

SYNTHESIS AND SPECTROSCOPIC INVESTIGATION OF (ACETYLAMINO)PYRIDINES

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Received April 23, 2009

Accepted June 26, 2009

Published online September 3, 2009

The self-association of 2- and 3-(acetylamino)pyridines in a condensed phase was investigated by conventional and linear-polarized IR spectroscopy. Interpretation of spectra of the monomer and associated forms was carried out by the reducing-difference procedure. Theoretical quantum chemical calculations at the B3LYP level of theory and with 6-31+G** basis set were performed in order to obtain the electronic structure and vibrational characteristics of both compounds.

Keywords: 2-(Acetylamino)pyridine; 3-(Acetylamino)pyridine; Self-association; IR-LD spectroscopic analysis; Theoretical calculation.

The design and creation of specific structural ensembles in condensed phase continues to be a subject of current interest in the context of development of new materials with significant electro-optical, electric or catalytic properties. The elucidation of the hydrogen bonds formation is one of the key factors and can be use as powerful instrument to understand the molecules organization and recognition in a condensed phase which is appeared an important strategy¹⁻³. Self-association of 2- and 3-aminopyridine has been intensively studied over the recent years both in solution and in the solid state due to the rudimentary binding qualities of their molecules. Typical of 2-aminopyridine is the formation of stable dimers in condensed phase through NH...N intermolecular hydrogen bonds^{4,5}. In the solid state, 3-aminopyridine forms infinite chains by the interactions of the same type, while in solution linear and cyclic dimers have been observed⁴⁻⁷. If we modify these compounds with the acetyl group, it should be interesting

to know how the self-organization of the molecules will be affected. For example, the solid state single crystal X-ray diffraction data for 5-amino-2-methoxypyridine ester amide of squaric acid ethyl ester⁸ show that interactions of the $\text{NH}\cdots\text{O}=\text{C}$ type are preferred instead of those of $\text{NH}\cdots\text{N}$. However, the high-temperature form of the compound is characterized by the classical interactions of the latter type⁹.

Herein, we have presented self-association of 2-(acetylamino)pyridine **1** and 3-(acetylamino)pyridine **2** (Chart 1) both in solution and in the solid state by conventional and linear-polarized IR (IR-LD) spectroscopy and especially by application of the reducing-difference procedure for interpretation of non-polarized and polarized IR spectra.

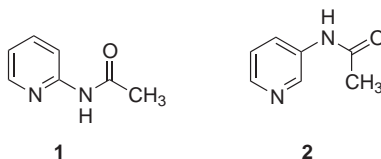
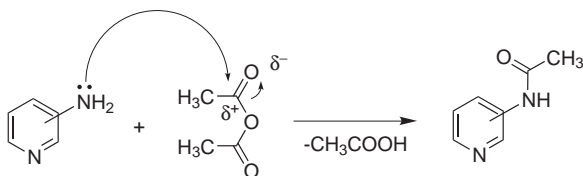


CHART 1

EXPERIMENTAL

Synthesis

The reaction scheme for the synthesis of 2-(acetylamino)pyridine **1** and 3-(acetylamino)pyridine **2** is presented in Scheme 1. 2-Aminopyridine (4.0 g) or 3-aminopyridine (2.5 g) (both Merck products) are mixed with acetic anhydride (5.6 or 3.5 ml) under continuous stirring at 100 °C for 1 h. Then H_2O (50 ml) is added and the stirring is continued for 30 min. A 30% aqueous NaOH is added for neutralization. The final products are extracted with CH_2Cl_2 . For $\text{C}_7\text{H}_8\text{N}_2\text{O}$ calculated: 61.75% C, 5.92% H, 20.57% N; found: 61.71% C, 5.92% H, 20.58% N for **1** and 61.70% C, 5.91% H, 20.59% N for **2**. The most intensive peaks in mass spectra of compounds **1** and **2** are observed at 137.45 and 137.51, respectively, corresponding to the single-charged cation $[\text{C}_7\text{H}_8\text{N}_2\text{O}]^+$ with molecular weight 137.15.



SCHEME 1

Materials, Measurements and Methods

The IR spectra have been recorded on a Bomem–Michelson 100 FT-IR-spectrometer in the 4000–400 cm^{-1} region at 2 cm^{-1} resolution. The conventional (non-polarized) IR spectra have been obtained using the Nujol mull technique with 5–10% concentration. The IR spectra in a chloroform solution (Uvasol, Merck) are obtained using the KBr cell with thickness of 0.04 cm, and at 1×10^{-2} and 5×10^{-3} M (dilute solution) concentrations. The oriented samples are obtained as a suspension in a nematic liquid crystal (ZLI-1695, Merck). We used the following technique to orient the sample. Compound **1** or **2** in a nematic solution of ca. 10-wt.% concentrations in ZLI-1695 and a 0.0025-cm cell thickness was chosen in order to achieve a reasonable solution orientation. In addition, the cell windows were rubbed out and polished in one direction. The IR spectra were obtained from 150 scans.

The theoretical approach, experimental technique for preparation of samples, procedures for interpretation of polarized IR spectra and validation of the new method of linear-dichroic infrared (IR-LD) orientation are presented with respect to its accuracy and precision. The influence of the liquid-crystal medium on peak positions and integral absorbances of the guest molecule bands, the nature and balance of the forces in the nematic liquid-crystal suspension and morphology of the suspended particles are also discussed^{10–13}.

Analyses of the samples by HPLC-ESI MS/MS were performed with a Thermo Finnigan surveyor LC-Pump. The compounds were separated on a Luna C18 column (150 \times 2 mm, 4 μm particle size) from Phenomenex (Torrance (CA), USA). The mobile phases were of water with 0.1% HCOOH (A) and acetonitrile with 0.1% HCOOH (B) using a gradient program, and are presented in Table I.

Thermogravimetric study was carried out using a Perkin–Elmer TGS2 instrument. Calorimetric measurements were performed on a DSC-2C Perkin–Elmer apparatus under argon.

Reducing-Difference Analysis of Non-Polarized IR Spectra

The method for *n*-component systems is extended¹¹ and consists of subtraction of two IR spectral curves corresponding to samples containing diverse concentrations of given structural units. The measurements of both samples must be made under the same conditions

TABLE I
HPLC MS/MS conditions

No.	<i>t</i> , min	A, %	B, %	Rate, $\mu\text{l min}^{-1}$
0	0.00	100	0	200
1	3.00	100	0	200
2	8.00	65	35	200
3	9.00	0	100	200
4	14.00	0	100	200
5	14.50	100	0	200
6	20.00	100	0	200

and using the same preparation techniques (e.g. liquids, solutions in selected solvents, Nujol mull or KBr technique). The subtraction procedure is performed until a definite band is eliminated in the obtained reducing-difference IR spectrum.

Reducing-Difference Procedure for Polarized IR-LD Spectra

This method was suggested by Thulstrup and Eggers¹⁴ for polarized UV-spectral interpretation. The procedure involves consecutive elimination of the spectral bands of a given polarization by subtracting the perpendicular spectrum multiplied by a coefficient from the parallel spectrum. This procedure was extended by Spanget-Larsen¹⁵, and Korte and Thulstrup¹⁶ to samples oriented in stretched polyethylene and nematic solution, respectively. A systematic analysis of this approach and its application to IR-band assignment according to their symmetry was developed by Jordanov and co-workers¹⁷⁻¹⁹ for polarized IR-LD spectra in nematic liquid-crystal solution. The method consists of subtraction of the perpendicular spectrum (IR_{\perp} ; a result of the 90° angle between the polarized light beam electric vector and the orientation of the sample) from the parallel spectrum (IR_{\parallel}) obtained with a colinear mutual orientation. The recorded difference spectrum ($IR_{\parallel} - IR_{\perp}$) divides the integrated absorbance of each band into positive bands originating from transition moments, which form average angles with the orientation direction (n) between 0 and 54.7° (magic angle), and negative bands corresponding to transition moments, which are directed between 54.7 and 90°. In the reducing-difference procedure, the perpendicular spectrum multiplied by the parameter c is subtracted from the parallel one and c is varied until at least one band or a set of bands is eliminated. The simultaneous disappearance of these bands in the obtained reduced IR-LD spectrum ($IR_{\parallel} - cIR_{\perp}$) indicates colinearity of the direction of the corresponding transition moments, providing information about the mutual disposition of the molecular fragments.

The interpretation of IR spectra containing multiple or strong by overlapping peaks is possible not only in polarized but also in conventional IR spectra. That requires first of all the number of peaks to be determined and their next curve-fitting as a result of v_i and integral absorption A_i values²⁰⁻²³. The deconvolution based on the Fourier self-deconvolution method and the subsequent peak-fitting procedure are applied²⁴.

The curve-fitting of peaks includes the Levenberg-Marquardt method²⁵⁻²⁹, where the algorithm continually iterates until a minimum value of the reduced χ^2 is reached. The χ^2 is a statistical measure of goodness-of-fit, based on the known variance in the data. This approach is defined as curve-fitting or a peak-fitting procedure. During the curve-fitting of the IR-spectral curve, three peak functions should be chosen – a Lorentzian, Gaussian or mixed Gaussian-Lorentzian²⁰⁻²³. The mixed (50:50) Gaussian-Lorentzian peak function turns out to be the most useful in the IR-spectral interpretation. Two of the most used line shapes are Gaussian-Lorentzian mixtures.

All the IR-spectra interpretations are made using the GRAMS AI/7 IR-program package³⁰ and Statistica 5.11 for statistic relationships³¹.

The geometry optimization of the studied structures and subsequent vibrational analysis was carried out using DFT (B3LYP) calculations and 6-31+G** basis set. All calculations were carried out using Gaussian 98 and Dalton 2.0 packages^{32,33}. The visualization of the output files was carried out using ChemCraft 5.0 (ref.³⁴). For every structure, the stationary points found on the potential energy hypersurfaces are characterized by using a standard analytical harmonic vibrational analysis. The experimental data were compared with the theoretically

calculated parameters (including vibrational frequencies and intensities) to establish which type of experimental data coincide the best with theoretically calculated. A scaling factor of 0.9614 was used.

RESULTS AND DISCUSSION

Self-Association in Solid State

The non-polarized IR and difference IR-LD spectra of **1** and **2** are presented in Fig. 1. As can be seen, a significant degree of macro-orientation of suspended particles is observed^{10–13}. A specific feature in the IR spectra of these compounds is the absence of a well-defined band of amide NH stretching bands (ν_{NH}), especially in the case of **1**. The observed broad band in the 3300–2500 cm^{-1} region is typical of protonated amines or systems, where the NH participates in very strong intermolecular interactions of the N–H...N type, such as in 4-aminopyridinium hemiperchlorate³⁵. In our systems, we can explain this phenomenon by the presence of the acetylamino group, which affects the basicity of the N_{py} atom. This may also mean, that a strong NH...N interaction is observed in these systems.

The intensive bands at 1691 cm^{-1} of **1** and 1689 cm^{-1} of **2** correspond to the Amide I ($\nu_{\text{C=O}}$) stretching mode. They correlate well with the typical values of acetylamino derivatives³⁶ at $1690 \pm 45 \text{ cm}^{-1}$. Within the interval of $1540 \pm 60 \text{ cm}^{-1}$, the strong intensive band of δ_{NH} (Amide II), typical of

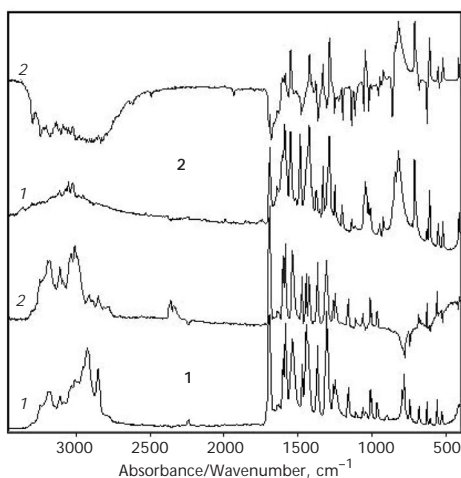


FIG. 1
Non-polarized IR (1) and difference IR-LD (2) spectra of **1** and **2**

this functional group, is usually observed³⁶. In our systems, the bands at 1533 cm^{-1} for **1** and 1554 cm^{-1} for **2** are attributed to the discussed mode. The low-intensive absorption maxima at 1625 , 1575 and 1525 cm^{-1} are associated with the in-plane stretching modes of substituted pyridines (py modes). Their elimination at an equal dichroic ratio confirms the assignment of these bands as A_1 modes. Amide III ($\nu_{\text{C-N}}$) is also observed as an intensive band within the $1275 \pm 55\text{ cm}^{-1}$.

For **1** and **2**, this mode can be assigned to the bands at 1303 and 1288 cm^{-1} , respectively. The IR-spectroscopic region $900\text{--}400\text{ cm}^{-1}$ is characterized by a series of bands of $\gamma(\omega)_{\text{NH}}$ (Amide V), $\delta_{\text{C=O}}$ (Amide IV), $\gamma_{\text{C=O}}$ (Amide VI), δ_{NCC} and γ_{Ph} out-of-plane modes of different substituted pyridines³⁶. If we describe the γ_{Ph} bands of 1,2- and 1,3-disubstituted benzenes, they are observed at $755 \pm 35/705 \pm 35\text{ cm}^{-1}$ and $685 \pm 25/530 \pm 90\text{ cm}^{-1}$, respectively³⁶. In some acetylmino derivatives, the band of $\gamma(\omega)_{\text{NH}}$ is observed as a strong and broad band at $840 \pm 20\text{ cm}^{-1}$. The elimination of the 777 cm^{-1} band leads to disappearance of the bands at 790 and 740 cm^{-1} (Fig. 2 (2)). These results suggest that the former band corresponds to γ_{NH} , while the latter pairs of maxima to γ_{Ph} modes. The other bands at 676 , 624 and 655 cm^{-1} can be assigned to $\delta_{\text{C=O}}$, $\gamma_{\text{C=O}}$ and δ_{NCC} , respectively. The obtained characteristic bands are selected in Table II.

The obtained results suggest that the molecules of **1** can associate in the solid state as stable cyclic dimers or infinite chains stabilized by strong $\text{NH}\cdots\text{N}$ intermolecular interactions. However, the investigation of the asso-

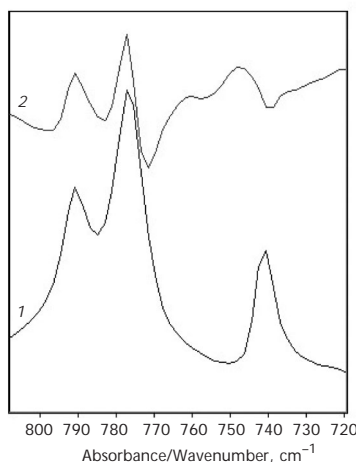
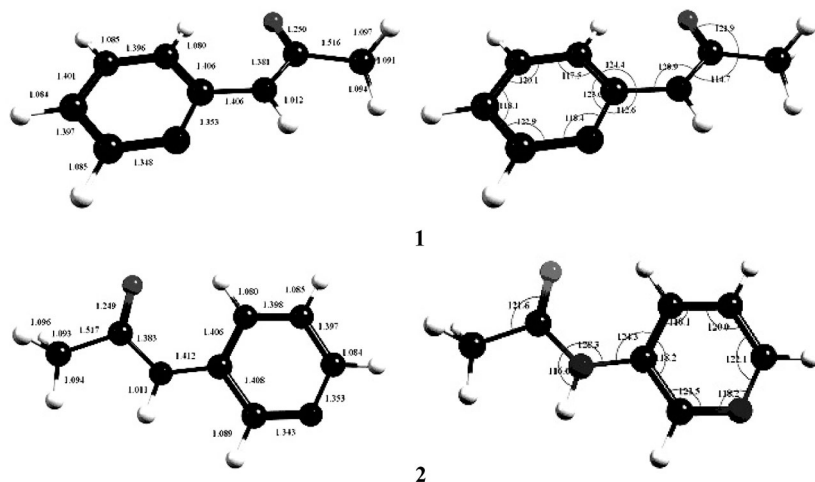


FIG. 2
Non-polarized IR (1) and reduced IR-LD (2) spectra of **1** after elimination of the band at 777 cm^{-1}

Simultaneous elimination of the γ_{NH} and γ_{ph} modes at an equal dichroic ratio suggests that both transition moments are colinearly oriented not only in the isolated molecule of **1** but in the frame of the dimer as well.

Assignment	1		2	
	Theor.	Exp.	Theor.	Exp.
ν_{NH}	3421	3300	3422	3300
Amide I ($\nu_{\text{C=O}}$)	1698	1691	1699	1689
Amide II (δ_{NH})	1543	1533	1560	1554
i. p. (py) modes	1624, 1577, 1525	1625, 1576, 1525	1623, 1577, 1513	1625, 1575, 1515
Amide III ($\nu_{\text{C-N}}$)	1300	1303	1300	1288



SCHEME 2
Optimized molecular geometries of **1** and **2** at B3LYP/6-311+G**

The obtained experimental results correlate well with the theoretically predicted geometry (Scheme 2). As can be seen, the molecule of **1** is flat with a maximum deviation from total planarity of $0.0(2)^\circ$. The amide and pyridine planes are coplanar with an angle of 0.0° . The obtained geometric parameters such as bond lengths and angles correlate well with the crystallographic data of pyridine derivatives^{37,38}, where the obtained differences between the values are less than 0.0123 \AA and 2.1° , respectively. The amide CO-NH group is flat with *trans*-configuration and a dihedral angle of 179.6° .

The analysis of **2** in the solid state shows that the elimination of the band at 1630 cm^{-1} leads to disappearance of all the A_1 bands at 1588 , 1122 and 1000 cm^{-1} . However, this procedure provokes the disappearance of the bands at 707 and 603 cm^{-1} , typical of out-of-plane γ_{Ph} modes (Fig. 3 (2)). In the frame of one molecule of **2**, bands of the A_1 and B_1 symmetry cannot be eliminated at an equal dichroic ratio. This means that compound **2** is self-associated in the solid state as infinite zigzag chains by strong $\text{NH}\cdots\text{N}$ interactions (Scheme 3). In these chains, the molecules of **2** can be disposed in a manner leading to colinearity of the transition moments direction of vibrations of the A_1 and B_1 symmetry class. A similar association and reducing-difference result is observed in the case of 4-aminopyridine in the solid state, where the elimination of A_1 and B_2 modes at an equal dichroic ratio is possible in the frame of infinite chains, formed by 4-AP molecules through $\text{NH}\cdots\text{N}$ interactions³⁹.

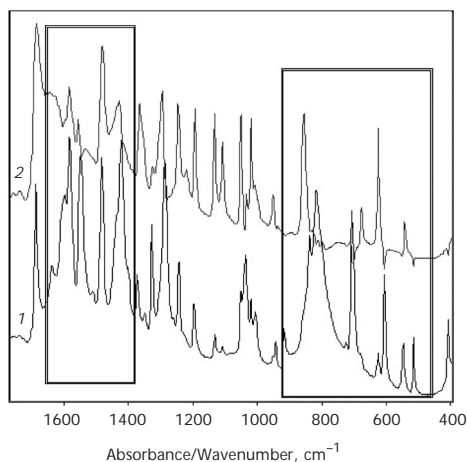
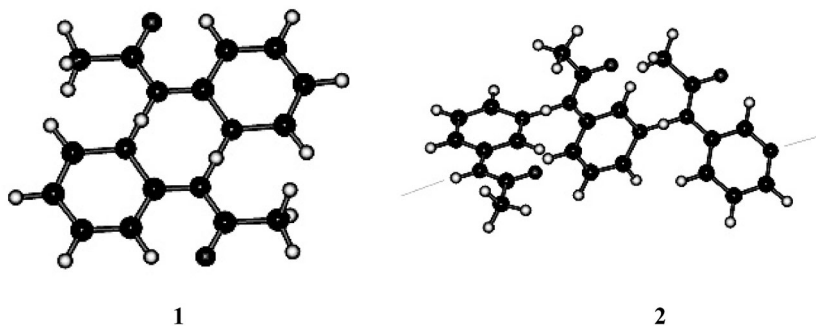


FIG. 3
Non-polarized IR (1) and reduced IR-LD (2) spectra of **2** after elimination of the band at 707 cm^{-1}

Our theoretical calculations of the molecular geometry of **2** show that the molecule is flat with a coplanar disposition of the planes of amide and pyridine rings at an angle of 0.1° (Scheme 2). Like in **1**, the obtained geometric parameters – bond lengths and angles – correlate well with those of *N*-[2-(furan-3-yl)pyridin-3-yl]acetamide⁴⁰, where differences less than 0.0342 \AA and 2.1° are obtained. The amide fragment is flat with *trans*-configuration and a dihedral angle of 179.8° .



SCHEME 3
Self-association of **1** and **2** in the solid state

Self-Association in Solution

Analysis of the self-associates of **1** and **2** is carried out using the difference procedure of non-polarized IR spectra^{10–13}. Non-polarized IR spectra of **1** and **2** in chloroform solutions are presented in Fig. 4. The bands of ca. 3425 cm^{-1} in both compounds correspond to the ν_{NH} stretching vibration of the non-associated NH group. The typical values³⁶ are within $3410 \pm 70 \text{ cm}^{-1}$. The band of $\nu_{\text{C=O}}$ is shifted to low frequencies by $4\text{--}7 \text{ cm}^{-1}$. The in-plane modes within the $1600\text{--}1450 \text{ cm}^{-1}$ region are affected only weakly, with a difference less than 2 cm^{-1} . The δ_{NH} bands, which are observed at 1513 cm^{-1} for **1** and 1519 cm^{-1} for **2**, are dramatically influenced (Fig. 4).

The obtained values correlate well with the theoretically predicted IR bands shown in Fig. 7. The obtained differences less than 5 cm^{-1} between the theoretically and experimentally obtained IR-spectroscopic data in solution indicate a good applicability of the theoretical approximation method. This result confirms the conclusions of the solid-state IR spectra that the self-association of **1** and **2** is due to strong $\text{NH}\cdots\text{N}$ interactions. The importance of this conclusion is associated with other phenomena as well.

Using the spectra in chloroform solutions of **1** and **2** at different concentrations (see Experimental and Figs 5 and 6), and applying the reducing difference procedure to the bands corresponding to the non-associated ν_{NH} at ca. 3425 cm^{-1} and to the associated δ_{NH} band at 1533 cm^{-1} , we can isolate

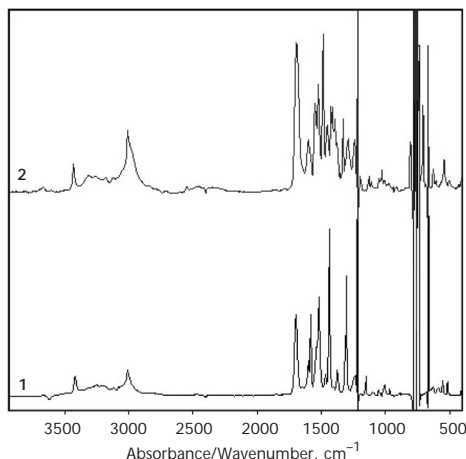


FIG. 4

IR spectra of **1** and **2** in chloroform solution (10^{-2} M concentration)

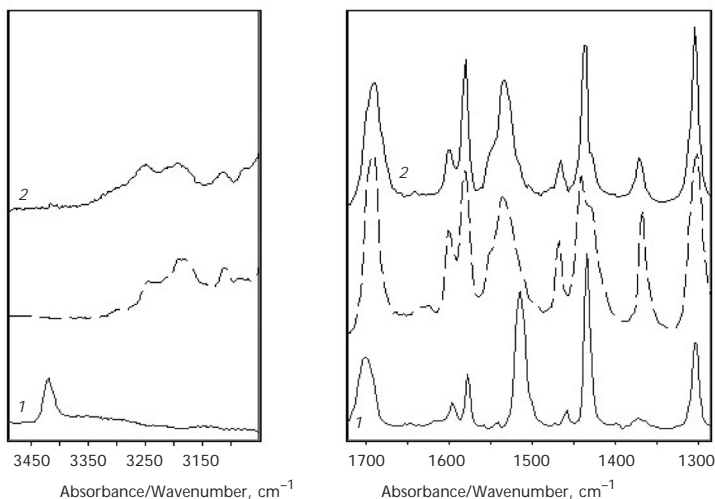


FIG. 5

Reduced IR spectra of monomeric (1) and associated (2) forms of **1** in solution; solid-state IR spectrum (dotted line)

(according to the theory¹¹) the IR bands of non-associated molecules of **1** and those of the associated form. As can be seen, the spectrum of the free molecules of **1** (Figs 4 (**1**) and 5 (*1*)) is similar to that in chloroform, while the spectrum of the associates (Fig. 5 (*2*)) is surprisingly identical with those in the solid state. This result suggests that the dimers are characterized as self-associates in solution of **1**.

The same analysis to the IR spectra of chloroform solutions of **2** shows that the characteristics of the reduced IR spectrum of **2** (Fig. 6) differ from the solid-state spectra. The spectrum of isolated molecules in solution (Fig. 6 (*1*)) correlates well with those, theoretically predicted in Fig. 7,

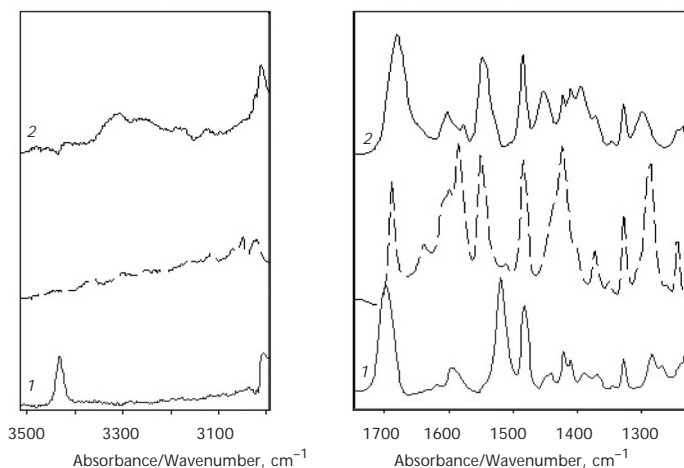


FIG. 6
Reduced IR spectra of monomeric (*1*) and associated (*2*) forms of **2** in solution; solid-state IR spectrum (dotted line)

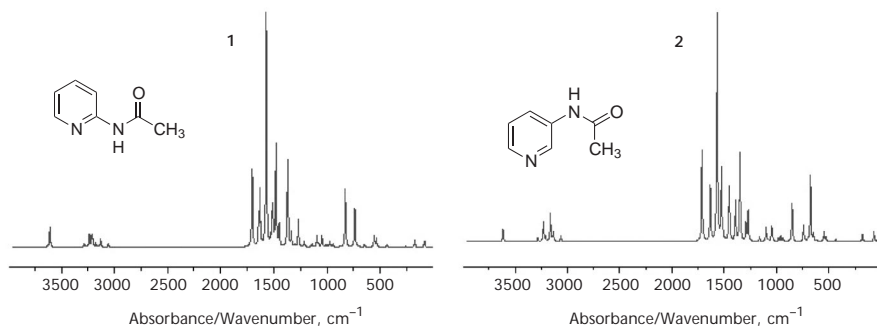


FIG. 7
Theoretical IR spectra of **1** and **2**

where the obtained difference is less than 6 cm^{-1} . The values are very close to those obtained with **1**, thus confirming again successful application of the theoretical method in vibrational analysis.

The IR spectrum of the associated form (Fig. 6 (2)) is characterized by a pair of bands at 1689 and 1679 cm^{-1} suggesting two "different" $\text{C}=\text{O}$ groups according to their mode of hydrogen bonding. Pair of bands is observed for δ_{NH} as well as at 1554 and 1534 cm^{-1} . In parallel with the broad band at $3200\text{--}2200\text{ cm}^{-1}$, a relatively intensive band is observed at 3330 cm^{-1} , a value typical of ν_{NH} for moderate intermolecular interactions^{8,9}. The first type of interactions suggests that a dimer of **2** formed by the molecular $\text{NH}\cdots\text{N}$ interaction is characteristic of the system. Similar dimers are proposed for the unsubstituted 3-aminopyridine by ^1H NMR in solution⁵.

However, the existence of the dimers associated by the $\text{NH}\cdots\text{O}=\text{C}$ interactions can be suggested as well. Moreover, the change in the IR-spectroscopic pattern of **2** is similar to that of 5-amino-2-methoxypyridine ester amide of squaric acid ethyl ester, where, as it has been mentioned, the type of the interaction is proved by the comparison of IR-LD spectroscopic analysis and single-crystal X-ray diffraction data⁸.

CONCLUSIONS

The self-association of 2-(acetylamino)pyridine and 3-(acetylamino)pyridine both in the solution and solid state is investigated by conventional and linear-polarized IR spectroscopy. The application of the reducing-difference procedure for the interpretation of the non-linear and linear-polarized IR spectra allows the assignment of the IR characteristics to both non-associated and associated compounds in condensed phase. Similar to unsubstituted aminopyridines in the solid state and solution, 2-(acetylamino)pyridine forms stable dimers by strong $\text{NH}\cdots\text{N}$ intermolecular hydrogen bonding. In contrast, 3-(acetylamino)pyridine forms infinite zig-zag chains in the solid state by $\text{NH}\cdots\text{N}$ interactions, but in solution two types of self-associates, dimers with $\text{NH}\cdots\text{N}$ bonding and $\text{NH}\cdots\text{O}=\text{C}$ bonding are characterized. These results are similar to other pyridine derivatives, where in the solid state, the crystallographically refined $\text{NH}\cdots\text{O}=\text{C}$ interactions⁸ are preferable. The theoretical calculated IR spectra confirm the obtained experimental results showing the applicability of the used method for such type investigation.

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