Asian Journal of Chemistry Vol. 9, No. 2 (1997), 288–292

Infrared Spectral Studies of Some Substituted Pyridines

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The present study has been undertaken on the infrared spectra of 2-hydroxypyridine, 2-chloropyridine and 2-bromopyridine molecules recorded on Perkin-Elmer spectrophotometer in the region 4000–200 cm^{-1}. The probable assignments of the above molecules are based on group frequency approach together with the data available for similar molecules.

INTRODUCTION

Among the biomolecules, the study in n-heterocyclic molecules has become quite interesting because they are the constituents of nucleic aicds (DNA and RNA). In these molecules recent spectroscopic studies[1–3] of pyridine have been motivated by studying the vibrational spectra for understanding the specific biological processes and analysis of a relatively complex system. The pyridine ring system is also very important as a structural unit in the natural products and compounds of pharmaceutical interest. Madhi[4] and Goel[5] have studied the spectra of pyridine. A few investigators[6, 7] gave only some modes of the title molecules without giving complete interpretation. Hence the current study has been planned out completely to interpret the IR spectra of all the title molecules with their structural formulae and all vibrational modes by using Wilson enumeration.

EXPERIMENTAL

The spec-pure compounds 2-hydroxypyridine (2-Hp) 2-chloropyridine (2-Clp) and 2-bromopyridine (2-Brp) (Figs. 1–3) were obtained from Sigma. However, their purity was confirmed by elemental analysis and m.p. determination and were

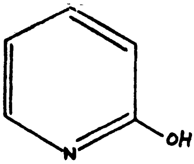

fig-1→ 2-HP

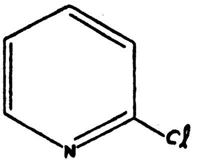

fig-2→ 2clP

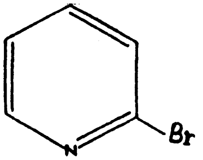

fig-3→ 2BrP

used as such without further purification. The IR spectra of all molecules were recorded on Perkin-Elmer spectrophotometer in the region 4000–200 cm^{-1} by KBr-pallet technique.

RESULTS AND DISCUSSION

The spectra have been interpreted on the basis of magnitude and relative intensities and group frequency approach. Much aid has been taken from the assignments made by earlier workers[2, 5]. From the structural point of view the molecule 2-Hp belongs to C_s point group symmetry, whereas 2-Clp and 2-Brp belong to C_{2v} point group symmetry. The tentative assignments with relative modes and intensity along with the comparison of pyridine are presented in Table-1 using Wilson's notations.

TABLE-1
VIBRATIONAL FREQUENCIES (cm^{-1}) OF 2-HYDROXY PYRIDINE, 2-CHLOROPYRIDINE AND 2-BROMOPYRIDINE

Wilson No. (a)	Assignments*	2-Hp	2-Clp	2-Brp	Pyridine (a)
1	ν(C—C) ring breathing	985 vs	990 vs	988 vs	992
2	ν(C—H)	3070 vw	3055 s	3055 s	3054
4	γ(C—C)	710 vvw	730 vw	700 s	700
5	γ(C—H)	900 sh, m	—	—	942
6a	β(C—C)	620 vvw	620 w	610 m	605
6b	β(C—C)	660 vvw	—	—	652
8a	ν(C—C)	1510 vvw	1575 s	1565 s	1583
8b	ν(C—C)	1640 vs	1585 vs	1575 vs	1592
9a	β(C—H)	1230 vvs	1285 m	1240 s	1218
9b	β(C—H)	1140 vs	1155 vvs	1148 s	—
10b	γ(C—H)	930 vvw	890 ms	820 mw	886
11	γ(C—H)	750 vvw	770 vs	790 mw	—
12	(C—C—C) Trig. ben.	1010 m	—	1100 vs	1030
14	ν(C—C)	1310 m	—	—	1375
16a	γ(C—C)	410 w	405 m	405 w	374
16b	γ(C—C)	450 m	486 vs	—	405
18a	β(C—H)	—	1040 s	1042 ms	1068
18b	β(C—H)	1085 vs	1080 s	1078 vs	1085
19a	ν(C—C)	1450 vw	1455 s	1452 vs	1482
19b	ν(C—C)	1410 vs	1425 s	1416 vs	1439
20a	ν(C—H)	2990 m	—	3000 w	3036

Assignments*	2-Hp	2-Clp	2-Brp	Pyridine
OH Group Vib.				
ν(C—OH)	1260 s	—	—	—
β(OH)	1230 vvs	—	—	—
Torsional (OH)	395 ms	—	—	—
γ(OH)	340 s	—	—	—
Cl-group-vib.				
ν(C—Cl)	—	1130 vs	—	—
β(C—Cl)	—	340 s	—	—
γ(C—Cl)	—	225 s	—	—
Br-group-vib.				
ν(C—Br)	—	—	614 vs	—
β(C—Br)	—	—	295 s	—
β(C—Br)	—	—	280 vs	—
γ(C—Br)	—	—	240 s	—

*Visual intensities are shown against each wave number: s–strong, vs–very strong, vvs–very-very strong, sh–shoulder, m–medium, w–weak, mw–medium weak, vw–very weak, vvw–very-very weak, ν–stretching, β–in-plane bending and γ–out–of–plane–bending.

a = K.K. Innes, J.P. Byrne and I.G. Ross, *J. Mole. Spectrosc.* **22**, 125 (1967).

C—H Vibrations

Bellamy[8] pointed out that the (C—H) valence oscillation mode exists between 3100–3000 cm^{-1}, which permits ready identification for structure and is not affected by substituents. Thus in the present case the vibrational modes ν_2 and ν_{20a} have been identified at 3070 cm^{-1} and 2990 cm^{-1} in 2-Hp, at 3055 cm^{-1} in 2-Clp and at 3055 cm^{-1} and 3000 cm^{-1} in 2-Brp showing (C—H) stretching vibrations. These assignments are in agreement with Green[9] and modes of pyridine[5].

Studies on the benzene spectra show the presence of modes ν_3, ν_9, ν_{15}, ν_{18} involving (C—H) in-plane bending in the region 1300–1000 cm^{-1}. Hence the frequencies under the modes ν_{9a}, ν_{9b}, ν_{18a}, ν_{18b} are well assigned to (C—H) in-plane bending in 2-Hp, 2-Clp and 2-Brp and with correlation to pyridine are described in Table-1 in detail, which are in accordance with the work of Moony[10] and Joshi[11]. Thomson[12] and Varasani[13] suggested that the (C—H) out-of-plane vibrations result from ν_5, ν_{10}, ν_{11} and ν_{17} modes of benzene and are expected to occur in the region 1000–600 cm^{-1}. These are almost independent of their nature. Thus the frequencies found under the modes ν_5, ν_{10}, ν_{11} for the present molecules 2-Hp, 2-Clp and 2-Brp are presented with the pyridine frequencies[5, 16] in Table-1.

C—C Vibrations

In all substituted benzenes[8], four bands are usually observed in the region 1650–1400 cm^{-1}. These bands are the components of the vibrational modes ν_8

and ν_{19} corresponding to C—C stretching vibration of benzene. Thus the modes ν_{8a} and ν_{8b} have been found at 1640 cm^{-1} and 1583 cm^{-1} in 2-Hp, at 1585 cm^{-1} and 1575 cm^{-1} in 2-Clp and at 1575 cm^{-1} and 1565 cm^{-1} in 2-Brp. The vibrations ν_{19a} and ν_{19b} have been detected at 1450 cm^{-1} 1410 cm^{-1} for 2-Hp, at 1455 cm^{-1} and 1425 cm^{-1} for 2-Clp and at 1452 cm^{-1} 1416 cm^{-1} for 2-Brp as shown in Table-1 and supported by other workers[5, 15, 17].

The C—C vibration ν_{14} occurs in the region 1300–1240 cm^{-1}. But this mode has been found only in 2-Hp at 1310 cm^{-1}, while in the present study at 1375 cm^{-1}, in pyridine. As suggested by Ingold[19] the frequency of the ring breathing vibration ν_1 of benzene is quite reduced in the C_s or C_{2V} symmetry due to interaction with closely lying vibration of benzene under the C_s or C_{2V} symmetry. Both these vibrations belong to the same symmetry type a′ or a_1. The modes ν_1 have been found at 985 cm^{-1} in 2-Hp, 990 cm^{-1} in 2-Clp and 988 cm^{-1} in 2-Brp whereas they have been found at 992 cm^{-1} for pyridine. The vibration ν_{12} is thought to remain virtually undisplaced and thus has been identified as 1010 cm^{-1} only in 2-Hp. The components ν_{6a}, ν_{6b}, ν_{16a}, ν_{16b} corresponding to C—C in-plane and out-of-plane deformation modes have been identified in their respective regions (Table-1) and the present assignments find support from literature values[5, 15, 17, 21]. The out-of-plane ν_4 vibration is found to be constant in substituted benzene[16] and in the present study the bands at 710 cm^{-1} in 2-Hp, 730 cm^{-1} in 2-Clp and 700 cm^{-1} in 2-Brp respectively have been assigned to this vibration.

C—X Vibration

In the high frequency region the O—H stretching frequency could not appear in 2-Hp. Kletz and Price[20] have suggested the occurrence of the C—OH stretching mode near 1300 cm^{-1}, while Bellamy[8] suggested that the O—H in-plane bending mode lies at lower frequency near 1200 cm^{-1}. So the bands found at 1260 cm^{-1} and 1230 cm^{-1} have been attributed to C—OH stretching and O—H in-plane bending mode respectively. Gupta[15] *et al.* reported the torsional mode and C—OH out-of-plane bending mode at 379 cm^{-1} and 328 cm^{-1} in phenols. In view of above the bands at 395 cm^{-1} and 340 cm^{-1} have been attributed to OH torsional and C—OH out-of-plane bending modes. This work is in accordance with the previous workers[17, 18].

Sherrer *etal.*[21] assigned the C—Cl stretching mode at 1070 cm^{-1} and 1152 cm^{-1} in *m*-dichlorobenzene. So the IR bands found at 1130 cm^{-1} in 2-Clp have been attributed to C—Cl stretching mode and supported by many workers. Green *et al.*[22] have assigned C—Cl out-of-plane bending mode between 200–110 cm^{-1} in various chloro-substituted benzenes. Thus the band found at 225 cm^{-1} in 2-Clp has been assigned to C—Cl out-of-plane bending mode. On the other hand the band observed at 340 cm^{-1} has been attributed to C—Cl in-plane bending mode. The above work is in accordance with the previous workers[1, 4, 5, 10, 16]

Little work has been done on bromo-substituted pyridines. The C—Br stretching frequency usually appears in the region 700–500 cm^{-1}. Green *et al.*[23] assigned C—Br stretching mode at 610 cm^{-1} in 2,4-dibromofluorobenzene. In the present case of 2-Brp the frequency at 614 cm^{-1} has been attributed to C—Br stretching, while Szymanski[18] assigned the mode at 650 cm^{-1} in bromo-substituted alkenes. Varsanyi[13] assigned the C—Br in-plane bending at 275 cm^{-1} and 170 cm^{-1} and C—Br out-of-plane bending deformation at 210 cm^{-1} in 2,6-dibromo-4-cyanophenol; hence the band at 280 cm^{-1} and 275 cm^{-1} has been taken to represent the C—Br in-plane bending vibrations while those at 240 cm^{-1} represent the C—Br out-of-plane bending deformation and supported by several workers[5, 15–17].

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(*Received*: 17 September 1996; *Accepted*: 2 December 1996) AJC-1196