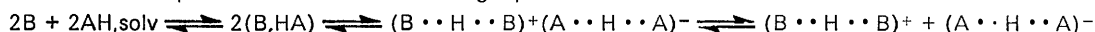


## Hydrogen Bonding in Complexes of Heterocyclic *N*-Oxides with Halogenoacetic Acids. Part VII.<sup>1</sup> An Infrared and Nuclear Magnetic Resonance Study of 4-Methylpyridine *N*-oxide Complexes

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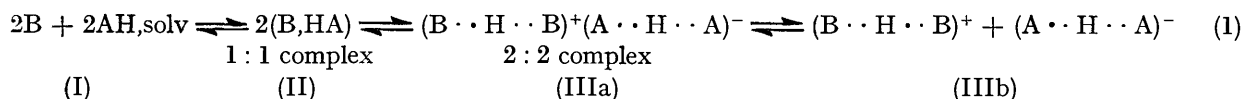
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I.r. and n.m.r. spectra of complexes of 4-methylpyridine *N*-oxide with trifluoroacetic, trichloroacetic, dichloroacetic, and monochloroacetic acids have been measured in order to study the association through hydrogen bonding. The complex with trichloroacetic acid was prepared in two crystal modifications. The observed spectral variations were so large that it was necessary to postulate several different structures. The n.m.r. chemical shift of the proton in the hydrogen bond was dependent on both the concentration and the nature of solvent. The i.r. spectra, in contrast, were not noticeably affected by concentration in the range 0.1–0.6M or the nature of the solvent (below 1800 cm<sup>-1</sup>). A linear relationship was observed between chemical shift and Δp*K*<sub>a</sub>. The experimental results can be interpreted in terms of the following equilibria:



We have recently shown<sup>1-4</sup> that the interaction of 4-methylquinoline *N*-oxide (B) with halogenoacetic acids (HA) in complexes in benzene, toluene, chloroform, methylene chloride, acetonitrile, and acetone can be described by equation (1). Spectroscopic evidence was obtained for the existence of structure (III) in crystalline state of some complexes.<sup>2</sup>

Hadži *et al.*<sup>5-8</sup> investigated complexes of pyridine *N*-oxide with trichloroacetic and dichloroacetic acids in the crystalline and liquid states, and suggested structure (II) for these materials. We believe that structures



(IIIa) and (IIIb) are also important and have sought evidence for their existence in the present study of similar complexes of 4-methylpyridine *N*-oxide. The 4-methyl derivative was chosen rather than pyridine *N*-oxide because (i) it forms crystalline and more stable complexes with halogenoacetic acids and (ii) it has similar p*K*<sub>a</sub> value to 4-methylquinoline *N*-oxide;<sup>9</sup> however it has the same symmetry as pyridine *N*-oxide.

### EXPERIMENTAL

4-Methylpyridine *N*-oxide was prepared from 4-methylpyridine according to the method of Ochiai<sup>10</sup> and recrystallized from benzene.

The crystalline complexes were prepared by dissolving the anhydrous *N*-oxide in a small volume of chloroform-carbon tetrachloride (3 : 1) and adding the appropriate halogenoacetic acid. All the complexes, except those of trifluoroacetic acid, were recrystallized from chloroform-carbon tetrachloride (3 : 1). The complex with trifluoroacetic acid was recrystallized from carbon tetrachloride. The complex with trichloroacetic acid was obtained in two crystal modifications. One (form 1) is obtained by inducing rapid crystallization from a saturated and pre-

<sup>1</sup> Part VI, Z. Dega-Szafran, M. Z. Naskręt-Barciszewska, and M. Szafran, *Roczniki Chem.*, 1973, **47**, 749.

<sup>2</sup> M. Szafran and Z. Dega-Szafran, *Roczniki Chem.*, 1970, **44**, 793.

<sup>3</sup> Z. Dega-Szafran, E. Grech, and M. Szafran, *J.C.S. Perkin II*, 1972, 1839.

<sup>4</sup> Z. Dega-Szafran, E. Grech, M. Z. Naskręt-Barciszewska, and M. Szafran, *Adv. Mol. Relaxation Processes*, 1973, **5**, 89.

cooled solution in chloroform-carbon tetrachloride (3 : 1). The other (form 2) is formed by slow growth of crystals. The complex with trichloroacetic acid decomposes rapidly in acetonitrile solution, apparently with decarboxylation. M.p.s and analyses are given in the Table.

I.r. absorption spectra were recorded on a UR-10 Zeiss-Jena spectrometer. All substances were examined as Nujol and hexachlorobutadiene mulls, and in solution in chloroform, benzene, and acetonitrile (0.3M; in 0.1 mm NaCl cells).

N.m.r. spectra were measured at 80 MHz on a Tesla BS 487 A spectrometer for solutions in deuteriochloroform,

benzene, and acetonitrile at 27 ± 1 °C. Spectra were calibrated with respect to internal tetramethylsilane. The chemical shifts quoted are averages of at least four

### 4-Methylpyridine *N*-oxide complexes with halogenoacetic acids

Acid	M.p. (°C)	C (%)		H (%)		N (%)	
		Calc.	Found	Calc.	Found	Calc.	Found
TFA	34	43.05	42.9	3.6	3.6	6.3	6.3
TCA, form 1	56 †	35.25	35.45	2.95	2.9	5.15	5.15
form 2	66 †	35.25	34.9	2.95	2.9	5.15	5.15
DCA	40	40.35	40.25	3.8	3.85	5.9	5.9
MCA	49	47.2	47.05	4.95	5.05	6.9	6.85

† Decomp.

determinations, usually on two separate solutions. The complexes show a single 'average' resonance at very low field. Hereafter the chemical shift of this resonance will be called the H-bond shift. The H-bond shift values were usually reproducible to within ± 5 Hz.

Solvents were purified by standard methods. Benzene and chloroform were in addition passed through alumina immediately prior to use. Acetonitrile was stored over 4A molecular sieves.

<sup>5</sup> D. Hadži, *J. Chem. Soc.*, 1962, 5128.

<sup>6</sup> D. Hadži and N. Kobilarov, *J. Chem. Soc. (A)*, 1966, 439.

<sup>7</sup> D. Hadži, H. Ratajczak, and L. Sobczyk, *J. Chem. Soc. (A)*, 1967, 48.

<sup>8</sup> L. Golič, D. Hadži, and F. Lazarini, *Chem. Comm.*, 1971, 860.

<sup>9</sup> C. I. Popp and R. O. Ragsdale, *J. Chem. Soc. (A)*, 1969, 1892.

<sup>10</sup> E. Ochiai, *J. Org. Chem.*, 1953, **18**, 534.

## RESULTS AND DISCUSSION

*Infrared Spectra.*—Figure 1 shows the spectra of the two crystal modifications of the complex with trichloroacetic acid (TCA). The spectra of the solid state are different, but solution spectra are essentially the same for all solvents. The most striking differences in the solid state spectra are in the contour and position of the carbonyl band and the broad absorption associated with the hydrogen bond. Form 2 is characterized

This is a strong argument for a 2:2 complex (III). The spectrum of form 2 is also similar to that obtained previously with the 4-methylpyridine *N*-oxide complex.

Form 1 evidently has a different structure; we suggest structure (II). A reasonable explanation for the difference between the spectra in the solid state (form 2) and in solution may be found in the fact that in solution there exists an equilibrium of structures (II) and (III). Structure (II) is recognized from the broad

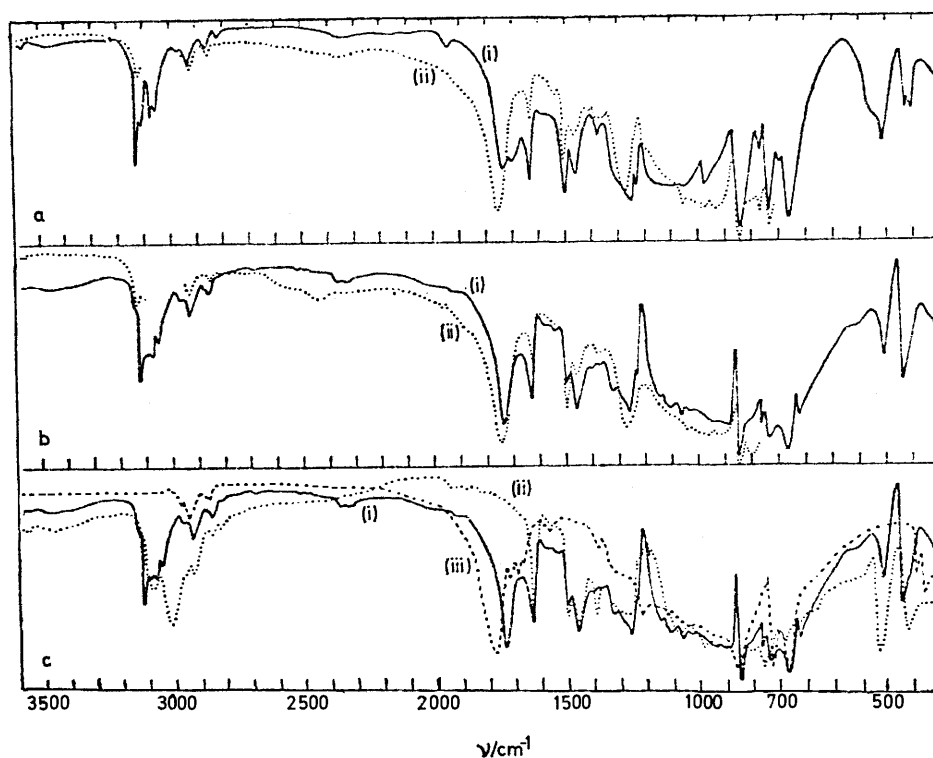


FIGURE 1 I.r. spectra of (a) (i) 4-methylpyridine *N*-oxide-TCA solid state, form 1; (ii) same, but in  $\text{CHCl}_3$ ; (b) (i) 4-methylpyridine *N*-oxide-TCA, solid state, form 2; (ii) same, but in  $\text{C}_6\text{H}_6$ ; (c) (i) 4-methylpyridine *N*-oxide-TCA, solid state, form 2; (ii)  $(4\text{-methylpyridine } N\text{-oxide})_2\text{HBr}$ , solid state; (iii)  $(\text{CCl}_3\cdot\text{CO}_2)_2\text{HK}$ , solid state

by a typical carbonyl band at  $1745\text{ cm}^{-1}$  and a very strong, broad absorption centred at about  $950\text{ cm}^{-1}$ . The spectrum resembles that obtained previously<sup>2</sup> for the 4-methylquinoline *N*-oxide complex with TCA. The spectrum of form 1 shows two bands at  $1735$  and  $1695\text{ cm}^{-1}$  which are probably attributable to  $\nu(\text{C}=\text{O})$  and  $\nu_{\text{as}}(\text{CO}\cdot\text{O})$ , respectively. The strong and broad absorption is centred in the  $1100\text{ cm}^{-1}$  region. In solution, the strong and broad absorption is nearly identical with that from the solid state of form 2. The solvent does influence the details of the broad absorption band and there is some increase in background absorption in the  $2800\text{--}1800\text{ cm}^{-1}$  region. The carbonyl band is shifted slightly to higher frequency. Careful i.r. analysis shows that the spectrum of form 2 (Figure 1c) is essentially the sum of the absorptions of 4-methylpyridine *N*-oxide hemihydrobromide  $[(\text{B}\cdot\text{H}\cdot\text{B})^+\text{Br}^-]$ <sup>11</sup> and the acid salt of TCA  $[(\text{A}\cdot\text{H}\cdot\text{A})^-\text{K}^+]$ .<sup>12</sup>

<sup>11</sup> M. Szafran, *Bull. Acad. Polon. Sci. ser. sci. chim.*, 1963, **11**, 111.

and relatively weak absorption in  $2800\text{--}1800\text{ cm}^{-1}$  region, and structure (III) from the broad and strong absorption centred at about  $950\text{ cm}^{-1}$ . The difference in strength of the broad band in the  $2800\text{--}1800\text{ cm}^{-1}$  region between the solid state (form 1) and solution spectra (Figure 1a) is probably caused by the difference in environment of the complex. Speakman<sup>13</sup> suggests that the environment of the complex in the crystal might exert a significant influence in shortening a short hydrogen bond.

Complexes with trifluoroacetic (TFA), dichloroacetic (DCA), and monochloroacetic (MCA) acids were each obtained in one crystal modification only. Their solid state spectra are similar to the spectrum of form 1 of the complex with TCA (Figure 2), suggesting that these complexes are of the 1:1 type in the crystalline state.

<sup>12</sup> M. Szafran, *Bull. Acad. Polon. Sci. ser. sci. chim.*, 1964, **12**, 383.

<sup>13</sup> J. C. Speakman, *Structure and Bonding*, 1972, **12**, 141.

The solution spectra of the complexes are very sensitive to the nature of the acid (Figures 2 and 3). In particular the broad absorption in the region below  $1200\text{ cm}^{-1}$  shows significant intensity changes with differences in acid strength (Figure 3). With stronger acids, *e.g.* TFA, the absorption becomes even broader at lower frequencies in comparison with that in the

(II) and (III) in solution. The solution spectra, are similar to those obtained previously<sup>2</sup> for 4-methylquinoline *N*-oxide complexes, and appear to be independent of the nature of the solvent in the region below  $1800\text{ cm}^{-1}$ . Additional differences among the spectra of solutions in several solvents are observed in the strength of the broad band in the  $2800\text{--}1800\text{ cm}^{-1}$  region. All

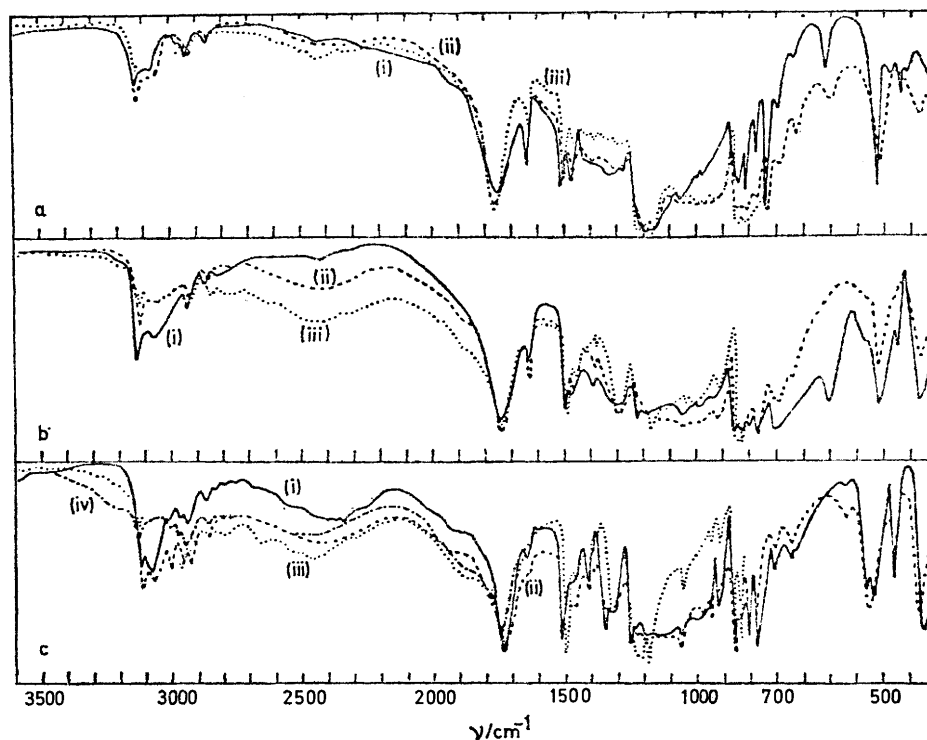


FIGURE 2 I.r. spectra of complexes of 4-methylpyridine *N*-oxide with (a) TFA, (b) DCA, and (c) MCA; (i) solid state, (ii) molten, (iii) in  $\text{CHCl}_3$ , (iv) in  $\text{CH}_3\text{CN}$

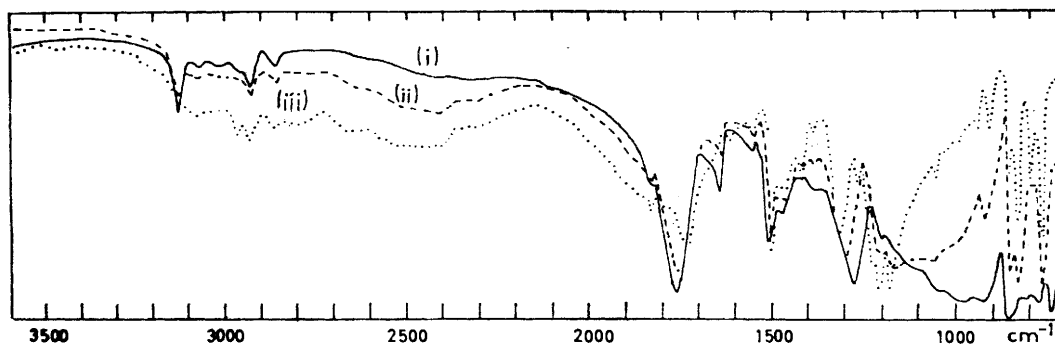


FIGURE 3 I.r. spectra in benzene of 4-methylpyridine *N*-oxide complexes with (i) TCA, (ii) DCA, and (iii) MCA

solid state (Figure 2). In complexes with weaker acids, *e.g.* MCA, this relationship is reversed. In all the solution spectra a greater background absorption in the region  $2800\text{--}1800\text{ cm}^{-1}$  is observed. The intensity of this feature becomes more pronounced for the weaker acids (Figure 3).

In summary, the observed differences between the spectra of the solid state and of solution may be explained in terms of an equilibrium between structures

spectra of solutions in acetonitrile (Figure 2c) show a weak band in the  $3250\text{--}2900\text{ cm}^{-1}$  region. The position of this band has been shown to be related to the  $\text{p}K_a$  value of the acid, and the absorption may be assigned to OH stretching in the monomeric acid ( $\text{AH}_{\text{solv}}$ ).<sup>14</sup>

The spectra of  $0.1\text{--}0.6\text{M}$  solutions in chloroform are practically independent of concentration. However,

<sup>14</sup> L. J. Bellamy, A. R. Osborn, and R. I. Pace, *J. Chem. Soc.*, 1963, 3749.

Gusakova, Denisov, *et al.*,<sup>15</sup> who studied complexes of pyridine with halogenoacetic acids in chloroform, observed concentration dependence up to 0.7M. In order to clarify this problem the spectra of molten complexes were investigated (Figure 2). Comparison of the molten state spectra with those of solutions in chloroform showed in two cases (Figure 2b and c) an increase in the broad absorption below 1200  $\text{cm}^{-1}$

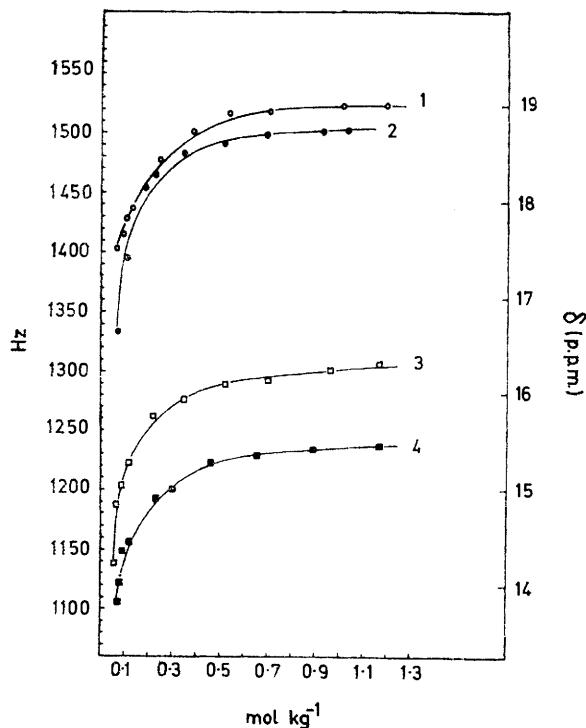


FIGURE 4 H-Bond shifts as a function of concentration in complexes of 4-methylpyridine *N*-oxide with (1) TFA, (2) TCA, (3) DCA, and (4) MCA in benzene

and in all spectra a decrease in absorption in the region 2800–1800  $\text{cm}^{-1}$ . We deduce that in the molten complexes there is some increase in the proportion of form (III) and some decrease in that of form (II) as compared with the solution state.

**Nuclear Magnetic Resonance Spectra.**—The H-bond shifts observed for solutions in benzene, deuteriochloroform and acetonitrile at several concentrations are shown in Figures 4–6. These resonances have a marked concentration dependence, as expected for a system in which protons are present in various molecular species which are in rapid equilibrium. The concentration dependence is similar to that obtained previously<sup>1,3,4</sup> with 4-methylquinoline *N*-oxide complexes and reflects changes in the relative amounts of these molecular species.

We have previously<sup>4</sup> shown that the H-bond shift for 4-substituted quinoline *N*-oxide complexes in deuteriochloroform is related to the difference between the dissociation constants of *N*-oxides and acids in

<sup>15</sup> G. V. Gusakova, G. S. Denisov, A. L. Smoljanski, and W. M. Schreiber, *Doklady Akad. Nauk S.S.S.R.*, 1970, **193**, 1065.

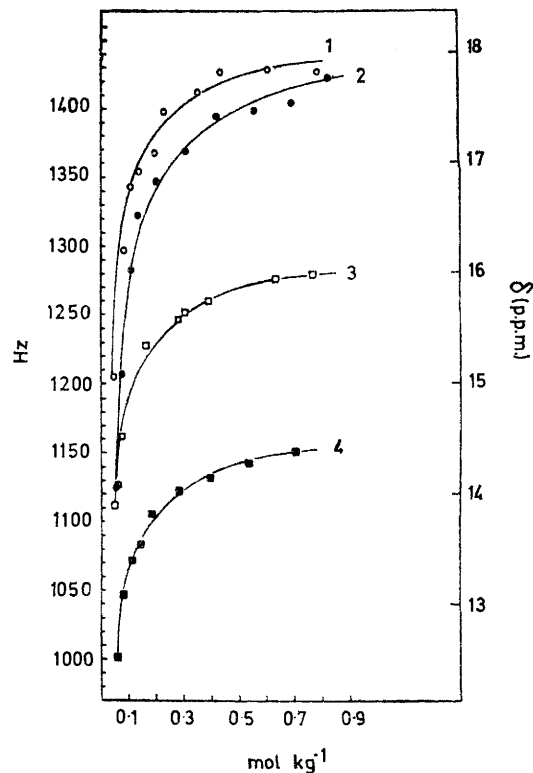


FIGURE 5 H-Bond shifts as a function of concentration in complexes of 4-methylpyridine *N*-oxide with (1) TFA, (2) TCA, (3) DCA, and (4) MCA in deuteriochloroform

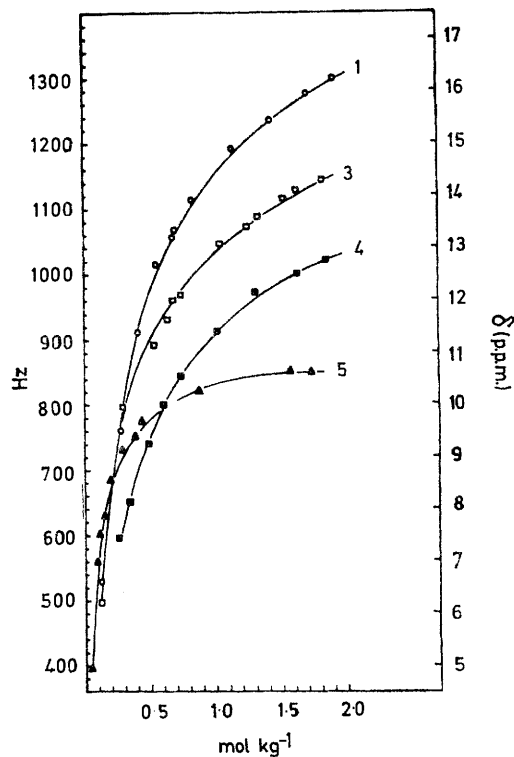


FIGURE 6 H-Bond shifts as a function of concentration in complexes of 4-methylpyridine *N*-oxide with (1) TFA, (3) DCA, and (4) MCA in acetonitrile and (5) TFA in acetonitrile

aqueous solution by equation (2). The chemical

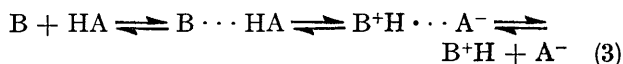
$$\delta = 16.02 + 1.24\Delta pK_a \quad (2)$$

shifts for 4-methylpyridine *N*-oxide complexes show fair agreement with this relation.

N.m.r. spectra are strongly dependent upon the nature of solvent. The observed H-bond shifts decrease in the order benzene > deuteriochloroform > acetonitrile. By analogy with the 4-methylquinoline *N*-oxide complexes, the interaction between 4-methylpyridine *N*-oxide and halogenoacetic acids is described by equation (1). In benzene and deuteriochloroform equilibria, (II) and (III) are probably the most important and the 2 : 2 complex forms conjugated ion pairs (IIIa). In acetonitrile solution the situation is complicated by the presence of monomeric acid (I) and the conjugate ion pair is solvated (IIIb). The H-bond shift is greatest in acetonitrile for the complexes involving the strongest acids, *e.g.* TFA. In such cases the solvating power of the solvent is least likely to break up acid-base complexes.

#### CONCLUSION

It is generally recognized that the interaction of bases (B) with carboxylic acids (HA) in a 1 : 1 ratio is described by equation (3).<sup>16</sup> The results obtained in

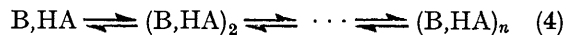


this and previous<sup>3</sup> work indicate clearly that this is true for dilute solutions. At higher concentrations,

<sup>16</sup> M. M. Davis, in 'The Chemistry of Non-aqueous Solvents,' ed. J. J. Lagowski, Academic Press New York 1970.

<sup>17</sup> A. S. Kertes and G. Markovits, *J. Phys. Chem.*, 1968, **72**, 4202.

formation of dimers and perhaps higher oligomers also has to be considered [equation (4)], in agreement with



the studies of Kertes and Markovits<sup>17</sup> on ammonium salts.

The considerable difference between the structures of complexes of 4-methylpyridine *N*-oxide (except form 2) and those of 4-methylquinoline *N*-oxide in the solid state may be attributable to steric constraints; presumably these are imposed by the optimum energy packing arrangement. This conclusion agrees with results of Evans and Lo<sup>18</sup> for the salts  $R_4N^+(ClHCl)^-$ .

Spectra of systems containing hydrogen bonds with a single minimum of potential energy [type (ii) in Hadži's classification<sup>19</sup>] are characterized by (i) the absence of an OH stretching band in the region above 1800  $cm^{-1}$  and (ii) a broad and strong absorption centred between 1200 and 600  $cm^{-1}$ .

The analysis of the spectra of 4-methylpyridine *N*-oxide complexes with TCA indicates clearly that the main evidence for the type of hydrogen bonding is the position of the strong and broad absorption band. As observed in this paper and in ref. 20, the OH stretching vibration appears as a weak band in some spectra and is difficult to detect experimentally.

We thank Professor N. Sheppard for his interest, and the Polish Academy of Sciences (PAN 3) for their support.

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<sup>18</sup> J. C. Evans and G. Y. S. Lo, *J. Phys. Chem.*, 1966, **70**, 11.

<sup>19</sup> D. Hadži, *J. Pure Appl. Chem.*, 1965, **11**, 435; *Chimia (Switz.)*, 1972, **26**, 9.

<sup>20</sup> T. Dziembowska and M. Szafran, *Roczniki Chem.*, in the press.