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Intermolecular Hydrogen Bond Involving a π Base as the Proton Acceptor. VI. Hydrogen Bonding of Phenols and Naphthols to Aromatic Hydrocarbons. Entropy Anomaly and the Role of Charge-Transfer

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Using a series of alkylphenols and naphthols as the proton donors, the hydrogen bond shifts and the association constants of hydrogen-bonded complexes involving methyl benzenes, naphthalene, and phenanthrene as the proton acceptors have been determined from the infrared spectra in carbon tetrachloride. The frequency shifts ($\Delta\nu$) of the hydroxyl stretching vibration and the free energy changes ($-\Delta F$) for complex formation increase with decreasing pK_a of the proton donors. Linear correlation between $-\Delta F$ and $\Delta\nu$ are obtained for each proton donor interacting with methyl benzenes. The entropy anomaly discovered previously was confirmed. Charge-transfer arguments of Basila and co-workers are reconsidered for the hydrogen-bonded systems involving a π base as the proton acceptor.

Recently, there has been increasing evidence for hydrogen bond formation involving olefins and aromatics as the proton acceptors,[1,2] and this has been quantitatively studied by several investigators.[3-5] A good linear correlation of pK_a *vs.* the hydrogen-bonded frequency shift exists for many compounds of entirely different functional types.[1] Recently we have developed such a correlation for the hydrogen bonding of 4-substituted-2,6-xylenols to mesitylene.[6]

The purpose of this paper is to confirm (A) the existence of this correlation through methyl benzenes, naphthalene, and phenanthrene as the proton acceptor and (B) the correlation between the association constants and $\Delta\nu$. Another objective is to show the importance of charge-transfer type contributions[7] to hydrogen bond which are revealed from the results of infrared spectroscopic measurements.

Experimental

The OH stretching absorption spectra were scanned on a Shimadzu IR 600 (high precision grating spectrophotometer) with spectral slit width 1.5 cm^{-1} in the region of 3 μ. The cells had an optical path length of 0.2 cm, and were equipped with NaCl windows. The

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1) For a review, see E. M. Arnett, "Progress in Physical Organic Chemistry," ed. by S. G. Cohen, A. Streitwieser, Jr., and R. W. Taft, Vol. 1, Interscience Publ., New York (1963), p. 259.

2) a) L. P. Kuhn and R. E. Bowman, *Spectrochim. Acta*, **23A**, 189 (1967). b) R. J. Oullette, D. L. Marks and D. Miller, *J. Am. Chem. Soc.*, **89**, 913 (1967). c) M. R. Basila, E. L. Saier and L. R. Cousins, *ibid.*, **87**, 1665 (1965). d) C. J. Collins, *ibid.*, **89**, 1652 (1967).

3) M. Ōki and H. Iwamura, *J. Am. Chem. Soc.*, **89**, 567 (1967) and the preceding papers.

4) L. Joris, P. v. R. Schleyer and R. Gleiter, *ibid.*, **90**, 327 (1968) and the preceding papers.

5) a) Z. Yoshida and E. Ōsawa, *J. Am. Chem. Soc.*, **87**, 1467 (1965). b) Z. Yoshida and E. Ōsawa, *ibid.*, **88**, 4019 (1966). c) Z. Yoshida and N. Ishibe, *ibid.*, **91**, (1969), in press.

6) Z. Yoshida and N. Ishibe, to be published.

7) For a review, see S. Bratoz, "Advances in Quantum Chemistry," ed. by L. O. Lowdin, Vol. 3, Academic Press, New York (1967), p. 209.

TABLE 1. HYDROGEN BOND SHIFT $\Delta\nu_{OH}$ AND FREE ENERGY CHANGE $-\Delta F$ DUE TO 1:1 HYDROGEN BONDED COMPLEX FORMATION AND APPARENT INTEGRATED MOLAR ABSORPTION COEFFICIENT OF BONDED OH BAND A^b IN CCl_4 AT 26°C

(A) $\Delta\nu_{OH}$ (cm^{-1})

Proton donor	nil (ν_f)	π-Base								
		1	2	3	4	5	6	7	8	9
		Benzene	Toluene	*m*-Xylene	*o*-Xylene	*p*-Xylene	Mesitylene	Hexamethyl-benzene	Naphthalene	Phenanthrene
α-Naphthol	3608.0±0.4	51.9±0.8	58.9±0.8	69.3±0.8	69.4±0.8	70.0±0.8	80.0±0.6	108.7±0.5	47.0±0.8	48.1±0.7
β-Naphthol	3609.2±0.4	50.2±0.8	57.5±0.8	68.0±0.8	68.5±0.8	69.5±0.7	79.1±0.7	105.1±0.5	46.5±0.9	46.8±0.8
Phenol[a]	3610.0±0.4	49.2±0.8	57.0±0.8	66.5±0.7	66.5±0.7	69.0±0.7	77.0±0.6	104.8±0.5	46.2±0.8	46.8±0.8
m-Cresol	3611.0±0.5	48.0±0.7	55.0±0.8	65.0±0.8	66.5±0.8	67.0±0.7	76.0±0.6	103.0±0.6	44.3±0.7	46.2±0.7
p-Cresol	3611.8±0.4	47.3±0.7	54.6±0.8	63.5±0.7	65.0±0.7	66.0±0.8	74.8±0.7	102.0±0.6	43.0±0.8	45.5±0.8
o-Cresol	3612.5±0.5	46.5±0.8	53.5±0.8	63.2±0.8	65.0±0.7	65.5±0.8	74.2±0.7	102.0±0.5	43.0±0.9	45.3±0.7
p-*t*-Butylphenol	3613.0±0.5	46.5±0.8	53.3±0.8	62.7±0.8	64.2±0.8	64.0±0.8	74.0±0.6	101.0±0.6	43.0±0.9	45.2±0.8

(B) $-\Delta F$ (kcal/mol)

Proton donor	π-Base								
	1	2	3	4	5	6	7	8	9
	Benzene	Toluene	*m*-Xylene	*o*-Xylene	*p*-Xylene	Mesitylene	Hexamethyl-benzene	Naphthalene	Phenanthrene
α-Naphthol	−0.69±0.03	−0.58±0.02	−0.45±0.03	−0.44±0.04	−0.40±0.04	−0.26±0.02	0.11±0.03	−0.26±0.02	−0.22±0.06
β-Naphthol	−0.71±0.02	−0.62±0.03	−0.47±0.06	−0.46±0.03	−0.43±0.03	−0.28±0.02	0.10±0.02	−0.27±0.01	−0.23±0.02
Phenol[a]	−0.73±0.03	−0.62±0.02	−0.51±0.01	−0.47±0.03	−0.45±0.02	−0.30±0.03	0.03±0.03	−0.27±0.04	−0.23±0.03
m-Cresol	−0.75±0.01	−0.65±0.03	−0.51±0.04	−0.50±0.04	−0.47±0.03	−0.35±0.02	0.01±0.01	−0.28±0.03	−0.25±0.04
p-Cresol	−0.78±0.01	−0.69±0.01	−0.54±0.02	−0.53±0.02	−0.49±0.02	−0.39±0.01	−0.04±0.02	−0.30±0.03	−0.27±0.03
o-Cresol	−0.81±0.05	−0.71±0.02	−0.58±0.03	−0.56±0.01	−0.53±0.02	−0.41±0.02	−0.10±0.01	−0.31±0.04	−0.26±0.05
p-*t*-Butylphenol	−0.80±0.02	−0.73±0.03	−0.60±0.04	−0.59±0.03	−0.54±0.04	−0.45±0.02	−0.13±0.04	−0.31±0.05	−0.26±0.05

(C) A^b ($l\cdot mol^{-1}\cdot cm^{-1}\times10^{-4}$) (In part)

Proton donor	π-Base								
	1	2	3	4	5	6	7	8	9
	Benzene	Toluene	*m*-Xylene	*o*-Xylene	*p*-Xylene	Mesitylene	Hexamethyl-benzene	Naphthalene	Phenanthrene
α-Naphthol	1.97±0.33	1.99±0.20	2.44±0.02	2.24±0.14	2.50±0.20	2.64±0.21	2.79±0.32	2.26±0.37	2.50±0.14
Phenol	1.95±0.20	2.16±0.13	2.27±0.10	2.43±0.20	2.54±0.10	2.71±0.16	3.03±0.18	2.09±0.21	2.29±0.30
p-*t*-Butylphenol	1.46±0.10	1.55±0.15	1.77±0.13	1.94±0.14	1.82±0.09	2.05±0.16	2.21±0.13	1.69±0.11	1.82±0.21

a) Literature values are summarized in Ref. 5a and 5b.

concentration of phenols and naphthols in carbon tetrachloride was kept below 0.015—0.010 mol/*l* to avoid self-association of the proton donor. Concentration of π bases ranged from 0.2 to 4 mol/*l*. All measurements were carried out at average room temperature of 26°C. Two peaks were observed on all spectra, as is well-known in hydrogen-bonded systems.[8] A previously described procedure was employed for calculating the equilibrium constants and the apparent integrated molar absorption intensities of the OH$\cdots\pi$ complexes and for analyzing the infrared spectra to obtain the hydrogen-bonded frequency shifts.[5a]

All materials used were commerciall products and purified by the usual methods.

Results

In the presence of aromatic hydrocarbons, the spectra of the hydroxyl stretching vibration of alkylphenols and naphthols in carbon tetrachloride were seen as doublets. Table 1 summarizes: (A) Shifts of ν_{OH} of alkylphenols and naphthols due to interaction with the added π base ($\Delta\nu$); (B) free energy change, $-\Delta F$, due to 1 : 1 hydrogen bond complex formation; and (C) apparent integrated molar absorption coefficient, A^b, of the bonded OH bond.

Discussion

Effect of the pK_a of proton donors on $\Delta\nu$ and $-\Delta F$: The previous works with *t*-BuOH,[2c] pyrrole,[9] and phenol[5a,10] as proton donors showed a regular increase of $\Delta\nu$ with a number of methyl groups on the benzene ring. We have observed a similar increase using different proton donors. The linear correlation between $\Delta\nu$ and the pK_a of proton donors[11] (Fig. 1) is in agreement with the relation observed for ordinary hydrogen bonds involving lone pair electrons on oxygen and nitrogen atoms.[12,13] The slopes of all lines in Fig. 1 are virtually the same. The pK_a in aqueous solution of the proton donors includes both the enthalpy and entropy terms. The linear relationships, therefore, indicate that the proton donors used in this study have the same effect on $\Delta\nu$ when each infrared frequency shifts are measured in a solvent (CCl_4) different from water; consequently, one might conclude that the base strength of a series of π bases can be obtained by using a proton donor as reference. The "$\Delta\nu$" becomes a convenient measure for the base strength, as pointed out by Arnett.[1]

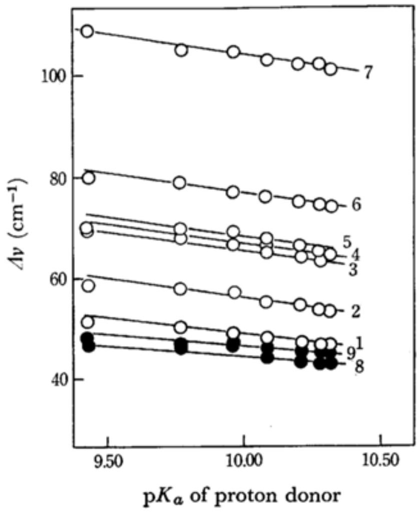

Fig. 1. Relationship between $\Delta\nu$ and pK_a of the proton donors. Numbers correspond to the π bases listed in Table 1.

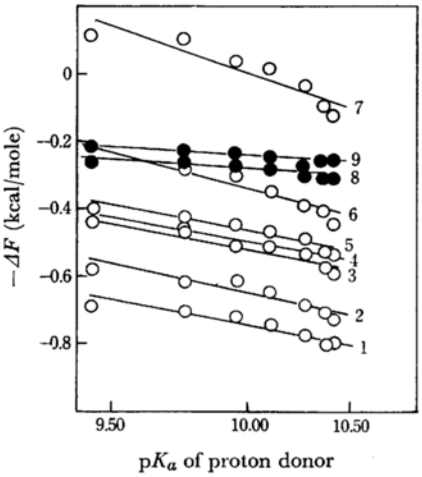

Fig. 2. Plots of $-\Delta F$ *vs.* pK_a of the proton donors. Numbers correspond to the π bases listed in Table 1.

As shown in Fig. 2, when the free energy changes of hydrogen bond formation ($-\Delta F$) are plotted against the pK_a values of the proton donors, linear correlations are obtained for each π base except *p*-*t*-butylphenol (pK_a 10.31 at 26°C) and α-naphthol (pK_a 9.43 at 26°C) as the proton donor. While

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[8] G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," Freeman and Co., San Francisco (1960), p. 67.

[9] N. Fuson, P. Pineau and M. I. Josien, *J. Chim. Phys.*, **55**, 464 (1958).

[10] R. West, *J. Am. Chem. Soc.*, **81**, 1614 (1959).

[11] The titration curve of various proton donors in water was obtained by using the automatic potentiometric titration method at 26°C. The slopes of observed curves were so steep that the break point in the curve could not be determined precisely as in the case of carboxylic acids. The dissociation constants were, therefore, determined at the point where the observed curve meets the theoretical one.

[12] Ref. 1, p. 256.

[13] R. Denger, A. Gilchirst, J. Pegg, J. Smith, T. Thompson and L. Sutton, *J. Chem. Soc.*, **1955**, 3889; J. Gordon, *J. Org. Chem.*, **26**, 738 (1961).

the slope of the lines for methyl benzenes increases with basicity ($-\Delta F$) of the proton acceptors,[14] the slopes for phenanthrene and naphthalene are very small, in spite of the high $-\Delta F$ values. In contrast, the dependence of $\Delta\nu$ on the pK_a values of the proton donor is essentially the same for these polycyclic compounds as it is for the methyl benzenes (Fig. 1). This observation can be interpreted by assuming a large entropy effect. By comparing the $\Delta\nu$- and $-\Delta F$-values for each of the proton donors, a larger entropy effect with the polycyclic compounds than with the methyl benzenes is confirmed. This entropy anomaly has been reported in the hydrogen bonding of phenol with aromatic π base.[5a,15]

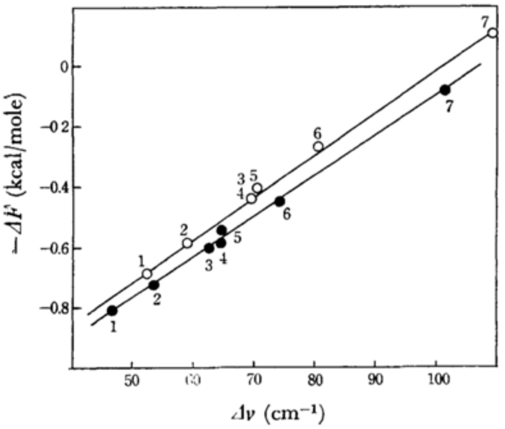

Fig. 3. Plots of $-\Delta F$ *vs.* $\Delta\nu$ for the α-naphthol- and *p*-*t*-butylphenol-methylbenzene systems. ○ : α-Naphthol, ● : *p*-*t*-Butylphenol. Numbers correspond to the π bases listed in Table 1.

Linear correlations between $-\Delta F$ and $\Delta\nu$ were obtained for each proton donor (even for *p*-*t*-butylphenol and α-naphthol as shown in Fig. 3) interacting with methyl benzenes. The value of the slopes was 0.014 ± 0.001 kcal/mol·cm^{-1}. This value agrees with the one obtained by Joesten and Drago[16] for thermodynamic measurements of the phenol adducts.

On the role of charge transfer: The possibility of detecting experimentally the role of charge-transfer involving π electrons from the proton acceptor to the proton donors has been anticipated.[17] The arguments of Basila, Saier, and Cousins[2c] is based on quantitative infrared spectroscopic studies of *t*-butyl alcohol-methyl benzene complexes. Their observed deviations for benzene, ethyl benzene, and mesitylene, when compared with other π bases, were not well explained. Although they consider 1 : 2 as well as 1 : 1 complexes involving these three π bases, the reexamination of their experiments proved that the deviations were due to the use of cells which were too long (15 mm).[5b] For these reasons, it seems best to reconsider their arguments.

The first argument for the importance of charge-transfer in hydrogen bonding is the linear relationship between ionization potential of the proton acceptor, I_D, and the frequency function, $\nu^f/\Delta\nu$:

$$I_D = C_1 \times (\nu^f/\Delta\nu)^{1/2} + C_2$$

where ν^f is the stretching frequency of the free OH. According to the Puranik-Kumar equation,[18] based on Mulliken's second-order perturbation theory for loose 1 : 1 complexes,[19] the plot of I_D *vs.* $(\nu^f/\Delta\nu)^{1/2}$ should be a straight line for a series of related proton acceptors with a given proton donor. Figure 4 shows the plots for phenol-aromatic hydrocarbon complexes as well as those for phenol-olefin complexes.[20] The methyl benzenes fit the straight line. The same relations were obtained with other proton donor-aromatic hydrocarbon complexes. A linear correlation was also obtained for phenol-olefin complexes, although

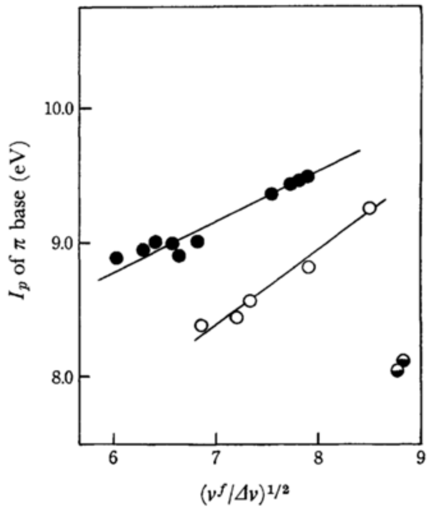

Fig. 4. Correlation between the ionization potential of π bases and $(\nu^f/\Delta\nu)^{1/2}$. ●, olefins; ○, Methylbenzene; ◒, Polyacenes.

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[14] This trend has been observed in the ordinary hydrogen bond: S. Nagakura, *J. Am. Chem. Soc.*, **76**, 3070 (1954).

[15] R. West, International Symposium on Molecular Structure and Spectroscopy, Tokyo, 1962, D-117.

[16] M. D. Joesten and R. S. Drago, *J. Am. Chem. Soc.*, **84**, 3817 (1962).

[17] L. N. Ferguson, "The Modern Structural Theory of Organic Chemistry," Prentice-Hall, Inc., Englewood Cliffs, N. J. (1963), p. 134.

[18] P. G. Puranik and V. Kumar, *Proc. Indian Acad. Sci., Sec. A*, **58**, 29 (1963).

[19] R. S. Mulliken, *J. Am. Chem. Soc.*, **74**, 811 (1952); *J. Phys. Chem.*, **56**, 80 (1952).

[20] Z. Yoshida and N. Ishibe, to be published.

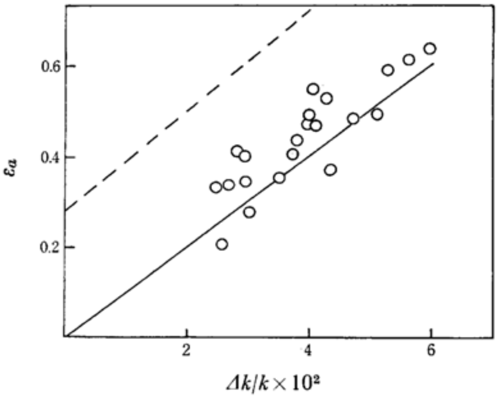

Fig. 5. Plots of the added effective nuclear change ε_a *vs.* the relative change in force constant $\Delta k/k$. The solid line is the one expected from the model discussed in the text and the dashed one is the one reported by Person *et al.* Ref. 23).

some of the ionization potentials of the olefins[21] used in this plot were not determined experimentally.[22] Naphthalene and phenanthrene both show large deviations from the correlation line found for the methyl benzenes; this implies that the polycondensed aromatics fit another line. This could be expected from the fact that the parameters C_1 and C_2 involve terms such as (1) overlap integral between the molecular orbital of the proton acceptor molecule and that of the negative ion of the proton donor molecule, and (2) polarity of the proton donor orbital.

The second argument of Basila and co-workers[2c)] is based on the linear relation between ε_a, the added effective charge on the oxygen atom of the OH group due to the hydrogen bonding, and $\Delta k/k$, the relative change of the force constant of the OH stretching vibration due to hydrogen bonding. This correlation, proposed by Person and co-workes,[23] is based on the "van der Waals interaction-charge-transfer" resonance model, (a)↔(b), for some charge-transfer complexes. Figure 5 shows the result of this plot for complexes with

$$\underset{\text{(a)}}{\text{A–H}\cdots\cdots\text{B}} \longleftrightarrow \underset{\text{(b)}}{\text{A}^-\cdots\cdots(\text{H–B})^+}$$

α-naphthol, phenol, and *p-t*-butylphenol. It should be noted that the plots are between the line obtained by Person *et al.* and the theoretical line obtained by assuming that the structures (a) and (b) would be equally important (*i. e* $\Delta k/k=0.50$, $\varepsilon_a=4.8$).

As additional evidence, Fig. 6 shows the plots of $\Delta\nu$ *vs.* the increment of the apparent absorption coefficient of the OH stretching band due to hydrogen bond formation, ΔA, for complexes where β-naphthol, phenol, and *p-t*-butylphenol are the proton donors. In the hydrogen bonding with lone-pair electrons Huggins and Pimentel[24] found a much larger ratio of $\Delta A/\Delta\nu$ (dashed line in Fig. 6). Since ΔA is a measure of the increased polarity of the OH group due to hydrogen bonding, Fig. 6 suggests that not only electrostatic interactoins but also charge-transfer interactions are important.

The results of three different treatments lead to the same conclusion, that is, charge-transfer from the proton acceptor to the vacant antibonding orbital of the proton donor plays an important role in the hydrogen bonding with π electrons.

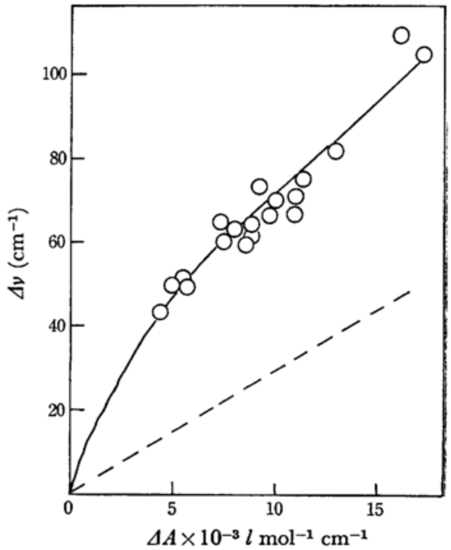

Fig. 6. Plots of $\Delta\nu$ *vs.* the difference between the integrated molar absorption intensity of the hydrogen bonded OH band and that of the free one. The dashed line is the one obtained by Huggins and Pimentel (Ref. 24).

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[21] a) K. Watanabe, T. Kayama and J. Mottl, "Final Report on Ionization Potentials of Molecules by a Photoionization Method," Department of Army No. 5B-99-01-004, ORD TB 2-0001-00R-1624 (1959). b) K. Watanabe, *J. Chem. Phys.*, **26**, 542 (1957).

[22] Ionization potentials of some olefins were calculated from the relation described by Turner. D. W. Turner, "Determination of Organic Structure by Physical Methods," ed. by F. C. Nachod and W. D. Phillips, Vol. 2, Academic Press, New York (1962), p. 354.

[23] W. B. Person, R. H. Humphrey, W. A. Deskin and A. J. Popov, *J. Am. Chem. Soc.*, **80**, 2049 (1958); W. B. Person, R. H. Humphrey and A. I. Popov, *ibid.*, **81**, 273 (1959); W. B. Person, R. E. Erickson and R. E. Buckles, *ibid.*, **82**, 29 (1960).

[24] C. M. Huggins and G. C. Pimentel, *J. Phys. Chem.*, **60**, 1615 (1956).