Journal of Thermal Analysis, Vol. 45 (1995) 751-759

THE INTERMOLECULAR INTERACTIONS IN BINARIES Pyridine base+hydrocarbon, on the base of experimental enthalpy of mixing data

H. Wilczura, T. Kasprzycka-Guttman, M. Jarosz-Jarszewska and A. Myslinski

Department of Chemistry, University of Warsaw, 02–093 Warsaw, Pasteura 1, Poland

Abstract

The recapitulation of systematical investigations of excess enthalpy of mixing in binary mixtures: pyridine base+*n*-alkane or some of arenes is presented. On the base of experimental results as well as model calculations (PFP, ERAS) the discussion of intermolecular interactions in pyridine bases is given.

Keywords: excess enthalpy of mixing, intermolecular interactions, PFP and ERAS models, self-association of pyridine bases

Introduction

The problem of intermolecular interactions in pure pyridine bases is very complicated, and precisely not explained till now. In the literature is available some information on the self-association of pyridine and its methyl derivatives [1–11]. The results of spectroscopic investigations indicate the presence of some complexes in these substances [12–13]. The self-association of pyridine bases was confirmed by dipol moment investigations [11, 14], as well as by large differences between the enthalpy of vaporization values for pyridine bases and their homomorphic substances (benzene, cyclohexane and their methyl derivatives) [15].

Our experimental data of excess enthalpy of mixing for binaries consisted of pyridine base and hydrocarbon (aliphatic or some aromatic) indicate very strong intermolecular interactions in such solutions [16–20]. Experimental method and detailed results of measurements of $H^E=f(x)$ for pyridine bases (pyridine, α-, β-, γ-picoline, 2,4-, 2,6-lutidine, 2,4,6-collidine) with hydrocarbons (*n*-alkanes: hexane to decane, and arenes: benzene, toluene, *o*-xylene) at 298.15 K were published earlier [16–21, 35].

Two models of nonelectrolyte solutions: Prigogine-Flory-Patterson (PFP) and Extended Real Associated Solution (ERAS) [23–34] have been used for de-

0368–4466/95/ $ 4.00
© 1995 Akadémiai Kiadó, Budapest

John Wiley & Sons, Limited
Chichester

scription of H^E data. The separation of the chemical contribution H^E_{ch} from total H^E values allowed to discusse the problem of self-association of pyridine bases.

In the present paper the recapitulation of systematical investigations of excess enthalpy of mixing in binaries formed by pyridine bases with aliphatic hydrocarbons, and some of arenes is given. The paper includes also discussion of intermolecular interactions in pyridine bases.

Results

The excess enthalpies of mixing for binaries: pyridine or its methyl derivative+hydrocarbon (aliphatic or aromatic) have been measured at 298.15 K. The experimental results and description by PFP and ERAS models for pyridine bases with *n*-alkanes have been published earlier [16–20] except the data for 2,4,6-collidine+*n*-alkanes.

The H^E data and their description by PFP model for some systems of pyridine bases with benzene were published previously [35], whereas for pyridines with toluene and *o*-xylene are in publishing in J. Thermal Anal.

The results and theoretical description of H^E for the following mixtures; 2,4,6-collidine+*n*-alkanes+benzene, 2,4-lutidine+toluene, α-, β-, γ-picoline+toluene are in publishing too.

In the all above binary systems excess enthalpies of mixing are endothermic except of 2,4,6-collidine+toluene with *S*-shaped H^E curve. The maximum values of H^E for mixtures: pyridine base$_{(1)}$+*n*-alkane are within the limits of 800÷1945 J·mol^{-1}. H^E curves are nearly symmetrical (the maximum is found for $0.50 < x_1 < 0.60$). The maximum values of the enthalpy of mixing decrease in the following order:

pyridine > γ- > β-> α-picoline > 2,4- > 2,6-lutidine > 2,4,6-collidine

For binaries formed by pyridine bases with benzene the maximum values of H^E are contained between 10.1÷168.3 J·mol^{-1} for $0.30 < x_1 < 0.72$ and increase in a sequence:

pyridine < β- < γ- α-picoline < 2,6- < 2,4-lutidine < 2,4,6-collidine

In the later cases H^E curves are not so symmetrical as for mixtures of pyridine with normal alkanes.

For pyridine bases$_{(1)}$ (except of 2,4,6-collidine) with toluene the maximum values of enthalpy of mixing are in the range of 46.6÷176.4 J·mol^{-1} for $0.38 < x_1 < 0.45$ and decrease in the sequence:

pyridine > α- > γ-picoline > 2,4-lutidine > β-picoline > 2,6-lutidine.

The *S*-shaped H^E curve for 2,4,6-collidine$_{(1)}$+toluene mixture has two extremes: +3.6 J·mol^{-1} for $x_1=0.03$, and –35.8 J·mol^{-1} for $x_1=0.62$.

The maximum H^E values for systems: pyridine base$_{(1)}$+*o*-xylene are in the range: 21.9÷378.2 J·mol^{-1} for $0.35 < x_1 < 0.51$ and decrease as follows:

pyridine > α- > γ- > β-picoline > 2,6- > 2,4- lutidine > 2,4,6-collidine

H^E data for some of above presented mixtures are also available in the literature [22, 36–40]. A discussion and comparison of these data with our results was given in the previous paper [35].

For all our systems have been found satisfactory agreement of the values computed by PFP and ERAS methods and the experimental H^E data.

Theory

The PFP model [23–32] considering only a contribution of the physical interactions to the excess properties of mixture have been used to description of experimental H^E data for the all above binaries. Information about the self-association of pyridine bases has been reported in the literature [1–11]. The self-association of these substances was confirmed by UV spectroscopic investigation [12], as well as by NMR method [13]. Taking this into account the ERAS model [33, 34] was used for calculation of H^E data for mixtures formed by pyridine bases with *n*-alkanes. In the ERAS model the PFP physical contribution is supplemented by the chemical term directly expressing a contribution of association to the excess properties. The methods of computation of pyridines self-association parameters (K, Δh^*, Δv^*) for ERAS H^E_{ch} term have been reported previously [16–20]. As a homomorphic substances for pyridine bases were taken: benzene, toluene and *o*-xylene respectively.

The H^E_{ch} contribution to the ERAS model for α-, β-, γ-picoline+*n*-alkanes systems was shown and discussed earlier [41]. Values of H^E_{ch} for the remaining binaries: pyridine base$_{(1)}$+*n*-alkane are presented Fig. 1.

For all investigated mixtures of pyridines with *n*-alkanes a small dependence of H^E_{ch} values on the chain length of the hydrocarbon component have been observed. The H^E_{ch} contribution amounts about 15% of the total H^E value.

In the ERAS model dimerization has been assumed as the only form of association of pyridine bases due to hydrogen bond with the pyridine-ring nitrogen atom. The structure of 2,4,6-collidine, and 2,6-lutidine molecules makes impossible formation of hydrogen bonds on this way. The number and position of the methyl groups determine the possibility of hydrogen bond creation in the remaining picolines and lutidines. The dimerization ability of picolines has been discussed previously [41]. In conclusion two main effects were pointed out as responsible for the dimerization: the influence of $-CH_3$ group position on the lone pair of electrons of the nitrogen atom, and the steric hindrance at the nitrogen atom caused by the α positioned $-CH_3$ group. Thus the degrees of associa-

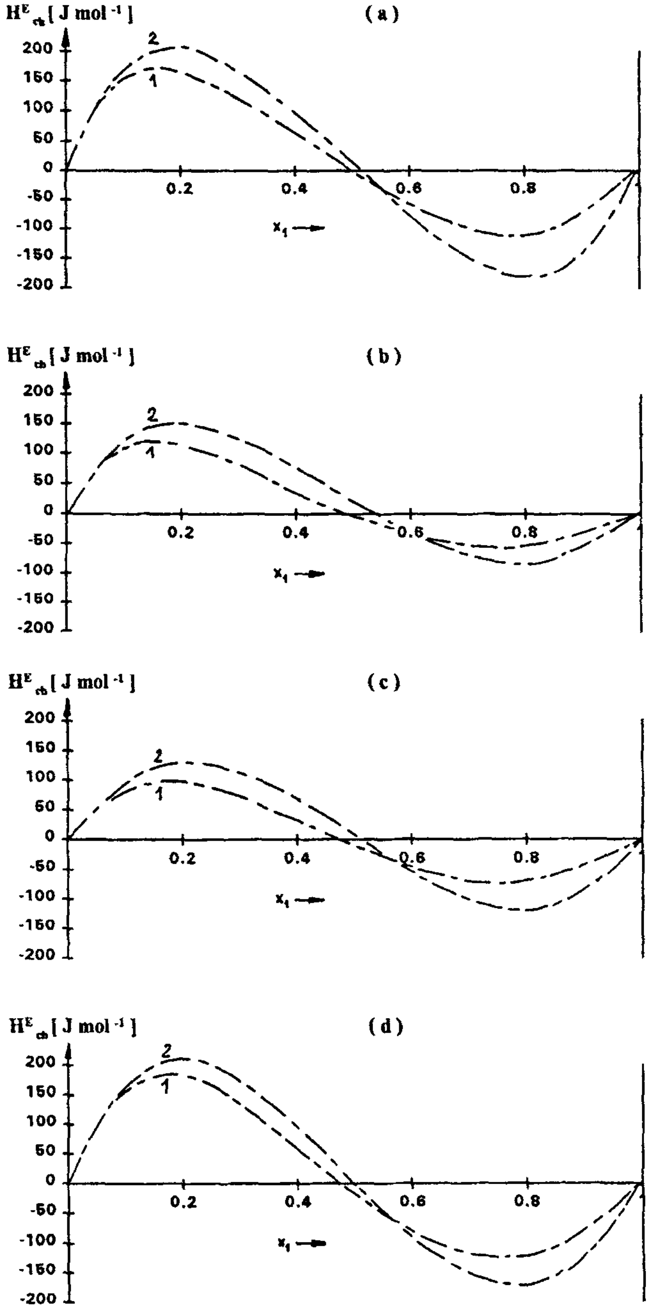


Fig. 1 H^E_{ch} for mixtures: a) pyridine+C_6 (1), pyridine+C_{10} (2); b) 2,4-lutidine+C_6 (1), 2,4-lutidine+C_{10} (2); c) 2,6-lutidine+C_6 (1), 2,6-lutidine+C_{10} (2); d) 2,4,6-collidine+C_6 (1), 2,4,6-collidine+C_{10} (2)

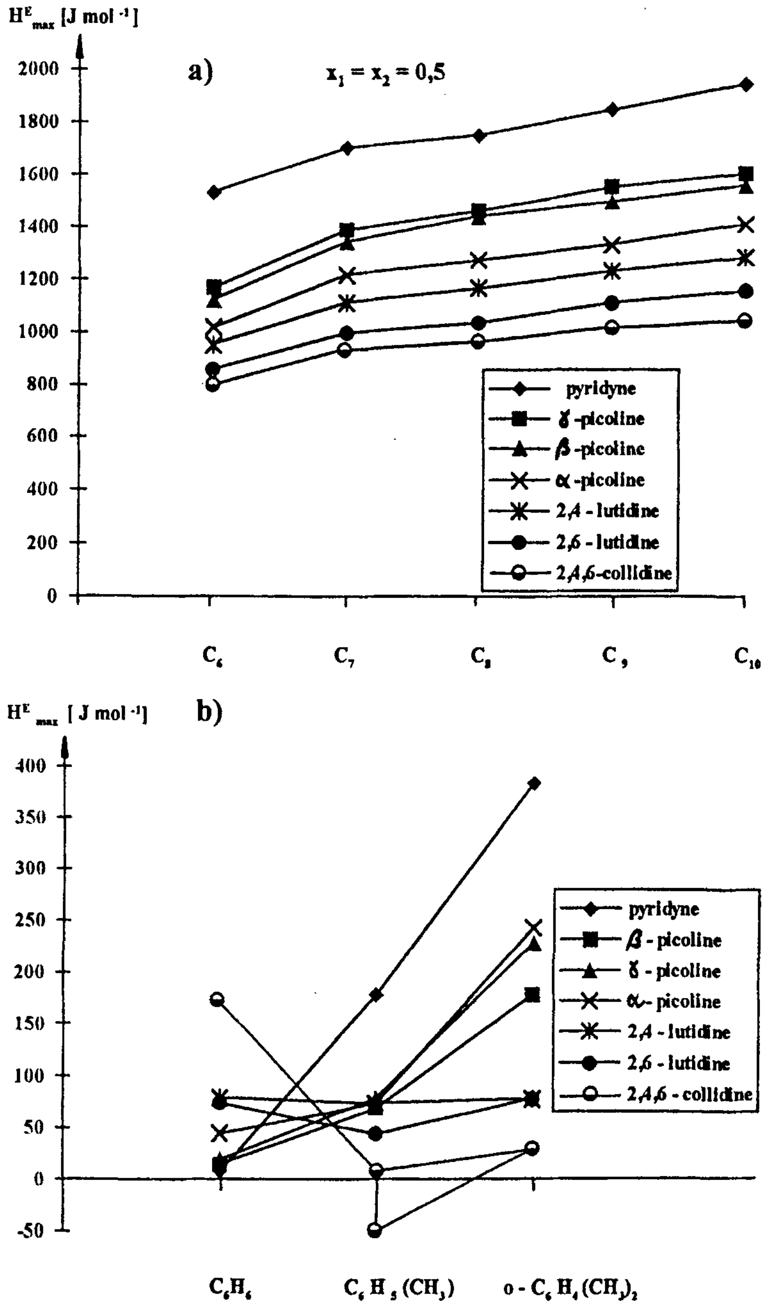


Fig. 2 Maximum H^E values for pyridine bases viz. a) carbon atom number of hydrocarbon components: b) methyl group number of aromatic hydrocarbon components

tion of β- and γ-picoline should be nearly equal and both distinctly greater than that of α-picoline [2, 4, 42]. The values of association constants [42], as well as the dipol moments [43] of pure picolines (α-picoline 1.97D, β-picoline 2.4D, γ-picoline 2.6D) confirmed these conclusions.

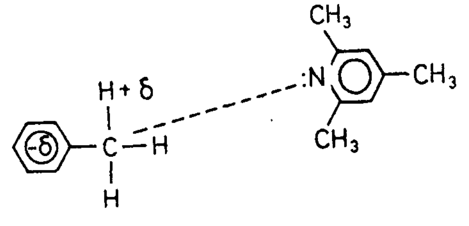
The maximum values of the enthalpy of mixing in pyridine bases+*n*-alkanes binaries are much higher than corresponding data for pyridines with arenes (Fig. 2). Probably it is a result of much higher energy of destruction of the pure components structure as compared with the intermolecular interaction energies in solutions. In these cases when aromatic hydrocarbon is a one of components of mixture the mixing course is more complicated. First of all, the structures of both components are destroyed (endothermic contribution to the H^E value) and than intermolecular interactions between different molecules appear in solutions (exothermic contribution to the H^E). Total H^E is the resultant of these main effects.

The thermal effect of mixing for pyridine with benzene equal 10 J·mol^{-1} is a consequence of compensation of *n*-π, and π-π type interactions in pyridine, π-π interactions in benzene, and both *n*-π and π-π in pyridine-benzene solution. It agrees with the suggestion given by Woycicki [22] on the intermolecular interactions in solutions formed by pyridines. Some of the authors suggest that the self-association of pyridine bases is going by the lone electron pair of electrons of the nitrogen atom and π electrons [42, 43].

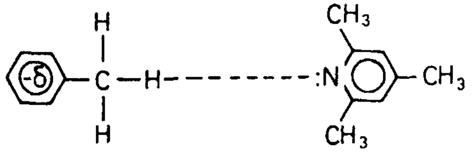
For the mixtures: pyridine, α-, β-, γ-picoline+aromatic hydrocarbon H^E_{max} values increase with increasing number of methyl groups in arene molecule. For binaries: 2,4-, 2,6-lutidine, 2,4,6-collidine+arene this dependence is more complicated (Fig. 2). The presence of two $-CH_3$ groups in 2,4- and 2,6-positions in pyridine molecules a little changes H^E for mixtures with benzene, toluene and *o*-xylene. The putting on of three methyl groups into the pyridine molecule causes the following of H^E values with arenes:

$$C_6H_6 > C_6H_5CH_3 < C_6H_4(CH_3)_2$$

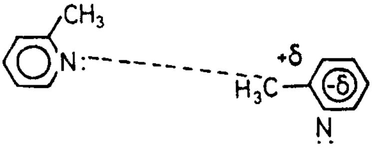
The *S*-shaped H^E curve for 2,4,6-collidine with toluene mixtures suggests that for $x_1>0.1$ intermolecular interactions between different molecules are stronger than forces between molecules of the same type. The exothermic effect observed for this system probably is a consequence of formation the following structures:



or



On the other hand the substitution of α-positioned hydrogen atom by methyl group makes the lone pair of electron on the nitrogen atom more labile. It makes possible the schema proposed by Singh and coworkers [9].



Taking this into account the influence of $-CH_3$ group in picolines on the lone electron pair is as follows:

α-picoline > β-picoline > γ-picoline

Nakanishi and others [4] found that steric hindrance at the nitrogen atom caused by the α-positioned methyl group change degree of association of pyridines in sequences:

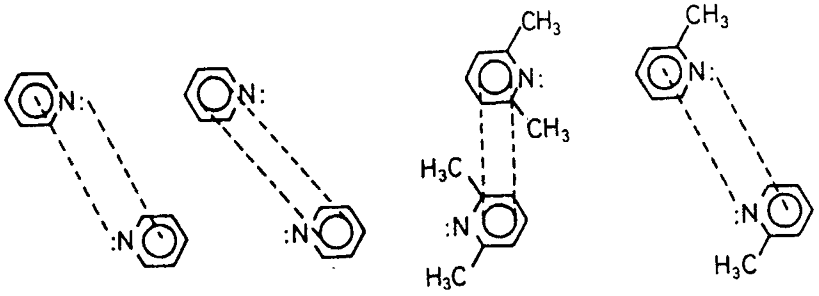
pyridine > β-picoline > γ-picoline > α-picoline > 2,6-lutidine.

The presence of methyl groups in pyridine molecules differentiates radically their dipol moments, which according to Cumper *et al.*, [42] are:

γ-picoline >	β-picoline >	2,4-lutidine >	pyridine >	α-picoline >	2,6-lutidine
μ=2.6D	2.4D	2.3D	2.21D	1.97D	1.66D

On the base of experimental H^E data it has been found that within the isomer group the order of the H^E_{max} values is the same as that of the isomer dipol moments.

The discussion of the course of H^E functions for investigated systems, as well as their description by PFP and ERAS methods indicate that the main contributions to the H^E values are made by nonspecific intermolecular interactions. In the pure pyridine bases besides of the dispersion and dipol–dipol forces, strong n-π and π-π type interactions occur. The self-association of pyridines is a result of the n-π and π-π interactions. These interactions are the main cause for the creation of dimer structures e.g.:



A small value of the H^{E}_{chem} contribution to the total H^E values for mixtures of pyridine with *n*-alkanes is in agree with this conception.

Table 1 Association parameters of pyridine bases

Component	$K_{at\ 298.15K}$	Δh^*/J·mol^{-1}	Δv^*/cm^3·mol^{-1}
pyridine	9.70	–8221	–4.38
α-picoline	4.16	–7743	–5.30
β-picoline	10.28	–8748	–6.01
γ-picoline	10.87	–8721	–5.79
2,4-lutidine	4.59	–7414	–3.77
2,6-lutidine	1.33	–10072	–3.61
2,4,6-collidine	2.20	–12889	–6.51

References

1 L. Sacconi, P. Paoletti and M. Ciampolini, J. Am. Chem. Soc., 82 (1960) 3828.
2 K. W. Marcom and D. N. Travers, Trans. Faraday Soc., 62 (1966) 2063.
3 T. J. V. Findlay, J. S. Keniry and A. D. Kidmann, Trans. Faraday Soc., 63 (1967) 846.
4 J.-J. Abe, K. Nakanishi and H. Touhara, J. Chem. Thermodyn., 10 (1978) 483.
5 S. Warycha and J. H. Rytting, J. Sol. Chem., 13 (1984) 589.
6 M. Woycicka and Z. Kurtyka, Bull. Acad. Polon. Sci. Ser. Chim., XIII(7) (1965) 469.
7 W. Woycicki, Bull. Acad. Polon. Sci. Ser. Chim., XV(12) (1967) 613.
8 P. P. Singh, P. S. Arora and R. C. Phutela, Z. Phys. Chem. (Leipzig), 258 (1977) 225.
9 P. P. Singh, R. K. Nigam and S. P. Sharma, Thermochim. Acta, 63 (1983) 237.
10 S. Warycha and I. Wawer, Advances in Molecular Relaxation and Interaction Proceses, 14 (1979) 29.
11 R. Smets and P. Huyskens, Bull. Soc. Chem. France, (5–6) (1978) 173.
12 Y. Yukawa, 'Handbook of Organic Structural Analysis', W. A. Benjamin Inc., 1965.
13 I. Wawer and S. Warycha, Pol. J. Chem., 59 (1985) 565.
14 H. Bertagnolli and T. Engelhardt, Ber. Bunsenges. Phys. Chem., 90, 512.
15 R. R. Dreisbach, 'Physical Properties of Chemical Compounds', American Chemical Society, 1955.

16 T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 158 (1990) 1.
17 T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 184 (1991) 321.
18 T. Kasprzycka-Guttman, H. Wilczura and A. Myslinski, J. Thermal Anal., 38 (1991) 1357.
19 T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 198 (1992) 405.
20 T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 209 (1992) 25.
21 H. Wilczura, T. Kasprzycka-Guttman and S. Randzio, Bull. Acad. Polon. Sci. Ser. Chim., 34 (1986) 483.
22 W. Woycicki and K. Sadowska, Bull. Acad. Polon. Sci. Ser. Chim., XVI, 3 (1968) 147. ibid., XVI, 6 (1968) 329.
23 I. Prigogine, 'The Molecular Theory of Solutions', North-Holland, Amsterdam 1957.
24 P. J. Flory, R. A. Orwoll and A. Vrij, J. Am. Chem. Soc., 86 (1964) 3507; ibid., 86 (1964) 3515; ibid., 86 (1964) 3563.
25 P. J. Flory, Discuss. Faraday Soc., 49 (1970) 7.
26 E. Eichinger and P. J. Flory, Trans. Faraday Soc., 64 (1968) 2035.
27 P. J. Flory, J. Am. Chem. Soc., 87 (1965) 1833.
28 A. Abe and P. J. Flory, J. Am. Chem. Soc., 87 (1965) 1838.
29 M. Barbe and D. Patterson, J. Sol. Chem., 9 (1980) 753.
30 H. Tra Van and D. Patterson, J. Sol. Chem., 11 (1982) 793.
31 M. Costas and D. Patterson, J. Sol. Chem., 11 (1982) 807.
32 S. N. Bhattacharyya, M. Costas, D. Patterson and H. Tra Van, Fluid Phase Equilib., 20 (1985) 27.
33 A. Heintz and R. Lichtenthaler, Ber. Bunsenges, Phys. Chem., 84 (1980) 727.
34 A. Heintz, Ber. Bunsenges. Phys. Chem., 89 (1985) 172.
35 T. Kasprzycka-Guttman and H. Wilczura, Thermochim. Acta, 225 (1993) 31.
36 T. J. Findlay, Australian J. Chem., 14 (1961) 646.
37 J. Merlin and A. Ait-Kaci, Selected Data on Mixtures, Ser. A. (1) 34(1982).
38 T. Murakami, S. Murakami and R. Fujishiro, Bull. Chem. Soc. Jpn., 42 (1969) 35.
39 P. Garrett, J. Pollock and K. Marcom, J. Chem. Thermodyn., 17 (1971) 135; ibid., 9 (1977) 561.
40 D. Diez, F. Ruiz, M. Royo, A. Gutierrez and C. Losa, J. Chem. Thermodyn., 17 (1985) 371.
41 H. Wilczura, B. Semeniuk, A. Myslinski and T. Kasprzycka-Guttman, J. Thermal. Anal., 38 (1992) 2011.
42 C. W. Cumper, J. J. Vogel and S. Walker, J. Chem. Soc., 3621 (1956).
43 R. K. Nigam, P. P. Singh and S. Sharma, Fluid Phase Equilib., 16 (1984) 25.

Zusammenfassung — Es wird eine kurze Zusammenfassung der systematischen Untersuchungen der Mischungsüberschußenthalpie in binären Gemischen dargelegt: Pyridinbase + *n*-Alkan oder Aren. Sowohl auf der Grundlage von experimentellen Ergebnissen als auch von Modellberechnungen (PFP, ERAS) werden die intermolekularen Wechselwirkungen in Pyridinbasen diskutiert.