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Vibrational Spectra of 2,4-Dimethyl-6-Hydroxy Pyrimidine

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The vibrational (infrared and Raman) spectra of 2,4-dimethyl-6-hydroxy pyrimidine are reported. The assignments of fundamentals are proposed and discussed by assuming the molecule under C_{2V} point group symmetry. Tautomeric behaviour of the compound is also discussed.

INTRODUCTION

Infrared and Raman spectroscopic studies are widely used in biological research on nucleic acids and related compounds. The N-heterocyclic molecules *e.g.* pyrimidine, cytosine, uracil and their derivatives are of great biological importance as they play a key role in the structure and properties of nucleic acids[1]. The vibrational spectra of simple pyrimidines and their derivatives have been extensively studied both experimentally and theoretically[2, 3].

In view of above discussion the present paper reports vibrational spectral (infrared and Raman) studies and tautomeric behaviour of the compound 2,4-dimethyl-6-hydroxy pyrimidine (2,4,6-DMHP) (Fig. 1).

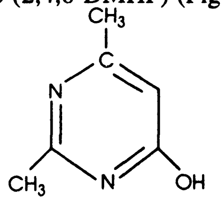

Fig. 1

EXPERIMENTAL

Spec-pure grade solid sample of 2,4-dimethyl-6-hydroxy pyrimidine was obtained from M/s Aldrich Chemie, West Germany and used as such. Its purity was confirmed by elemental analysis and melting point determination. The infrared (IR) spectrum was recorded on Perkin-Elmer M-683 spectrophotometer in the region 4000–200 cm^{-1} using KBr pellets and in the region 4000–400 cm^{-1} using nujol mull, ethanol and methanol solvents. The laser Raman spectrum was recorded on Spex-Rama Lab spectrophotometer using 52 MG argon-krypton laser of wavelength 488 nm.

RESULTS AND DISCUSSION

The IR spectrum of 2,4,6-DMHP in KBr pellets is shown in Fig. 2, while the laser Raman spectrum of this compound is shown in Fig. 3. The observed fundamental frequencies and their proposed assignments are given in Table-1. The comparison of methyl group frequencies of 2,4,6-DMHP with the similar

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molecules is given in Table-2. Tautomeric forms of the compound 2,4,6-DMHP are shown in Fig. 4.

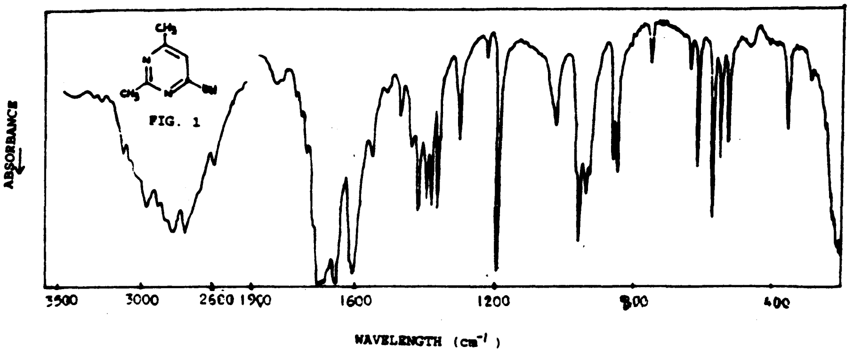

Fig. 2. IR spectra of 2,4,6-DMHP in KBr pallets

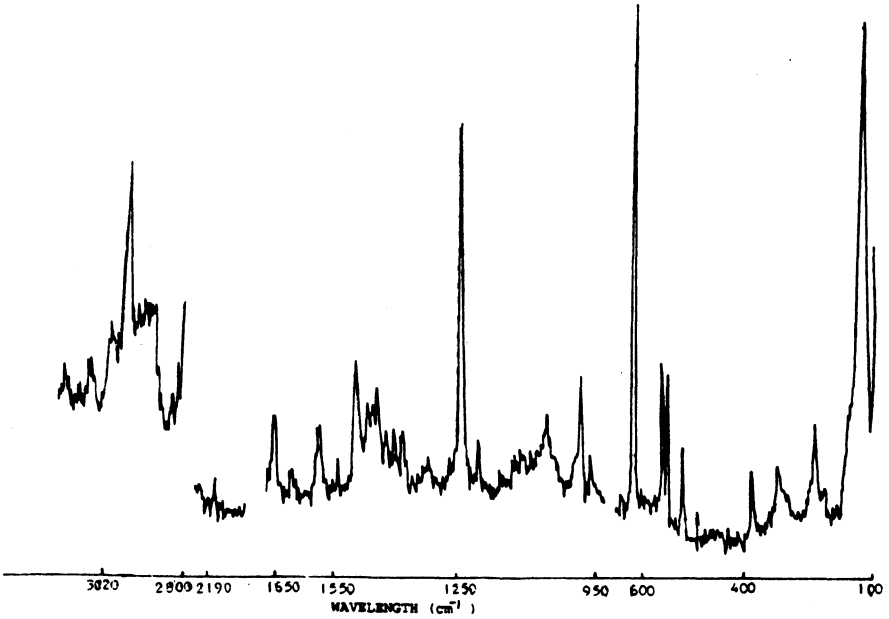

Fig. 3. Laser Raman spectrum of 2,4,6-DMHP

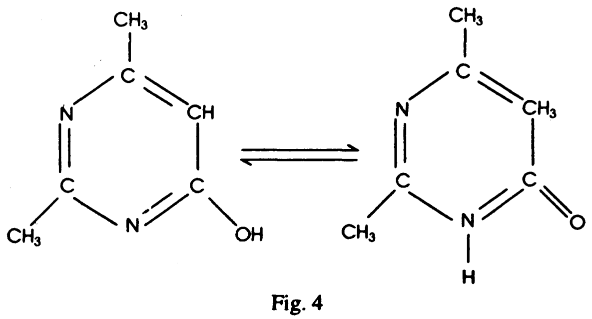

Fig. 4

TABLE-1
VIBRATIONAL FREQUENCIES (cm^{-1}) FOR 2,4,6-DMHP AND THEIR ASIGNMENTS

Raman	IR				Assignments
	KBr	Nujol mull	Ethanol	Methanol	
90 m	—	—	—	—	Lattice vibration
111 vw	—	—	—	—	Lattice vibration
118 vw	—	—	—	—	Lattice vibration
121 vvs	—	—	—	—	Lattice vibration
221 s	220 vw	—	—	—	CH_3 torsion
—	230 vw	—	—	—	CH_3 torsion
—	250 vw	—	—	—	γ(C—OH)
305 m	290 w	—	—	—	γ(C—CH_3)
360 m	360 s	—	—	—	β(C—CH_3), γ(C=O)
—	415 vw	410 w	410 m	410 m	γ ring
—	—	420 w	420 m	420 s	γ ring
—	—	—	440 s	—	(O—H) torsion
520 s	—	—	520 vw	—	γ ring
—	530 s	530 vs	—	—	β(C=O)
555 s	550 s	550 s	—	540 vw	β(C—OH)
565 vs	570 vs	570 vs	—	580 vw	β ring, β(C—CH_3)
630 vvs	620 vs	620 vs	—	630 vw	β ring
—	640 m	650 m	—	—	β ring
—	—	660 w	670 s	670 m	ν ring
—	—	730 s	—	—	—
—	760 m	760 m	—	—	ring breathing
—	860 sb	860 s	—	—	γ(C_5—H)
—	865 s	870 w	880 s	—	—
958 m	950 m	950 s	—	—	β(C_5—H)
978 s	970 s	970 m	—	—	β ring
—	1030 sb	1030 s	—	1040 s	CH_3 rocking
1048 m	—	1050 vw	1050 vs	1069 vs	CH_3 rocking
—	—	—	1090 vs	—	CH_3 rocking
—	1190 vs	1190 vw	—	—	ν(C—CH_3)
—	—	1200 vs	—	—	ν(C—CH_3)
1242 vs	1230 m	1240 m	—	—	ν(C—OH)
—	—	—	1280 s	—	β(O—H)
—	1305 s	1320 s	1330 s	—	ν ring
—	1365 s	—	—	1360 vw	ν ring
—	1385 s	1390 vs	1380 s	1380 vw	CH_3 sym. deformation

Raman	IR				Assignments
	KBr	Nujol mull	Ethanol	Methanol	
1401 w	1400 s	1410 s	—	—	CH_3 sym. deformation
—	1425 s	1425 s	1420 m	1420 w	CH_3 sym. deformation
1436 m	1445 w	—	—	1440 w	CH_3 sym. deformation
—	—	1470 vs	1460 m	1460 s	CH_3 sym. deformation
1484 s	1480 m	—	—	1480 s	CH_3 asym. deformation
—	1505 vw	—	—	1490 m	CH_3 asym. deformation
1524 m	1515 vw	1520 vw	—	1510 s	CH_3 asym. deformation
—	1530 vw	1530 vw	1540 vw	1540 s	ν ring
1565 m	1560 m	1560 m	1560 vw	1560 s	ν ring
—	1610 s	1620 s	—	1640 s	ν(C═C)
1664 m	1650 mb	1660 vs	1650 vs	1660 s	β(N—H)
—	—	1700 s	—	1700 m	ν(C═O)
—	—	—	—	1720 s	—
—	—	1850 s	—	1850 w	—
—	—	2380 s	2380 m	—	—
2800 w	—	2780 vw	—	—	CH_3 sym. stretching
—	—	2860 s	—	2850 m	CH_3 sym. stretching
2931 vs	2920 vw	2920 s	2940 m	2920 s	CH_3 sym. stretching
—	—	2960 w	—	2960 w	CH_3 asym. stretching
—	2980 vw	—	2980 vs	—	CH_3 asym. stretching
3021 m	3050 vw	—	—	—	ν(C—H)
—	—	3100 vw	—	—	ν(N—H)
—	—	—	3400 sb	3420 sb	ν(O—H)
—	—	3840 vw	3840 vw	3840 s	—

where ν = stretching, sym. = symmetric, asym. = asymmetric, w = weak, m = medium, mb = medium broad, β = in-plane bending, γ = out-of-plane bending, deform. = deformation, vs = very strong, vw = very weak, vvs = very very strong, s = strong.

The molecule 2,4,6-DMHP is trisubstituted pyrimidine, hence only one C—H valence oscillation is expected. This C—H stretching mode lies in the region 3100–3000 cm^{-1}.[4] In view of this, a very weak IR band at 3050 cm^{-1} (in KBr), with the corresponding Raman value 3021 cm^{-1} has been taken to represent C—H stretching mode. The N—H stretching vibration in uracil and similar molecules was reported in the region 3200–3100 cm^{-1};[5, 6] hence the band at 3100 cm^{-1} (in nujol) may be assigned to N—H stretching mode, which may be due to the migration of one hydrogen atom from the hydroxy group to the nitrogen of the ring[7]. Sanyal *et al*[8] have assigned (C—H) in-plane bending and out-of-plane bending modes at 940 and 848 cm^{-1} respectively in 4,6-dihydroxy-2-methyl pyrimidine. In view of this IR bands observed at 950 cm^{-1} (in KBr and nujol) with the corresponding Raman value 958 cm^{-1} and 860 cm^{-1} (in KBr and nujol) have been assigned to the above modes respectively in the present molecule. The N-heterocyclic ring breathing vibration occurs at 760, 791 and 779 cm^{-1} in uracil, cytosine and cytosine-d_3 respectively.[9–11] In the present study, the IR band with medium intensity at 760 cm^{-1} (in KBr and nujol) has been taken to represent ring breathing mode. The IR values 1650 cm^{-1} (in KBr and ethanol)/1660 cm^{-1} (in nujol and methanol) with the corresponding Raman value 1664 cm^{-1} may be taken to represent (N—H) in-plane bending mode which is in agreement with literature value[12]. Assignments of ring stretching (CC, CN) in-plane bending and out-of-plane bending modes are given in Table-1. These assignments are in accordance with the literature values[8, 12, 13].

Goel *et al.*[14] have assigned (C—OH) stretching mode at 1254 cm^{-1} in 2,4-diamino-6-hydroxy pyrimidine. In the present molecule IR band observed at 1230 cm^{-1} (in KBr)/1240 cm^{-1} (in nujol) with the corresponding Raman value 1242 cm^{-1} has been taken to represent (C—OH) stretching mode which also find support from the literature value[15]. The IR bands observed at 550 cm^{-1} (in KBr and nujol)/540 cm^{-1} (in methanol) with the correponding Raman value 555 cm^{-1} have been assigned to (C—OH) in-plane bending mode and out-of-plane bending mode has been identified at 250 cm^{-1} (KBr) under the present investigation.[8]

TABLE-2

ASSIGNMENTS OF METHYL GROUP FREQUENCIES (cm^{-1}) IN 2,4,6-DMHP AND THEIR COMPARISON WITH SIMILAR MOLECULESn[8].

Assigments	5,6-DMU	4,6-DMP	2,4,6-AHMP	4,2,6-ADMP	4,6,2-DHMP	2,4,6-DMHP
v sym. CH_3	2829 vs	2852 sb	2855 s	2860 vw	—	2850 m
v sym. CH_3	2804 vs	—	—	2780 m	—	2780 vw
v asym. CH_3	2951 vs	2960 vs	—	2938 w	—	2960 w
v asym. CH_3	2884 s	2920 vs	2880 s	—	—	2920 s
v asym. CH_3	2994 m	—	2898 ms	2980 w	—	2980 vs
CH_3 sym. defor.	1389 vs	1375 s	1388 vs	1350 ms	—	1385 s
CH_3 sym. defor.	1404 ms	1442 vs	—	—	1460 mw	1445 w
CH_3 asy. defor.	1480 vw	1500 vs	1470 w	1490 vs	1500 w	1480 s
CH_3 asy. defor.	1466 vw	1460 vs	1432 s	1450 vs	1470 mw	1460 sb
CH_3 rocking	1088 vw	—	1048 vs	1065 ms	—	1060 s
CH_3 rocking	1014 vw	1002 s	1020 s	1040 s	1050 vs	1030 s
CH_3 rocking	1140 s	—	—	—	1140 ms	1090 vs

where 5,6-DMU = dimethyl uracil [Ref. 18], 4,6-DMP = 4,6-dimethyl pyrimidine [Ref. 18], 2,4,6-AHMP = 2-amino-4-hydroxy-6-methyl pyrimidine [Ref. 19], 4,2,6-ADMP = 4-amino-2,6-dimethylpyrimidine [Ref. 7], 4,6,2-DHMP = 4,6-dihydroxy-2-methyl pyrimidine [Ref. 8].

The C═O stretching frequency has been assigned at 1694 cm^{-1} (in KBr)/1692 cm^{-1} (in nujol) in 2,4-diamino-6-hydroxy pyrimidine[14]. In the present study a band occurring at 1700 cm^{-1} (in nujol and methanol) has been assigned to this mode, while the IR bands observed at 530 cm^{-1} (in KBr and nujol) and at 360 cm^{-1} (in KBr) with the corresponding Raman value 360 cm^{-1} have been assigned to C═O in-plane bending and out-of-plane bending modes respectively in 2,4,6-DMHP. These assignments are in accordance with the literature value[9, 12, 14]. The molecule 2,4,6-DMHP has two methyl groups at 2 and 4 positions; hence two C—CH_3 valence oscillations are expected. It has been shown that the C—CH stretching vibrations appear in the range 1300–1200 cm^{-1}.[16] In view of this the IR bands observed at 1200 and 1190 cm^{-1} have been assigned to C—CH_3 stretching modes in 2,4,6-DMHP. The IR bands observed at 570 cm^{-1} (in KBr and nujol)/580 cm^{-1} (in methanol) with Raman value 565 cm^{-1} and at 360 cm^{-1} (in KBr) with Raman band value 360 cm^{-1} may be assigned to (C—CH_3) out-of-plane bending modes, while only one (C—CH_3) out-of-plane bending mode is observed, which has been assigned at 290 cm^{-1} (in KBr) with the corresponding Raman band with medium intensity at 305 cm^{-1} in the study of present molecule. These assignments find support from the literature value[7, 8, 13].

The CH_3 stretching and deformation modes of the methyl groups in 2,4,6-DMHP are well assigned in their respective regions in Table 1, which are in agreement with the literature value[16–18]. Salik Ahmad *et al*[7] have assigned CH_3 rocking modes at 1065, 1040, 970 and 950 cm^{-1} in 4-amino-2, 6-dimethyl pyrimidine while at 1140, 1088, 1014 and 994 cm^{-1} in 5,6-dimethyl uracil[18]. In view of these assignments, the IR bands at 1030 cm^{-1} (in KBr and nujol)/1040 cm^{-1} (in methanol), 1050 cm^{-1} (in nujol and ethanol)/1060 cm^{-1} (in methanol) with the corresponding Raman band at 1048 cm^{-1} with medium intensity and 1090 cm^{-1} (in ethanol) have been assigned to CH_3 rocking modes in the study of present molecule. The IR bands observed at 230 cm^{-1}, 220 cm^{-1} (in KBr) with Raman band at 221 cm^{-1} are assigned to CH_3 torsional modes in the present molecule which correlates with the literature[7, 18].

Gupta *et al*[19] have assigned O—H stretching mode at 3430 cm^{-1} in 4-amino-6-hydroxy-2-mercapto pyrimidine. In the present study the O—H stretching mode is assigned at 3400 cm^{-1} (in ethanol)/3420 cm^{-1} (in methanol). The strong IR bands observed at 1280 cm^{-1} and 440 cm^{-1} (in ethanol) have been assigned to (O—H) in-plane bending and torsional modes respectively which correlates with the literature[12].

Tautomeric behaviour

A medium strong band at 1700 cm^{-1} has been identified in C═O region corresponding to ν(C═O) stretching mode and C═O in-plane and out-of-plane bending modes have been indentified at 530 and 360 cm^{-1} respectively in the present molecule, which are in agreement with literature value[13]. This indicates that the tautomerism is due to OH group at 6-position. However, as O—H stretching and bending vibrations also appear, the existance of tautomerism may be taken to be very weak. The present molecule 2,4-dimethyl-6-hydroxy pyrimidine, therefore, tautomerise to give 2,4-dimethyl-6-pyrimidinol.

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