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The Effects of Solvents on the IR and PMR Spectra of Intramolecular OH···π and OH···O Hydrogen Bonded Systems[1)]

Shinichi Ueji

Institute of Chemistry, College of General Education, Kobe University, Tsurukabuto, Nada, Kobe 657

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The effects of solvents on the intramolecular OH···π and OH···O hydrogen bonding in 2-arylphenols and 2,6-diarylphenols have been studied by examining the OH stretching IR absorption spectra in a range of solvents. The solvent shifts of the hydrogen bonded bands, νOH···π and νOH···O, followed the *G* correlation and the BHW plot. The success of both correlations suggests that the solvent shifts are primarily due to a specific solvent-solute association, even in relatively non-polar solvents. The solvent sensitivity of the OH···π and OH···O hydrogen bonded bands depended on the stereo-chemical environment around the hydrogen bonded system rather than on such electronic factors as the strength of the hydrogen bonding. On the basis of the relationship between the solvent sensitivity and the structural changes over a group of phenols, a simplified model for the solvent-solute association is put forward. Furthermore, this simplified model is also discussed in terms of the aromatic solvent-induced shifts in the PMR spectra.

Since the first observation of the solvent sensitivity of the hydrogen bonded OH frequency,[2)] considerable attention has been focused on the solvent effects on IR frequency shifts.[3)–6)] However, the problem is not yet completely settled.

In the IR study of the solvent effects on the hydrogen bonded bands, Bellamy, Morgan, and Pace[3)] attributed the origin of solvent shifts to the specific association of solvents with the hydrogen bonded complex;

$$\text{S-H} \cdots \text{O-H} \cdots \text{B(Base)},$$

where S-H denotes the solvent molecule. Later, Yoshida and Ōsawa[4)] interpreted the solvent shifts in terms of the dipolar association model, in which the solvent is preferentially oriented with its bond dipole toward the lone pair dipole of the hydroxyl group in the hydrogen bonded system. Furthermore, they assumed that the dipolar association exists as the following geometry.[4a)]

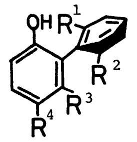
$$\begin{array}{l} \overset{\delta-}{\text{O}}\text{H} \cdots \overset{\delta+}{\text{B}} \\ \vdots \\ \underset{\delta+}{\text{H}}\text{-}\underset{\delta-}{\text{S}} \end{array}$$

Most of the studies in this field have been concerned with the intermolecular hydrogen bonding. However, there has been little systematic study of the intramolecular hydrogen bonding, primarily because of the complexity of the factors affecting the solvent sensitivity. In case of the intramolecular hydrogen bonding, the solvent shifts can be expected to be affected by the geometric effects as well as the electronic effects if the specific solvent-solute association is an important factor in determining the solvent shifts.

In this paper, the effects of solvents on the intramolecular OH···π and OH···O hydrogen bonding in 2-arylphenols (**1**—**7**) and 2,6-diarylphenols (**8**—**13**) are investigated by means of IR spectroscopy, and the solvent-solute association model is discussed through the geometric effects on the solvent sensitivity.

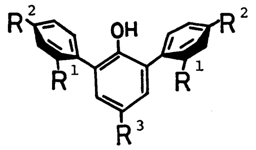
^{1}H NMR spectroscopy is also a powerful method for the study of the geometry for the solvent-solute association model. The aromatic solvent-induced shifts in the PMR spectra of Compound (**8**) are nicely explained in terms of the model derived from the IR study.

2-arylphenols



1 $R^1=R^2=R^3=R^4=H$
2 $R^1=R^2=R^4=H$, $R^3=CH_3$
3 $R^1=R^3=CH_3$, $R^2=R^4=H$
4 $R^1=OH$, $R^2=R^3=R^4=H$
5 $R^1=OH$, $R^2=R^3=CH_3$, $R^4=H$
6 $R^1=OCH_3$, $R^2=R^3={}^4R=H$
7 $R^1=R^2=R^3=H$, $R^4=NO_2$

2,6-diarylphenol



8 $R^1=R^2=R^3=H$
9 $R^1=CH_3$, $R^2=R^3=H$
10 $R^1=R^2=H$, $R^3=NO_2$
11 $R^1=CH_3$, $R^2=H$, $R^3=NO_2$
12 $R^1=H$, $R^2=CH_3$, $R^3=NO_2$
13 $R^1=H$, $R^2=C(CH_3)_3$, $R^3=NO_2$

Results and Discussion

IR Spectra. In nonpolar solvents such as CCl_4, 2-arylphenols (**1**, **2**, **3**, **5**, and **7**) show the doublet νOH absorptions, corresponding to the free and the intramolecularly OH···π hydrogen bonded hydroxyl groups, while 2,6-diarylphenols (**8**—**13**) have only a singlet νOH due to the intramolecular OH···π hydrogen bonding. In addition to the observed doublet, the other 2-arylphenols (**4** and **6**) exhibit a broad third band centered at about 3450 cm^{-1}, indicating the presence of intramolecular OH···O hydrogen bonding. These assignments are based on the reported IR spectra of similar compounds.[7,8)] Some typical νOH absorption spectra are reproduced in Fig. 1.

Table 1 summarizes the intramolecularly OH···π and OH···O hydrogen-bonded OH stretching frequencies in the same set of solvents, together with the solvent constants. The OH···π and OH···O frequencies in the

TABLE 1. INTRAMOLECULAR OH···π AND OH···O HYDROGEN BONDED OH STRETCHING FREQUENCIES (cm^{-1}) IN THE SAME SET OF SOLVENTS[a] AND SOLVENTS CONSTANTS

Solvent	Solvent constants		1	2	3	4		5
	G	$\Delta\nu/\nu$				OH···π	OH···O	
(Vapor)	0	0	(3587)	(3580)	(3571)	(3569)	(3538)	(3553)
Hexane	44	7.0	3573.0	3566.6	3558.3	3558.4	—b)	3544.3
Cyclohexane	49	7.6	3570.2	3564.2	3557.5	3556.6	—b)	3543.9
Decalin	58	8.8	3566.6	3563.0	3555.7	3555.7	3483	3542.0
Tetrachloroethylene	64	9.4	3565.7	3560.2	3553.0	3554.8	3478	3541.1
Carbon tetrachloride	69	9.9	3564.8	3561.1	3553.9	3555.7	3474	3542.0
Benzene	80	11.1						
Dichloromethane	100	14.0	3554.8	3550.5	3542.7	3549.3	3440	3534.8
Bromoform	118	17.0	3547.5	3544.0	3539.4	3540.3	3429	3530.5

Solvent	6		7	8	9	10	11	12	13
	OH···π	OH···O							
(Vapor)	(3579)	(3499)	(3569)	(3573)	(3567)	(3554)	(3545)	(3547)	(3546)
Haxane	3566.6	3460	3551.1	3560.2	3554.8	3539.3	3532.0	3533.0	3533.0
Cyclohexane	3564.1	3456	3548.4	3558.5	3553.8	3536.6	3531.4	3531.4	3531.4
Decalin	3563.9	3450	3543.9	3555.5	3551.0	3533.9	3525.7	3527.5	3526.6
Tetrachloroethylene	3561.4	3442	3542.0	3555.7	3549.4	3531.1	3524.8	3525.0	3526.4
Carbon tetrachloride	3562.0	3441	3543.9	3555.7	3550.0	3532.0	3527.5	3527.5	3527.5
Benzene				3549.3	3544.1	3524.0	3518.6	3518.0	3516.7
Dichloromethane	3551.7	3409	3527.6	3543.8	3539.0	3519.7	3513.0	3512.8	3513.0
Bromoform	3545.5	3397	3520.9	3540.2	3535.7	3514.1	3511.0	3510.5	3511.0

a) The νOH frequencies differ slightly from the results for the same materials reported in a preliminary communication.[1] The data were obtained in separate experimental studies on different spectrometers. b) The apparent intensity was too weak to obtain a reliable value.

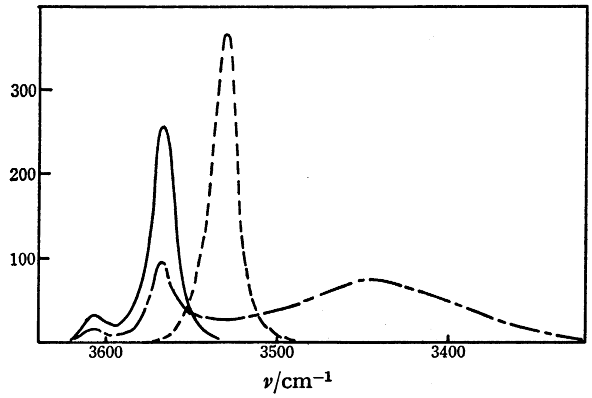


Fig. 1. νOH Absorptions of **1**, **6**, and **10** in CCl_4.
——(**1**), ———(**6**), ----(**10**).

vapor phase were estimated by interception at $G=0$ in the G correlations (see Fig. 2), according to the previously reported procedure.[2,4] The G value is the solvent constant empirically assigned to the solvent by Allerhand and Schleyer in order to explain the solvent sensitive IR bands.[2] The relative solvent shifts, $\Delta\nu/\nu$, of the νC=O of acetophenone are used as the reference value in the Bellamy-Hallam-Williams (BHW) plot.[9] The choice of solvents was limited to inert solvents which can not act as proton acceptors, because the proton acceptor solvents produce intermolecular hydrogen bonding.[10,11]

It is found from Table 1 that the frequencies of the hydrogen bonded bands, νOH···π and νOH···O, are fairly sensitive to the change of solvent. These solvent shifts correlate linearly with both the G and $\Delta\nu/\nu$ values. Figures 2 and 3 show the G correlation and the BHW plot respectively. The success of both correlations suggests that the operation of the solvation mechanism in the OH···π bonded system is similar to that in the

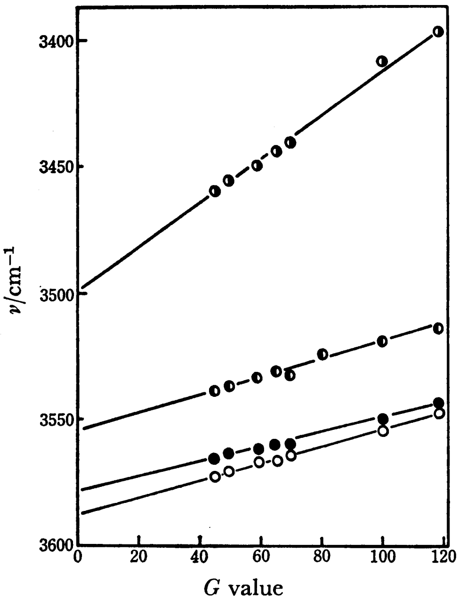


Fig. 2. Correlation of the OH stretching frequencies of OH···π and OH···O hydrogen bonds with the G values of the solvents.
1 (○), **6** (OH···π, ●; OH···O, ◑), **10** (◐).

TABLE 2. SOLVENT SENSITIVITY, IR SPECTRAL DATA, AND DIHEDRAL ANGLE OF THE OH···π AND OH···O HYDROGEN-BONDED SYSTEMS

		a	$1/S$	$\Delta\nu_{\max}/\mathrm{cm}^{-1}$ a)	A_i/A_f b)	Dihedral angle (θ)/deg	K band $\lambda_{\max}$/nm
2-Arylphenols							
1		0.33	0.69	42.2	6.7	50° e)	245.5
2		0.30	0.64	47.5	11.2	60° e)	245.5
3		0.27	0.56	54.5	16.4	70° e)	240.0
4	OH···π	0.23	0.50	44.5	9.1		
	OH···O	0.94	2.00	126	— c)		
5		0.19	0.40	62.7	42.0	70°—90°	Submerged
6	OH···π	0.28	0.60	42.8	7.8		
	OH···O	0.85	1.90	164	39.7		
7		0.40	0.87	47.3	9.6		
2,6-Diarylphenols				$\nu_{i\,\max}/\mathrm{cm}^{-1}$ d)	$A_i\times10^{-4}$ f)		
8		0.28	0.61	3555.7	1.89	60°(52°) g)	241.0
9		0.27	0.58	3550.0	2.01	70°	236.0
10		0.34	0.74	3532.0	2.60	(58°) g)	
11		0.30	0.67	3527.5	2.85		
12		0.32	0.74	3527.5	2.73		
13		0.32	0.75	3527.5	3.04		

a) νOH(free)–νOH(OH···π or OH···O). b) Relative integrated intensities; A_i(OH···π or OH···O)/A_f(free). c) The A_i value could not be determined because of the very weak intensity. d) νOH···π. e) See Ref. 8. f) Integrated intensisies; A_i(OH···π)/mol^{-1} l cm^{-2}. g) Our X-ray results; see Ref. 20.

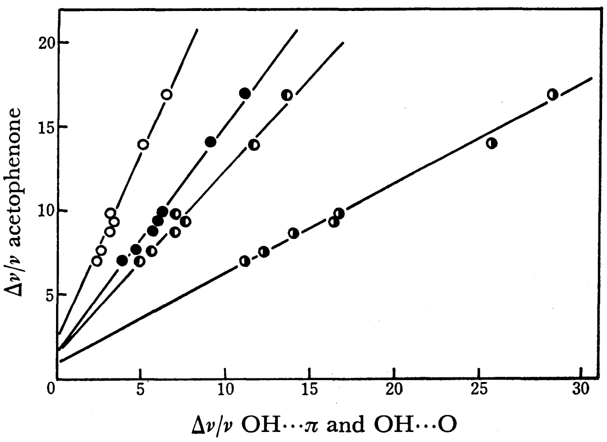


Fig. 3. BHW plots of νOH···π and νOH···O frequencies against the νC=0 frequencies of acetophenone. **1** (●), **5** (○), **7** (◐), **6** (OH···O; ◑).

carbonyl group12) and that the solvent shifts are mainly produced by a specific solvent-solute association rather than by general dielectric effects, because (1) Bellamy *et al.* showed that the solvent dependency of the νC=O frequency is primarily due to a specific solvent-solute association,9) and (2) the G value does not fit the KBM, Pullin, and Buckingham equations based on the dielectric theory.2)

As can be seen from Figs. 2 and 3, the slopes in both correlations vary widely from compound to compound. It is known that the slope of the G correlation (a)2) and the reciprocal slope of the BHW plot $(1/S)$13) become direct measures of the solvent sensitivity.

Table 2 lists the a and $1/S$ values, the IR spectral data, and the dihedral angle between the phenol ring and the proton acceptor ring. In the IR data, both A_i/A_f and $\Delta\nu_{\max}$ can indicate the strength of the hydrogen bonding in 2-arylphenols.14) With 2,6-diarylphenols without a free hydroxyl group, both A_i and $\nu_{i\,\max}$ are adopted as a measure of the strength of the OH···π bonding.15) The dihedral angle was roughly estimated from the K-band maxima of these compounds in heptane in the UV spectra, according to the established method.8,16) From the data in Table 2, the strength of the OH···π hydrogen bonding is found to increase with the increase in the dihedral angle. This trend is consistent with those reported by Ōki and Iwamura,8) who studied the steric effects on the OH···π hydrogen bonding in 2-arylphenols.

For the intermolecular hydrogen bonding, Yoshida *et al.*4) reported the parallelism between the $1/S$ value and the strength of the hydrogen bonding. This fact is consistent with the dipolar association theory, in which the bond dipole of the solvent associates with the lone pair dipole of the hydrogen bonded system, because the lone pair dipole increases with the strength of the hydrogen bonding.

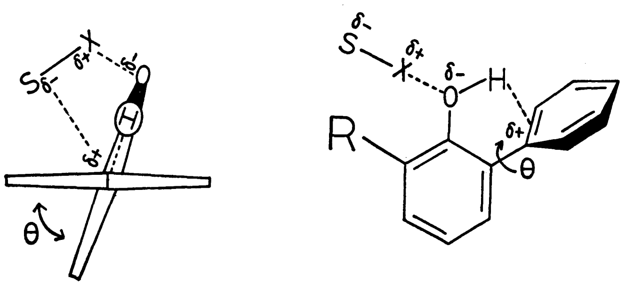
In case of the OH···π hydrogen bonding, the component of the dipole electric field is in the $\overset{\delta-}{\mathrm{O}}\mathrm{H}\cdots\!\leftarrow\overset{\delta+}{\pi}$ direction, because the charge-transfer plays an important role in this hydrogen bonded system.17) Furthermore, the oxygen lone pair dipole on the OH group reinforces the component of the dipole due to the charge-transfer. Therefore, the dipolar association theory can also be applied to the intramolecular OH···π hydrogen bonding now being studied, as with the ordinary hydrogen bonding.

In contrast to Yoshida's result, it is clear from Table 2 that the proportional correlation between the solvent sensitivity and the strength of the OH···π bonding does not hold in this case; rather, both the a and $1/S$ values seem to be inversely proportional to the A_i, A_i/A_f, ν_i, and $\Delta\nu$ values. However, it seems that our observation can be reconciled with Yoshida's dipolar association theory by considering the difference between inter- and intramolecular hydrogen bonded system.

For the intermolecular hydrogen bonding, such electronic effects as the strength of the hydrogen bonding are important factors in the dipolar association. On the other hand, for the intramolecular hydrogen bonding, the steric effects on the dipolar association seem to play a larger part than the electronic effects,[18] since the OH···π bonded system is fixed in the same molecule by the molecular geometry. Therefore, the lack of the correlation proposed by Yoshida *et al.* can be interpreted by assuming that the steric effects are so great that the electronic effects are masked.

By comparing the solvent sensitivity for the compound pairs of **1** and **7**, **8** and **10**, and **9** and **11**, it is noted that the nitrophenols (**7**, **10**, and **11**) show a and $1/S$ values larger than those for the corresponding phenols without the nitro group (**1**, **8**, and **9**) (see Table 2). The electron withdrawing nitro substituent produces a stronger OH···π hydrogen bonding, but does not greatly alter the stereochemical environment around the dipole of the OH···π bonded system. For these pairs of compounds, therefore, only the electronic effects can be operative in determining the solvent sensitivity. This result supports the dipolar association theory.

In order to investigate the steric effects on the dipolar association, both a and $1/S$ values are compared with the structural changes over a group of phenols. As can be seen from Table 2, both a and $1/S$ values appear to decrease with an increase in the dihedral angle; the observed order in the solvent sensitivity for the similar structural class is as follows; **7**>**1**>**2**>**3**, **4**>**5**, **8**>**9**, **10**>**11**, **10**≃**12**≃**13**. This suggests that the solvent sensitivity is greatly affected by the steric factors, and supports the specific dipolar association mechanism in solvation to the OH···π bonded system.



R=H or aryl.

geometry (I) geometry (II)

Fig. 4. Schematic representation of the dipolar association between the bond dipole of the solvent and the dipole of the OH···π bonded system. S–X; solvent, θ; dihedral angle.

From the dihedral angular dependence of the solvent sensitivity, we propose a simplified model with the geometry (I) for the dipolar association between the dipole of the OH···π bonded system (involving the lone pair dipole) and the bond dipole of the solvent molecule, as is shown in Fig. 4. This model is based on a specific 1:1 solvent-solute interaction. The geometry (I) indicates that the approach of the bond dipole of the solvent to the dipole of the OH···π bonded system is made difficult by the larger dihedral angle, since the steric repulsion between the solvent molecule and the proton acceptor ring becomes more severe with an increase in the dihedral angle.

As another model, the geometry (II), in which the positive end of the dipole of the solvent associates with negative end of the dipole (the lone pair electrons) of the OH···π bonded system, is also shown in Fig. 4. In this model, however, there are no steric effects on the solvent-solute association, and so Yoshida's correlation should be held throughout all the phenols studied here. It seems that this model is significant only in a protic solvent[19] because of the formation of hydrogen bonding.

In the competitive intramolecular hydrogen bond formation between the OH···π and OH···O systems in **4** and **6**, the latter system shows a remarkably large solvent sensitivity. The OH···O hydrogen bonding in the biphenyl skeleton is possible only in either a planar or nearly planar conformation,[7b] while the OH···π hydrogen bonding is favored for the conformation in which the dihedral angle becomes larger.[8] For example, 2-arylphenol (**5**), with a nearly perpendicular conformation, shows no OH···O bonding, but a strong OH···π interaction (see Table 2). Furthermore, in general, the strength of the OH···O bonding is greater than that of the OH···π bonding (see Table 2). Therefore, the trend in the observed solvent sensitivity can be interpreted in terms of both electronic and dihedral angular effects, supporting the model with the geometry (I).

Another steric factor which can affect the solvent sensitivity is the presence of alkyl substituents in the proton acceptor ring. In addition to the dihedral angular effects, an *ortho* methyl group in the proton acceptor ring also hinders the bond dipole of the solvent from approaching the dipole of the OH···π bonded system, as is anticipated from the geometry (I). Furthermore, the introduction of the alkyl group to the *para* position of the proton acceptor ring (**12** and **13**) produces little variation in the solvent sensitivity (see Table 2). If the dipolar association exists in the geometry (II), the dipolar association will be made difficult by the presence of the *para* alkyl group, because the *para* alkyl group on the opposite side of the OH···π bond is expected to hinder the approach of the solvent molecule (the positive end of the dipole) to the lone pair electrons on the oxygen atom (the negative end of the dipole). Therefore, the absence of any effects of the *para* alkyl group on the solvent sensitivity agrees with the geometry (I), because the alkyl group at the *para* position is well removed from the site of the dipolar association.

PMR Spectra. The chemical shifts (δ) of the PMR spectra of 2,6-diphenylphenol (**8**) in CCl_4, in benzene-d_6, and hexafluorobenzene and the solvent shifts ($\Delta\delta=\delta_{\mathrm{CCl_4}}-\delta_{\mathrm{C_6D_6\ or\ C_6F_6}}$) are given in Table 3. For comparison, this Table also includes the IR frequency shifts in these solvents. Compound (**8**) with a single polar site was selected for this study, because the aromatic solvent-induced shifts (ASIS) become more complex for a compound with multiple polar sites.[21] The observed ASIS are due to the dipolar association of the aromatic solvent with the OH···π bonded system,

Table 3. Proton chemical shifts (δ) and OH stretching frequencies (νOH) in CCl_4, C_6D_6, and C_6F_6 and solvent shifts ($\Delta\delta$ and $\Delta\nu$OH) of 2,6-diphenylphenol

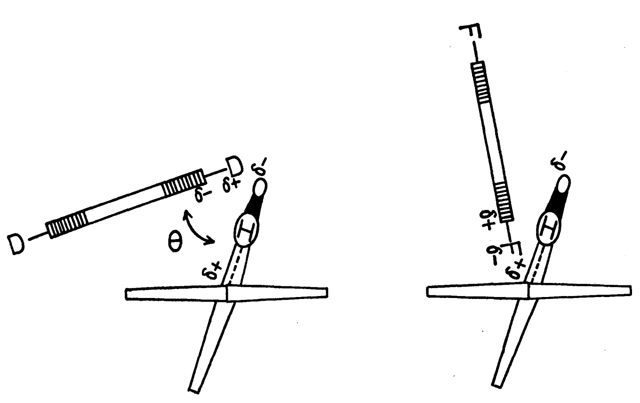
Proton chemical shifts (ppm)			
	OH proton		
	CCl_4	C_6D_6	C_6F_6
δ	5.12	5.15	5.36
$\Delta\delta$		−0.03	−0.24
	2,6-Ring protons[a]		
	CCl_4	C_6D_6	C_6F_6
δ	7.42	7.13	7.43
$\Delta\delta$		0.28	−0.01
OH stretching frequencies (cm^{-1})			
	CCl_4	C_6H_6	C_6F_6
νOH	3555.7	3549.3	3559.3
$\Delta\nu$OH		6.4	−3.6

a) Estimated from the δ value of the strongest peak.

not to the intermolecular OH···π bond formation,[22] since these IR shifts follow a common pattern obtained for other inert solvents studied here (see Figs. 2 and 3).

It is known[24] that the direction of the ASIS with C_6D_6 is opposed to that with C_6F_6. As may be seen in Table 3, however, both C_6D_6 and C_6F_6 produced more complex ASIS results. This seeming anomaly can be interpreted by assuming the asymmetric deformation of the geometry for the dipolar association caused by the steric requirement. In order to explain these ASIS results, the schematic representation of the dipolar association between the bond dipole of C_6D_6 and of C_6F_6 solvent molecules and the dipole of the OH···π bonded system is shown in Fig. 5; the direction of the bond dipole of the $\overset{\delta-}{\mathrm{C}}\leftarrow\overset{\delta+}{\mathrm{D}}$ bond in C_6D_6 shows a sign opposite to that of the $\overset{\delta+}{\mathrm{C}}\rightharpoonup\overset{\delta-}{\mathrm{F}}$ in C_6F_6.[24a)]

In C_6D_6 solvent, a slight downfield shift for the OH proton and an upfield shift for the ring protons at the 2,6-positions of the phenol are observed. As is shown in model A, the π-electron cloud on the C_6D_6 molecule, which is attracted by the dipolar association, will be repelled by the π-electron cloud on the proton acceptor ring, thus increasing the angle, θ, between the dipole of the OH···π bonded system and the bond dipole of the overlying C_6D_6 solvent molecule. The large angle should cause a large remove of the OH proton from the center of the C_6D_6 molecule, so that the OH proton may be expected to lie near the edge of the aromatic shielding cone or the weak deshielding region of the C_6D_6 molecule. As another possible source of the ASIS effects, the charge polarization and variation in the bond order for the OH bond arising from a change in the solvent must be considered. On passing from CCl_4 to C_6H_6, the OH stretching frequency falls by 6.4 cm^{-1} (see Table 3). This electronic effect will cause the downfield ASIS of the OH proton. Thus, the slight deshielding of the OH proton in C_6D_6 can be explained in terms of the combination of the ring current and electronic effects. Furthermore, the upfield shifts for the ring protons must be eonsidered in the same model. When the C_6D_6 solvent molecule approaches the proton acceptor ring (hereafter abbreviated as Ring I) with the positive end of the dipole, the other ring (hereafter Ring II) will be further removed from the same C_6D_6 solvent molecule. Therefore, the protons on Ring I will be strongly shielded, and those on Ring II, weakly deshielded. As the average ASIS effect, therefore, the upfield shift was observed in C_6D_6 solvent, supporting the model A.[25]



model (A) model (B)

Fig. 5. Schematic representation of the dipolar association between the bond dipole of benzene and of hexafluorobenzene and the dipole of the OH···π bonded system.

On the other hand, C_6F_6 gives a downfield shift in the OH proton and little variation in the ASIS of the ring protons. It is possible to expect the approach of the fluorine of the C_6F_6 periphery to the positive end of the dipole of the OH···π bonded system, since the van der Waals radius for fluorine (1.35 Å) is almost equal to that for hydrogen (1.2 Å). As is to be anticipated from the model B, the OH proton will be in the deshielding region of the C_6F_6 ring, in spite of the repulsion of the π-electron cloud on the C_6F_6 solvent molecule and the oxygen lone pair electrons. Accordingly, the OH proton should have a downfield shift, although the OH stretching frequency rises by 3.6 cm^{-1}. At the same time, this model shows that the protons on Ring I and II are in the deshielding and shielding region of the C_6F_6 solvent molecule respectively, since the C_6F_6 could be situated along the dipole of the OH···π bonded system. These ASIS, therefore, should cancel each other. In short, the direction of the ASIS can be nicely explained in terms of the model B.

Consequently, it is found that these ASIS results support the model derived from the IR study.

Experimental

Measurement of the Spectra. The infrared spectra were recorded on a JASCO DS-701G grating spectrometer. The spectral slit width under high resolution conditions was 2 cm^{-1} in the region 3200—3700 cm^{-1}. Sodium chloride cells of 1 and 2 mm thicknesses were used. The concentration of phenols was about 5×10^{-3} M. The frequencies were calibrated by the standard absorption line of water vapor (3568.5 and 3447.2 cm^{-1}). The precision of the measurements on νOH was about 2 cm^{-1} for the OH$\cdots\pi$ band and about 5 cm^{-1} for the broader OH$\cdots$O band. All the measurements were carried out at 35 °C. Proton chemical shifts were measured on a JEOL PS-100 spectrometer operating at 100 MHz by using TMS as the internal standard at normal probe temperatures (*ca.* 35 °C). Frequency calibration was provided by the use of standard side-band techniques employing an audio-frequency counter. The measured relative chemical shifts are believed accurate to ± 0.1 Hz. The ultraviolet absorption was obtained with a Hitachi 124 automatic recording spectrophtometer in 1.0 cm quartz cells at room temperature. The concentration of the samples in heptane was 10^{-5}—10^{-4} M.

Materials. Most of the solvents for spectra measurements were spectro-grade solvents and were used without further purification. Bromoform and decalin were purified by known methods.[27] Compound (**1**) was a commercial sample, recrystallized before use. Compounds (**2**),[8] (**3**),[8] (**4**),[28] (**5**),[29] (**6**),[28] (**7**),[7a] and (**12**)[30] were prepared according to the published procedures. Compounds (**8**)—(**11**) were prepared earlier.[10]

Preparation of 13. To a mixture of *t*-butyl chloride (4.3 g, 46.5 mmol) and **10** (2 g, 6.9 mmol) was added powered aluminium chloride (0.4 g, 3 mmol) at 40 °C. The mixture was then stirred for 5 h. A subsequent in the usual way gave a brown solid which was chromatographed on silica gel; elution with benzene–hexane (5: 1) afforded **13** (1.4 g, 52%). Recrystallization from benzene–hexane gave yellow plates; mp 162—164 °C. Found: C, 77.49; H, 7.29; N, 3.50%. Calcd for $C_{26}H_{29}O_3N$: C, 77.39; H, 7.24; N, 3.47%.

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