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IR-SPECTRAL STUDY OF SELF-ASSOCIATION EFFECTS OF 2-AMINOPYRIDINE IN SOLUTION

Key words: IR-spectra, 2-Aminopyridine, Self-association in solution

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ABSTRACT

A comparative IR-spectral study of solute-solute hydrogen bond formation in carbon tetrachloride and chloroform solutions of 2-aminopyridine is reported. The presence of chain-like self-associates is confirmed in contrast to the solid state where the stabilization of the cyclic dimeric structure takes place. This conclusion is suggested on the basis of the NH_2 stretching region data obtained by changing the solute concentration as well as by comparing with the corresponding data about melted and solid state 2-aminopyridine and 3-aminopyridine samples.

INTRODUCTION

In recent papers ^{1, 2} we have discussed the results obtained in our comparative IR- and UV-spectral study on Pd (II) complexes with 2-amino-pyridine (2-AP), synthesized both in sulphuric acid and in alkaline solution. It was found that sulphato-2-aminopyridine-palladium complex exhibits a polynuclear structure as a result of the bridging bidentate co-ordination of both sulphato group and 2-AP. The complex keeps its structure in alkaline medium, in which the substitution of SO_4^{2-} by OH^- yields hydroxo-2-amino-pyridine-palladium complex.

In principle 2-AP exhibits a monodentate co-ordination via the pyridine nitrogen because of its considerably greater electron-donating power than the amino group ³. The formation of additional $\text{Pd}^{2+} \leftarrow \text{N}(\text{amino})$ dative bond by a bidentate 2-AP complexation should specifically affect the NH_2 characteristic frequencies, but the wide overlapping bands in the $3700\text{--}3100\text{ cm}^{-1}$ spectra of both sulphato- and hydroxo-2-amino-pyridine-palladium (II) are not suitable for NH_2 stretching bands identification ¹. Similarly, the bending NH_2 mode (δNH_2) appears in the $1635\text{--}1595\text{ cm}^{-1}$ range ² with a low intensity peak additionally overlapping with the pyridine skeleton band at about 1600 cm^{-1} .

The data discussed refer to the solid state IR-spectra of the complexes where the supplementary association effects should be also manifested. 2-AP itself forms cyclic dimers in the solid state ⁴ (Scheme I) which give the characteristic peculiarity of the corresponding IR-spectrum (see below). This structure does not exist after complexation, but the possibilities of additional chain-like $\text{NH}\dots\text{N}(\text{amino})$ bond formation in the case of monodentate 2-AP co-ordination as well as the existence of $\text{NH}\dots\text{O}=\text{S}$ and $\text{NH}\dots\text{OH}$ hydrogen bonds in the complexes investigated by us are likely.

For these reasons, the present paper deals with the IR-spectral investigation on the solute-solute hydrogen bond formation in carbon tetrachloride and chloroform solutions of *2-AP* where we have found the presence of chain-like self-associates. This conclusion is suggested on the basis of the NH_2 stretching region data obtained by changing the solute concentration and by comparing with the IR-spectra of melted and solid state *2-AP* and 3-aminopyridine (*3-AP*) as well.

The study is restricted by the low solubility of the compounds in carbon tetrachloride in which the solvent effects are negligible. Both *2-AP* and *3-AP* are soluble in chloroform, but weak specific solute-solvent interaction has been reported about *2-AP* diluted solutions in this solvent ⁵. Furthermore, the enhanced chloroform polarity shifts the equilibrium between the monomeric and self-associated solute molecules to the free species. Hence, the results obtained about dilute chloroform solutions are not easy for interpretation and we discuss only the data about 1 M and 5 M solute concentration.

EXPERIMENTAL

2-AP and *3-AP* (Fluka, purum), recrystallized from n-hexane were used. Spectral quality solvents (Uvasol, Merck) were employed and only triethylamine (Carlo Erba, purum) was additionally redistilled and dried over molecular sieves.

A Bomem-Michelson 100 spectrometer served as an IR-instrument. The following sample cells were used: 5 cm quartz for the dilute (≤ 0.0005 M) carbon tetrachloride solutions of *2-AP* and *3-AP*; 0.01 cm KBr for 0.1 M and 0.5 M solute concentration in various solvents; 0.002 cm KBr for 1M and 5 M solutions in chloroform.

The IR-spectra of the melted samples were obtained by 80⁰ C heating between KBr plates. The solid state 2-AP- and 3-AP spectra were recorded as Nujol mulls and from melt crystallized film as well.

The curve fitting was performed with the program Spectra Calc.

RESULTS AND DISCUSSION

IR-spectral data of 2-AP including a normal coordinate treatment ⁶ have been reported by a great number of authors ⁷⁻¹⁵, but no detailed analysis on hydrogen bond formation has been worked out. *Sugeta* has developed a calculation procedure for spectrophotometric determination of molar absorption coefficients of constituent species in a multicomponent equilibrium system which is applied to IR-spectral analysis of 2-AP self-association in 0.1 M and 0.5 M carbon tetrachloride solutions ¹⁶. The calculations prove that the dimerization could be predominating in the employed concentration range and by analogy with the results from X-ray study ⁴ a cyclic dimeric structure (I) is assumed. However, this conclusion is not acceptable, since the solution IR-spectra are markedly different from those in the solid state.

The pointed above X-ray investigation on the crystalline 2-AP structure suggests that the molecules are linked together in centrosymmetric dimers (I), without any additional NH...N(amino) hydrogen bond formation between the separate units ⁴. On the basis of this assumption, the following assignment of the NH₂ stretching bands of the solid state IR-spectrum (Fig. 1.1 and Table 1) is available:

- The absorption maximum at 3446 cm⁻¹ corresponds to the antisymmetric stretch (ν_{as} NH₂). Compared to ν_{as} NH₂ of the monomeric 2-AP at 3510 cm⁻¹ (Fig. 1.2 and Table 1), this value is 64 cm⁻¹ low-

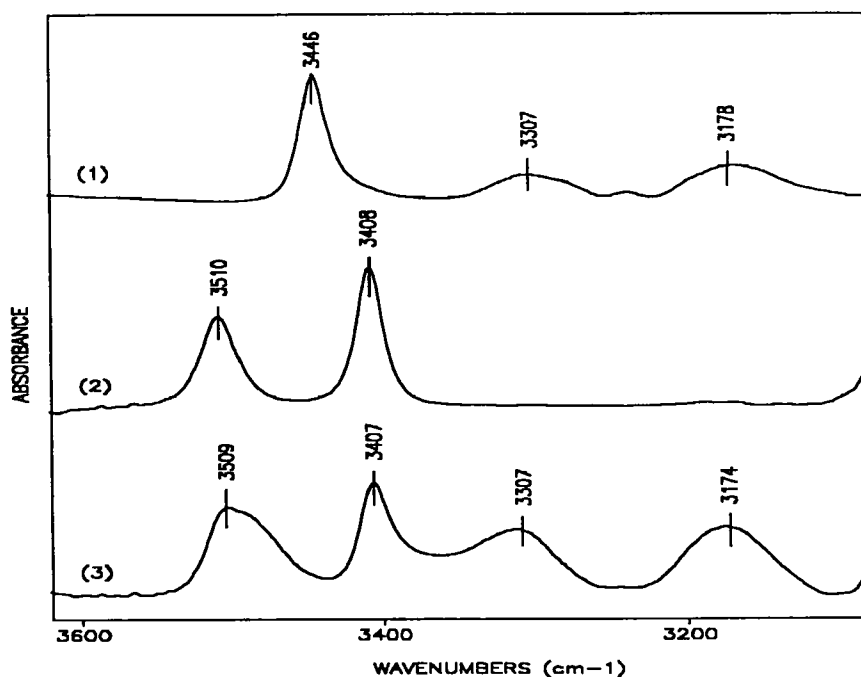


Fig. 1. IR-spectra of 2-AP: solid state, Nujol mull (1); solution in carbon tetrachloride, 0.0005 M (2) and 0.5 M (3)

frequency shifted. Similar $\Delta\nu_{as} NH_2$ (69 cm^{-1}) is observed by comparison of benzamide IR-spectrum in dilute carbon tetrachloride solution¹⁵ with that in a melt, where cyclic dimerization without any additional interaction between the separate dimers also takes place¹⁷.

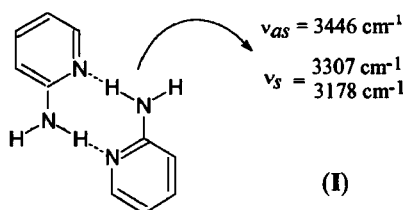
- The bands at 3307 cm^{-1} and 3178 cm^{-1} belong to the Fermi-doublet caused by a resonance between the symmetric NH_2 frequency ($\nu_s NH_2$) of the dimeric 2-AP and its $2\delta NH_2$ overtone. This effect is typical of $NH\dots N$ hydrogen bond formation with the participation of NH_2 group^{16, 18-22}. The frequencies and the intensities ratio of the discussed bands are used for the

Table I
 NH₂ stretching frequencies (cm⁻¹) of 2-Aminopyridine

Solvent	Concen- ration (mol.l ⁻¹)	Monomer		Dimer					Trimer	
		ν_{as}^f	ν_s^f	ν_{as}^f	ν_s^f	ν_{as}^b	ν_s^b	ν_{as}^b	ν_{as}^b	ν_s^b
carbon tetra- chloride	0.0005	3510	3408							
	0.1	3510	3408	3488	3393	3311	3170	3232	3250	
	0.5	3509	3407	3489	3396	3307	3174	3238	3249	
chloro- form	1	3510	3408	3488	3391	3316	3173	3238	3251	3371
	5	3507	3405	3480	3384	3314	3177	3236	3248	3366
triethyl- amine	0.1	3508	3407			3314	3174	3237	3252	3370
Liquid (melt)*				3465	3385	3310	3175			
Solid state nujol from melt *								3236	3249	
								3446	3446	

^{f, b} - free and hydrogen bonded species, respectively; ^{1, 2} - experimental values of Fermi-resonance doublet;
⁰ - calculated value of unperturbed ν_s^b NH₂; δ - calculated value of δ NH₂ overtone; * - without curve fitting

calculation of the unperturbed by Fermi-resonance symmetric NH_2 vibration at 3236 cm^{-1} (Table 1), using the method applied by *Wolff* and *Horn* ²⁰. With respect to $\nu_s \text{NH}_2$ of the monomeric *2-AP* at 3408 cm^{-1} (Fig. 1.2 and Table 1), this denotes a $\Delta\nu_s \text{NH}_2$ value of 172 cm^{-1} . The larger low-frequency shift of the $\nu_s \text{NH}_2$ band compared to the $\nu_{as} \text{NH}_2$ perturbation is in agreement with the fact that only one amino group hydrogen atom is involved in hydrogen bond ^{18, 20-24} (Scheme I).

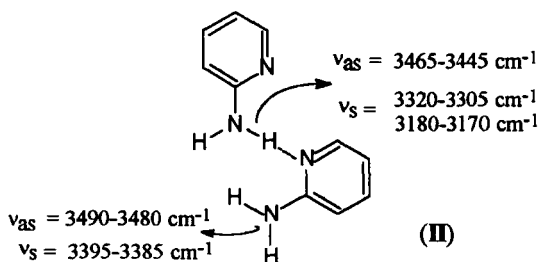


The difference between *2-AP* IR-spectra obtained in the solid state and in carbon tetrachloride solution is illustrated in Fig. 1. The self-association is not observed in solutions of *2-AP* concentration below 0.001 M (Fig. 1.2), and the discussed absorption maxima at 3510 cm^{-1} and 3408 cm^{-1} characterize the $\nu_{as} \text{NH}_2$ and $\nu_s \text{NH}_2$ stretching frequencies, respectively, in the free species (see also ^{5, 9, 16}). The increasing concentration of the solute provokes the $\text{NH}\cdots\text{N(Py)}$ intermolecular hydrogen bond formation leading to a broadening of the low-frequency flank of the NH_2 monomeric bands as well as to the appearance of the Fermi-doublet absorption maxima (Fig. 1.3). The specification of these effects is obtained by an IR-spectral curve fitting of solutions with increasing solute concentration (Table 1). The following intensities changes are affected:

- Both the absorption maxima at 3510 cm^{-1} and 3408 cm^{-1} decrease while the Fermi-resonance doublet at $3320\text{--}3305\text{ cm}^{-1}$ and $3180\text{--}3170\text{ cm}^{-1}$ grows up in parallel with a new band pair at $3490\text{--}3475\text{ cm}^{-1}$ and $3396\text{--}3384\text{ cm}^{-1}$ (see Fig. 2). The $\Delta\nu\text{NH}_2$ value ($\Delta\nu\text{NH}_2 = \nu_{\text{as}}\text{NH}_2 - \nu_{\text{s}}\text{NH}_2$) of this slightly shifted band pair varies within $90\text{--}100\text{ cm}^{-1}$ similarly to the $\Delta\nu\text{NH}_2$ difference of the free species (Table 1). Therefore, the discussed peaks can be assigned to $\nu_{\text{as}}\text{NH}_2$ and $\nu_{\text{s}}\text{NH}_2$, respectively, of the non-hydrogen-bonded amino group¹⁵.

- A new absorption maximum at about $3370\text{--}3360\text{ cm}^{-1}$ appears on increasing the solute concentration (Table 1). The effect is clearly perceptible of the spectrum of 5 M solution (Fig. 3).

The results are in agreement with the assumption that in carbon tetrachloride and chloroform solutions 2-AP forms *chain like (open)* dimers (II). In this case the discussed band pair at about 3480 cm^{-1} and 3380 cm^{-1} corresponds to the non-hydrogen-bonded NH_2 group. Since the other amino



group contains only one hydrogen atom involved in hydrogen bonding, the belonging $\nu_{\text{s}}\text{NH}_2$ band should be strongly low-frequency shifted. The $\nu_{\text{s}}\text{NH}_2$ values between 3230 cm^{-1} and 3240 cm^{-1} (Table 1), calculated from the Fermi-resonance doublets, is in agreement with this suggestion. The

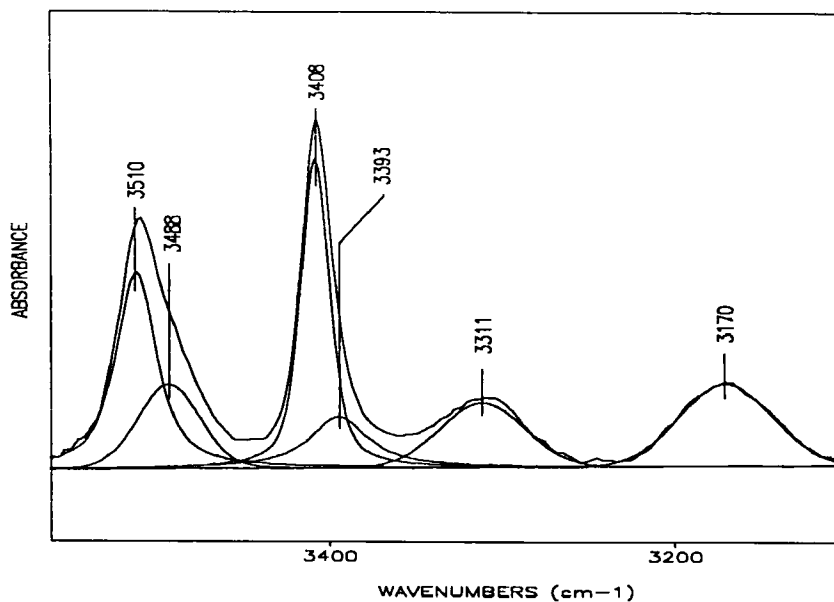


Fig. 2. Curve fitting (3550-3100 cm^{-1}) of the 2-AP IR-spectrum, 0.1 M solution in carbon tetrachloride

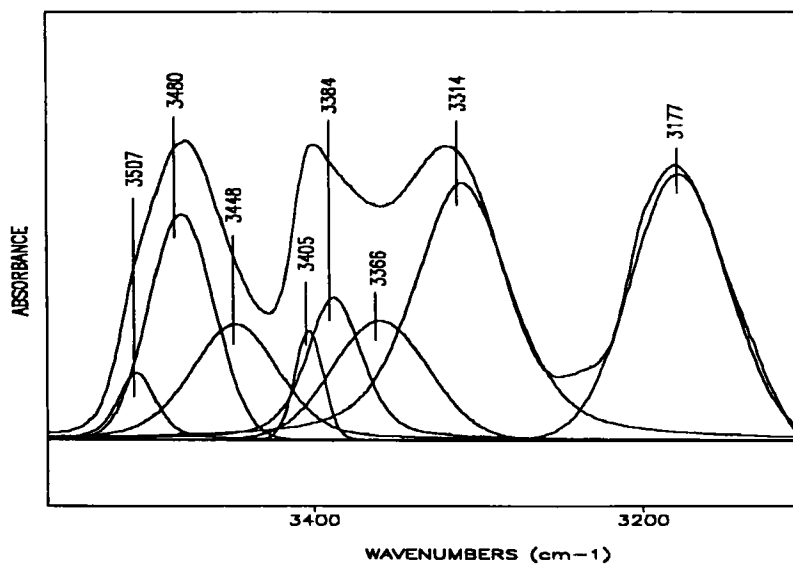
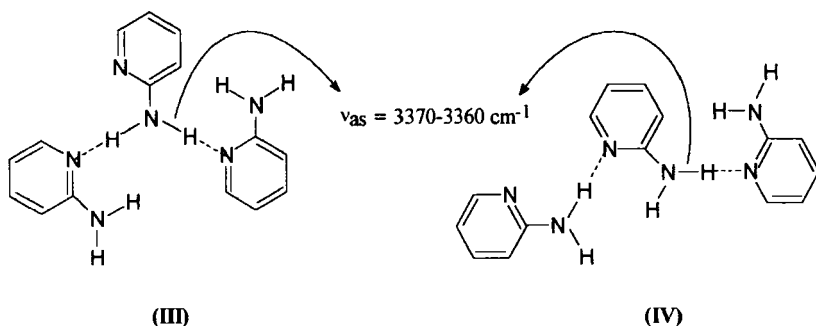


Fig. 3. Curve fitting (3550-3100 cm^{-1}) of the 2-AP IR-spectrum, 5 M solution in chloroform

corresponding antisymmetric NH_2 vibration is weakly affected^{18, 20, 21, 23, 24} and the respective band is not observed in the spectra of low-concentration 2-AP solutions because of a strong overlapping with the $\nu_{as} \text{NH}_2$ absorption maximum of the non-bonded dimeric NH_2 group (Fig. 2). With increasing concentration of the dimeric species the respective peak at 3465-3445 cm^{-1} is resolved (Fig. 3 and Table 1).



The appearance of a new band in the 3370-3360 cm^{-1} region at higher solute concentration indicates that under these conditions 2-AP also forms some amount of higher order (mainly trimeric) self-associates (Fig. 3 and Table 1). Two possible structures could be considered: the symmetric (III) or head-to tail associates (IV). The eventual formation of (III) where both the hydrogen atoms of the amino group are hydrogen bonded, should mostly affect the antisymmetric NH_2 stretching frequency and the discussed absorption maximum can be attributed to this mode. Moreover, the $\nu_s \text{NH}_2$ and consequently the Fermi-resonance caused band splitting should show almost the same values as well as in the case of the dimeric species (II)^{20, 21, 23, 24}. These suggestions concur with the previously reported results about the IR-spectra of 1:2 adducts of primary amines with trimethyl-, triethyl-

and tri-*n*-propylamine as proton acceptors^{19, 21} and are additionally assumed by our IR-spectral study of 2-*AP* in triethylamine (Fig. 4 and Table 1). Because of the steric hindrance of the bulky triethyl group of the solvent, some amount of non-solvated solute is present and the spectrum exhibits the corresponding weak-intensity bands at 3508 cm⁻¹ and 3407 cm⁻¹ (Fig. 4). Since the triethylamine is low-polar²⁵, the absorption maxima are not solvatochromically affected (compare with Fig 1.2). The band at 3480 cm⁻¹ (ν_{as} NH₂) as well as the Fermi-doublet at 3314 cm⁻¹ and 3174 cm⁻¹ (ν_s NH₂), characterize the 1:1 adduct of 2-*AP* and triethylamine. The peak at 3370 cm⁻¹ should be assigned to the presence of trimeric associates (1:2 adducts).

We have verified the alternative assumption of structure (IV) formation in 2-*AP* solutions by a comparative IR-spectral study of 3-*AP*. The X-ray data²⁶ of the crystalline compound demonstrate that 3-*AP* molecules are chain-linked to each other by (H)NH...N(Py) hydrogen bonds and this head-to-tail association forms infinite chains parallel to one of the crystallographic axes.

The solid state 3-*AP* IR-spectrum is given in Fig. 5.1. The Fermi-doublet at 3306 cm⁻¹ and 3158 cm⁻¹ (ν_s NH₂), and particularly the band at 3377 cm⁻¹ (ν_{as} NH₂) characterize the head-to-tail hydrogen bonded units of 3-*AP* which are structurally analogous to the central 2-*AP* molecule of Scheme (IV). The melting of the 3-*AP* sample breaks the infinite chains and this leads to intensity decrease of the 3377 cm⁻¹ absorption maximum and high-frequency shift of the Fermi-doublet peaks. Simultaneously, additional bands appear in the 3465-3390 cm⁻¹ range (Fig. 5.2), which should be assigned to NH₂ modes of the final units of broken 3-*AP* chains. These units are included in chain residues through hydrogen bonded amino groups of "dimeric type"

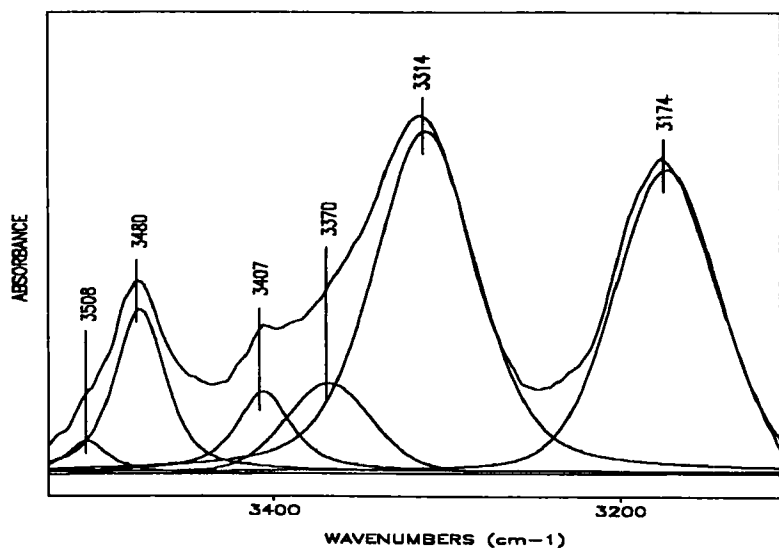


Fig. 4. Curve fitting (3500-3100 cm⁻¹) of the 2-AP IR-spectrum, 0.1 M solution in triethylamine

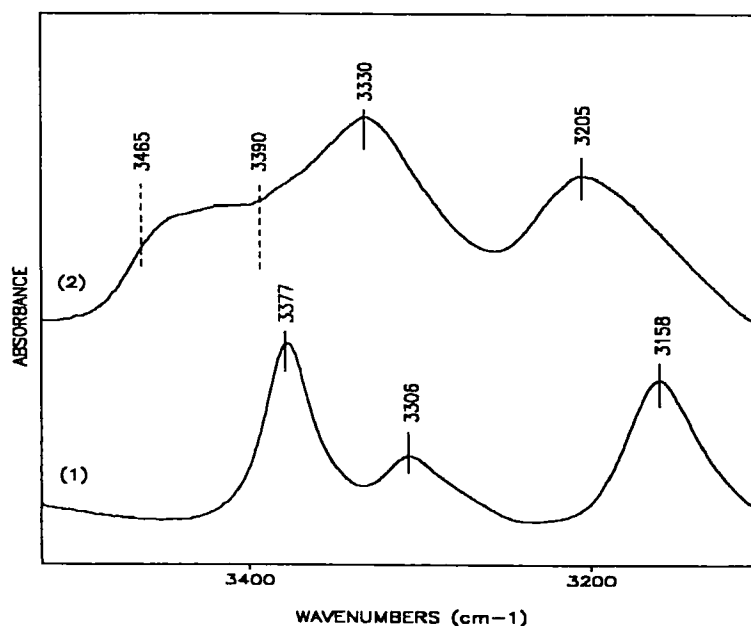
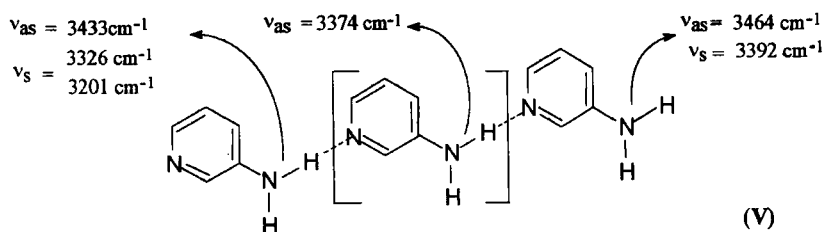


Fig. 5. IR-spectra of 3-AP: solid state, Nujol mull (1); liquid, melt (2);

(Scheme V), analogous of the outside 2-AP units in Scheme (IV). The IR-spectrum curve fitting of 5M 3-AP solution in chloroform resolves the discussed maxima (Fig. 6). The additional bands at 3486 cm^{-1} and 3401 cm^{-1} should be attributed to the $\nu_{as} \text{NH}_2$ and $\nu_s \text{NH}_2$ vibrations of the monomeric 3-AP, respectively, and the data obtained for high-diluted 3-AP chloroform solutions confirm this suggestion. The assignment of the other bands is given in Scheme (V).



The results stated above suggest that the presence of $3370\text{--}3360\text{ cm}^{-1}$ band is typical of both 2-AP structures (III) and (IV), and it is not characteristic for their identification. However, the pointed similarity between the 2-AP and 3-AP IR-spectra illustrated in Figs. 3 and 6, respectively, indicates that 2-AP forms *head-to-tail* self-associates. The same conclusion is obtained by comparing the spectra of melted 3-AP- and 2-AP samples (Figs. 5.2 and 7.1). Like 3-AP, the corresponding 2-AP IR-spectrum exhibits absorption maxima at 3465 cm^{-1} and 3390 cm^{-1} (Fig. 7.1, compare with Fig. 5.2), characteristic of the final units in chain-linked self-associates. These bands disappear after crystallizing of the melt where the peak at 3446 cm^{-1} which is typical of 2-AP cyclic dimers (I) comes to the fore (Fig. 7.2).

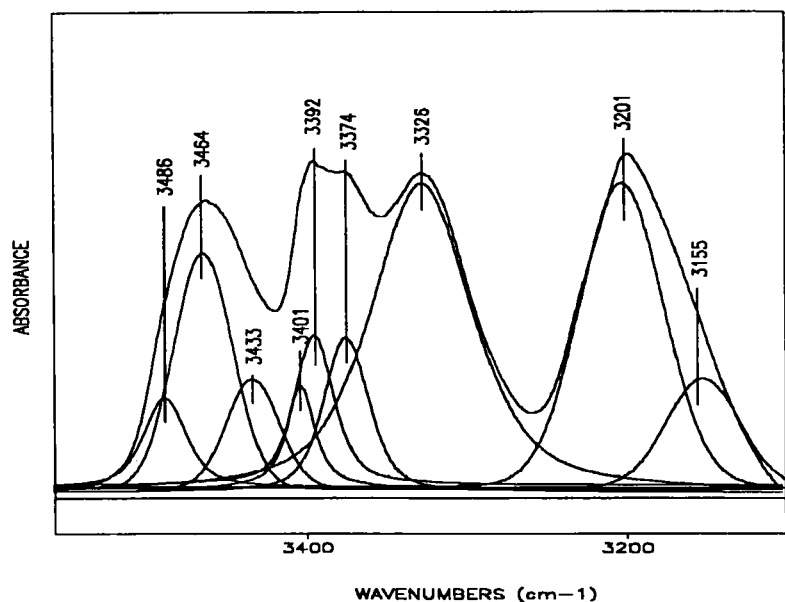


Fig. 6. Curve fitting (3550-3100 cm^{-1}) of the 3-AP IR-spectrum, 5 M solution in chloroform

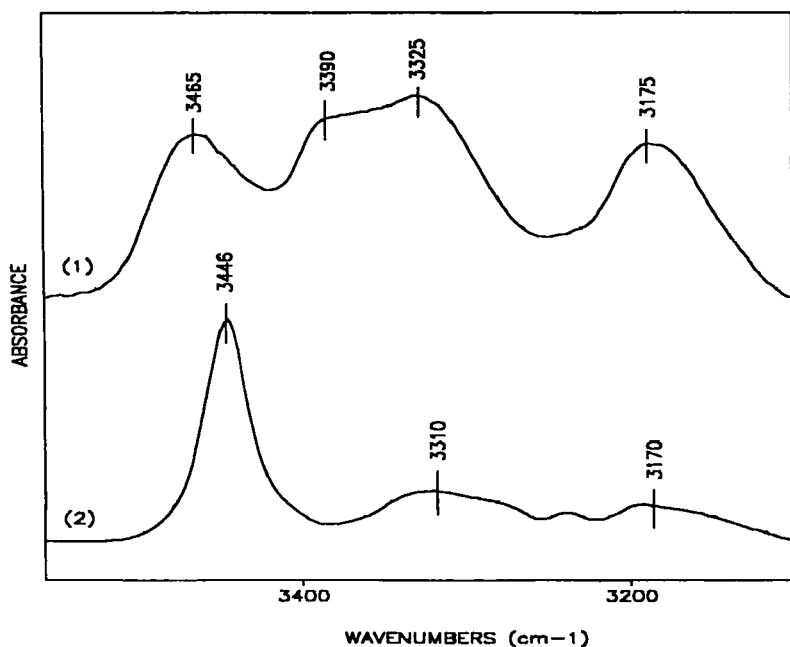


Fig. 7. IR-spectra of 2-AP: liquid, melt (1); solid state, from melt (2)

CONCLUSIONS

The study carried out proves that *2-AP* forms chain-like self-associates in solutions, in contrast to solid state where cyclic dimer structure takes place. This result applies to the liquid *2-AP* too.

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