Infrared and ^1H Nuclear Magnetic Resonance Studies of Hydrogen Bonds in Some Pyridine *N*-Oxide Trifluoroacetates and their Deuteriated Analogues in Dichloromethane

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The i.r. and ^1H n.m.r. spectra of 11 substituted pyridine *N*-oxides with CF_3COOH and CF_3COOD were examined in dry dichloromethane. All the investigated complexes show a typical carbonyl band. The variation of $\nu(C{=}O)$ frequency with ΔpK_a, its shape and band-width, and changes on deuteraition confirm the assumption that the structure of complexes with strong OHO hydrogen bonding is altered gradually with the rise of the interaction energy, from the molecular A-H . . . B, to the ionic, A^- . . . $H\text{-}B^+$. If the centre of gravity ($\bar{\nu}_H$ or $\bar{\nu}_D$) and the chemical shift of hydrogen-bonded protons (δ) are plotted against ΔpK_a, points fall on two intersecting straight lines. These correlations are used to compare the hydrogen bond strength in complexes of pyridines and their *N*-oxides. A discrepancy between the i.r. and ^1H n.m.r. data was found and discussed with respect to the contribution of charge to the shielding of strongly hydrogen-bonded protons. A plot of $\bar{\nu}_H/\bar{\nu}_D$ against $\bar{\nu}_H$ shows a characteristic shape with a minimum, similar to that found by Novak. The variations of $\bar{\nu}_H/\bar{\nu}_D$ with proton acceptor properties of *N*-oxides are consistent with the 'quasi-symmetrical' structure A . . . H . . . B postulated in the literature.

CONSIDERABLE interest has been shown during the last 40 years in the interaction between acids and bases in liquids.[1-9] The main types of structures have been specified and the influence of the solvent recognized. The interaction between comparatively weak partners results in the formation of a molecular complex (A–H · · · B), while that between strong partners results in the formation of an intimate ionic pair (A^- · · · $H\text{–}B^+$). The dissociation of an ionic pair into free ions in solvents like hydrocarbons and their halogen derivatives is extremely unlikely. Instead, most ionic pairs in such solvents exist in the form of higher aggregates $(AHB)_n$.[10,11] The structures of complexes formed by partners of intermediate strength are of special interest. Such complexes usually show a very low ν(AH) frequency and a very high chemical shift for the AH proton. The shape of the ν(AH) band is very complex and it may be determined by many factors having no direct relation to proton migration in the hydrogen bridge.[12] A reliable determination of the structure of the complexes of intermediate-interaction energy is difficult and requires a study of each complex over a wide range of the spectrum.

An equilibrium between a molecular complex and an ionic pair of the OH · · · N $\rightleftharpoons$ O^- · · · $H\text{–}N^+$ type has been found from the i.r. spectra in the carbonyl–carboxylate region[13-17] and skeletal[18] vibrations of partner molecules, from u.v. spectra,[19,20] and from ^1H n.m.r. spectra at low temperatures.[21] The frequency of the reversible proton transfer in the OH · · · N complexes is above 10^5 s^{-1}, but much slower in complexes with CH · · · N bonding.[9] Thus the fact of proton migration in complexes of OHN and CHN types in inert media is not in doubt. In the case of OH · · · O complexes not a single example of molecular–ionic tautomerism has been reported. It seems that their structure is altered gradually with an increase in the interacting energy, from the molecular, A–H · · · B, to the ionic, A^- · · · $H\text{–}B^+$.[22-24] In the intermediate case (*e.g.* complexes of CF_3COOH with some oxides[23,25,26]) the spectral features of such complexes resemble those of some acid salts of carboxylic acids $MH(OOCR)_2$, whose potential surface for the interaction has only one minimum corresponding to a central position for the proton.[27,28] Matrosov and Kabachnik[23] proposed a 'quasi-symmetrical' hydrogen bond structure ($A^{\delta-}$ · · · H · · · $B^{\delta+}$) for the intermediate complex.

Further information can be derived from the isotope effect. An interesting correlation between the ratio $\nu(OH)/\nu(OD)$ and the bond length R(O · · · O) or frequency ν(OH) has been demonstrated by Novak.[29] It has been shown that this ratio decreases from *ca.* 1.35 for a weak (long) hydrogen bond up to 1.0 for a very strong (short) bond. In a case of short, probably symmetrical type hydrogen bonds, the value $\nu(OH)/\nu(OD)$ becomes bigger than $\sqrt{2}$. The theory of an anomalous isotope frequency shift has been studied by Sokolov and Savel'ev[30,31] and Guissani and Ratajczak.[32]

In this paper we investigate the carbonyl region and $\nu(OH)/\nu(OD)$ ratio for complexes of the trifluoroacetic acid with various pyridine *N*-oxides in dichloromethane in order to obtain more information on changes in the hydrogen bond with a change in acceptor properties of the *N*-oxides. ^1H N.m.r. spectra are also investigated and discussed in terms of a positive charge effect on the chemical shift of hydrogen-bonded protons.

EXPERIMENTAL

Complexes were prepared as previously.[26] Dichloromethane was passed through alumina, stored over Linde 4Å molecular sieves, and used within ten days. Dichloromethane for deuteriated complexes was washed with D_2O, distilled, and then dried. The percentage of deuterium in complexes was monitored by ^1H n.m.r. spectroscopy, and was >95%. All solutions were prepared and non-aqueous solutions were transferred in a dry box.

I.r. spectra were recorded on a Perkin-Elmer 180 spectrophotometer, using cells with KBr (0.124 mm, 0.2M),

CaF_2 (0.025 mm, 0.97M), and NaCl (1.0 mm, 0.01M) windows. ^1H N.m.r. spectra were measured at 60 MHz on a Varian EM 360 spectrometer at 24 ± 2 °C. All chemical shifts were taken downfield relative to the resonance of the solvent and then converted to δ values.

The ionization constant of 4-ethoxypyridine *N*-oxide was determined by a spectrophotometric method (analytical wavelengths 264 and 270 nm) at 20 °C; $pK_a = 1.97 \pm 0.03$.

Centres of gravity of the reconstructed bands were obtained as $\bar{\nu} = \int A(\nu)\nu d\nu / \int A(\nu) d\nu$ by numerical integration as described previously.[17] To simplify, the following abbreviations are used $\bar{\nu}(OH) \equiv \bar{\nu}_H$ and $\bar{\nu}(OD) \equiv \bar{\nu}_D$.

RESULTS AND DISCUSSION

There are two bands, 1 805 and 1 782 cm^{-1}, in the ν(C=O) region of the i.r. spectrum of a trifluoroacetic acid solution in dichloromethane (Figure 1a). The first band corresponds to the monomeric acid since the intensity strongly increases with dilution. Additional proof is provided by the ν(OH) band at 3 440 cm^{-1} whose intensity increases with dilution too. The band at 1 782 cm^{-1} is attributed to ν(C=O) of the dimeric species. Deuteriation causes not only a shift to lower frequencies (1 804 and 1 780 cm^{-1}) but also a narrowing of the dimer band ($\Delta\nu^{H}_{3/4}$ 17, $\Delta\nu^{D}_{3/4}$ 16 cm^{-1}). In the case of complexes the ν(C=O) frequency decreases with increasing proton-acceptor properties of the *N*-oxides (Table 1). The band-width is three or more times larger than that in the dimer. The observed increase of the band-width is partly caused by the superposition of the OH stretching vibration (Figure 1). In the spectra of complexes with the weakest *N*-oxides (*e.g.* the 4-nitro- and 4-cyano-derivatives) the uncomplexed acid can be recognized [ν(C=O) at 1 800 cm^{-1} as a shoulder and ν(OH) at 3 440 cm^{-1}]. For the strongest *N*-oxides (*e.g.* the 4-dimethylamino-derivative) the uncomplexed acid was not observed, even for a dilute solution (0.01M). Deuteriation lowers ν(C=O) by 10—25 cm^{-1}. For the very strong, probably symmetrical hydrogen bond, such as that found in the crystal of KH-$(OOCCF_3)_2$ the carbonyl band shifts from 1 790 to 1 735 cm^{-1} on deuteriation.[28]

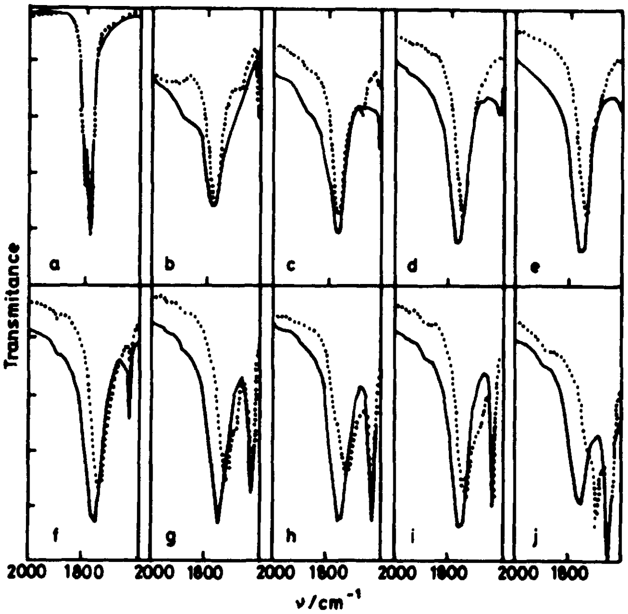


FIGURE 1 I.r. spectra of trifluoroacetic acid (——) and trifluoroacetic [^{2}H]acid (· · · ·) and their complexes with substituted pyridine *N*-oxides in dichloromethane: a, acid and b—j complexes; b, 4-CN; c, 4-Cl; d, H; e, 3-Me; f, 4-Me; g, 4-OEt; h, 4-OMe-2-Me; i, 4-OPh; j, 4-NMe$_2$

The spectrum of the 4-dimethylamino pyridine *N*-oxide complex requires comment. Figure 1 shows that the smooth ν(C=O) band at 1 745 cm^{-1} is replaced on deuteriation by a very narrow band at 1 688 cm^{-1} and a shoulder at 1 725 cm^{-1}. The narrow band lies in the $\nu_{as}(COO^-)$ region of trifluoroacetates, but its width is at least three times smaller than that of a typical carboxylic band.[17] Thus the shoulder (1 725 cm^{-1}) can be ascribed to the perturbed vibration ν(C=O) of the complex and the band at 1 688 cm^{-1} to some other perturbed internal mode. The observed broadening of the ν(C=O) band for some other complexes (the last three columns of Table 1, Figure 1h—j) supports the above suggestion. Finally it should be mentioned that the tautomeric equilibrium between a molecular complex and an ionic pair requires a broadening of the absorption in the carbonyl region of medium—strong bases (see *e.g.* ref. 17). A short hydrogen bond strongly perturbed the structure of the carboxylate anion and only the carbonyl band is observed in *e.g.* potassium hydrogen bis(trifluoroacetate).[28] Thus a strong hydrogen-bonded ionic pair can absorb in the carbonyl region and this would cause a broadening of the band. In the investigated complexes most bands are smooth and have nearly constant width, and the observed exceptions can be explained by other facts. Thus there is strong evidence in favour of a continuous shift of the proton from the carboxy to the *N*-oxide group with increasing proton-acceptor properties of *N*-oxides.

The i.r. spectra of *N*-oxidopyridine trifluoroacetates show, as for other compounds with strong hydrogen-bonds,[12] an extremely broad absorption that extends from *ca.* 3 000 down to 400 cm^{-1} and is topped by some badly defined maxima (A > 2 800, B *ca.* 2 500, C *ca.* 1 900, D *ca.* 1 100, and E *ca.* 850 cm^{-1}). This absorption is assigned to the OH stretching vibration of the strongly hydrogen-bonded *N*-oxidopyridine trifluoroacetates (Figure 2). Deuteriation reduces this absorption (Figure 3). Table 1 lists the centres of gravity ($\bar{\nu}_H$ and $\bar{\nu}_D$) of the very broad stretching vibration and the isotopic frequency ratio ($\bar{\nu}_H/\bar{\nu}_D$). Figures 4 and 5 show a generally good correlation between the centre of gravity ($\bar{\nu}_H$ and $\bar{\nu}_D$) and ΔpK_a. A deviation from the correlation lines is seen for 4-phenoxypyridine *N*-oxide complex.

Recently, we have reported the same type of correlation between the chemical shift of hydrogen-bonded protons and ΔpK_a [26] in four solvents excluding dichloromethane. Since in the previous paper we had only two points on the right-hand side of a diagram, and one of them was 4-phenoxypyridine *N*-oxide, we extend the investigation of ^1H n.m.r. spectra. The results are shown in Figure 6. Since the point of 4-PhO-pyridine

TABLE 1

Characteristic i.r. bands and chemical shifts of hydrogen-bonded protons of substituted N-oxidopyridine trifluoroacetates in dichloromethane (0.2M)

No.	Substituent	ΔpK_a	$\nu(C=O)/cm^{-1}$		$\Delta\nu_{3/4}(C=O)/cm^{-1}$		$\bar{\nu}_H/cm^{-1}$	$\bar{\nu}_D/cm^{-1}$	$\bar{\nu}_H/\bar{\nu}_D$	δ
			H	D	H	D				
1	4-NO_2	−1.93	1 800 sh 1 775	1 800 sh 1 765	67	38	2 012	1 646	1.222	15.03 *
2	4-CN	−1.40	1 800 sh 1 775	1 800 sh 1 765	67	40	1 955	1 644	1.189	15.40 *
3	4-Cl	0.13	1 770	1 760	57.5	40	1 420	1 263	1.124	17.77
4	H	0.56	1 765	1 755	52	45	1 302	1 170	1.113	18.33
5	3-Me	0.85	1 760	1 750	52	45	1 218	1 115	1.092	18.57
6	4-Me	1.06	1 755	1 745	52	50	1 167	1 030	1.133	18.82
7	4-OEt	1.74	1 750	1 725 1 688 sh	55	52	1 165	1 036	1.124	18.90
8	4-OMe	1.82	1 750	1 725	50	55	1 164	1 040	1.119	18.67
9	4-OMe-2-Me	2.18	1 750	1 725 1 695 sh	55	65	1 238	1 130	1.096	18.33
10	4-OPh	2.44	1 755	1 730 1 680 sh	52	62	1 173	1 070	1.096	18.97
11	4-NMe_2	3.65	1 745	1 725 sh 1 688	70		1 527	1 329	1.149	17.42

* With excess of base (C_B/C_{AH} = 2 : 1).

N-oxide complex is well removed from the correlation line it is clear that the data for the intersection point described previously are overstated. The correct data are listed in Table 2.

Previously, we have shown [33] that complexes of pyridine N-oxides and quinoline N-oxides with trifluoroacetic acid generate their own lines correlating the chemical shift of hydrogen-bonded protons with ΔpK_a values. The difference between the behaviour of these two families of N-oxides may be explained in terms of the diamagnetic anisotropy of the benzene ring and association through dipole–dipole interactions. Hence, the deviation from the correlation lines observed for the 4-phenoxypyridine N-oxide complex suggests that this compound should be considered as one of another family of bases. A 4-phenoxy-substituent diminishes the dipole–dipole association.[10]

An examination of Figures 4—6 shows that the charac-

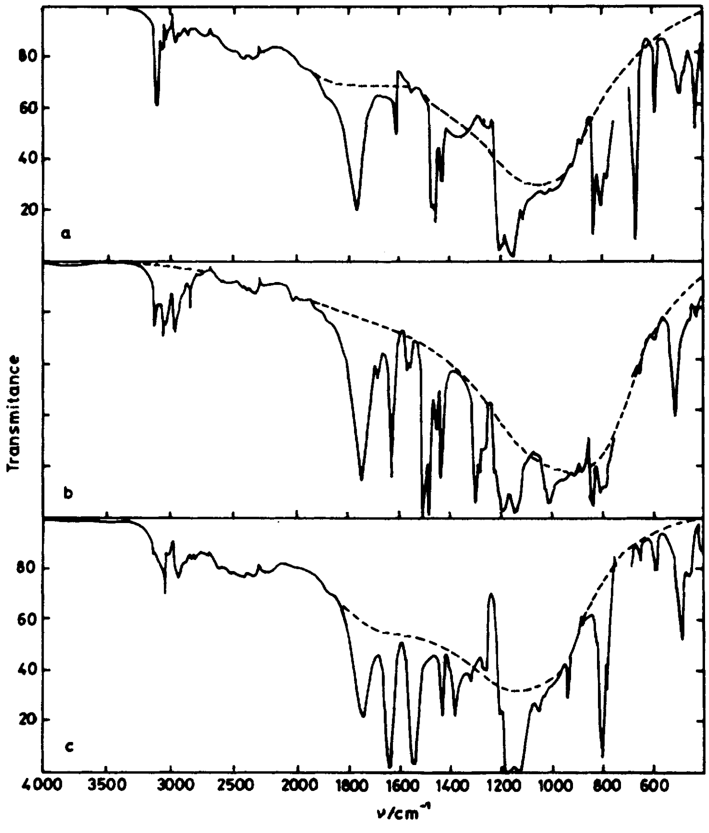


FIGURE 2 I.r. spectra of complexes of substituted pyridine N-oxides with trifluoroacetic acid in dichloromethane: a, 4-Cl; b, 4-OMe; c, 4-NMe_2

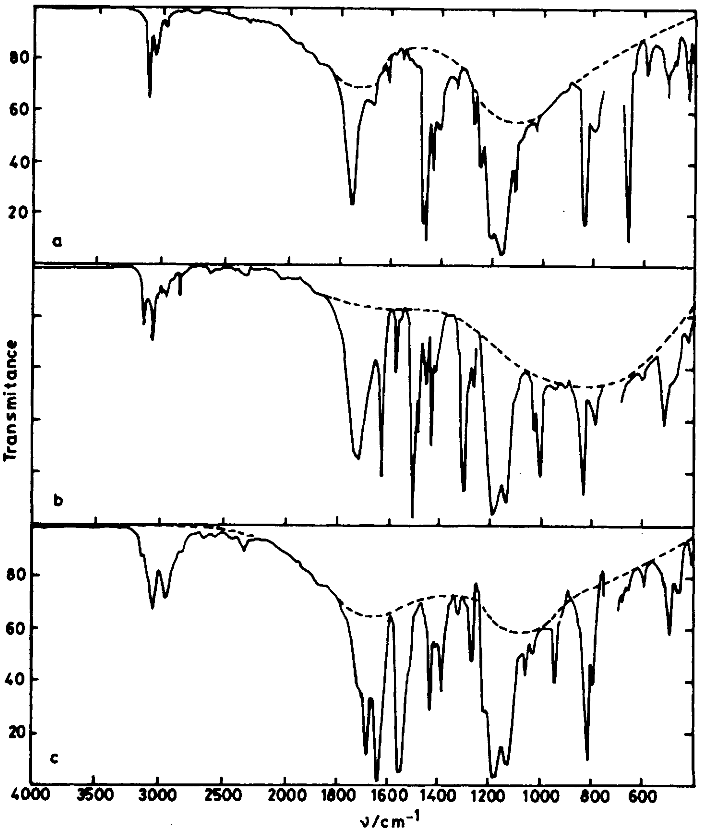


FIGURE 3 I.r. spectra of complexes of substituted pyridine *N*-oxides with trifluoroacetic [^{2}H]acid in dichloromethane: a, 4-Cl; b, 4-OMe; c, 4-NMe$_2$

teristic alterations of both the centre of gravity of the complex absorption and the chemical shift with ΔpK_a reflect the variations of the hydrogen bond strength. The strongest hydrogen bond appears in complexes which are close to the intersection point.

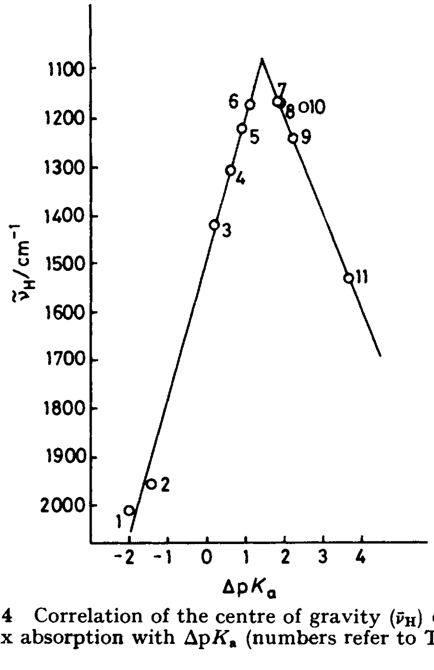


FIGURE 4 Correlation of the centre of gravity ($\tilde{\nu}_H$) of ν(AH) complex absorption with ΔpK_a (numbers refer to Table 1)

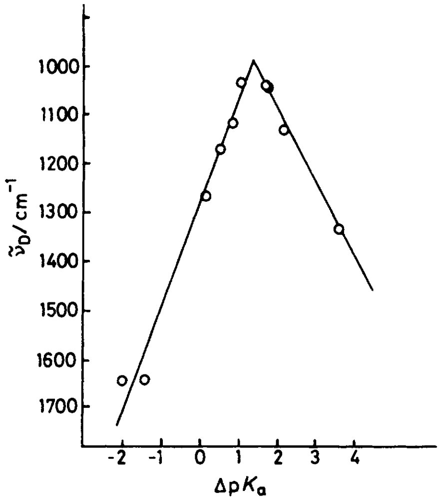


FIGURE 5 Correlation of the centre of gravity ($\tilde{\nu}_D$) of ν(AD) complex absorption with ΔpK_a (numbers refer to Table 1)

An interesting comparison can be made between complexes of pyridines and their *N*-oxides with trifluoroacetic acid, because for the former complexes correlations similar to those in Figures 4—6 have been described.[17,34,35] The lower frequencies ($\tilde{\nu}_H$ and $\tilde{\nu}_D$) obtained for complexes of pyridine *N*-oxides support the claim that the OHO hydrogen bond is stronger than that of OHN. However, the reverse conclusion is derived from comparison of the

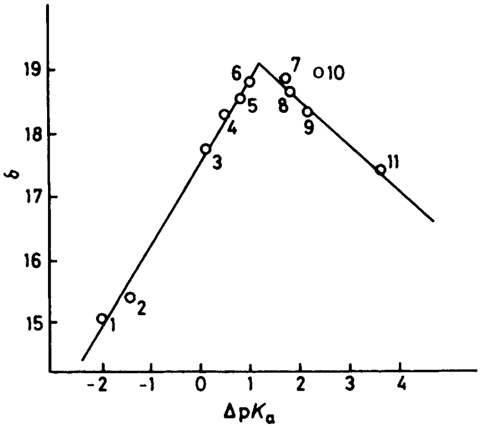


FIGURE 6 Correlation of the chemical shift of hydrogen-bonded protons (δ) with ΔpK_a (numbers refer to Table 1)

chemical shift of hydrogen-bonded protons. In complexes of pyridine hydrogen-bonded protons show a significant downfield shift of *ca.* 1 p.p.m. when compared to those in the *N*-oxides. The conclusive evidence that the discrepancy is probably due to the effect of a positive charge came from the correlation between the chemical shift and the centre of gravity. This showed a single line for complexes of pyridine *N*-oxides (Figure 7) and two lines for complexes of pyridines.[34,35] Our interpretation is that these results are due to the charge transfer caused by the proton transfer as in (A) and (B).

TABLE 2

Comparison of data at the intersecting points

Correlation	ΔpK_a	δ	$\tilde{\nu}_{\rm H}$/cm^{-1}	$\tilde{\nu}_{\rm D}$/cm^{-1}
$\delta = f(\Delta pK_a)$	1.23	19.13		
$\tilde{\nu}_{\rm H} = f(\Delta pK_a)$	1.33		1 077	
$\tilde{\nu}_{\rm D} = f(\Delta pK_a)$	1.39			988
Average	1.32 ± 0.08			

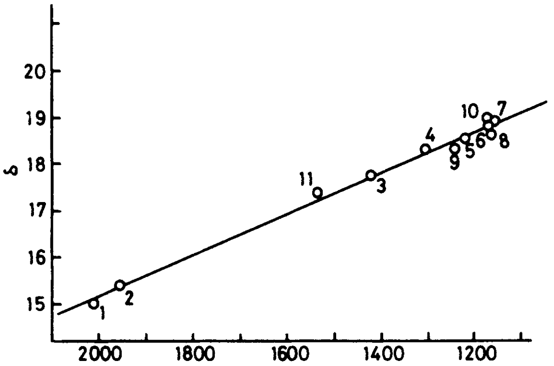
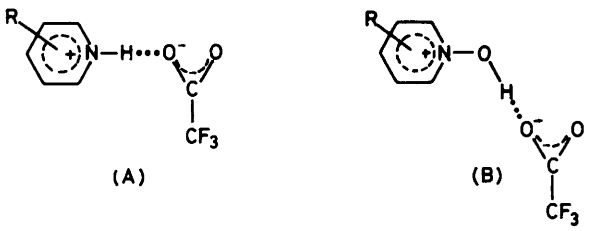


FIGURE 7 Correlation of the chemical shift of hydrogen-bonded protons (δ) with the centre of gravity ($\tilde{\nu}_{\rm H}$) of ν(AH) complex absorption (numbers refer to Table 1)

As the separation of a positive charge in complexes of pyridine *N*-oxides is greater than in pyridine series the deshielding effect in the former complexes is lower and the chemical shift of the hydrogen-bonded protons in a molecular complex approaches that of an ionic pair. The above mentioned discrepancy between the behaviour of i.r. and n.m.r. data implies that the contribution of charge to shielding of strongly hydrogen-bonded protons is important.



A plot of the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ isotope frequency ratio against $\tilde{\nu}_{\rm H}$ (Figure 8) is very similar to that found by Novak[29] for some crystals and calculated by Romanowski and Sobczyk.[36] The decreasing part of the curve is also in satisfactory agreement with Savel'ev and Sokolov's[30,31] calculations.

In Figure 8 the curve shows that the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ value decreases slowly with lower frequencies. The potentials (double or single minimum) are strongly asymmetric and the proton stays preferentially in one well. Values of the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ ratio of *ca.* 1.1 are observed when $\tilde{\nu}_{\rm H}$ shifts to 1 220 cm^{-1}. This range may correspond to the potentials which are strongly asymmetric near the first excited level.[32] Finally, the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ ratio increase. We expect a further increase in the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ ratio for complexes close to the intersection points (Figures 4—6), since their frequencies are predicted to be in the 1 080 cm^{-1} region (Table 2). As the investigated complexes are asymmetric (with respect to molecular symmetry) the strong hydrogen bond in complexes at the intersection point can be described by a quasi-single minimum potential with sufficient anharmonicity. Theoretical calculations of the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ ratio for quasi-single minimum have been carried out, giving values ranging between 1.1 and 1.3.[32] The analysis indicates that there is a good agreement between our approach and the theoretical calculations. Thus, the expected values of the $\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$ ratio for a complex at the intersection point is consistent with the 'quasi-symmetrical' structure of the hydrogen bond.

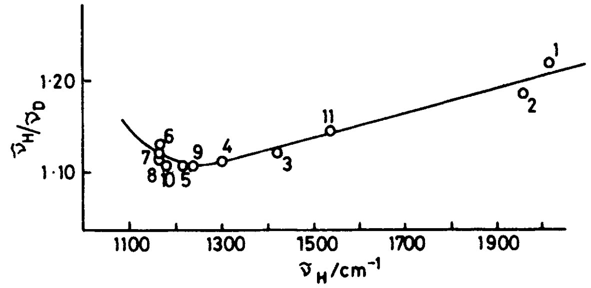


FIGURE 8 Correlation of the isotope frequency ratio ($\tilde{\nu}_{\rm H}/\tilde{\nu}_{\rm D}$) with the centre of gravity ($\tilde{\nu}_{\rm H}$) of ν(AH) complex absorption (numbers refer to Table 1)

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