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Infrared Spectra of 4-Chloro-2,6-Diaminopyrimidine

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The present study contains infrared spectra of 4-chloro-2,6-diaminopyrimidine recorded on Perkin-Elmer spectrophotometer in the region 4000–200 cm^{-1} using KBr-Pallet technique. The spectra have been analysed assuming C_{2v} point group symmetry for the molecule. The tentative assignments to the observed fundamental frequency with structural feature have been made to different modes of vibration on the basis of magnitude and relative intensity of recorded spectra and group frequency approach and also in analogy with similar molecules using Wilson's notation.

INTRODUCTION

N-Heterocylic molecules *e.g.*, pyrimidine, pyridine, cytosine, uracil and their derivatives are of greater biological importance as they play a central role in the structure and properties of nucleic acids. However, owing to their great complexity and low symmetry the analysis of their spectra is difficult and little spectroscopic work[1–10] has appeared on pyrimidines and their substituted analogues. A full understanding of the vibrational spectra of nucleic acid bases is of great importance in biophysical research.[10–12] The study on aminopyrimidine is also available in literature.[13–16] The present study has been undertaken to investigate the IR spectra of 4-chloro-2,6-diaminopyrimidine. (Fig. 1).

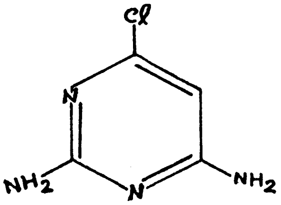

Fig. 1. 4,2,6-CDAP

EXPERIMENTAL

The spec-pure compound 4-chloro-2-6-diaminopyrimidine (hereafter referred as 4,2,6-CDAP) was obtained from Sigma-Aldrich (USA), and used as such

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without further purification however its purity was confirmed by elemental analysis and m.p. determination. The IR spectrum of 4,2,6-CDAP molecule has been recorded on Perkin-Elmer spectrophotometer in the region 4000–200 cm^{-1} using KBr pellet technique.

RESULTS AND DISCUSSION

It is assumed that the NH_2 group behaves as a mass point and the molecule 4,2,6-CDAP may be considered under the C_{2v} point group symmetry. The observed IR fundamental frequencies with assignment are given in Table-1.

TABLE-1
VIBRATIONAL FREQUENCIES OF 4-CHLORO-2,6 DIAMINOPYRIMIDINE (4,2,6-CDAP)

Frequencies of 4,2,6-CDAP	Intensity	Assignments
310	s	$\gamma(C—NH_2)$
380	s	β(C—Cl)
410	s	γ(C—C)
620	vs	ν(C—Cl)
740	m	β(C—C)
800	m	γ(C—C)
880	vvs	Ring breathing
965	vs	β(C—C—C)
1040	vvw	$\beta(C—NH_2)$
1150	vvs	γ(C—H)
1265	vvs	β(C - H)
1370	vvs	$\nu(C—CH_2)$, ν(C—C)
1440	vvs	ν(C—C)
1540	ms	ν(C—C)
1580	ms	ν(C—C)
1640	vvs	ν(C—C)
3140	m	ν(C—H)
3200	vvw	ν(N—H)
3350	vvs	$\nu_{sym}(N—H)$
3450	vvs	$\nu_{asym}(N—H)$

s = strong, vs = very strong, vvs = very very strong, m = medium, ms = medium strong, w = weak, vw =very weak, vvw = very very weak, ν—stretching, β—in-plane bending, γ—out-of-plane bending.

In substituted benzenes, one out of the 2 ring modes ν_1 and ν_{12} decreases to 820 cm^{-1} while the other keeps itself 1000 cm^{-1}. Patel *et al.*[17] have shown that for different substituents, it is the potential energy distribution of the substituent sensitive mode that closely corresponds to ν_1 in benzene. In view of the above a very strong band at 880 cm^{-1} and the band 965 cm^{-1} have been assigned as ν_1 and ν_{12} respectively. This finds support from the recent works of Kartha *et al.*[18] The ν_8 and ν_{19} modes only show relatively small changes on substitution. The bands at 1640 cm^{-1} and 1580 cm^{-1} have been assigned to the ν(C—C) mode, while the pair of bands at 1540 cm^{-1} and 1440 cm^{-1} have been assigned to the ν_{19} mode. The ring stretching vibrations have been identified at 1370 cm^{-1}. All these assignments are in well agreement with the literature values.[19, 20]

Out-of-plane modes ν_4 and ν_{16} show an increase on substitution. Thus in view of it the ν_4 mode has been assigned at 800 cm^{-1} and ν_{16} assigned at 410 cm^{-1}. Patel *et al.*[17] has shown that the frequencies of the modes, which closely resemble ν_6 mode—in the region 800–650 cm^{-1}. In the present spectrum the ν_6 mode has ben identified at 740 cm^{-1}. As the molecule 4,2,6-CDAP is penta-substituted benzene, so only one C—H valence oscillation is expected and is assigned at 3140 cm^{-1} in accordance with literature. It is observed[21] that when the number of adjacent hydrogen atoms attached to the ring is decreased, the C—H out-of-plane vibration in general shows a shift to higher magnitude. Thus a strong IR band 1150 cm^{-1} has been assigned as the C—H out-of-plane bending mode while an IR band at 1265 cm^{-1} has been assigned as C—H in-plane bending mode in present case.

Mostly in all primary aromatic amines the amino group involves symmetrical and asymmetrical N—H stretching vibration. According to Bellamy[22] these two bands occur in the region 3550–3350 cm^{-1}. It has been also pointed out that in N-actamide in chloroform solution, the NH_2 absorption band occurs at 3550 cm^{-1} and 3415 cm^{-1} but it also shows additional bands at 3498 cm^{-1} and 3345 cm^{-1}. In solid states it gives two broader N—H peaks near 3350 cm^{-1} and 3169 cm^{-1} in substituted nitroanilines N—H symm. and asymm. stretching bands are assigned at 3350 cm^{-1} and 3470 cm^{-1} respectively. In view of these assignments the bands observed at 3450 cm^{-1} and 3350 cm^{-1} have been assigned to as N—H asymm. and symm. stretching vibrations in the present molecule. These asymmetrical and symmetrical frequencies are found to obey the following relation.

$$\nu_{sym} = 345.53 + 0.878\ \nu_{asym}$$

It has been found in various cases[23] that C—NH_2 stretching vibration appears near 1350 cm^{-1}. In the present molecule the said band has been assigned at 1370 cm^{-1}. It also has contribution from C—C stretching vibration. NH_2 in-plane bending and out-of-plane bending vibration have been assigned near region 1100 and 300 cm^{-1} respectively by some workers.[24] In the present investigation the bands found at 1040 cm^{-1} have been assigned to NH_2 in-plane bending and out-of-plane bending

Many workers[6, 25] observed the C—Cl stretching modes in the region 650–550 cm^{-1}. The very strong band observed at 620 cm^{-1} has been assigned as the C—Cl stretching mode in the 4,2,6-CDAP molecule. These find support from literature.[26, 27] Green *et al.*[28] assigned the C—Cl out-of-plane bending modes in the region 200–110 cm^{-1} in the vibrational spectra of various chloro-substituted benzenes but no such type of band has been found here. The C—Cl in-plane bending modes have been identified at 380 cm^{-1} in accordance with the work already reported by some workers.[13, 29]

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