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Studies of Hydrogen Bonding

Part III *. Intermolecular Hydrogen Bond Association between Nitrogen Compounds and Methanol, Phenol, α-Napththol and Pentachlorophenol

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A linear relationship is shown to exist between the logarithms of the association constants and the pK_a values of the proton acceptors for the system pyridines-phenol. This relationship is not applicable to the aliphatic amines. Pentachlorophenol, unlike phenol, forms 2:1 and 3:1 as well as 1:1 hydrogen bonded complexes with tertiary amines. The effect of steric factors on hydrogen bonding is discussed.

In two previous publications [1,2] it was shown that the logarithms of the association constants, K_{ass}, between organophosphorus compounds and methanol, phenol, α-naphthol and pentachlorophenol respectively, form a linear relationship with the frequency shift, $\Delta\nu_{OH}$, of the O-H band, which accompanies the formation of the hydrogen bond. Furthermore, we concluded that the linear relationships between frequency shift and ΔH, ΔF, ΔS, $\nu_{½}$ and $\nu_{½} \times \varepsilon_{max}$, respectively, were only valid when kept to one system, *e.g.*, OPC-phenol, OPC-methanol etc. It was also shown that the curves ΔH and ΔS *vs.* the frequency shift, $\Delta\nu_{OH}$, flatten with increasing acidity of the proton donors, the sequence of decreasing slope being, methanol > phenol > α-naphthol > pentachlorophenol. The effect of solvent interaction on the hydrogen bond association was considered and the following conclusions drawn: For the system organophosphorus compounds OPC-methanol, the solvent interaction is mainly due to the solvation effect around the hydrogen bonded complex. As the proton-donating power increases, solvent interaction with the proton donor becomes more pronounced, *i.e.*, for the systems OPC-phenol and OPC-α-naphthol both the solvation and the solvent-proton donor effects came into play, and for the system OPC-pentachlorophenol the solvent-proton donor effect predominates. This interpretation may also explain the anomalies ob-

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served with pentachlorophenol in comparison with phenol with regard to their relative ability to form intermolecular hydrogen bonds with organophosphorus compounds.

Since hydrogen bond energies between a proton donor and nitrogen compounds have not as yet been studied systematically, we found it of interest to extend our study to compounds containing nitrogen. A particularly interesting paper in this field is that by Sutton *et al.*[3], who present the results of a study of complex formation by partition of a reactant between the vapour phase and solution. By this method they determined K_{ass}, ΔF, ΔH and ΔS values for association between trimethylamine and some hydroxy-compounds and found a linear relationship between the logarithms of the dissociation constants of some hydroxy compounds and their association constants with trimethylamine in cyclohexane as solvent. In a previous paper[4] they had measured the changes of dielectric dipole moment, $\Delta\mu$, which occur when trimethylamine forms complexes with weakly acidic hydroxy-compounds in cyclohexane solution. Here they found that, in general, there is a fairly good correlation between $(\Delta\mu)^2$ and K_{ass}. Another interesting study on ternary solutions has been carried out by Nagakura and Gouterman[5] using ultraviolet spectroscopy. They found the association constants at 25°C in heptane between triethylamine and phenol, α-naphthol and β-naphthol to be 83.8, 121.0 and 103, respectively. For comparison it should be mentioned that the association constants at 25°C obtained by Sutton *et al.*[3] between trimethylamine and phenol, α-naph-

Table 1. Data on hydrogen bonding between nitrogen compounds and phenol

Proton acceptor	PHENOL						
	K_{ass} 20°C	K_{ass} 50°C	ΔH kcal	ΔF kcal	ΔS e.u.	$\Delta\nu_{OH}$ cm^{-1}	$\nu_{½}$ cm^{-1}
Triethylamine	90.9	26.2	−7.8	−2.6	−17.7	380	500
Tripropylamine	22.4	8.7	−5.9	−1.8	−14.1	330	420
Tributylamine	29.2	9.7	−6.9	−2.0	−16.9	350	420
Tribenzylamine	2.7	2.1	−1.6	−0.6	− 3.4	90	406
N-Diethylaniline	2.6	2.1	−1.3	−0.6	− 2.7	67	550
Pyridine	59.8	19.7	−7.0	−2.4	−15.6	492	454
Collidine	137.1	41.6	−7.5	−2.7	−15.7	531	430
2,6-Lutidine	95.2	31.8	−6.9	−2.7	−14.4	535	504
2,4-Lutidine	103.9	35.0	−6.8	−2.7	−14.1	516	466
2-Picoline	74.7	24.8	−6.9	−2.5	−15.0	520	484
3-Picoline	73.1	25.8	−6.5	−2.5	−13.8	491	418
4-Picoline	80.0	27.8	−6.6	−2.6	−13.9	500	404
4-Benzylpyridine	78.3	28.9	−6.2	−2.5	−12.6	—	—
Quinoline	57.4	18.3	−7.2	−2.4	−16.4	498	450
Isoquinoline	61.4	20.4	−6.9	−2.4	−15.4	529	484
Quinaldine	79.9	25.7	−7.1	−2.6	−15.6	532	466
Acridine	67.2	23.4	−6.6	−2.5	−14.1	520	464

thol, and β-naphthol were found to be 86.0, 110, and 230, respectively. The anomalies observed for β-naphthol in comparison with α-naphthol by Sutton *et. al.* with trimethylamine were not observed by Nagakura and Gouterman with triethylamine. Fuson, Pineau and Josien[6] have found by infrared spectroscopy an association constant of 55 for phenol with pyridine in carbon tetrachloride solution. Halleux[7] has also reported some association constants between phenol and a number of pyridines. With regard to hydrogen bond energies only very few results are available. Among the few comparisons that can be made with previously reported values of the enthalpy of association are those obtained by Tsuboi[8], Sutton *et al.*[3] and Becker[9]. Tsuboi's value of −3 kcal/mole and Becker's value of −3,9 kcal/mole for the system methanol-pyridine in CCl_4 solution are consistent with our value of −3.2 kcal/mole (see Table 1), while Tsuboi's value of −5 kcal/mole for phenol-pyridine in CCl_4 solution is somewhat lower than that obtained by us, namely −7.0 kcal/mole.

EXPERIMENTAL

Materials. The following materials were used without further purification: "Merck Guaranteed Reagent" phenol, α-naphthol and carbon disulphide. "Merck Spectroscopic Grade" methanol and carbon tetrachloride. "Fluka puriss" pentachlorophenol. All the nitrogen compounds were of a high standard of purity and in all cases they were purified either by fractional distillation from KOH or by recrystallisation just before use. The *triethylammonium pentachlorophenolate* was prepared by mixing pentachlorophenol (1 g) with an excess of triethylamine (5 g). The mixture was shaken vigorously for a few minutes until all the pentachlorophenol was dissolved, and after few minutes the triethylammonium pentachlorophenolate precipitated out (0.94 g, 68 %. Found: C 39.30; H 4.39; N 3.81; Cl 45.60. $C_{12}H_{16}ONCl_5$ requires C 39.20; H 4.35; N 3.81; Cl 48.27). The salt was purified by washing with ether; it was not appreciably hygroscopic. Attempts to prepare the salt by using solvents, *e.g.*, cyclohexane, ether, ligroin and dioxane were unsuccessful.

Infrared measurements. The instrument, the instrumental conditions and the method of running the spectra were the same as described earlier[2]. For the determination of the frequency shift of the ground state stretching vibration of the O-H band which accompanies the formation of a hydrogen bond, the concentration of the proton donors was kept at 0.06 M, and that of the nitrogen compounds at 0.03 M. The exceptions were, tribenzylamine and N-diethylaniline with phenol, and the systems phenol-pyridines and methanol-amines. The concentrations of the proton acceptors in these systems were 0.12, 0.04 and 0.3 M, and of the proton donors, 0.06, 0.01 and 0.06 M, respectively.

Near-infrared measurements. The instrument, the instrumental conditions, the method of running the spectra, and the method of calculation of association constant were the same as described earlier[2]. The spectra were run immediately after preparing the solutions because of the reaction of the amines, particularly triethylamine, with carbon tetrachloride. This reaction was sufficiently slow, at the low concentrations used, not to interfere seriously. For all thermodynamic data in Table 1, the concentration of the proton donors was kept at 0.006 M to prevent self-association. The concentrations of the proton acceptors were 0.003, 0.006 and 0.012 M, except for the system methanol-nitrogen compounds where they were 0.06, 0.12 and 0.20 M. The concentration range of the proton donors and the acceptors shown in Table 2 is 0−0.006 M.

Refractive index measurements. The refractive index measurements were carried out with a Bausch & Lomb Precision Refractometer, 33−45−02−01, at 20°C. The concentration range of the proton donors and acceptors is 0−0.12 M. The results are shown in Figs. 3 and 4.

Table 2. Data on hydrogen bonding between nitrogen compounds and methanol and α-naphthol.

Proton acceptor	METHANOL							α-NAPHTHOL						
	K_{ass} 20°C	K_{ass} 50°C	$-\Delta H$ kcal	$-\Delta F$ kcal	$-\Delta S$ e.u.	$\Delta\nu_{OH}$ cm^{-1}	$\nu_{½}$ cm^{-1}	K_{ass} 20°C	K_{ass} 50°C	$-\Delta H$ kcal	$-\Delta F$ kcal	$-\Delta S$ e.u.	$\Delta\nu_{OH}$ cm^{-1}	$\nu_{½}$ cm^{-1}
Triethylamine	6.4	3.5	3.8	1.1	9.2	427	352	108.9	38.2	6.6	2.7	13.1	—	—
Tripropylamine	3.4	2.2	2.7	0.7	6.9	413	526	30.9	11.6	6.1	2.0	14.2	380	418
Tributylamine	4.1	2.4	3.5	1.0	8.8	413	532	44.5	17.4	5.9	2.2	12.6	383	342
Tribenzylamine	3.4	2.7	1.5	0.7	2.5	—	—	1.9	1.5	1.3	0.4	3.4	—	—
N-Diethylaniline	1.7	1.3	1.5	0.3	4.1	—	—	—	—	—	—	—	—	—
Pyridine	6.0	3.6	3.2	1.0	7.4	300	304	82.5	33.5	5.7	2.6	10.5	530	514
Collidine	7.6	4.3	3.6	1.2	8.2	356	256	200.8	69.5	6.7	3.1	12.2	535	610

RESULTS AND DISCUSSION

Nitrogen compounds-phenol. The sharp distinction between systems shown to exist in two previous publications [1,2] has further been confirmed in this work. As can be seen in Table 1, the association constants for the system nitrogen compounds-phenol are very small in relation to the great frequency shift, $\Delta\nu_{OH}$, *e.g.*, triethylamine-phenol, K_{ass} = 90.9, $\Delta\nu_{OH}$ = 380, compared with $(C_2H_5)_2NP(O)(OC_2H_5)_2$-phenol[2], K_{ass} = 518.2, $\Delta\nu_{OH}$ = 395. Thus the hydrogen bonding ability of the phosphorus compound with phenol is about 5.5 times that of triethylamine although the frequency shift is almost the same. In general, the ability to form intermolecular hydrogen bonds in relation to frequency shift is very much smaller for nitrogen compounds than for organophosphorus compounds containing the P=O group. Another interesting finding is the marked decrease in hydrogen bonding ability of tripropylamine and tributylamine in comparison with triethylamine (see Table 1). This observation is in agreement with the data reported by Tamres *et al.* [10], who measured the heats of mixing of nitrogen bases with chloroform. They found that the heat of mixing of equimolecular quantities of the nitrogen compound and chloroform is much greater for triethylamine than for tributylamine, *i.e.*, 870 and 438 cal/mole, respectively. These results should be compared with those obtained by us for triethylamine-phenol, K_{ass} = 90.9, ΔH = −7.8 kcal, and for tributylamine-phenol, K_{ass} = 29.2, ΔH = −6.9 kcal (see Table 1). Furthermore, we have found, as shown in Fig. 1, that the correlation between the logarithms of the association constants of nitrogen bases with phenol and the heat of mixing of the same nitrogen bases with chloroform measured by Tamres *et al.* [10] is close to a linear relation, with the exception of triethylamine and tributylamine. This means that the abilities of

pyridines and quinolines to form hydrogen bonds are related to their heat of mixing with chloroform in a linear manner, and that this relationship is not applicable to the aliphatic tertiary bases. There should also exist a linear relationship between the heats of mixing with chloroform and the ΔH values from Table 1, but the calculated enthalpies are too inaccurate for this purpose. It should, however, be noted that the hydrogen bonding abilities of tributylamine and isoquinoline with phenol are very different, K_{ass} = 29.7 and 61.6 l/mole, respectively, although their heats of mixing with chloroform (438 and 440 cal/mole, respectively) and the enthalpies with phenol (—6.9 kcal) are the same. This again supports the view that we have to distinguish between aliphatic tertiary amines and pyridines with regard to their ability to form hydrogen bonds. We have also found, as shown in Fig. 2, a linear relationship between the logarithms of the association constants of pyridines (and quinolines) with phenol and the pK_a values of the bases. The corresponding points for aliphatic tertiary amines are far below the straight lines in Fig. 2. Similar observations have been reported by Halleux[7] who states that there appears to be a linear relationship between log K_{ass} and pK_a for the association of phenol with several pyridines.

The more unfavourable entropy of formation of phenol-nitrogen compounds complexes in comparison with organophosphorus compounds-phenol complexes may depend on (*a*) different solvent interactions on the proton acceptors, *i.e.*, we have to take into account the solvent interaction on the nitrogen compounds in comparison with organophosphorus compounds; (*b*) different steric properties of the complexes, since it is well known that tertiary amines cannot be separated into enantiomers due to the fact that the nitrogen atom is oscillating very quickly through the plane connecting the three different substituents (this oscillating effect may also play a part when aliphatic tertiary amines are compared with pyridines with regard to their ability to form hydrogen bond); (*c*) a difference of polarity in the two types of hydrogen bonds — as pointed out earlier[2], an increase in dipole moment will give a greater orientation of the solvent molecules around the complex which will contribute to a negative entropy of reaction; (*d*) a difference in the mode of formation of the hydrogen bonds, *i.e.*, we have to distinguish between two types of association complexes, one in which there is principally and electronic attraction between the hydrogen atom of the original acid and an electron rich area of the base, and one in which a proton mainly shares the electron pair of another atom to form a covalent bond with the proton acceptor, so that now the bond between the proton

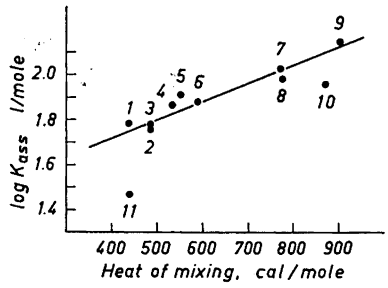


Fig. 1. The relation between the logarithms of the association constants at 20°C for hydrogen bonded complexes between nitrogen compounds and phenol and the heat of mixing of the same bases with chloroform; (1) isoquinoline; (2) quinoline; (3) pyridine; (4) 3-picoline; (5) 4-picoline; (6) 2-picoline; (7) 2,4-lutidine; (8) 2,6-lutidine; (9) 2,4,6-collidine; (10) triethylamine; (11) tributylamine.

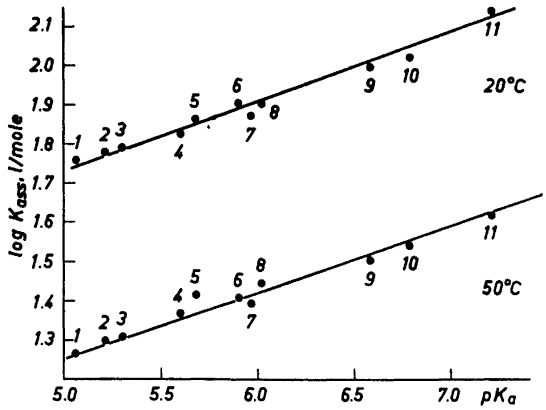


Fig. 2. The relation between pK_a values of proton acceptors and the logarithms of the association constants of the same acceptors with phenol; (1) quinoline; (2) pyridine; (3) isoquinoline; (4) acridine; (5) 3-picoline; (6) quinaldine; (7) 2-picoline; (8) 4-picoline; (9) 2,6-lutidine; (10) 2,4-lutidine; (11) 2,4,6-collidine. Solvent, carbon tetrachloride.

donor and the hydrogen atom becomes mainly electrostatic in character. In the latter case proton-transfer takes place. In the association complex the hydrogen bond is in both cases of the same, unsymmetrical type, but in the latter case the original base holds the hydrogen atom covalently and thus plays the role of the original acid in the former case. A typical example of hydrogen bonding in which electrostatic attraction between proton donor and base predominates is the interaction between phenol and organophosphorus compounds. From this point of view the hydrogen bonding studies in the system organophosphorus compounds-phenol may be considered as a study of the relative electron densities around the oxygen atom in the P=O group. With the nitrogen compounds, however, we should have both types of hydrogen bonds in which either electrostatic attraction or proton-transfer predominates. In the pyridines and quinolines the π electrons in the ring may contribute to the electron density on the nitrogen since nitrogen is more electronegative than carbon. The unshared electron pair on the nitrogen, however, is less available for covalent bond formation because it takes part in resonance in the ring. This may explain the greater hydrogen bonding ability in the electrostatic, non-proton transfer sense of pyridines and quinolines compared with tertiary aliphatic amines in relation to their basicity.

Due to the high electron density around the nitrogen atom in pyridines and quinolines we assume that electrostatic attraction predominates in the hydrogen bonding whereas with amines proton-transfer predominates. However, Table 1 shows that $\Delta\nu_{OH}$ is always $\lesssim$ 380 cm^{-1} for the association of phenol wich tertiary amines, whereas with pyridines it is always $\gtrsim$ 490 cm^{-1}. The smaller frequency shift values for amines-phenol in comparison with pyridines-phenol could be taken to mean that in the latter case the proton-transfer structure should be more pronounced than in the former case, and hence contradict the theory above. The reason for these anomalies may be attributed to steric effects. Strong evidence in support of this view is as shown in Table 2, the greater frequency shift for the system amines-methanol in comparison with pyridines-methanol. This is just the reverse of what is the case with phenol. Furthermore, the association of amines with phenol clearly shows that the effect of steric interaction plays a big part, whereas there is no evidence of steric effects with the system pyridines-phenol, and not even for one between acridine and phenol. The pronounced decrease in the value of the association constant as we proceed from trimethylamine (Sutton *et al.*[3] has found the association constant between trimethylamine and phenol to be 86 l/mole at 25°C) and triethylamine to tripropylamine and tributylamine may also be due to steric effects, *i.e.*, steric interaction between the end of the carbon chain and phenol.

Table 3. Data on hydrogen bonding between nitrogen compounds and pentachlorophenol.

Proton acceptor	PENTACHLOROPHENOL						
	K_{ass} 20°C	K_{ass} 50°C	ΔH kcal	ΔF kcal	ΔS e.u.	$\Delta\nu_{OH}$ cm^{-1}	$\nu_{½}$ cm^{-1}
Triethylamine	—	—	—	—	—	1155	—
Tripropylamine	—	—	—	—	—	1100	—
Tributylamine	—	—	—	—	—	1125	—
Tribenzylamine	1.3	0.8	−3.	−0.2	−10.0	—	—
Pyridine	111.4	44.2	−5.8	−2.7	−10.4	805	922
Collidine	224.7	67.2	−7.6	−3.2	−15.1	1098	1016

Nitrogen compounds-methanol and nitrogen compounds-α-naphthol. It has been found (see Table 2) that the steric effect with amines is less pronounced when phenol is replaced by methanol. This is best illustrated by comparison of tribenzylamine-phenol with tribenzylamine-methanol. Otherwise the association constant and the enthalpies are markedly lower due to the low acidity of methanol. With α-naphthol no enhanced steric effect was observed except with tribenzylamine. As can be seen from Tables 1 and 2, both phenol and α-naphthol have greater frequency shifts with pyridines than for amines, whereas for methanol the reverse is the case. Since the methanol molecule is small there is little steric effect with the amines. This suggests that $\Delta\nu_{OH}$ is larger for amines than for pyridines due to lower basicity of the latter.

Nitrogen compounds-pentachlorophenol. As shown in a previous paper [2] when in the system organophosphorus compounds-phenol and in the system amides-phenol [11] phenol is replaced by pentachlorophenol a drop in association constant occurs, which was suggested to be due to solvent interaction. With the system nitrogen compounds-pentachlorophenol no such drop in association constants was observed. Actually, the association constants, as can be seen in Table 3, are increased considerably on replacing phenol with pentachlorophenol. We suggest that this may be due to the fact that the unshared electron pair on the nitrogen atom in pyridines is more available for covalent bond formation than are those of the oxygen in the P=O group, *i.e.*, there will be a shift in the equilibrium between the electrostatic (I) and the proton-transfer structure (II), towards the latter as the proton-donating power and the ability of the base to form a covalent bond increases.

$$\overset{\delta-}{RO}-H\cdots:\overset{\delta+}{N}- \rightleftharpoons R\overset{-}{O}\cdots H:\overset{+}{N}-$$

(I) (II)

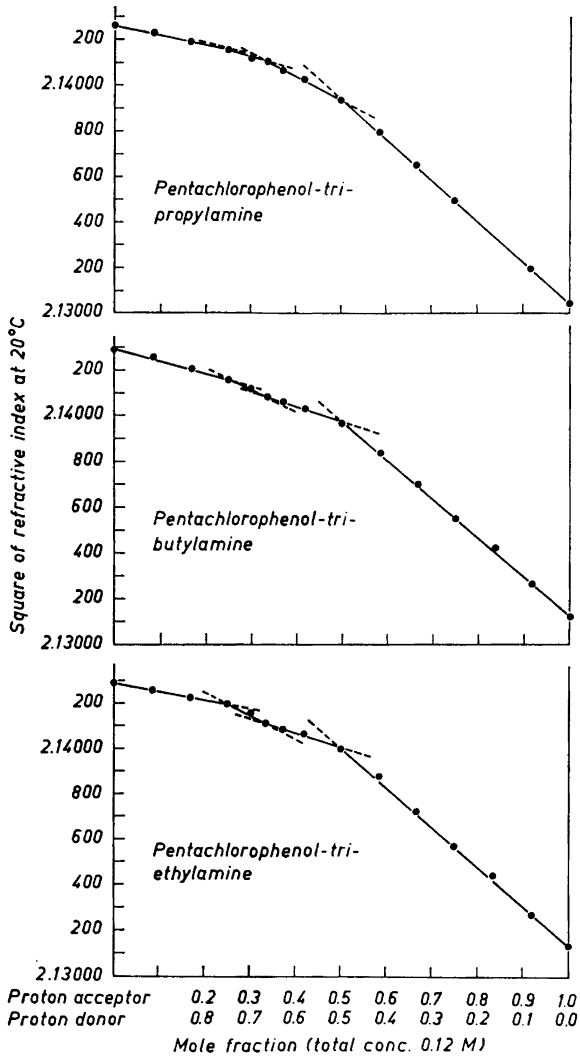


Fig. 3. Square of refractive index *vs.* mole fraction of some hydrogen bonded complexes. The curves show three slope changes corresponding to intermolecular complexes of 1:1, 1:2 and 1:3 ratio. Solvent, carbon tetrachloride.

This view is supported by the fact that the frequency shift $\Delta\nu_{OH}$, and the broadening of the O-H band contour are very much enhanced for the system pyridines-pentachlorophenol in comparison with the system pyridines-phenol, which again may be due to the higher polarity of the proton-transfer structure. In general we suppose that for the system pyridines-phenol the electrostatic structure (I) will predominate. However, as the proton-donating power is

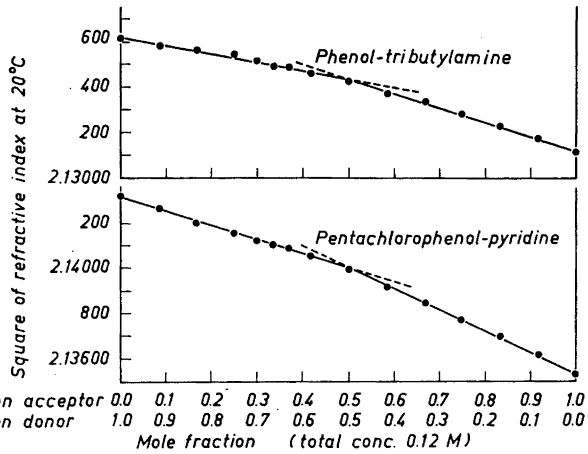


Fig. 4. Square of refractive index *vs.* mole fraction of some hydrogen complexes. The curves show only one slope change corresponding to 1:1 complex. Solvent, carbon tetrachloride.

increased, for example by replacing phenol with pentachlorophenol, the proton-transfer structure (II) becomes more favourable, pyridine utilising its unshared electron pair to form a proton-transfer structure (II) as the acidity of the proton donor increases. This structure is even more pronounced when in the system pyridines-pentachlorophenol the pyridine is replaced by a tertiary aliphatic amine. Due to the stronger basicity of amine the unshared electron pair on the nitrogen will capture the proton and hence the proton-transfer structure will predominate.

Furthermore, it has been found that the polarity of the complexes between amines and pentachlorophenol is increased to such an extent that they react further to give a mixture of 1:1, 1:2 and 1:3 complexes. The results are shown in Fig. 3, using a method described by Giles *et al.*[12] The figure shows the relationship between the square of the refraction index of the solution and the mole fraction of proton donor and acceptor. As can be seen at least 1:1, 2:1 and 3:1 complexes are formed between pentachlorophenol and the amines. For comparison we have shown in Fig. 4, that pyridine-pentachlorophenol and tributylamine-phenol only form 1:1 complexes. Further data on hydrogen bonded complexes are given in Table 4. From this table it can bee seen that if the formal concentrations of, for example, triethylamine and pentachlorophenol are 0.6×10^{-3} and 5.4×10^{-3} moles/l respectively, then the concentration of pentachlorophenol which participates in the complex formation is 0.898×10^{-3} moles/l. This means that the complex must contain more of the proton donor than of the acceptor. This is also the case, as shown in Table 4, for tripropylamine and tributylamine with pentachlorophenol, but not for pyridine and collidine with pentachlorophenol and tributylamine with phenol. These results agree very well with those shown in Figs. 3 and 4. In Fig. 5 some of the

Table 4. Data on hydrogen bonded complexes. Cell length, 10.0 cm. Solvent, carbon tetrachloride. Temperatures, 20° and 50° C (in brackets).

Concentration moles/l × 10^3		Pentachlorophenol + Triethylamine		Pentachlorophenol + Tripropylamine	
Proton donor	Proton acceptor	D^* × 10^2	C^{**} × 10^3	D × 10^2	C × 10^3
6.0	0.0	12.49(12.32)	0	13.31(13.08)	0
5.4	0.6	9.37(10.07)	0.898(0.495)	10.40(11.01)	0.712(0.347)
5.0	1.0	7.47 (8.72)	1.411(0.753)	8.57 (9.85)	1.137(0.480)
4.8	1.2	6.80 (8.09)	1.532(0.859)	7.73 (9.15)	1.315(0.601)
4.5	1.5	5.55 (7.11)	1.833(1.037)	6.60 (8.41)	1.525(0.641)
4.2	1.8	4.58 (6.30)	1.999(1.132)	5.65 (7.62)	1.653(0.703)
4.0	2.0	3.91 (5.80)	2.121(1.175)	5.06 (7.16)	1.718(0.714)
3.6	2.4	2.78 (4.77)	2.264(1.276)	4.10 (6.20)	1.752(0.755)
3.4	2.6	2.37 (4.24)	2.261(1.335)	3.62 (5.75)	1.768(0.762)
3.2	2.8	1.95 (3.86)	2.263(1.320)	3.29 (5.31)	1.717(0.764)
3.0	3.0	1.64 (3.43)	2.212(1.330)	2.92 (4.91)	1.683(0.747)
2.4	3.6	0.88 (2.46)	1.977(1.202)	2.09 (3.67)	1.458(0.715)
2.0	4.0	0.66 (1.95)	1.683(1.050)	1.64 (3.01)	1.261(0.619)
1.0	5.0	0.22 (0.83)	0.894(0.596)	0.61 (1.32)	0.725(0.394)

Concentration moles/l × 10^3		Pentachlorophenol + Tributylamine		Pentachlorophenol + Pyridine	
Proton donor	Proton acceptor	D × 10^2	C × 10^3	D × 10^2	C × 10^3
6.0	0.0	12.90(12.73)	0	13.31(13.08)	0
5.4	0.6	9.69(10.51)	0.893(0.445)	11.49(11.52)	0.219(0.115)
5.0	1.0	8.20 (9.37)	1.185(0.583)	10.35(10.51)	0.334(0.178)
4.8	1.2	7.42 (8.83)	1.349(0.637)	9.75(10.02)	0.405(0.202)
4.5	1.5	6.30 (8.04)	1.568(0.725)	8.94 (9.26)	0.470(0.251)
4.2	1.8	5.26 (7.06)	1.754(0.825)	8.14 (8.57)	0.529(0.268)
4.0	2.0	4.77 (6.70)	1.804(0.841)	7.62 (8.09)	0.564(0.288)
3.6	2.4	3.67 (5.75)	1.893(0.889)	6.65 (7.16)	0.603(0.314)
3.4	2.6	3.29 (5.35)	1.869(0.887)	6.20 (6.75)	0.604(0.303)
3.2	2.8	2.92 (4.91)	1.842(0.885)	5.75 (6.30)	0.608(0.309)
3.0	3.0	2.50 (4.53)	1.838(0.865)	5.26 (5.85)	0.629(0.315)
2.4	3.6	2.68 (3.34)	1.620(0.826)	4.00 (4.58)	0.597(0.298)
2.0	4.0	1.19 (2.69)	1.447(0.731)	3.20 (3.76)	0.558(0.274)
1.0	5.0	0.44 (1.14)	0.795(0.463)	1.46 (1.82)	0.342(0.165)

Table 4, cont.

Concentration moles/l × 10^3		Pentachlorophenol + Collidine		Phenol + Tributylamine	
Proton donor	Proton acceptor	$D \times 10^2$	$C \times 10^3$	$D \times 10^2$	$C \times 10^3$
6.0	0.0	13.08(12.90)	0		0
5.4	0.6	11.07(11.29)	0.321(0.148)	15.49(13.58)	0.081(0.033)
5.0	1.0	9.80(10.24)	0.506(0.237)	12.61(12.55)	0.116(0.039)
4.8	1.2	9.18 (9.72)	0.588(0.278)	12.03(12.00)	0.140(0.057)
4.5	1.5	8.30 (8.94)	0.691(0.341)	11.18(11.24)	0.170(0.056)
4.2	1.8	7.42 (8.25)	0.795(0.362)	10.29(10.46)	0.214(0.065)
4.0	2.0	6.91 (7.73)	0.829(0.404)	9.80 (9.93)	0.204(0.076)
3.6	2.4	5.88 (6.85)	0.901(0.414)	8.72 (8.91)	0.222(0.078)
3.4	2.6	5.40 (6.35)	0.922(0.446)	8.20 (8.41)	0.223(0.076)
3.2	2.8	4.91 (5.90)	0.947(0.455)	7.68 (7.88)	0.225(0.085)
3.0	3.0	4.48 (5.45)	0.944(0.465)	7.16 (7.37)	0.227(0.086)
2.4	3.6	3.27 (4.29)	0.899(0.405)	5.65 (5.88)	0.211(0.075)
2.0	4.0	2.55 (3.48)	0.830(0.381)	4.67 (4.87)	0.191(0.075)
1.0	5.0	1.10 (1.64)	0.495(0.237)	2.27 (2.41)	0.121(0.047)

* D means optical density of free O-H band.
** C means concentration, moles/l, of proton donor participating in complex formation.

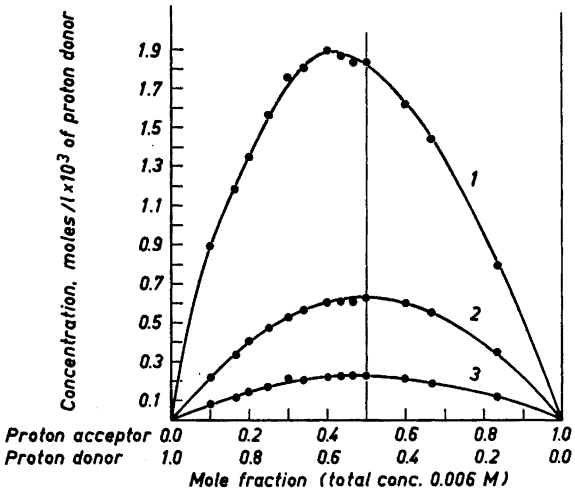


Fig. 5. Concentration of proton donor which participates in hydrogen bonds *vs.* mole fraction. (1) tributylamine-pentachlorophenol; (2) pyridine-pentachlorophenol; (3) tributylamine-phenol. Temperature 20°C.

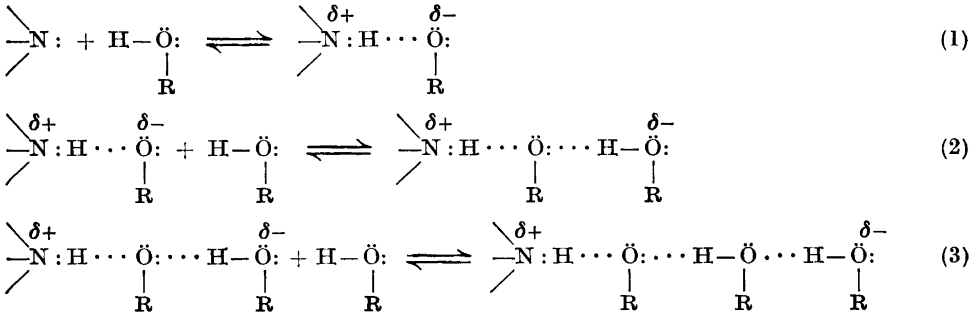
Table 5. A comparison of thermodynamic data for hydrogen bonds in different solvents.

Compound	K_{ass} 20°C	K_{ass} 50°C	ΔH kcal	ΔF kcal	ΔS e.u.	Solvent
Phenol + Tributylamine	29.2	9.7	−6.9	−2.0	−16.9	CCl_4
	34.3	14.5*	−7.9	−2.1	−19.7	CS_2
Phenol + Pyridine	59.8	19.7	−7.0	−2.4	−15.6	CCl_4
	71.5	31.5*	−7.5	−2.5	−17.0	CS_2
Pentachlorophenol + Pyridine	111.4	44.2	−5.8	−2.7	−10.4	CCl_4
	108.1	48.5*	−7.3	−2.2	−17.5	CS_2

* measured at 40°C.

figures in Table 4 have been plotted to show more clearly the correlation between the concentration of the proton donor participating in complex formation and the mole fraction of the proton donor and acceptor. As can be seen from this figure, the variation of concentration of the proton donor participating in complex formation of pyridine with pentachlorophenol and of tributylamine with phenol is symmetrical with a maximum at mole fraction = 0.5, *i.e.*, we have 1:1 association [13], whereas this is not the case with tributylamine-pentachlorophenol.

We therefore propose the following association scheme for pentachlorophenol with amines:



(1)

(2)

(3)

etc.

Eqn. (1) represents the formation of a proton-transfer structure due to the strong acidity of pentachlorophenol. This proton-transfer structure has been confirmed by comparison of its infrared spectrum with that of triethylammonium pentachlorophenolate. Both spectra have a very strong and broad band in the region 1700 to 2800 cm^{-1} and

differ greatly from the spectra of the amines-phenol system. Also, the difference in frequency shift, $\Delta\nu_{OH}$, should be noticed, *e.g.*, 380 cm^{-1} and 1155 cm^{-1}, respectively, for phenol and pentachlorophenol with triethylamine. It is likely that the latter should be attributed to a shift of the N-H frequency upon hydrogen bonding (see eqn. 1). Nevertheless, the electron density on the oxygen atom in pentachlorophenol due to the strong polarity of the complex will increase to such an extent that it will act as base towards a second pentachlorophenol molecule and the result is shown in eqn. (2). This will continue as shown in eqn. (3) until the electron density on the oxygen atoms in the complex due to reduced polarity, is lowered to such an extent that the next pentachlorophenol molecule will associate with a new molecule of amine.

Solvent interaction. As shown in part II [2], the thermodynamic data on hydrogen bonds are very much affected by solvent interaction. It was suggested that the fall in association constants for the system organophosphorus compounds-pentachlorophenol compared with the system organophosphorus compounds-phenol was due at least partly to hydrogen bond formation between the proton donor and the solvent. As discussed above no such fall was found in the association constants in the case of nitrogen compounds. We have found, however, a marked increase in association constants with regard to phenol, but not to pentachlorophenol which remains almost constant, by replacing carbon tetrachloride with carbon disulphide (see Table 5). The reason for this anomaly is not yet clear, and much work needs still to be done, for example by using more differentiated solvents, to reveal the full effect of solvent interaction on hydrogen bonding.

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