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Fourier transform infrared and laser Raman spectroscopic investigations on 2–N–(benzoylamino)pyridine

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Abstract : This paper is completely devoted to the analysis of the vibrational spectra of 2-N-(benzoylamino) pyridine. The Fourier transform infrared spectrum of 2–N–(benzoylamino) pyridine has been recorded in the range 4000–400 cm $^{-1}$ and the laser Raman spectrum was measured over the region 4000-10 cm $^{-1}$. The spectra have been analysed on the basis of C_s symmetry and the observed bands have been assigned to different specific modes of vibration. The assignments of the Infrared and Raman bands are made on the basis of magnitude and relative intensities of the observed bands. The assignments made for the complex compounds under investigation are found to be satisfactory with the earlier work on some pyridine derivatives.

Keywords : Vibration spectroscopy, 2-N–(benzoylamino)pyridine, vibrational assignments

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The vibrational spectra of biological important pyridine derivatives have been examined previously [1-4] but the high complexity and low symmetry of these molecules have made detailed interpretation very difficult. Differences of absorption depend on the number and position of substituents in the pyridine ring as well as on the nature of these substituents. The majority of the absorption bands in the 3300 cm $^{-1}$ region have been identified and a number of frequencies in the 2000-600 cm $^{-1}$ region characteristic of the fundamental vibrations have been observed [1-4]. It was shown that the presence of hydrogen bonding in certain pyridine derivatives could be clearly detected by infrared spectroscopy [1–4]. The infrared spectroscopic investigation, however, formed part of a larger programme of work involving the examination of the vibrational spectra from 4000-600 cm $^{-1}$ of pyridine and of substituted pyridines containing two, three and four substituents. The objective of this investigation is to identify the vibrational frequencies corresponding to each substituent, whether they are stretching vibrations or associated bending vibrations. It was also studied that the vibrations were dependent on the total number of substituents and their positions in the ring.

The Fourier transform infrared spectrum of 2-N-(benzoylamino)pyridine is reported in the region 4000–400 cm^{-1}. The laser Raman spectrum was recorded over the region 4000-10 cm ^{1}. The samples were obtained from spectracol, England (Grade I) and used without further purification. The spectra were measured at Central Leather Research Institute and Indian Institute of Technology, Madras. The spectra are given in Figures 1 and 2.

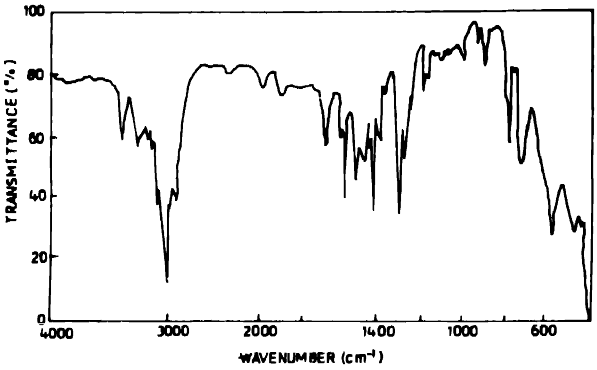

Figure 1. Fourier transform infrared spectrum of 2-N-(benzoylamino) pyridine.

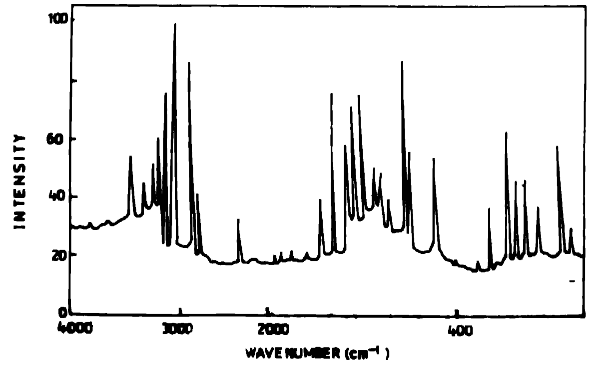

Figure 2. Laser Raman spectrum of 2-N-(benzoylamino) pyridine.

The observed bands in the infrared and Raman spectra of 2-N-(benzoylamino) pyridine are summarised in Table 1. All the sharp bands are expected to be accurate to ± 1 cm^{-1}.

Table 1. Assignment of the vibrational frequencies of 2–N–(benzoylamino) pyridine.

Laser Raman		Infrared		Assignment		
Freq.	Int.	Freq.	Int.			
3402	M	3400	M	ν	(N – H)	sym. stretch
3075	M	3089	M	ν	(C – H)	Aromatic stretch
3050	W	3055	S	ν	(C – H)	Aromatic stretch
3015	VW	3011	VS	ν	(C – H)	Aromatic stretch
2927	M	2925	S	ν	(C – H)	Stetching
1686	S	1680	S	ν	(C = O)	Stretching
1602	M	1610	MS	ν	(C–C)	Ring stretching
1595	S	1590	S	ν	(C–C)	Ring stretching
1538	S	1530	M	ν	(C–C)	Ring stretching
1510	S	1500	S	ν	Ring	C=N stretching
1471	W	1465	M	ν	(C–C)	Ring stretching
1441	VS	1440	S	ν	(C–C,C=N)	Ring stretching
1265	M	1280	S	β	(C–H)	In-plane bending
1261	M	1250	M	β	(C–H)	In-plane bending
1230	W	1242	M	ν	(C–N)	Stretching
1160	M	1158	M	ϕ	(C–H)	In-plane bending
847	W	850	W	ν	(C–N)	Stretching
780	MS	785	W	β	(C–H)	Out-of-plane bending
770	VS	770	MS	ν	(C–C)	Stretch-breathing type
756	M	750	W	ϕ	(C–H)	Out-of-plane bending
718	M	715	M	ν	(C–C)	Stretch-breathing type
701	M	695	MS	ϕ	(C–H)	Out-of-plane bending
620	W	638	W	ϕ	(C–C)	Out–of-plane bending
561	M	560	S	β	(C–C)	In-plane bending
454	M	460	M	ϕ	(C–C)	Out-of-plane bending
412	MW	410	M	ϕ	(C–C)	Out-of-plane bending

VS – Very strong; S – Strong; M –Medium;
MS – Medium strong; W – Weak; VW – Very weak

As the similarity in the infrared spectra of benzene and pyridine has often been observed, the absorption frequencies of benzene and pyridine can be compared and are seen to be very similar. It would be expected that the replacement of each of two CH groups in benzene by nitrogen atom would not appreciably alter the vibrations other than those of the hydrogen atoms. The previous works [5-9] have shown that the ring vibrations of pyridine parallel to those of the benzene can be readily located and the hydrogen vibrations of pyridine show considerable divergence from those of benzene and can only be tentatively assigned. In general, transition from benzene to pyridine causes a displacement of the hydrogen frequencies towards lower frequencies. The complex studied in the present investigation is monosubstituted pyridine derivative. Its aromatic nature indicates that this complex would belong to the symmetry of C_s. This is possible due to the assumption of C_6H_5 group as single point mass. In view of C_s symmetry, the molecule will have only two types of vibrations (planar and non-planar) and will be active both in Raman and infrared. Apart from these vibrations the fundamental frequencies associated with C_6H_5 group will also appear. The remaining frequencies have been assigned to combinations and overtones of the fundamental vibrations. We therefore proceed to assign the frequencies as shown in Table 1.

For simplicity and convenience, the modes of vibrations of aromatic compounds are considered as guidelines. However, as with any 'complex' molecule, the vibrational interactions occur and the labels really indicate only the predominant vibrations.

Considering the complex 2-N-(benzoylamino)pyridine as substituted pyridine on one hand and a substituted benzene on the other, the observed fundamental frequencies in the spectra of these complexes can be discussed as follows :

Aromatic C–H stretching vibrations ;

Most mononuclear and polynuclear aromatic compounds have three or four peaks in the region 3080-3010 cm $^{-1}$, these being due to the stretching vibrations of the ring C–H bonds, and these are of strong-to-medium intensity. As might be expected, monosubstituted benzenes usually exhibit more peaks than di or tri substituted benzenes. The frequencies 3015, 3050 and 3075 cm^{-1} in infrared spectrum and 3015, 3055 and 3081 cm^{-1} in laser Raman spectrum have been assigned to C- H stretching modes.

Aromatic in-plane and out -of-plane C- H deformation vibrations :

A number of C–H in-plane deformation bands occur in the region 1290-1000 cm $^{-1}$, the bands usually being sharp, but of weak-to-medium intensity. However, these bands are not normally of importance for interpretation purposes although they can be used. In fact, a number of interactions are possible, thus necessitating great care in interpretation of bands in this region. Polar ring substituents may result in an increase in the intensity of these bands. Additional difficulties may also arise due to the presence of other bands in this region.

The frequencies of the C–H out-of-plane deformation vibrations are mainly determined by the number of adjacent hydrogen atoms on the ring and not very much affected by the nature of the substituent [10-11] although strongly electron attracting substituent groups can result in an increase of about 30 cm $^{-1}$ in the frequency of the vibration. These bands give an important means for determining the type of aromatic substitution. Although normally strong, they are often not only strong bands in the region. The three C–H in-plane bending and three C–H out–of–plane bending vibrations of 2-N–(benzoylamino)pyridine are given in Table 1.

Aromatic ring stretching vibrations :

The ring carbon-carbon stretching vibrations occur in the region 1625-1530 cm^{-1} [12-16]. For aromatic six-membered rings e.g., benzenes and pyridines, there are two or three bands in this region due to skeletal vibrations, the strongest usually being at about 1500 cm^{-1}. In general, the bands are of variable intensity and are observed at 1625-1590 cm^{-1}, 1590–1575 cm^{-1}, 1525-1470 cm^{-1} and 1465-1430 cm^{-1} for substituted benzenes.

For monosubstituted benzenes with strong electron acceptor or donor groups, the bands at 1625-1590 cm^{-1} and 1590–1575 cm^{-1} are of medium intensity, the second band being the weaker, but for weakly-interacting groups these bands are weak.

For meta disubstituted benzenes, the intensity of the band at about 1600 cm^{-1} is directly dependent on the sum of the electronic effects of the substituents whereas for para-disubstituted benzenes it is dependent on the difference of the electronic effects of the substituents. For example, due to the large dipole changes possible for para-disubstituted compounds in which one group is ortho para-directing and the other is meta-directing, the band at 1625-1590 cm^{-1} is quite intense. In general, mono-meta-di– and 1,3,5, trisubstituted benzenes have strong bands at 1625-1590 cm^{-1} [1]

A fairly weak band is observed in the region 1465-1430 cm^{-1} for aromatic compounds, except para-disubstituted benzenes for which the range is 1420-1400 cm^{-1}. A band in the range 1510–1470 cm^{-1} is observed for mono-substituted, ortho– and meta-substituted and 1,2,3–trisubstituted benzenes, whereas for para-disubstituted and 1,2,4 trisubstituted compounds this band occurs at 1525–1480 cm^{-1} This is relatively strong for electron donor groups but is otherwise weak or absent, e.g., for the carbonyl group it is very weak. The bands at 1500–1400 cm^{-1} cannot be misinterpreted as due to olefinic C=C stretching vibrations since the latter lie outside this range. Four bands observed at 1610, 1590, 1530 and 1440 cm^{-1}. in 2–N–(benzoylamino)pyridine have been assigned to these ring carbon vibrations. Further the band at around 1500 cm^{-1}. may be due to the ring C=N stretching vibration.

Aromatic ring deformation vibrations :

Some bands in this region, are quite sensitive to change in the nature and position of substitutents [17-23] although other bands depend mainly on the disubstitution and number of substitutents rather than on their chemical nature or mass, so that these latter vibrations, together with the out–of–plane vibrations of the ring hydrogen atoms, are extremely useful in determining the positions of substituents.

Two bands usually observed are those due to the in-plane and out–of–plane ring deformation vibrations. The in-plane deformation vibration is at higher frequencies than the out–of–plane vibration and is generally weak for mono- and para-substituted benzenes. They are often masked by other stronger absorptions which may occur due to the substituent group.

For mono-substituted aromatics, the bands due to the out-of-plane ring deformation vibrations occur in the region 410-550 cm^{-1}. Hence, the bands observed around 638 and 560 cm^{-1} have been assigned to in-plane carbon bending vibrations and the peaks at around 410 and 460 cm^{-1} have been given for carbon out-of-plane bending vibrations.

Aliphatic vibrations :

The infrared spectrum of benzoyl derivatives of amino pyridines show a line of strong intensity in the region 1870-1540 cm^{-1} [24]. This line is due to C=O stretching vibrations of benzoyl derivatives of amino pyridines. Its relatively constant position, high intensity and relative freedom from interfering bands make this as one of the easiest band to recognise in infrared spectra. With its given range, the position of the C=C stretching band is determined by the physical state, electronic and mass effects of neighbouring substituents, conjugation hydrogen bonding and ring chain. Consideration of these factors leads to a considerable amount of information about the environment of the C=O group. In the present investigation, the band at 1680 cm^{-1} has been assigned to C = Ovibration.

The medium-to-weak absorption bands for the C-N linkages in aomines appear in the region of 1200-1020 cm^{-1} [24]. The characteristic strong band at around 1242 cm^{-1} in the spectra of the present compound has been assigned to C–N stretching vibration. Further, the band due to N–H stretching mode is observed around 3400 cm^{-1}.The remaining bands appear in the spectra may be due to the overtones and combinations of the fundamentals.

Thus a complete vibrational assignment has been made available for 2–N(benzoylamino) pyridine using Fourier transform infrared and laser Raman spectra in the present work.

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