

96556-35-3; 3-(benzyloxy)-1-butyl methyl ether, 96556-36-4; 4-(benzyloxy)-2-methyl-2-pentyl methyl ether, 96556-37-5; 3-methoxy-3-methyl-1-butyl benzyl ether, 96556-38-6; 4-methoxy-2-methyl-2-pentyl benzyl ether, 96556-39-7; 3-(benzyloxy)-2-methyl-1-propanol, 56850-59-0; 2-methyl-1,3-propanediol, 2163-42-0; 3-(benzyloxy)-2,2-dimethyl-1-propanol, 66582-32-9; 3-(benzyloxy)-2-methylpropanol, 73814-73-0; 3-(benzyloxy)-2,2-di-

methylpropanal, 38216-93-2; methyl 3-(benzyloxy)-2,2-dimethylpropionate, 96556-40-0; 3-(benzyloxy)-2-methyl-1-propanol-1-*d*, 96556-41-1; 3-(benzyloxy)-2,2-dimethyl-1-propanol-1,1-*d*<sub>2</sub>, 96556-44-4; 3-(benzyloxy)-2-methylpropyl *p*-toluenesulfonate, 96556-45-5; 3-(benzyloxy)-2,2-dimethylpropyl *p*-toluenesulfonate, 96556-46-6; 3-methoxy-2-methylpropyl benzyl ether, 96556-42-2; 3-methoxy-2,2-dimethylpropyl benzyl ether, 96556-43-3.

## Steric Effects on Hydrogen Bonding of 4-Nitro-2,6-diarylphenols with Bases

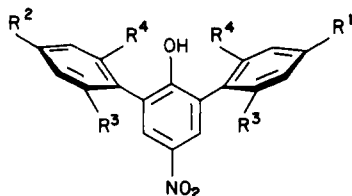
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The thermodynamics of hydrogen bonding of 4-nitro-2,6-diarylphenols with a variety of proton acceptor bases have been studied by examining the hydroxyl stretching IR absorption spectra in CCl<sub>4</sub> solution. Their IR spectra show the existence of competitive interaction between intramolecular OH···π and intermolecular OH···B (B = base) hydrogen bonding. For the intermolecular OH···B hydrogen bond formation, the <sup>1</sup>H NMR study suggests that the hydroxyl group is approximately coplanar with the phenol ring, even in these sterically hindered phenols. The variation of the thermodynamic parameters caused by the steric effects can be well understood on the basis of this model. The steric effects on the hydrogen bond formation are found to affect not only the enthalpy but also the entropy changes. In the correlation between -Δ*H* and -Δ*S* values, anomalous behavior is observed for hydrogen bonding with Me<sub>2</sub>SO.

There is little thermodynamic data available on hydrogen bonding between sterically hindered phenols and bases, in contrast to the extensive investigations of simple hydrogen bonded systems.<sup>1</sup> As to steric effects on hydrogen bonding, some discrepancies have appeared in the literature. Singh and Rao<sup>2</sup> reported that the enthalpies of hydrogen bonding are nearly equal for both unhindered and hindered systems. On the other hand, Yoshida and Ishibe<sup>3</sup> found that the steric effects on hydrogen bonding could influence not only the enthalpy but also the entropy factors. In most studies of the hindered hydrogen bonded systems, 2,6-dialkylphenols (like 2,6-dimethyl-<sup>3</sup> or 2,6-di-*tert*-butylphenols<sup>2</sup>) were used to investigate the steric effects on the hydrogen bonding. For this study, we have selected 4-nitro-2,6-diarylphenols<sup>4</sup> 1-6 in which the steric



1. R<sup>1</sup> = R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H
2. R<sup>1</sup> = R<sup>2</sup> = CH<sub>3</sub>; R<sup>3</sup> = R<sup>4</sup> = H
3. R<sup>1</sup> = R<sup>2</sup> = C(CH<sub>3</sub>)<sub>3</sub>; R<sup>3</sup> = R<sup>4</sup> = H
4. R<sup>1</sup> = R<sup>2</sup> = H; R<sup>3</sup> = CH<sub>3</sub>; R<sup>4</sup> = H
5. R<sup>1</sup> = R<sup>2</sup> = H; R<sup>3</sup> = R<sup>4</sup> = CH<sub>3</sub>
6. R<sup>1</sup> = C(CH<sub>3</sub>)<sub>3</sub>; R<sup>2</sup> = R<sup>3</sup> = R<sup>4</sup> = H

effects seem to be more serious than 2,6-dialkylphenols; the IR spectra of these phenols indicate a single hydroxyl stretching band (without a free OH band) due to an intramolecular OH···π bond in CCl<sub>4</sub> solution.<sup>5,6</sup>

In this paper, the thermodynamic values, -Δ*G*, -Δ*H*, and -Δ*S*, for the competitive interaction between the intramolecular OH···π and the intermolecular OH···B (B = base) hydrogen bonding were determined by the use of IR spectroscopy. The steric effects on these hindered hydrogen bonds are discussed in relation to the variation of the thermodynamic values obtained. The probable geometry for these hydrogen bonded systems is deduced roughly on the basis of the results of the steric effects and of their <sup>1</sup>H NMR spectra. The thermodynamic values obtained for the hindered systems are used to test the correlations of -Δ*H* vs. -Δ*S* and -Δ*H* vs. Δ*ν* [ν(OH···π) - ν(OH···B)].

### Experimental Section

**Materials.** Most of the solvents were spectrograde reagents and were distilled from calcium hydride immediately before use. Cyclohexanone and benzonitrile were purified by a known method.<sup>7</sup> Compounds 1-4 were prepared as previously.<sup>6</sup>

**4-Nitro-2,6-bis(2',6'-dimethylphenyl)phenol (5).** 1-Methoxy-2,6-diiodo-4-nitrobenzene<sup>8</sup> (3 g, 7.4 mmol), 2,6-dimethylbromobenzene (6.8 g, 37 mmol), and copper bronze (15 g) were mixed and heated at 180 °C for 1-2 h; after the reaction set in, the temperature was then raised to 250 °C. The reaction mixture was cooled to room temperature and extracted with acetone. The extract was concentrated and chromatographed on a silica gel column to give the crude product of 1-methoxy-2,6-bis(2',6'-dimethylphenyl)-4-nitrobenzene, which was used in the following demethylation without further purification. To a solution of the crude anisole derivative (0.32 g) in acetic acid (10 mL), aqueous hydrogen bromide (10 mL, 47%) and acetic anhydride (2 mL) were added, after which the mixture was heated for 6 h. The mixture was then poured onto ice water and extracted with chloroform. The recrystallization of the acidic part from CCl<sub>4</sub>-hexane gave 0.22 g of 5; mp 180-182 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 2.06 (s, 12 H), 5.17 (s, 1 H), 7.08-7.20 (m, 6 H), 8.01 (s, 2 H). Anal. Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>N: C, 76.06; H, 6.09; N, 4.03. Found: C, 76.11; H, 6.13; N, 4.01.

**4-Nitro-2-phenyl-6-(4'-*tert*-butylphenyl)phenol (6).** This phenol was formed as a byproduct (ca. 5%) in the preparation

(1) Joesten, M. D.; Schadd, L. J. "Hydrogen Bonding"; Marcel Dekker, Inc.: New York, 1974; pp 239-381.

(2) Singh, S.; Rao, C. N. R. *J. Am. Chem. Soc.* 1966, 88, 2142.

(3) Yoshida, Z.; Ishibe, N. *Bull. Chem. Soc. Jpn.* 1969, 42, 3259.

(4) Some of these phenols were used to discuss briefly the steric effects on hydrogen bonding with alkyl cyanides in the previous paper: Ueji, S.; Ueda, N.; Kinugasa, T. *J. Chem. Soc., Perkin Trans.* 2 1976, 178.

(5) Ōki, M.; Hosoya, H.; Iwamura, H. *Bull. Chem. Soc. Jpn.* 1961, 34, 1391, 1395.

(6) Ueji, S. *Bull. Chem. Soc. Jpn.* 1978, 51, 1799.

(7) Riddick, J. A.; Bunger, W. B. "Organic Solvent", 3rd ed.; Wiley-Interscience: New York, 1970; pp 729, 808.

(8) Block, P. J.; Powell, G. *J. Am. Chem. Soc.* 1942, 64, 1070.

**Table I. Thermodynamic Data for Hydrogen Bond Formation of 1-5 with Proton Acceptor Bases in CCl<sub>4</sub> at 28.5 °C**

bases		1	2	3	4	5
Me <sub>2</sub> SO	-ΔG <sup>a</sup>	2.00	1.53	1.45	2.10	2.00
	-ΔH <sup>b</sup>	5.98	4.79	4.69	5.51	5.30
	-ΔS <sup>c</sup>	13.2	10.8	10.7	11.3	10.9
benzotrile	-ΔG	0.12	0.09	-0.06	0.19	0.15
	-ΔH	4.11	3.04	2.65	4.07	4.00
	-ΔS	13.2	9.8	9.0	13.0	13.0
THF	-ΔG	0.57	0.36	0.32	0.62	0.60
	-ΔH	5.10	4.47	4.26	4.73	3.83
	-ΔS	15.0	13.6	13.1	13.6	10.7
dioxane	-ΔG	0.39	0.22	0.13	0.49	0.42
	-ΔH	4.37	3.17	2.93	4.25	3.55
	-ΔS	13.2	9.8	9.3	12.5	10.4
cyclohexanone	-ΔG	0.57	0.34	0.24	0.69	0.71
	-ΔH	4.76	3.11	2.84	4.33	3.87
	-ΔS	13.9	9.2	8.6	12.1	10.5

<sup>a</sup> kcal/mol. <sup>b</sup> kcal/mol. <sup>c</sup> cal/(mol deg).

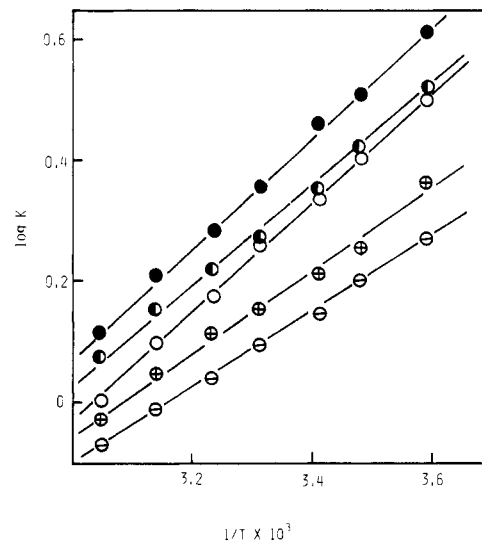
of 3:<sup>6</sup> mp 140–141 °C; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 1.34 (s, 9 H), 6.02 (s, 1 H), 7.40–7.63 (m, 9 H), 8.17 (s, 2 H). Anal. Calcd for C<sub>22</sub>H<sub>21</sub>O<sub>3</sub>N: C, 76.06; H, 6.09; N, 4.03. Found: C, 76.14; H, 6.05; N, 4.00.

**Measurement of Spectra.** All the IR spectra were recorded on a JASCO DS-701G grating spectrometer. The concentration ranged from 0.003 to 0.008 M for the phenols and from 0.07 to 0.4 M for the proton acceptor bases in CCl<sub>4</sub> solution. CaF<sub>2</sub> cells having path lengths of 2 mm were placed in a thermostated air bath and were permitted to stand for at least 15 min before running the spectra. The air bath was kept constant within ±0.1 °C, but the precision of the temperature in the sample was within ±1.0 °C in the range 5.5–20.0 °C and within ±0.5 °C in the range 28.5–55.0 °C. The other conditions for determination of the spectra were the same as in the previous paper.<sup>6</sup> The <sup>1</sup>H NMR spectra were obtained with a JEOL PS-100 spectrometer operating at 100 MHz in the same conditions described in the previous paper.<sup>6</sup>

**Analysis of IR Spectra.** In the presence of the proton acceptor bases (listed in Table I), the OH stretching IR absorption spectra of 1–5 in CCl<sub>4</sub> solution were all doublets. These IR spectra show that there is a competition between the intramolecular OH···π (sharp band) and the intermolecular OH···B (broad band) hydrogen bonds. The equilibrium constant *K* is calculated according to the equation  $K = C_1/C_2C_3$ , in which *C*<sub>1</sub>, *C*<sub>2</sub>, and *C*<sub>3</sub> are the concentrations of the intermolecular hydrogen bonded complex (OH···B), the intramolecular OH···π hydrogen bonded complex, and the unbonded acceptor base, respectively. Also,  $C_1 = C_2' - C_2$  in which *C*<sub>2</sub>' is initial concentration of the phenol, and *C*<sub>2</sub> can be calculated from the plots of absorbance against concentration for each phenol in CCl<sub>4</sub> solution (in the absence of the base), at temperatures (5.5, 14.0, 20.0, 28.5, 36.0, 45.5, and 55.0 °C) chosen for determination of the *K* values, as described in the previous paper.<sup>4</sup> Furthermore,  $C_3 = C_3' - C_1$  in which *C*<sub>3</sub>' is the initial concentration of the base. In determination of the *K* values, independent measurements were repeated several times for different concentrations of the proton acceptor base, because the value of -Δ*H* is very sensitive to errors in the *K* value. Then the -Δ*H* values were obtained from the plots of log *K* against 1/*T* (Figure 1). By use of the relations -Δ*G* = *RT* ln *K* and -Δ*G* = -Δ*H* + *T*Δ*S*, the values of -Δ*G* and -Δ*S* were obtained. The values of *K* are probably accurate to ±10%, of -Δ*H* to ±5% (the standard deviations, ±0.15 to ±0.25 kcal/mol), and of -Δ*S* to ±1 cal/(mol deg). The apparent absorptions were assumed to be the sum of the Lorentz curves and separated into the individual absorptions in doublet band.<sup>9</sup>

### Results and Discussion

Table I lists the values of -Δ*G*, -Δ*H*, and -Δ*S* obtained for the intermolecular hydrogen bonding of 1–5 with the bases in CCl<sub>4</sub> solution. The OH stretching frequencies ν(OH···B) and the frequency shifts Δν [ν(OH···π) - ν-



**Figure 1.** Plots of log *K* against 1/*T* for the intermolecular hydrogen bonding of 1–5 with dioxane: (○) 1, (⊕) 2, (⊖) 3, (●) 4, (⊙) 5.

**Table II. Frequencies<sup>a</sup> and Frequency Shifts<sup>b</sup> due to the Hydrogen Bond Formation in CCl<sub>4</sub> at 28.5 °C**

compd		dioxane	THF	benzotrile
1	ν(OH···B), cm <sup>-1</sup>	3285	3210	3360
	Δν(OH), cm <sup>-1</sup>	247	322	172
2	ν(OH···), cm <sup>-1</sup>	3305	3235	3375
	Δν(OH), cm <sup>-1</sup>	223	293	153
3	ν(OH···), cm <sup>-1</sup>	3295	3225	3390
	Δν(OH), cm <sup>-1</sup>	233	303	138
4	ν(OH···B), cm <sup>-1</sup>	3310	3230	3355
	Δν(OH), cm <sup>-1</sup>	218	298	173
5	ν(OH···B), cm <sup>-1</sup>	3310	3220	3355
	Δν(OH), cm <sup>-1</sup>	207	297	162

<sup>a</sup> The ν(OH···B) frequencies in Me<sub>2</sub>SO and cyclohexanone were omitted from the table. In Me<sub>2</sub>SO, the ν(OH···O) component so overlaps with ν(CH) that it is not easy to separate them. In cyclohexanone, the ν(OH···O) is too asymmetric to obtain reliable values; the same trend has been also observed in a simple phenol (Bellamy, L. J.; Pace, R. J. *Spectrochim. Acta, Part A* 1971, 27A, 705). <sup>b</sup> ν(OH···B).

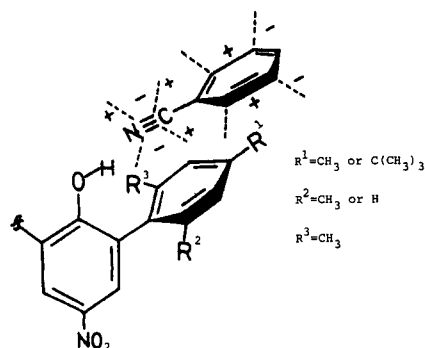
(OH···B)] as a measure of the strength of the OH···B hydrogen bonding are given in Table II.

For the comparison with recent thermodynamic data for hydrogen bonding of 4-nitrophenol with benzonitrile<sup>10</sup> [-Δ*G* = 1.96 kcal/mol, -Δ*H* = 6.54 kcal/mol, and -Δ*S* = 15.4 cal/(mol deg)] and dioxane<sup>11</sup> [-Δ*G* = 2.41 kcal/mol, -Δ*H* = 7.03 kcal/mol, and -Δ*S* = 15.5 cal/(mol deg)], introduction of the aryl groups to the 2- and 6-positions of 4-nitrophenol is found to cause a marked decrease of the thermodynamic values, because of the serious steric effects of 2,6-diaryl groups on the intermolecular hydrogen-bond formation (Table I). Furthermore, as can be seen from Table I, the thermodynamic values vary widely from compound to compound.

In order to investigate the probable geometry for the intermolecular hydrogen bonded system now being studied, the <sup>1</sup>H NMR spectra of 2–5 were measured in CDCl<sub>3</sub> and benzonitrile solvents. The base molecule we chose for this purpose is benzonitrile, because both the C≡N and the phenyl groups in this molecule have large anisotropy effects. The solvent shifts induced by their anisotropy are a sensitive probe for estimating the stereochemistry of the

(10) Jawed, I. *Bull. Chem. Soc. Jpn.* 1977, 50, 2602.

(11) Hudson, R. A.; Scoo, R. M.; Vinogradov, S. N. *J. Phys. Chem.* 1972, 76, 1989.



**Figure 2.** Schematic representation of the shielding (+) and deshielding (-) regions of benzonitrile molecule which is attracted by the intermolecular hydrogen bond formation.

**Table III. Chemical Shifts ( $\delta$ )<sup>a</sup> of Methyl and *tert*-Butyl Protons of 2-5 in  $\text{CDCl}_3$  and Benzonitrile and Solvent Shifts ( $\Delta$ )<sup>b</sup>**

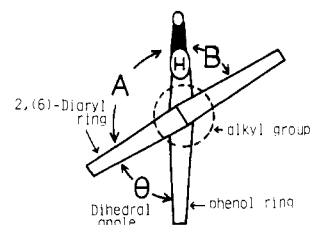
compd		$\text{CDCl}_3$	benzonitrile	$\Delta$
2	4'-Me	2.41	2.29	0.13
3	4'- <i>t</i> -Bu	1.35	1.28	0.07
4	2'-Me	2.19	2.25	-0.06
5	2',6'-Me	2.06	2.11	-0.05

<sup>a</sup> In parts per million to  $\text{Me}_4\text{Si}$ ; the error is within  $\pm 0.1$  Hz. <sup>b</sup>  $\delta$  ( $\text{CDCl}_3$ ) -  $\delta$  (benzonitrile).

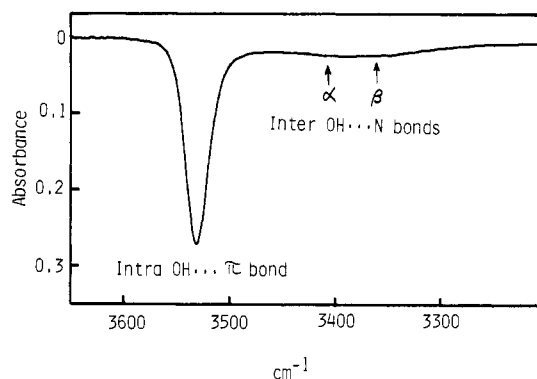
hydrogen bonded system. The chemical shifts  $\delta$  and the solvent shifts  $\Delta$  [ $\delta(\text{CDCl}_3) - \delta(\text{benzonitrile})$ ] of the alkyl groups of 2-5 are given in Table III. In benzonitrile solvent, 2 and 3 indicate the upfield shifts for the 4'-methyl and the 4'-*tert*-butyl protons, respectively, whereas 4 and 5 produce the downfield shifts for the 2'(6')-methyl proton(s). On the assumption that all of these solvent effects on the chemical shifts arise from the anisotropy effects of the benzonitrile molecule which is attracted by the intermolecular hydrogen bond formation, the geometrical model for the hydrogen bonded system is discussed briefly. In light of the anisotropy effects of the benzonitrile molecule, the direction of the NMR solvent shifts observed can be well understood by a simplified model in which the hydrogen bonding OH group is approximately coplanar with the phenol ring, even in these hindered phenols, as is shown in Figure 2. In this model, when the  $\text{OH}\cdots\text{N}$  distance is assumed to be 1.8-2.6 Å (see ref 12), the 4'-methyl group of 2 and 4'-*tert*-butyl group of 3 are immersed in the shielding region of the phenyl proton in the benzonitrile molecule, whereas the 2'(6')-methyl groups of 4 and 5 lie in the deshielding region of the nitrile portion in the benzonitrile molecule (Figure 2). For 3, the 4'-*tert*-butyl group will push up the overlaying benzonitrile molecule, causing the slant of its phenyl plane. Therefore, the 4'-*tert*-butyl protons may be expected to lie near the edge of the aromatic shielding cone of the slant phenyl plane, resulting in a smaller  $\Delta$  value (Table III). The model with a rather long  $\text{OH}\cdots\text{N}$  distance  $>3$  Å, however, cannot explain the feature of the NMR solvent shifts, because the 4'-alkyl groups are anticipated to be in the deshielding region of the nitrile portion of the benzonitrile molecule.

(12) In the estimation of the  $\text{OH}\cdots\text{N}$  distance, the following conditions should be fulfilled: (1) The limiting distance for the shortest  $\text{O}\cdots\text{N}$  is 2.5 Å.<sup>13</sup> (2) The limiting distance for the longest  $\text{H}\cdots\text{N}$  is based on Hamilton's criterion;<sup>13</sup>  $\text{H}\cdots\text{N}$  distance  $< W_{\text{H}} - W_{\text{N}} - 0.2$  Å, where  $W_{\text{H}}$  and  $W_{\text{N}}$  are the van der Waals radii of hydrogen (1.2 Å) and of nitrogen (1.6 Å), respectively. (3) The O-H distance (0.75 Å) for 1 obtained from our X-ray study<sup>14</sup> was used.

(13) Olovsson, I.; Jönsson, P. "The Hydrogen Bond"; Schuster, P., Zundel, G., Sandorfy, C., Eds.; North-Holland: New York, 1976; Vol. 2, Chapter 8.



**Figure 3.** Schematic representation of effects of the dihedral angle ( $\theta$ ) between the 2,6-diaryl rings and the phenol ring upon stereochemical environment around the hydroxyl group of the phenol.



**Figure 4.** OH stretching absorption spectrum of 4-nitro-2-phenyl-6-(4-*tert*-butylphenyl)phenol (6) (0.00489 M) in the presence of benzonitrile (0.347 M) in  $\text{CCl}_4$ .

In 1-3 (series I), the values of  $-\Delta G$ ,  $-\Delta H$ , and  $-\Delta S$  decrease in going from 1 to 3 and 2 and 3 show high  $\nu(\text{OH}\cdots\text{B})$  frequencies and small  $\Delta\nu(\text{OH})$  shifts as compared with 1. It is evident that the thermodynamic values decrease with increasing bulkiness of the 4'-alkyl group and that the presence of the 4'-alkyl group hinders the approach of the base molecule to the hydroxyl group of the phenols; the decrease of  $-\Delta H$  in series I may be attributed to a weaker bonding in a less restricted hydrogen bond configuration, and a smaller value for  $-\Delta S$  is therefore expected. Thus the steric effects of the 4'-alkyl groups in the thermodynamic data again suggest that the coplanarity of the hydrogen bonding OH group is not lost effectively, although the accuracy of the experimental results does not preclude the possibility of a slight twist of the OH group. As is shown in Figure 3, since 2,6-diarylphenols studied here have a rather large dihedral angle<sup>14</sup> between 2,6-diaryl rings and the phenol ring, the base molecule might be expected to approach the intramolecular  $\text{OH}\cdots\pi$  bonding OH group from a larger space, side A, with a minor loss of coplanarity of the OH group. If the OH group is markedly twisted away from the phenol ring, the steric effects of the 4'-alkyl groups will become insignificant. Furthermore, this model is also supported by the IR spectrum of 6, unsymmetrical 2,6-diarylphenol, which show the triplet  $\nu(\text{OH})$  with two kinds of the bonded  $\nu(\text{OH}\cdots\text{N})$  peaks unusually flat topped, in the presence of benzonitrile in  $\text{CCl}_4$  solution (Figure 4). The close doublet,  $\alpha$  and  $\beta$  bands, can be assigned to the OH group associated in the side of the phenyl ring with and without the *tert*-butyl group, respectively, on the basis of the  $\nu(\text{OH}\cdots\text{N})$  frequencies of 1 and 3 listed in Table II. The result of the coplanarity of the hydrogen bonding OH group is similar to those of Yoshida and Ishibe<sup>3</sup> and Tsuno et al.<sup>15</sup> who

(14) Ueji, S.; Nakatsu, K.; Yoshioka, H.; Kinoshita, K. *Tetrahedron Lett.* 1982, 23, 1173.

(15) Fujio, M.; Mishima, M.; Tsuno, Y.; Yukawa, Y.; Takai, Y. *Bull. Chem. Soc. Jpn.* 1975, 48, 2127.

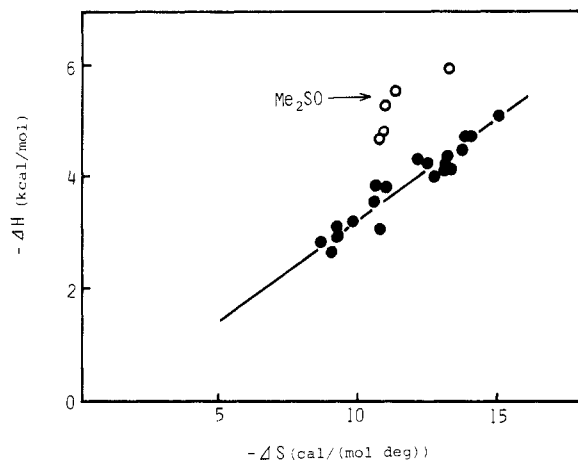


Figure 5. Correlation between  $-\Delta H$  and  $-\Delta S$ .

studied substituent effects on hydrogen bonding in 4-substituted 2,6-xylenols by the use of Hammett equation, although the phenols studied here are more seriously hindered systems than 2,6-xylenols.

On the other hand, for 1, 4, and 5 (series II), the steric effects of the 2'(6')-methyl group(s) are expected to be insignificant, because the hydrogen bonding site is well removed from the 2'(6')-methyl group(s) in the above model for the hydrogen bonded system. However, series II shows a complex variation of the thermodynamic values (Table I). Introduction of methyl group(s) to the 2'-and/or 6'-position(s) of 2,6-diaryl rings produces an increase of the dihedral angle between the 2,6-diaryl rings and the phenol ring. The values of  $-\Delta H$  and  $-\Delta S$  decrease with an increase of the dihedral angle,  $1 < 4 < 5$ , whereas the values of  $-\Delta G$  decrease slightly in the order of  $1 \geq 4 \approx 5$ ; no parallel trend was observed between  $-\Delta H$  and  $-\Delta G$  values. Also, in their IR spectra, 4 and 5 display a higher  $\nu(\text{OH}\cdots\text{B})$  and a smaller  $\Delta\nu(\text{OH})$  than 1 does. This result may best be understood when the competitive effects (dihedral angle effects and internal rotation effects about the pivot bond of the biphenyls) working in opposition upon the hydrogen bond formation are considered. In Figure 3, space A decreases with an increase of the dihedral angle, and then the approach of the base molecule to the OH group will be made difficult by the larger dihedral angle. Furthermore, this dihedral angle effects seem to depend strongly on the shape of the base molecule. For  $\text{Me}_2\text{SO}$  and benzonitrile molecules with a rod-shaped proton acceptor site ( $\text{S}=\text{O}$  and  $\text{C}\equiv\text{N}$ ), except for the case of cyclohexanone (see following discussion), the dihedral angle effects on the hydrogen bond formation are small (Table I), because the bulky portion of the base molecule is away from the  $\pi$  cloud on the 2,6-diaryl rings. On the other hand, THF and dioxane molecules in which the proton acceptor site, O atom, is included in the disk-shaped

molecule produce a clear steric effects caused by the variation of the dihedral angle (Table I); the plane of the base molecule comes into contact with the  $\pi$  cloud on the 2,6-diaryl rings for the hydrogen bond length assumed above, 1.8–2.6 Å. Cyclohexanone also has a rod-shaped proton acceptor site, but its equatorial protons adjacent to the carbonyl group in the chair form are expected to cause a small repulsion to the  $\pi$  cloud in the hydrogen bond formation. In fact, the variation of the  $-\Delta H$  values falls midway between the two kinds of the base groups discussed above. In addition to the dihedral angle effects, the effects of 2'(6')-methyl group(s) on the activation energy for the internal rotation about the pivot bond of the biphenyl skeleton should be considered, because the hydrogen bonding is easily destroyed by the internal rotation. If the effects of the internal rotation can only be operative in determining the equilibrium constant for the hydrogen bond formation, the  $-\Delta G$  values will increase with an increase of the activation energy for the internal rotation,  $5 > 4 > 1$ . Therefore, the interesting trend of the thermodynamic data in series II is mainly attributable to the competitive factors mentioned above, although the former factor is more important than the latter one.

Pimentel et al.<sup>16</sup> have reviewed linear correlations between  $-\Delta H$  and  $-\Delta S$  for intermolecular hydrogen bonding of phenols with bases. However, lack of the correlation was also reported for phenol<sup>17</sup> and *p*-fluorophenol<sup>18</sup> adducts. In the present data, when the  $-\Delta H$  values are plotted against the  $-\Delta S$  values, a rough correlation is obtained, except for the case of  $\text{Me}_2\text{SO}$  (Figure 5); the correlation seems to be valid for the closely related proton donors. Kamlet and Taft<sup>19</sup> also found that  $\text{Me}_2\text{SO}$  shows the anomalous behavior in the plot of  $\log K$  vs.  $^{19}\text{F}$  chemical shifts for *p*-fluorophenol–bases system. They assumed a dipolar complex between  $\text{Me}_2\text{SO}$  and the OH group.<sup>19</sup> Drago et al.<sup>20</sup> showed a general relationship  $\Delta H - \Delta\nu(\text{OH})$  [ $\nu(\text{OH}(\text{free})) - \nu(\text{OH}\cdots\text{B})$ ] for unhindered hydrogen bonded systems. However, there does not seem to be a clear relationship for the hindered system studied here. Drago's  $\Delta H - \Delta\nu(\text{OH})$  relationship should only be applied to unhindered systems.

**Registry No.** 1, 2423-73-6; 2, 67564-84-5; 3, 67564-85-6; 4, 58896-12-1; 5, 96556-24-0; 6, 96556-25-1; THF, 109-99-9;  $\text{Me}_2\text{SO}$ , 67-68-5; cyclohexanone, 108-94-1; benzonitrile, 100-47-0; 1-methoxy-2,6-diiodo-4-nitrobenzene, 31106-75-9; 2,6-dimethylbromobenzene, 576-22-7; 1-methoxy-2,6-bis(2',6'-dimethylphenyl)-4-nitrobenzene, 96556-26-2; dioxane, 123-91-1.

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