

Infrared Study of Hydrogen Bonds Involving *N*-Heterocyclic Bases and Phenols

Muriel Goethals [a], Boguslawa Czarnik-Matusiewicz [b]
and Thérèse Zeegers-Huyskens* [a]

[a] Department of Chemistry, University of Leuven, Celestijnenlaan 200F, B-3001 Heverlee, Belgium

[b] Faculty of Chemistry, University of Wrocław, 14 Joliot-Curie Street, 50 383, Poland

Received April 3, 1998

Revised September 9, 1998

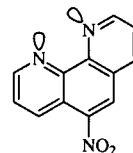
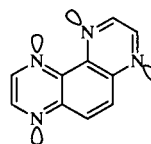
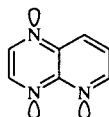
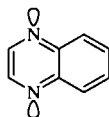
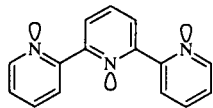
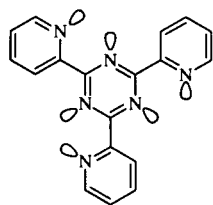
The hydrogen bond complexes between phenols and *N*-heteroaromatic bases 2,4,6-tri(2-pyridyl)-1,3,5-triazine, 2,2',2''-terpyridine, quinoxaline, pyrido[2,3-*b*]pyrazine, pyrazino[2,3-*f*]quinoxaline and 5-nitrophenanthroline are investigated by infrared spectroscopy in 1,2-dichloroethane. The stability constants of the complexes involving *N*-heteroaromatic bases characterized by two vicinal nitrogen atoms having lone pairs pointing to each other are higher than predicted from their basicity. Possible differences between protonation and hydrogen bond formation are discussed. *N*-heteroaromatic bases such as tri(2-pyridyl)-1,3,5-triazine or phenanthrolines cannot be considered as proton sponges but their behaviour is intermediate between that of the classical heteroaromatic bases and the proton sponges.

J. Heterocyclic Chem., **36**, 49 (1999).

Introduction.

Hydrogen bonds involving hydroxylic proton donors and simple heterocyclic nitrogen bases such as pyridines have been thoroughly investigated by spectrometric techniques [1-9] but so far there are only a few data on the complexing ability of azaaromatics formed by heteroaromatic rings connected through C-C single bonds. In a previous publication [10], we have investigated the hydrogen bond complexes between proton donors and 2,2'-bipyrimidine and have shown that the vicinity of two equivalent nitrogen atoms greatly enhances the proton accepting

power of the base. There is now a growing interest in polyazaaromatic bases for the determination of supramolecular structures and self-recognition processes [11]. For example, the linear sequence of connected 2,2',2''-terpyridine sites yields racks with individual terpyridine units and metal ions of octahedral symmetry. The choice of molecular shape and size, and especially the arrangement of hydrogen-bonding donor and acceptor sites are also crucial to the correct tessellation of a supramolecular array. This prompted us to investigate the hydrogen-bonding ability of the following important *N*-heteroaromatic ligands:



2,4,6-tri(2-pyridyl)-1,3,5-triazine

2,2',2''-terpyridine

quinoxaline

pyrido[2,3-*b*]pyrazine

pyrazino[2,3-*f*]quinoxaline

5-nitrophenanthroline

Table 1

Thermodynamic Data and Frequency Shifts of the $\nu(\text{OH})$ Vibration for the Interaction Between 2,4,6-tri(2-pyridyl)-1,3,5-triazine and Phenols

Phenol [a]	$K^{298\text{K}}$ l mol ⁻¹	$K^{323\text{K}}$ l mol ⁻¹	$-\Delta H$ kJ mol ⁻¹	$\Delta\nu$ cm ⁻¹
3,4-dimethylphenol (10.32)	29	14	23	440
4-methoxyphenol (10.21)	32	15	24	450
phenol (9.95)	40	18	26	470
4-chlorophenol (9.38)	89	34	31	500
4-bromophenol (9.34)	96	35	32	510
3,4-dichlorophenol (8.58)	218	74	35	550
3,5-dichlorophenol (8.18)	317	103	36	540

[a] The $\text{p}K_a^A$ of the phenols are indicated in parenthesis.

The hydrogen-bonding abilities of the above mentioned molecules are compared with those of model molecules such as pyridine, pyrazine, quinoline, 5-nitroquinoline

and 1,3,5-triazine. Thermodynamic data for the interaction between hydroxylic proton donors and pyridine, pyrazine or quinoline are usually measured in carbon

Table 2
Thermodynamic Data and Frequency Shifts of the $\nu(\text{OH})$ Vibration for the Interaction Between 2,2',2''-Terpyridine and Phenols

Phenol	$K^{293\text{K}}$ l mol^{-1}	$K^{323\text{K}}$ l mol^{-1}	$-\Delta H$ kJ mol^{-1}	$\Delta\nu(\text{OH})$ cm^{-1}
3,4-dimethylphenol	12	7	17	410
4-methoxyphenol	13	7	20	420
phenol	16	8	22	425
4-chlorophenol	31	15	23	440
4-bromophenol	34	16	24	450
3,4-dichlorophenol	61	28	25	475
3,5-dichlorophenol	80	34	27	495

Table 3
Thermodynamic Parameters and Frequency Shifts of the $\nu(\text{OH})$ Stretching Vibration for the Interaction Between Pyridine and Phenols

Phenol	$K^{298\text{K}}$ l mol^{-1}	$K^{328\text{K}}$ l mol^{-1}	$-\Delta H$ kJ mol^{-1}	$\Delta\nu(\text{OH})$ cm^{-1}
3,4-dimethylphenol	12 [a]	6	21 [a]	430
phenol	15	7	22	440
4-chlorophenol	31 [a]	14	23 [a]	455
4-bromophenol	31 [a]	14	23 [a]	460
3,4-dichlorophenol	56 [a]	25	24 [a]	490
3,5-dichlorophenol	72	31	25	510

[a] Values cited in reference 5.

Table 4
Equilibrium Data at 298K in 1,2-Dichloroethane for Complexes Involving *N*-Heteroaromatic Bases and Unsubstituted Phenol and $\text{p}K_{\text{a}}^{\text{B}}$ of the Bases

Base	$K^{298\text{K}}$ l mol^{-1}	$-\Delta G^{0,298\text{K}}$ kJ mol^{-1}	$\text{p}K_{\text{a}}^{\text{B}}$
Systems without proximity effect			
pyrazine	4(2) [a]	1.72	0.6
quinoxaline	4.5 (2)	2.01	0.7
pyrimidine	5.4 (2)	2.46	1.28
pyridazine	6.8 (2)	3.03	2.3
5-nitroquinoline	4 (1)	3.43	2.69
3-iodopyridine	4.2 (1)	3.55	3.25
1,7-phenanthroline	11.2 (2)	4.27	4
2,2,2''-terpyridine	16 (2)	5.15	4.33
quinoline	11 (1)	5.94	4.9
pyridine	15 (1)	6.71	5.17
4-ethylpyridine	21 (1)	7.54	6.02
Systems with proximity effect			
pyrazino[2,3- <i>f</i>]quinoxaline	11 (2)	4.22	0.5
pyrido[2,3- <i>b</i>]pyrazine	9 (1)	5.44	1.2
2,4,6-tri(2-pyridyl)-1,3,5-triazine	40 (3)	6.42	3.1
5-nitrophenanthroline	21 (2)	5.82	3.28
1,10-phenanthroline [b]	36.4 (2)	7.19	4.7
neocuproine [b]	46.7 (2)	7.80	4.85
bathocuproine [b]	107 (2)	9.86	6

[a] The applied statistical factors are indicated between parentheses. [b] From reference 17.

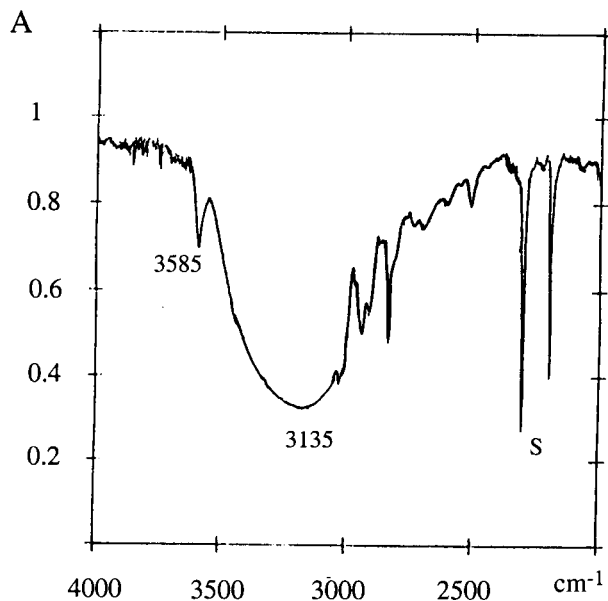


Figure 1. FT-IR spectrum (4000-2000 cm^{-1}) of a solution of 4-chlorophenol ($c = 0.04 \text{ mol dm}^{-3}$) and 2,4,6-tri(2-pyridyl)-1,3,5-triazine ($c = 0.05 \text{ mol dm}^{-3}$) in deuteriodichloromethane. Path length = 0.1 cm.

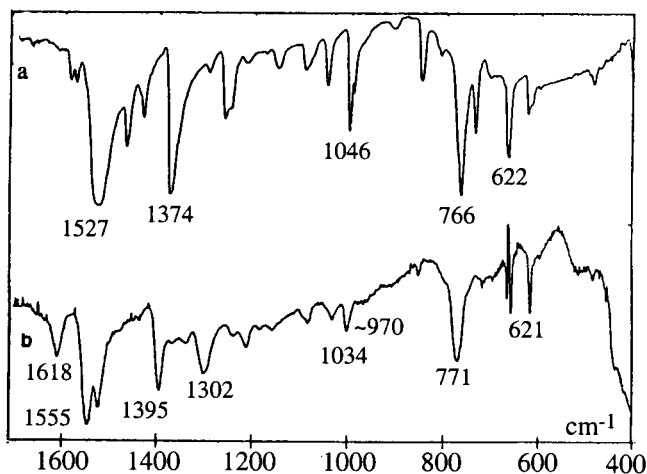


Figure 2. FT-IR spectrum of a: 2,4,6-tri(2-pyridyl)-1,3,5-triazine, b: 2,4,6-tri(2-pyridyl)-1,3,5-triazine·HCl in potassium bromide suspension.

tetrachloride [1-5, 12,13]. Owing to the very poor solubility of the above mentioned bases in this solvent, the equilibrium constants were determined in this work in 1,2-dichloroethane.

EXPERIMENTAL

Infrared data were obtained with a Perkin-Elmer 883 and FT-IR Bruker 88 and 66 instruments. The FT-Raman spectra were recorded on the Bruker 66 spectrometer equipped with a FRA-

106 Raman module (source = YAG laser operating at 9400 cm^{-1} with a power of 200 mW, CaF_2 beamsplitter, Ge cooled detector, resolution 2 cm^{-1}). The equilibrium constants (K) of the 1-1 adducts have been determined from the absorbance of the $\nu(\text{OH})$ stretching vibration of the phenols, using low concentrations of proton donors ($0.01\text{-}0.02 \text{ mol l}^{-1}$) in order to avoid self-association. The base concentrations ranged between 0.03 and 0.1 mol l^{-1} . In this limited concentration range, only complexes of 1-1 stoichiometry are formed. The enthalpies have been calculated from the K values at 298 and 323 K; measurements at intermediate temperatures did not yield better results. In order to avoid overlapping with the $\nu(\text{CH})$ vibrations, the frequency shifts of the $\nu(\text{OH})$ stretching vibration ($\Delta\nu(\text{OH})$) have been measured in deuteriodichloromethane.

TPT,s-triazine, NP and pyridine are from Fluka; pyrazine, PQ, QX and pyrazine are from Janssen Chimica, TP from Aldrich and 1,3,5-s-triazine from Merck. These products were used without further purification. 1,2-dichloroethane from Janssen Chimica was dried on molecular sieves. Deuteriodichloromethane is from Janssen Chimica. Phenols from Aldrich were crystallized in a petroleum-ether mixture. As suggested by the absence of absorption bands in the $3700\text{-}3500 \text{ cm}^{-1}$ region, no appreciable amount of water was present in the solutions.

Results and Discussion.

a) Complexes Between 2,4,6-Tri(2-pyridyl)-1,3,5-triazine, 2,2',2''-Terpyridine or Pyridine with Phenols.

In the first section of this work, the complexing abilities of 2,4,6-tri(2-pyridyl)-1,3,5-triazine and 2,2',2''-terpyridine are compared with those of the model molecules pyridine and 1,3,5-triazine.

Table 1 contains the formation constants determined at 298 and 323 K, the enthalpies of complex formation along with the frequency shifts of the $\nu(\text{OH})$ stretching vibration of the complexes between 2,4,6-tri(2-pyridyl)-1,3,5-triazine and some phenols derivatives. One spectrum in the $\nu(\text{OH})$ region is reproduced in Figure 1. The $\nu(\text{OH})$ band is broad and shows several submaxima characteristics for OH ... N bonds of medium strength. The error on $\Delta\nu(\text{OH})$ is $\pm 10 \text{ cm}^{-1}$ and the difference of 100 cm^{-1} observed between the weakest and strongest complex listed in Table 1 is significant.

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

$$\log K^{298\text{K}} = 6.62 - 0.50 \text{ pK}_a^A \quad r = 0.9978 \quad (1)$$

$$\log K^{323\text{K}} = 5.44 - 0.42 \text{ pK}_a^A \quad r = 0.9989 \quad (2)$$

r being the correlation coefficient.

In this limited $\Delta H\text{-}\Delta\nu$ range, the Badger-Bauer [14] correlation is valuable

$$\Delta H = -33.8 + 0.129 \Delta\nu(\text{OH}) \quad r = 0.9902 \quad (3)$$

These classical correlations will not be discussed for the other complexes investigated in this work.

In order to avoid any confusion with the pK_a^A of the proton donors, the pK_a of the acid conjugated to the base will be labelled pK_a^B . 2,4,6-Tri(2-pyridyl)-1,3,5-triazine has a pK_a^B value of 3.1 [15]. This molecule has three triazol N atoms and three pyridyl N centers available for protonation. Since the latter are readily protonated (pK_a^B values of 5.17 for pyridine and -2.31 for 1,3,5-triazine), the observed pK_a^B value probably reflects protonation occurring at one of these pyridyl N centers. This is also suggested by the observation of the typical vibra-

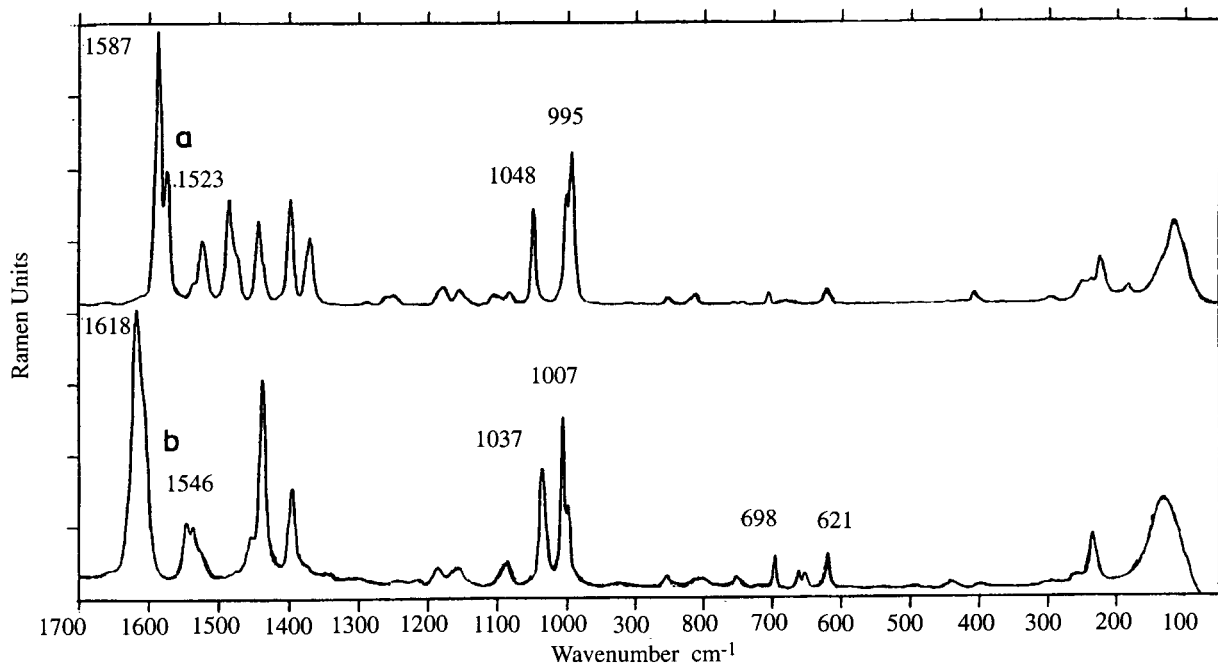


Figure 3. FT-Raman spectrum of a: 2,4,6-tri(2-pyridyl)1,3,5-triazine, b: 2,4,6-tri(2-pyridyl)-1,3,5-triazine•HCl.

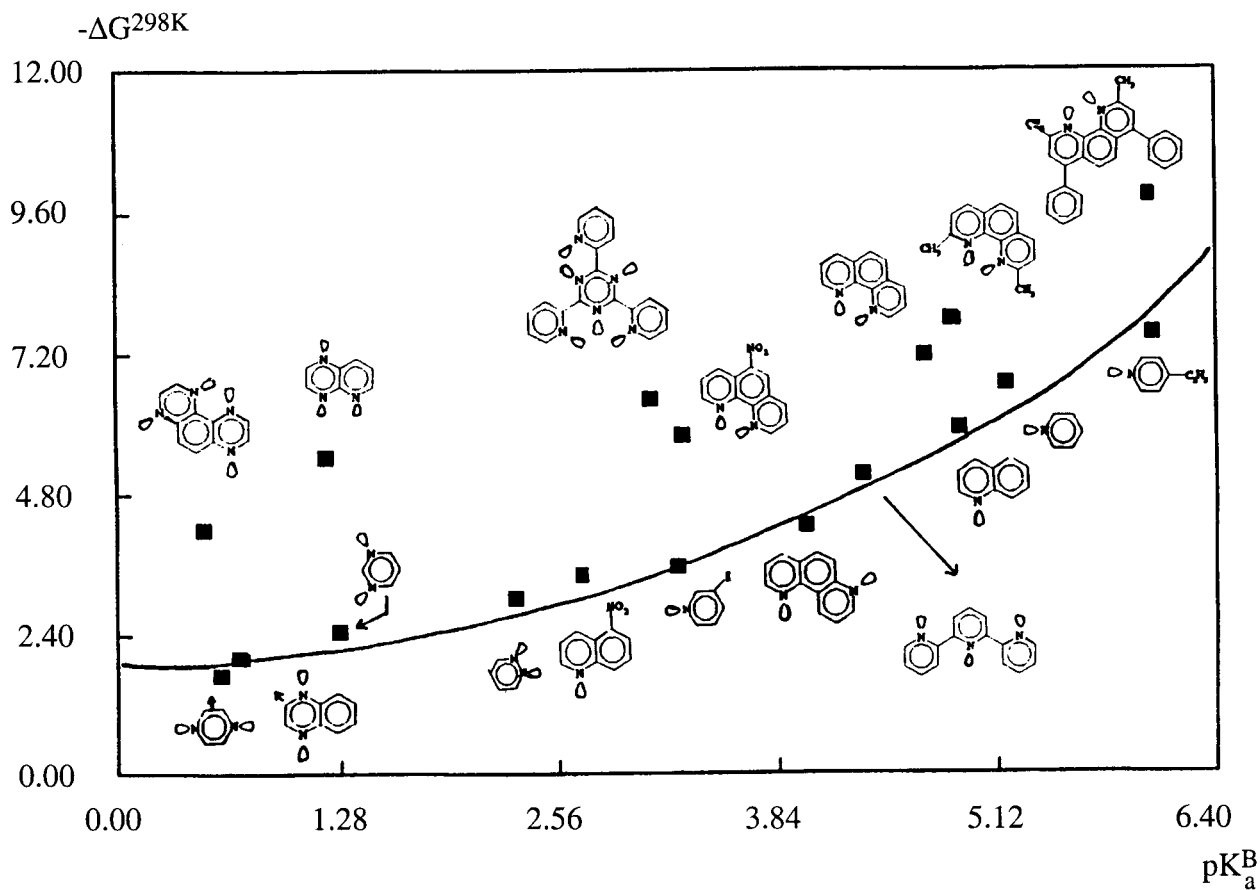


Figure 4. $-\Delta G^{0,2998\text{K}}$ as a function of the pK_a^{B} of the proton acceptor.

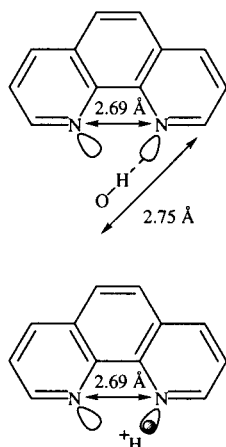


Figure 5. Structure of the complex between phenanthroline and phenol and protonated phenanthroline.

tions of the pyridinium ion [16] in the vibrational spectra of the ionic adduct of 2,4,6-tri(2-pyridyl)-1,3,5-triazine with hydrochloric acid which are reproduced in Figures 2 and 3. The pyridinium bands are observed at 1618 cm^{-1} (ν_{8a}), 1547 cm^{-1} (ν_{19b}), 1395 cm^{-1} (ν_{14}), 1034 cm^{-1} (ν_{12}), 771 cm^{-1} (ν_{10b}) and 621 cm^{-1} (ν_{6b}) in an infrared spectrum and the $\delta(\text{NH}^+)$ and $\gamma(\text{NH}^+)$ are observed at 1302 and about 970 cm^{-1} . The pyridinium absorptions are observed at 1618 , 1546 , 1037 , 1007 (ν_1), 698 (ν_4) and 621 cm^{-1} in the Raman spectrum. Comparison of the thermodynamic data and of the frequency shifts of the $\nu(\text{OH})$ stretching vibration of the 2,4,6-tri(2-pyridyl)-1,3,5-triazine with the experimental values for the corresponding pyridine complexes (indicated in Table 2) also suggests that complex formation occurs at one of the pyridyl-N centers. The triazine complexes are much weaker which can be deduced from the values of the formation constants and the infrared frequency shifts. For the phenol-1,3,5-triazine complex, the K value at 298K is 1.6 l mol^{-1} , and the $\Delta\nu(\text{OH})$ value 290 cm^{-1} ; for the 3,5-dichlorophenol complex, these values are respectively equal to 4.1 l mol^{-1} and 355 cm^{-1} . Owing to the weakness of the complexes, the $-\Delta H$ values could not be determined. The thermodynamic data and frequency shifts for the 2,2',2''-terpyridine complexes are listed in Table 3. This molecule adopts the *trans,trans*-configuration in the solid state [17] and only small twists of the terminal pyridine rings from the plane of the central pyridine occur in solution [18]. The pK_a^B of 2,2',2''-terpyridine is 4.33. Comparison of the data of Tables 1,2 and 3 shows that the equilibrium constants are not ordered according to the pK_a^B values of the bases. The K values obtained for the 2,4,6-tri(2-pyridyl)-1,3,5-triazine complexes are higher than those predicted from the pK_a^B values even when correcting the K values by a statistical factor of 3 taking into account the number of equivalent interaction sites. The enthalpies of complex formation and the frequency shifts are also higher for the 2,4,6-tri(2-pyridyl)-1,3,5-triazine complexes.

b) Formation Constants of the Hydrogen Bond Complexes Formed Between Phenol and other Heterocyclic Bases.

For the other systems, the formation constants have also been measured for different phenols. The results are summarized in Table 4 where the reference proton donor is phenol. This table indicates the K values measured at 298K and the statistical fac-

tor, the free energy $-\Delta G^{0,298\text{K}}$ ($=RT \ln K^{298\text{K}}$) and the pK_a^B values of the considered proton acceptor. Figure 4 shows the $-\Delta G^{0,298\text{K}}$ values plotted against the pK_a^B values of the corresponding bases and clearly indicates that the complexes can be divided into two sets. The first one includes complexes of bases characterized by only one N atom (pyridines, quinoline and 5-nitroquinoline) or bases characterized by two non-vicinal N atoms (pyrimidine, pyrazine, 1,7-phenanthroline, 2,2',2''-terpyridine, quinoxaline) or pyridazine where the two lone pairs are not pointing to each other. For these complexes, the free energies are related to the pK_a^B values of the base by the following exponential expression

$$-\Delta G^{0,298\text{K}} = 1.62e^{0.26pK_a^B} \quad r = 0.992 \quad (4)$$

which has a better correlation than the linear equation

$$-\Delta G^{0,298\text{K}} = 0.89 + 1.02 pK_a^B \quad r = 0.975 \quad (5)$$

The second set of complexes involves the bases where the two lone pairs are parallel pyrido[2,3-*b*]pyrazine or are pointing to each other (2,4,6-tri(2-pyridyl)-1,3,5-triazine, pyrazino[2,3-*f*]quinoxaline and phenanthrolines). For these systems, the free energies are notably higher than those predicted from the basicity of the proton acceptors in water. This effect cannot be accounted for by experimental errors on $-\Delta G^0$ which are equal to 10% for the weakest complexes (pyrido[2,3-*b*]pyrazine and pyrazino[2,3-*f*]quinoxaline) and 5% for the strongest complexes (2,4,6-tri(2-pyridyl)-1,3,5-triazine and phenanthrolines). For the phenol-bathocuproine complex for example, the experimental $-\Delta G^0$ value of $9.86 \pm 0.12\text{ kJ mol}^{-1}$, [19] is significantly higher than the value of 7.71 kJ mol^{-1} computed by equation (4). For the other complexes also, the deviations from the curve depicted in Figure 4 are much larger than the experimental errors. It is interesting to note here that the complexes between methanol and *N*-heteroaromatic bases have been previously studied [20]; the largest deviation in the $\Delta\nu(\text{OH})$ - pK_a^B plot is produced by 1,10-phenanthroline and its experimental pK_a^B is 2.7 units larger than would be expected on the basis of its spectral shift [20]. This feature, in contrast with the results of the present work, has been interpreted as arising from a strong intramolecular hydrogen bond in the protonated form of 1,10-phenanthroline. This conclusion disagrees with X-Ray Photoelectron Spectroscopy (ESCA) data [21]. Symmetric protonation which would lead to a single N1s X-Ray Photoelectron Spectroscopy line was not found experimentally. Peak separation of 2.1 eV is about the same as in *N*-methyl-1,10-phenanthroline and if intramolecular hydrogen bonding occurs, it is substantially less important than electron withdrawal from the ring system. The nmr measurements have also shown that in protonated phenanthroline, the proton may oscillate between the two nitrogen atoms with a very fast intramolecular exchange [22,23]. The measurement of a second protonation constant [24-26] also suggests that in strongly acidic aqueous media, the proton is not midway between the two nitrogen atoms.

The results of this work clearly show that 2,4,6-tri(2-pyridyl)-1,3,5-triazine, pyrido[2,3-*b*]pyrazine and the phenanthroline derivatives cannot be considered as proton sponges. A typical proton sponge such as 1,8-bis(dimethylamino)naphthalene interacts with phenol derivatives to give the protonated base and homoconjugated (OHO)⁻ anions and in several cases, complexes of higher stoichiometry are formed [27-29]. Further very broad absorptions extending from 3000 to 500 cm^{-1} are observed in the proton sponge complexes as well in solution as in the solid state [27-30]. These spectroscopic characteristics are not observed in

the present complexes and only one band is observed in the $\nu(\text{OH})$ region. This absorption which is characterized by several submaxima to the low frequency side (Figure 1) is typical for normal OH...N hydrogen bonds formed between phenols and N-heteroaromatic bases [31]. Steric strain relieved on protonation and very short intramolecular NH...N⁺ hydrogen bonds (about 2.6 Å) which are the leading factors contributing to the high basicity of the proton sponges [32-34], are not operating in the case of 2,4,6-tri(2-pyridyl)-1,3,5-triazine and phenanthrolines.

The difference between the structures of hydrogen bonded and protonated phenanthroline is illustrated in Figure 5. In both systems, the bond is formed in the direction of one of the free lone pairs [35]. In free phenanthroline, the N...N distance calculated from X-ray diffraction data is 2.69 Å [36]. In the phenanthroline-phenol complex, the O...N distance estimated from the relations of Nakamoto *et al* [37] is 2.75 Å. This distance is somewhat shorter in the stronger complexes (2.7 Å). In protonated phenanthroline, the NH⁺ distance was estimated as 1.1 Å and as discussed previously, the proton is not midway between the two nitrogen atoms. Figure 5 shows that in the hydrogen bond complex, the second lone pair is pointing in the vicinity of the OH bond of the phenol and can have some contribution to the charge transfer to the $\sigma^*(\text{HO})$ orbital. In protonated phenanthroline, the lone pair of the unprotonated nitrogen lies outside the interaction region of the NH⁺ bond owing to the smaller NH⁺ bond length as compared with the N...H...O distance.

It is interesting to note here that in *cis*-2,2'-bipyridine, the lone pair of the unprotonated nitrogen shows virtually no polarization when the adjacent nitrogen is protonated [38]. The proton affinity computed at the MP2/6-31G** level of *cis*-2,2'-bipyridine is 998.6 kJ mol⁻¹ and that of *trans*-2,2'-bipyridine 946.5 kJ mol⁻¹. In the protonated *cis*-structure, the N...H⁺ distance of 2.09 Å is longer than that found in proton sponges and the NH⁺...N angle of 108.5° is too acute for this to be considered as a strong cationic hydrogen bond [38]. In organic solvents, 2,2'-bipyridine has the *trans*-conformation and in contrast with 2,2'-bipyrimidine where two vicinal lone pairs are available for hydrogen bond formation, no proximity effect was observed [38].

Lastly it should be mentioned that the stability constants of the iodine complexes of 1,10-phenanthroline and its substituted derivatives (called twin-site electron donors) are higher when compared to those of 1,7-phenanthroline and other diazines and bipyridines. This effect has been accounted for by the simultaneous union of one iodine molecule to both the nitrogen atoms [39]. In view of the greater size of the iodine molecule as compared with that of an OH bond, the overlapping between the lone pairs of the two nitrogen atoms and the $\sigma^*_u(\text{I-I})$ orbital will be higher and a symmetric structure seems more likely in this case.

A proximity effect was also observed for the pyrido[2,3-*b*]pyrazine complexes where the two vicinal lone pairs are parallel. The origin of this effect is less clear because the overlapping of the free lone pair and the $\sigma^*(\text{OH})$ orbital must be much less effective. It must be noticed here that the $\text{p}K_a^{\text{B}}$ value of 1.2 is perhaps too low, the $\text{p}K_a^{\text{B}}$ values of the other triazanaphthalene derivatives ranging from 2.4 to 4.1 [15].

Acknowledgements.

The authors thank the Fund of Scientific Research of Flanders (FWO-VI) for financial support. M.G. thanks the IWT for a Ph.D. fellowship. B.C-M thanks the Flemish community for a

post-doctoral fellowship obtained in the frame of the bilateral collaboration between Flanders and Poland.

REFERENCES AND NOTES

- [1] J. Rubin and S. Panson, *J. Phys. Chem.*, **69**, 3089 (1965).
- [2] A. M. Dierckx, P. Huyskens and Th. Zeegers-Huyskens, *J. Chem. Phys.*, **62**, 1601 (1964).
- [3] M. D. Joesten and J. L. Schaad, *Hydrogen Bonding*, Marcel Dekker Inc., New York, 1974, and references therein.
- [4] D. Clotman, J. P. Muller and Th. Zeegers-Huyskens, *Bull. Soc. Chim. Belg.*, **79**, 689 (1970).
- [5] V. S. Pilyugin, S. V. Vasin and T. A. Maslova, *Zh. Obshch. Khim.*, **51**, 1460 (1981).
- [6] V. S. Pilyugin, S. V. Vasin and V. V. Zinov'ev, *Zh. Fiz. Khim.*, **58**, 937 (1984).
- [7] N. Spencer, J. Andrefsky, A. Grushow, J. Naghdy, L. M. Patti and J. F. Trader, *J. Phys. Chem.*, **91**, 1673 (1987).
- [8] E. V. Titov, V. I. Shurpach, G. A. Belkina and N. P. Gonchar, *J. Mol. Struct.*, **219**, 257 (1990).
- [9] M. Rospenk and Th. Zeegers-Huyskens, *J. Phys. Chem.*, **101**, 8428 (1997).
- [10] M. Goethals, K. Platteborze and Th. Zeegers-Huyskens, *Spectrochim. Acta*, **48A**, 671 (1992).
- [11] J. M. Lehn, *Supramolecular Chemistry. Concept and Perspectives*, VCH Weinheim, New York, Basel, Cambridge, 1995.
- [12] C. V. R. Rao, C. Jacob and A. K. Chandra, *J. Chem. Soc., Faraday Trans. 1*, **78**, 3025 (1982).
- [13] O. Kasende and Th. Zeegers-Huyskens, *J. Phys. Chem.*, **88**, 2132 (1984).
- [14] R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 839 (1937).
- [15] D. D. Perrin, *Dissociation Constants of Organic Bases*, Butterworths, London, 1965, and supplement, (1972).
- [16] F. R. Dollish, W. G. Fateley and F. F. Bentley, *Characteristics Raman Frequencies of Organic Compounds*, John Wiley & Sons, New York, London, Sydney, Toronto, 1974.
- [17] C. A. Bessel, R. F. See, D. L. Jameson, M. R. Churchill and K. J. Takeuchi, *J. Chem. Soc., Dalton Trans.*, 3223 (1992).
- [18] K. Nakamoto, *J. Phys. Chem.*, **64**, 1420 (1960).
- [19] G. Siegel and Th. Zeegers-Huyskens, *Spectrochim. Acta*, **45A**, 1297 (1989).
- [20] L. Joris and P. von Ragué-Schleyer, *Tetrahedron*, **24**, 5991 (1968).
- [21] L. E. Cox, J. J. Jack and D. M. Hercules, *J. Am. Chem. Soc.*, **94**, 6575 (1972).
- [22] H. Rosenberger, M. Pettig, K. Madya, G. Engelhardt and R. Radeaglia, *Ber. Bunsenges.*, **73**, 662 (1969).
- [23] G. D. Dimitrov, *C. R. Acad. Bulg. Sci.*, **28**, 1625 (1975).
- [24] H. H. Perkampus and H. Kohler, *Z. Elektrochem.*, **64**, 365 (1972).
- [25] R. H. Linnell and A. Kaczmarczyk, *J. Phys. Chem.*, **65**, 1196 (1961).
- [26] A. A. Scilt and W. E. Dunbar, *Tetrahedron*, **30**, 401 (1974).
- [27] Z. Pawelka and Th. Zeegers-Huyskens, *J. Mol. Struct. (Theochem)*, **200**, 565 (1989).
- [28] B. Brzezinski, E. Grech and Z. Malarski, *J. Chem. Soc., Faraday Trans.*, **86**, 1777 (1990).
- [29] P. Huyskens, K. Platteborze and Th. Zeegers-Huyskens, *J. Mol. Struct.*, **436**, 91 (1997).
- [30] T. Glowiak, Z. Malarski, L. Sobczyk and E. Grech, *J. Mol. Struct.*, **270**, 441 (1992).
- [31] A. Hall and J. L. Wood, *Spectrochim. Acta*, **23A**, 1257 (1967).
- [32] R. W. Alder, *Chem. Rev.*, **89**, 1215 (1989).
- [33] H. A. Staab, *Tetrahedron Letters*, **29**, 5629 (1988).

- [34] F. Hibbert and S. Philips, *J. Chem. Res.*, **90** (1990).
- [35] C. V. R. Rao, C. Jacob and A. K. Chandra, *J. Chem. Soc., Faraday Trans. I.*, **78**, 3025 (1982).
- [36] S. Nishigaki, H. Yoshioka and K. Nakatsu, *Acta Cryst.*, **B34**, 875 (1978).
- [37] K. Nakamoto, M. Margoshes and R. E. Rundle, *J. Am. Chem. Soc.*, **77**, 6480 (1955).
- [38] S. T. Howard, *J. Am. Chem. Soc.*, **118**, 10269 (1996).
- [39] M. Goethals and Th. Zeegers-Huyskens, *Spectrosc. Letters*, (in press).
- [40] N. S. Rao, G. B. Rao and D. Ziessow, *Spectrochim. Acta*, **46A**, 1107 (1990).