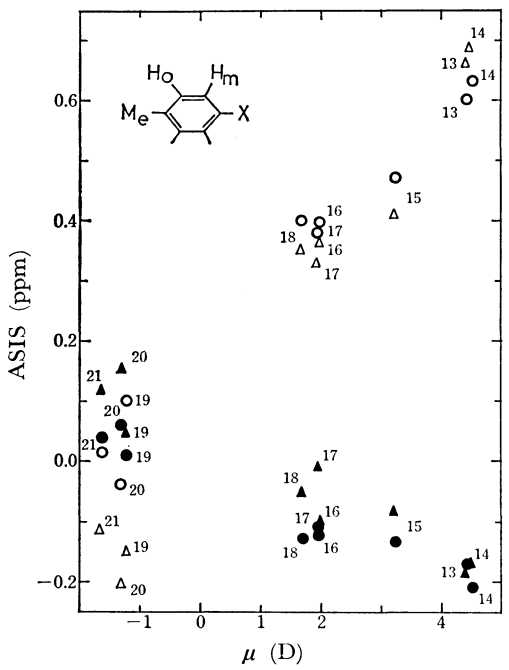


Fig. 5. ASIS values of methyl-protons (○: in C_6H_6 and ●: in C_6F_6) and *ortho*-protons (△: in C_6H_6 and ▲: in C_6F_6) *vs.* dipole moments (μ) for para substituted toluenes)(substituent; 13: CN, 14: NO_2, 15: CHO, 16: Br, 17: Cl, 18: I, 19: OCH_3, 20: $N(CH_3)_2$, 21: NH_2).

only in a qualitative manner, express ASIS values except for the proton near the dipole plane.

Figure 6 indicates that significiant differences between ASIS (C_6H_6) and ASIS(C_6F_6) are in the "sense" of the shifts and the position of the dipole planes. In hexafluorobenzene, the plane should be placed between the substituent and the center of the molecules.

As a general feature of the shifts, the magnitude of up-field shifts is larger than those of down-field shifts in benzene, while the magnitude of up-field shifts is comparable with down-field shifts in hexafluorobenzene, and the magnitude of ASIS(C_6H_6) is larger than those of ASIS(C_6F_6) for the same solute molecules. Those features of the ASIS are explainable in terms of the electrostatic interaction model. In a benzene solution, the more stable orientation of a solvent molecule around the solute dipole takes configuration (C) on the positive-charge region of the solute dipole while it takes configuration (D) on the negative-charge (see Figs. 2 and 8). As both benzene and hexafluorobenzene molecules have a flat, disk-like shape, the distance from the center of the solute dipole to the center of the solvent quadrupole is shorter in configuration (C) than in (D) ; furthermore the distance from the proton in question of the solute to the solvent molecules is also shorter in configuration (C) than in (D).

The stabilization energy of configuration (C) on the positive region is thus greater than that of (D) on the negative-region(see our previous paper[6]). In view of the known magnetic anisotropy of the benzene ring, configuration (C) should give an up-field shift,

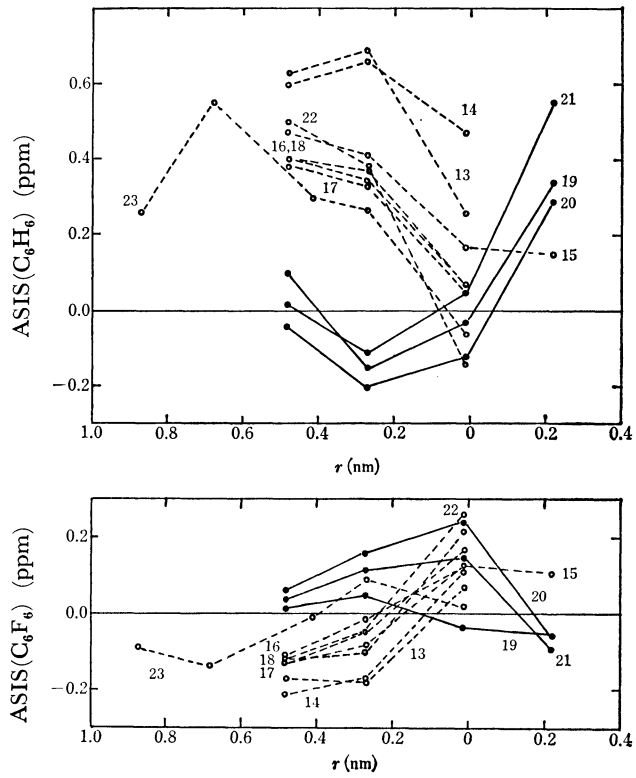


Fig. 6. The relations between ASIS values and the position of protons on para substituted toluenes and on 4-methyl-4′-nitrobiphenyl in C_6H_6 and in C_6F_6 (----: group (A) molecules and ——: group (B) molecules, substituent; 13: CN, 14: NO_2, 15: CHO, 16: Br, 17: Cl, 18: I, 19: OCH_3, 20: $N(CH_3)_2$, 21: NH_2, and molecules; 22: III′, 23: IV).

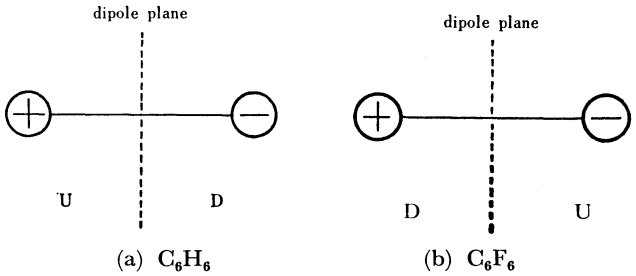


Fig. 7. A dipole plane rule in C_6H_6 (a) and in C_6F_6 (b). (U: up-field shift region and D: down-field shift region.)

while (D) should give a down-field shift for solute protons. Therefore the up-field shifts should show larger values than the down-field shifts.

In hexafluorobenzene solutions, however, the most stable orientation are configuration (D) on the positive-region of the solute dipole and configuration (C) on the negative-region. And the stabilized energy due to the dipole-quadrupole interaction on the positive-region is less than that on the negative-region; the effect of down-field shifts on the positive-region, is however, comparable with the up-field shifts on the negative-region, since the other attractive interaction between the local positive charge of the solute dipole and the localized dipole of C–F bond is not so small.

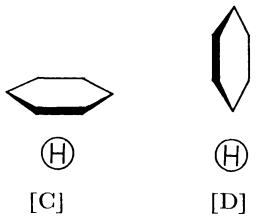


Fig. 8.

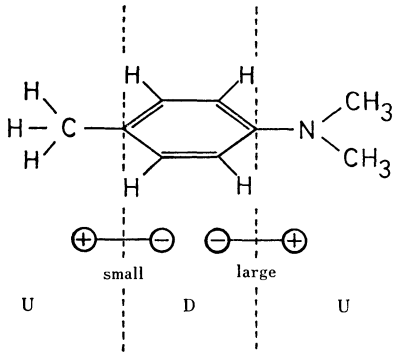


Fig. 9. Dipole plane rule on a *N,N*-dimethyl-*p*-toluidine. (U: up-field shift region and D: down-field shift region.)

Almost all the ASIS are interpreted by the orientation of the quadrupoles(solvent moleucles) around the solute dipole due to the electrostatic interaction, and are in good accord with the dipole plane rule. However, three exceptions were found.

One is the ASIS of methyl protons of the molecules in (III) when X=OCH_3, NH_2, or $N(CH_3)_2$. The ASIS values of these molecules showed a very slight up-field shift with hexafluorobenzene. These molecules are classified in group (B) and so the Hammett's σ_p values of the methyl group has the same sign as the Hammett's σ_p values of the OCH_3, NH_2, $N(CH_3)_2$ groups, but the direction of the bond dipole of the methyl group is opposite to that of the substituents in group (B). In this case, the effect of the bond dipole on the ASIS of the methyl group must be taken into consideration. This effect is especially great in the case of benzene solution, because benzene molecules around methyl protons are located in the positive-region of the methyl dipole, and so their more stable orientation gives large up-field shifts.(See Fig. 9.)

The second exception is a remarkable up-field shift found in the ASIS(C_6F_6) of *meta*-protons of the molecules in (III) in which X=$N(CH_3)_2$. As $N(CH_3)_2$ is a bulky substituent, no other solvent molecules are permitted to exist within it. As the exclusion space is located in the positive-region, the proton in question is not influenced by solvents that will cause down-field shifts. Herein the proton is considered to be influenced mainly by solvents in the negative-region and to show up-field shifts.

The third exception is that both solvents will induced a large up-field shift of protons on NH_2 on a group (III) molecule. It is presumed that the up-field shift is caused by the hydrogen bond-like interaction between the NH_2 group and π-electrons of the

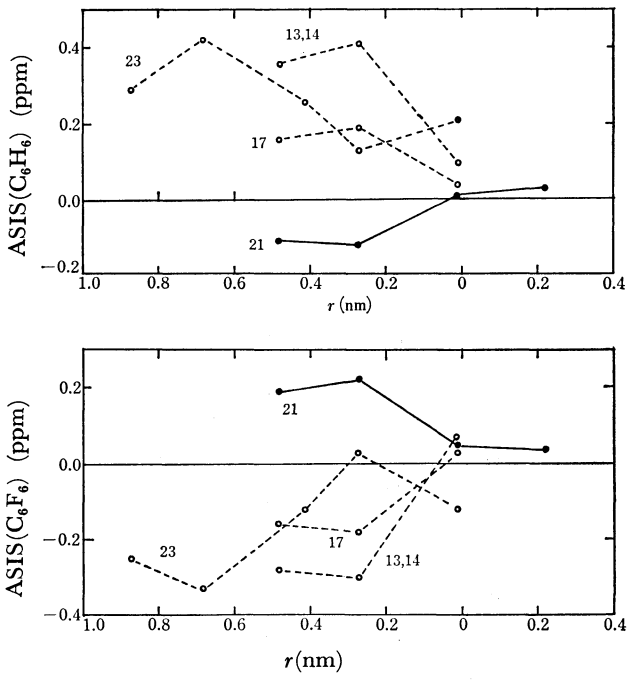


Fig. 10. The relations between calculated ASIS values and the position of protons on para substituted toluenes and on 4-methyl-4′-nitrobiphenyl in C_6H_6 and in C_6F_6 (substituent; 13: CN, 14: NO_2, 17: Cl, 21: NH_2, and molecule; 23: IV).

aromatic ring.

The calculated ASIS values of protons on para-substituted toluenes and 4-methyl-4′-nitrobiphenyl with benzene and hexafluorobenzene are illustrated in Fig. 10.

These exceptions are mostly due to the point-dipole and point-quadrupole approximations. Our model is, however, much more quantitative than the arbitrary models of Williams,[1] Ledaal,[7] and Verkade *et al.*[8–17] There is no need to say that a 1:1 complex is highly unlikely.

Our calculation is performed based on real physical numerical quantities without using the arbitary parameters such as in Laszlo *et al.*[2] The calculated values are in a good agreement with the observed values in the "sense" and in the order of magnitude. And the magnitude of shifts on the same molecule or on the molecules with a similar shape can be compared.

Thus, the ASIS of various solute molecules in ^1H NMR caused by benzene and hexafluorobenzene can be explained by the orientation of solvent molecules around a polar solute molecule(see Fig. 2) due to electrostatic interaction.

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