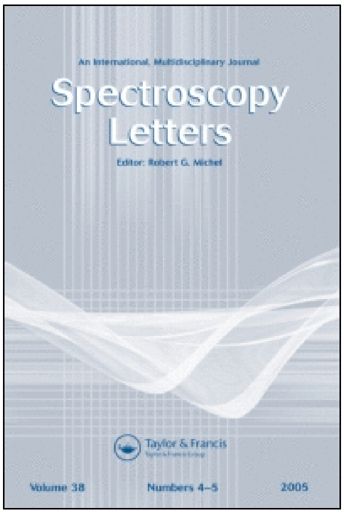

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INFRARED STUDY OF THE HYDROGEN BOND COMPLEXES INVOLVING 2,3-BIS-(2-PYRIDYL)-PYZAZINE AND PROTON DONORS. COMPARISON WITH MONOFUNCTIONAL HETEROCYCLIC N-BASES.

Keywords : 2,3-bis(2-pyridyl)-pyrazine, proton acceptor ability, infrared spectra.

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ABSTRACT

The hydrogen bond complexes between phenols and 2,3-bis(2-pyridyl)-pyrazine BPP) are investigated by infrared spectroscopy in carbon tetrachloride solution. The formation constants for the complexes of 1-1 stoichiometry are higher than those predicted from the pK_a of BPP. This is also the case for other N-heteroaromatic bases (pyridazine, 2,2'-bipyrimidine) characterized by two vicinal equivalent nitrogen atoms. The thermodynamic and infrared data of the complexes show that BPP cannot be considered as a proton sponge.

INTRODUCTION

The build-up of two dimensional and three-dimensional architectures requires the presence in the molecular components of two or more hydrogen bonding substrates whose position determines the final supramolecular structure. The polyfunctional N-heteroaromatic ligands such as ditopic bis-byridine, bis-pyrimidine, bis-pyrazine or hexaphenylhexaaza-derivatives form a very important class of ligands[1]. However, very few works on the proton acceptor ability of these bases have appeared in the literature. In this work , the hydrogen-bonding ability of 2,3-bis-(2-pyridyl)-pyrazine (BPP) is investigated , taking phenol derivatives as reference proton donors and compared with other N-heterocyclic bases

As shown in Figure 1, BPP has a crystallographic twofold axis through the mid-point of the pyrazine carbon-carbon bond. The dihedral angle between pyrazine and pyridine rings is 42.2° and between the two pyridine rings is 54.1° [2]

BPP form with metals coordination compounds and acts as a bidentate ligand through the two N-pyridine to form a seven-membered ring or through one pyridine-N and one pyrazine-N to form a five-membered ring [3-5].

The pK_a of BPP at 25°C is 3.1 [6] or 2.9 [7]. The molecule has two pyrazinyl N and two pyridyl N centers available for protonation. Since the latter are readily protonated (pK_a values of 5.17 for pyridine and 0.51 for pyrazine), the observed pK_a value probably reflects protonation occuring at one of these pyridyl N-centers. The infrared and Raman spectra of the ionic adducts of BPP with hydrogen chloride also strongly suggest that protonation takes place on one of the pyridyl N [8].

EXPERIMENTAL

The spectra have been recorded on the Perkin Elmer 883, on the Bruker 88 and on the Bruker 66 spectrometers.

The equilibrium constants characterizing the formation of complexes of 1-1 stoichiometry between BPP and phenols have been measured from the absorbance of the ν(OH) stretching vibration lying at 3610-3595 cm^{-1}. The concentrations of proton donors ranged between 0.005 and 0.007 mol dm^{-3} and BPP was always in excess in order to avoid self-association. The thermodynamic parameters have been measured in carbon tetrachloride.

BPP from Aldrich has been used without further purification. The phenols from Aldrich or Janssen Chimica have been crystallized from petroleum-ether-CCl_4 mixtures. CCl_4 from Janssen Chimica has been dried on molecular sieves.

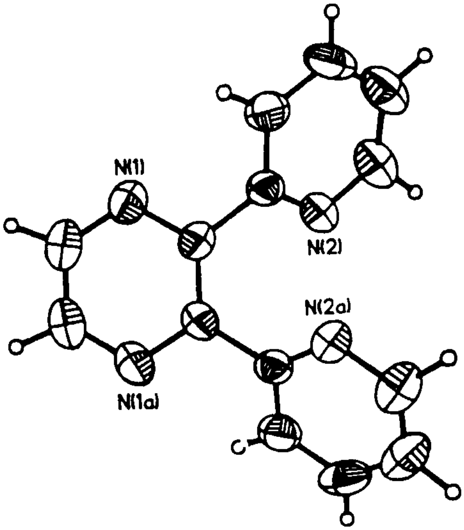

FIG. 1. X-ray structure of BPP (adapted from ref. 2)

RESULTS AND DISCUSSION

The thermodynamic data (equilibrium constants, enthalpies and entropies of complex formation) and the frequency shifts of the ν(OH) stretching vibration are indicated in Table 1

The logarithms of the equilibrium constants are linearly related to the pK_a^A values of the phenols :

$$\log K^{298K} = 7.68 - 0.59\, pK_a^A \quad (r = 0.998) \qquad (1)$$

$$\log K^{323K} = 7.76 - 0.53\, pK_a^A \quad (r = 0.997) \qquad (2)$$

In this limited $-\Delta H$-$\Delta\nu(OH)$ range, the Badger-Bauer correlation is valuable:

$$-\Delta H(\mathrm{kJ\ mol^{-1}}) = -23.3 + 0.106\, \Delta\nu(OH)\,(\mathrm{cm^{-1}}) \quad (r = 0.981) \qquad (3)$$

The data of Table 1 indicate that the complexes between phenols and BPP are of medium strength. The formation constants, the enthalpies of complex formation and the $\Delta\nu(OH)$ values are higher than for the pyrazine complexes [9] and from this it can

TABLE 1.

Thermodynamic data and Δν(OH) values for the interaction between phenols and BPP in carbon tetrachloride.

Phenol	K^{298K} ($dm^{-3}\,mol^{-1}$)	K^{323K} ($dm^{-3}\,mol^{-1}$)	-ΔH ($kJ\,mol^{-1}$)	-ΔS° ($kJ\,mol^{-1}$)	Δν(OH) (cm^{-1})
3,4-diCH_3	36	17	25	54	455
4-CH_3O	43	20	26	54	460
phenol	60	24	27	55	470
4-Cl	148	58	29	56	500
4-Br	151	67	29	56	505
3,4-diCl	418	156	32	58	530
3,5-diCl	588	225	34	59	535
3,4,5-triCl	1315	395	36	60	550

be anticipated that complex formation with hydroxylic proton donors will occur at the pyridyl-N atom. This is strengthened by the fact that some pyridine vibrations of BPP are shifted to higher wavenumbers in the complexes. The ν6a, ν1 and ν19a skeletal modes observed at 620, 992 and 1477 cm^{-1} in free BPP are shifted to 632, 1006 and 1484 cm^{-1}. These perturbations are similar to those observed in pyridine complexed with hydroxylic proton donors[10]. It must be pointed here that owing to the D_{2h} molecular symmetry of pyrazine, the symmetric skeletal vibrations ν1 and ν6a are not infrared active and are not observed in BPP so that the absorptions observed at 620 and 992 cm^{-1} could be assigned to pyridine-like modes. The ν1 mode of pyrazine is observed at 1014 cm^{-1} in a Raman spectrum [11].

Table 2 allows us to compare the stability constants at 298K for the interaction between 3,4-dichlorophenol and other N-heterocyclic bases (pyridines, diazines and 2,2'-bipyrimidine). This table also indicates the pK_a^B and the proton affinity (PA)[12] values of the proton acceptor and in some cases the enthalpies of complex formation and the $\Delta\nu(OH)$ values. In order to compare the stability constants in the different systems, a statistical correction taking into account the number of equivalent N in the base was applied. This statistical factor is indicated between parenthesis in the fourth column of Table 2.

Figure 2 where the logarithms of the formation constants at 298K is plotted against the pK_a^B values shows that bases 1 to 8 are situated on the same straight line, the equation of this line being

$$\log K^{298K} = 1.10 + 0.244\, pK_a^B \qquad (r = 0.978). \qquad (4)$$

For bases 9, 10 and 11, the K values are much higher than those predicted from their basicity. This effect is also found for the other phenols studied in this work and exceeds by far the experimental errors on K wich are of the order of magnitude of 5%.

Bases 1-8 are characterized by the presence in the heteroaromatic ring of one nitrogen atom (pyridine derivatives) or by two non-vicinal nitogen atoms. Bases 9, 10 and 11 are characterized by the presence of two vicinal N. In pyridazine, the two lone pairs are parallel. 2,2'-bipyrimidine is planar in the solid state and this is also the case in the dihydrate where two of the four N are bonded to the water molecules [15] In solvents of low polarity, the structure of 2,2'-bipyrimidine is also likely planar and the two lone pairs are pointing to each other. The approach of a hydroxylic proton donor is greatly favoured in the electron-rich region formed by two N. This effect does not exist in 2,2'-pyridine, owing to its transoid configuration [16] . Interestingly, the computed PA of *trans*-2,2'bipyridine is higher (1012 kJ mol^{-1}) than that of *cis*-2,2'bipyridine (946 kJ mol^{-1}) [17].

The same effect was also observed for the complexes between N-heteroaromatic bases and iodine. The K values of 1,10-phenanthroline are higher when compared to

TABLE 2.

Data for complexes involving heterocyclic N-bases and 3,5-dichlorophenol in carbon tetrachloride; pK_a and PA of the proton acceptor.

Base	pK_a^B	PA ($kJ\ mol^{-1}$)	K^{298K} dm^3mol^{-1}	$-\Delta H$ ($kJmol^{-1}$)	$\Delta\nu(OH)$ (cm^{-1})
(1) Pyrazine	0.51	874	34.3(2)[a]	26	433
(2) Pyrimidine	1.23	880	71(2)[a]	28	445
(3) 3-Br pyridine	2.84	906	56(1)	29	-
(4)3-Cl pyridine	2.84	899	53(1)	29	-
(5) 3-I pyridine	3.25	-	58(1)		
(6) Pyridine	5.17	923	208(1)	31	540
(7) 4-CH_3 pyridine	5.98	941	410(1)[b]	32	550
(8)3,5-di-CH_3 pyridine	6.15	945	490(1)[b]	-	
(9) Pyridazine	2.3	901	313(2)[a]	30	470
(10)2,2'-bipyrimidine	0.65	-	1550(4)[c]	35	335
(11) BPP	3	-	418(2)	32	530

a : ref 9 a : ref 13 c ref : 14

those of 1,7-phenanthroline and among the three diazabenzenes, pyridazine has the highest K value [18].

The data of Table 2 also indicate that for the pyridazine complex, the K value is higher than that predicted from its PA. For systems 9-11, the enthalpies of complex formation are also higher than those expected from the pK_a^B of the proton acceptors. this result must however be taken with caution, the errors on the determination of the enthalpies being ± 1.5 kJ mol^{-1}.

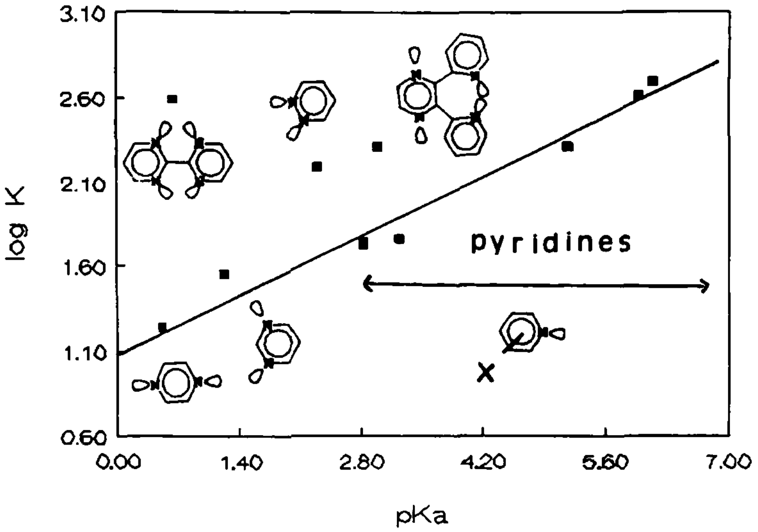

FIG.2. Log K (3,4-dichlorophenol-N-bases) as a function of pK_a^B

The presence of two vicinal N increases the stability of the complexes formed with hydroxylic proton donors. Bases 10-11 investigated in this work cannot be considered as proton sponges. The complexes formed between the proton sponge 1,8-bis(dimethylamino)naphtalene (DMAN) and phenols form in solution complexes of 1-2 stoichiometry and have a strong tendency to form protonated NH^+ and $(OHO)^-$ homoconjugated species. [19-20]. In DMAN, the distance between the two N atoms is short and the relief of electron repulsion seems to be a driving force for protonation; the pK_a^B value of DMAN (12.5) is also much higher. [21]. Further in the infrared spectra of the complexes in solution and in the solid state broad absorptions extending from 2800 to 500 cm^{-1} are observed. The isotopic ratio of the protonic bands is about one [22]. In the present complexes, no complexes of higher stoichiometry could be detected when the base was in excess and no broad absorption in the fingerprint region was observed. Further the isotopic ratio

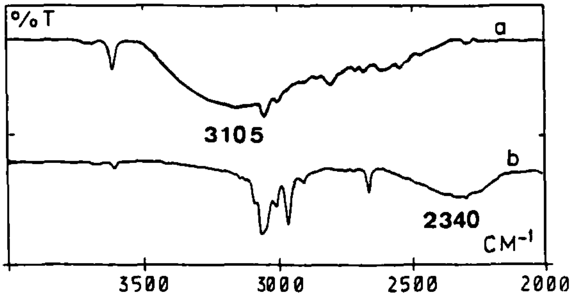

FIG.3. IR spectrum (4000-2000 cm^{-1}) of the complex between BPP and
a : 4-Br phenol-OH b : 4-Br phenol-OD
(c_{BPP} = 0.027 mol dm^{-3}, $c_{4\text{-Br phenol}}$ = 0.01 mol dm^{-3}, pathlength = 0.3 cm
Solvent = carbon tetrachloride).

ν(OH)/ν(OD) takes values between 1,32 and 1.33 for all the BPP complexes. This is illustrated in Figure 3 showing the infrared spectrum in the ν(OH) and ν(OD) region for 4-Br phenol-OH and 4-Br phenol-OD complexes with BPP where the ν(OH...N) and ν(OD...N) vibrations are observed at 3105 and 2340 cm^{-1} respectively. The value of this isotopic ratio suggests in the present case a localized proton and a relatively high barrier for the proton transfer [23]. Thus BPP cannot be considered as a proton sponge; the formation of complexes of high stability is generally followed by the formation of complexes of 1,2 stoichiometry and by the protonation [24] and in this sense, the behaviour of BPP announces that of the proton sponges. These conclusions are confirmed by experimental data on other N-bases such as 2,4,6,-tri-(2-pyridyl)-s-triazine and pyrazino(2,3-f)quinoxaline [25].

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