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Infrared Spectra of N-2 Pyridyl Formamide

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The infrared spectra of N-2 pyridyl formamide (2PF) has been reported for the first time with the tentative assignments of most of the fundamentals with the available limited experimental facilities for infrared study only.

INTRODUCTION

The vibrational assignments for pyridine were first reported by Wilmhurst and Bernstein[1] and later were modified slightly by Green *et al*[2]. Normal coordinate calculations for pyridine and some of its deuterated derivatives have also been reported[3,4] on the assumption of point group C_{2v} for 27 fundamental modes of vibration under the distribution and activity $10a_1$ (IR, Raman polarised) + $9b_2$ (IR, Raman depolarised) + $3a_2$ (Raman depolarised) + $5b_1$ (IR, Raman depolarised). The normal modes of vibrations of pyridine are very similar to those of benzene since nitrogen atom is isoelectronic with the —CH group and there are no drastic changes in force constants or in large mass effects in going from one molecule to other except that three carbon-hydrogen vibrations (a_1, C–H str, b_2, C–H in-plane deformation and b_1 out-of-plane deformation) will be absent in pyridine. The modes of 2, 3 and 4-methyl pyridines have been reported[5,6]. Other mono-substituted pyridine compounds investigated include the fluro, chloro, bromo, ethyl, aldehyde, methoxy, cyano, amino and hydroxy derivatives[7–14].

The frequency of the in-plane ring deformation is useful in distinguishing the substituent position in mono-substituted pyridines. For 2-, and 3-substitution of the ring, this band is found at about 615 cm^{-1} whereas for the substitution at the fourth position, it appears near 660 cm^{-1}. Therefore pyridine derivatives possessing —N—C—S group have been reported to be biologically versatile compounds. Several pyridine thiourea derivatives have been characterised as prospective agents for antiviral chemotherapy[15,16]. 2-Substituted pyridine derivatives with a suitable donor atom in the 2 position have attracted much attention as ligands for their diverse coordination potential[17,18]. Substituent effects across a pyridine ring are most effective when transmitted from the position 2 of the ring.

It was of interest in the present work to make an investigation of the infrared vibrational spectra of N–2 pyridyl formamide (2PF) (Fig. 1.), which combines the features of a 2-substituted pyridine as well as formamide. The assignment of

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the infrared bands is not aided for complete normal coordinate treatment for all the vibrations of the title compound on account of the limited facilities available for recording good Raman spectra and X-ray study to fix the proper point group for force field model.

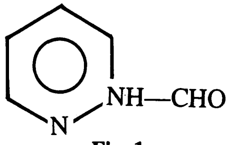

Fig. 1

EXPERIMENTAL

The procedure of Amarego[19] was followed for the synthesis of 2PF. A mixture of anhydrous formic acid (6.3 ml) and glacial acetic acid (16.4 ml) was heated at 50°C for 2 h. It was cooled and a solution of 2-aminopyridine (16.4 gm, 0.17 mol) in dry benzene (75 ml) was added. It was allowed to stand at 20°C for 48 h and then distilled. 2-pyridyl formamide which distils at 154°–156°/12 mm solidifies at room temp (m. pt. 69°–70°C). The product 2 (13 g, 0.1 mol) mixed with phosphorus pentasulphide supernatant xylene solution was decanted and cooled from which the yellow needles of the product separate out. The compound was washed with light petroleum and recrystallised from ethanol (m. p. 164°C) to get the yield of about 1 g. Infrared spectra were measured as Nujol mulls and KBr pellets using Perkin-Elmer 599 spectrometer.

RESULTS AND DISCUSSION

Salient features of the assignments of the vibrational spectra of 2PF are given in Table 1. The N–H stretching vibration of 2PF is fixed at 3160 cm^{-1} on the ground of sensitivity towards deuterator. The in-plane and out-of-plane NH bending modes are assigned at 1540 cm^{-1} and 690 cm^{-1} respectively. The ring stretching mode occurs at 1550 cm^{-1} and the weak breathing vibration at 1010 cm^{-1}. The ring deformation mode is attributed to an intense band at 615 cm^{-1}. The in-plane C—H bending modes are assigned in the region 1470 cm^{-1}–1230 cm^{-1} and the out-of-plane vibration in the range 1140 cm^{-1}–775 cm^{-1}. These assignments are analogous to those of several 2-substituted pyridines[20].

TABLE 1
INFRARED SPECTRA OF 2-PYRIDYL FORMAMIDE (2PF) OBSERVED FUNDAMENTALS (cm^{-1}) OF 2 PYRIDYL FORMAMIDE, THEIR RELATIVE STRENGTH AND ASSIGNMENTS

Wave number (cm^{-1})	Infrared spectrum	
	Relative strength	Assignments
3160	w	NH Str
3100		
3020	w	CH Str
2920	sh	

Wave number (cm^{-1})	Infrared spectrum	
	Relative strength	Assignments
1680	s	CO Str, CN Str
1600	ms	NH_2 Bend
1550	sh	Ring Str
1540 1530 1520	sh	NH Bend Ring Str, CN Str
1470	ms	CH Bend, CN Str
1410	s	CH Bend, Ring Str
1360	w	CH Bend + Ring Str
1315	w	CN Str
1290	s	N–C_{PY} Str, CH Bend
1260	sh, w	CH Bend, CN Str
1230	ms	NH Bend
1140	s	CH Bend OP
1010	w	Ring Breathing
840 785 775	m m s	CH Bend OP CH OP Bend
690	m	NH OP Bend
615	s	Ring def. O = C – N def.
500	m	C—C=O def. Ring torsion
320	w	NCO Bend, Ring def.

Note Str = stretching, Bend = bending, OP = out of plane, def = deformation,
s = strong, m = medium, w = weak, sh = shoulder, ms = medium strong.

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