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Infrared Spectrum and Thermodynamic Functions of 4-Amino-2,6-Dihydroxy Pyrimidine

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The present study comprises of the investigations carried on the infrared spectra of 4-amino-2,6-dihydroxy pyrimidine in the region 4000–400 cm^{-1}. The proposed assignments are based on the group frequency approach together with the data available for molecules similar in structure. The thermodynamic functions have been computed and discussed.

INTRODUCTION

The pyrimidine when substituted with OH or NH_2 gives us biologically important molecules like cytosine, thymine and uracils etc. Due to significant role of N-heterocyclic compounds in the strucutral problems of nucleic acids, investigations on substituted pyrimidines draw considerable attention. In such type of molecules the role of substituent is very important. Even so, a few detailed spectroscopic studies have been reported in literature for pyrimidine, substituted pyrimidine[1–8] and their nucleic acid constituents. It has been possible to have tautomeric structures with substituents like —OH and —NH_2 as reported in case of 4,5-diamino pyrimidine and 4,6-dihydroxy pyrimidine by Srivastava *et al.*[9, 10] In the present investigations the role of the NH_2 group by changing its position around the ring in the presence of two OH groups by spectroscopic methods is discussed. For this study the infrared spectrum of the molecule 4-amino-2,6-dihydroxy pyrimidine was recorded and the tautomeric behaviour of this molecular structure is discussed with vibrations associated with —NH_2 and —OH groups.

EXPERIMENTAL

The infrared spectra of 4-amino-2,6-dihydroxy pyrimidine (4,2,6-ADHP) has been recorded by nujol mull techniques. The accuracy of the bands is up to $\pm 10\ cm^{-1}$ in the region 2000–400 cm^{-1} and $\pm 20\ cm^{-1}$ in the region 4000–2000 cm^{-1}.

RESULTS AND DISCUSSION

In view of the position of the substituent the molecule 4,2,6-ADHP falls under

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C_s point group symmetry. In infrared spectrum of the molecule the ring vibrations, the vibrations associated with C—H bond along with different groups, have appeared. As general obsevations are true for all aromatic molecules so it has been observed that substituents do not exert much influence on the vibrations associated with C—H bond and other functional groups listed in Table-1. In this discussion only important ring vibrations are chosen.

TABLE-1
INFRARED ASSIGNMENTS OF 4-AMINO-2,6-DIHYDROXY PRIMIDINE

I.R. Bands (cm^{-1})	Intensity	Assignments
430	w	Ring out-of-plane bending
465	w	Ring out-of-plane bending
526	vs	Ring out-of-plane bending
552	s	(C—OH) in-plane bending
625	s	NH wagging
665	w	(C—OH) in-plane bending
690	w	Ring in-plane bending
710	w	(C—H) out-of-plane bending
780	s	Ring breathing
995	w	(C—H) in-plane bending
1020	m	Ring in-plane bending
1060	m	(C—NH_2) in-plane bending
1250	m	(C—OH) stretching
1295	m	(C—OH) stretching
1400	vs	(C—NH_2) stretching, Ring stretching
1480	ms	Ring stretching
1534	m	Ring stretching
1620	b	Ring stretching
3020	m	(C—H) stretching
3300	w	(N—H) symmetric stretching
3400	s	(N—H) asymmetric stretching

In infrared spectra of pyrimidine two pairs of absorption bands at 1461, 1400 cm^{-1} and 1610, 1569 cm^{-1} have been observed which have arisen due to interaction effects of the ring double bonds. It is believed that these four bonds are analogous to the components of $e_{1\mu}$ 1485 and e_{2g} 1595 cm^{-1} modes of benzene which are not much sensitive to substituents. By this argument the two pairs of band at 1480, 1400 cm^{-1} and 1620, 1534 cm^{-1} in 4,2,6-ADHP molecule have been assigned to the ring stretching vibrations. The spectral studies of pyrimidine and substituted pyrimidine show that breathing vibration corresponding to ν_1 mode of benzene is mass depending in accordance to that which is proposed by Lord *et al.*[11] By observed bands together with the data available for

trisubstituted benzenes the ν_1 mode has been assigned at 780 cm^{-1} in the present molecule. The ν_{12} and ν_{14} modes are not sensitive to the mass substituents, so these are assigned at 1020 and 1400 cm^{-1} in 4,2,6-ADHP molecule. The mode ν_6 is mass sensitive and is found in substituted aromatic molecules and trisubstituted benzenes; the pair of bands at 552 and 526 cm^{-1} in 4,2,6-ADHP molecule has been assigned as part of above mode.

The C—H stretching mode exists between 3100–3000 cm^{-1}. In view of this, the band at 3020 cm^{-1} with medium intensity has been assigned to C—H stretching mode in the title molecule 4,2,6-ADHP. According to Kletz and Price[12], C—OH stretching frequency occurs around 1300 cm^{-1} in substituted phenol. In view of above the observed bands at 1295 and 1250 cm^{-1} have been assigned as C—OH stretching mode in the present study due to OH group substitution at 2 and 6 positions. Many workers have found that C—NH_2 stretching vibration appears near 1350 cm^{-1}. However, in some spectra it may have had some contribution from C—C stretching of benzene. In the present study the strong band observed at 1400 cm^{-1} has been correlated to C—NH_2 stretching band. Bellamy and Williams have shown that symmetric and asymmetric N—H stretching vibrations obey the empirical relation

$$\nu_{sym} = 345.53 + 0.876\ \nu_{asym}$$

Under the present investigation the bands at 3400 and 3300 cm^{-1} have been correlated to symmetric and asymmetric stretching vibrations. Bellamy suggested that in N-octamide the NH_2 free absorption occurs at 3415 and 3530 cm^{-1} in chloroform solution and it also shows the additional bands at 3490, 3345, 3300 and 3182 cm^{-1}. This indicates the occurrence of different types of simultaneous association of free and bonded N—H bands. It supports the above assigned N—H stretching bands of the present molecule. Goel *et al.*[6] have assigned in-plane and out-of-plane bending vibrations respectively. In the present study the C—NH_2 in-plane bending vibration has been shown at 1060 cm^{-1}. The O—H valence vibration appears in the region 3700–3500 cm^{-1} in molecules having OH group. But such vibrations could not appear in the present study.

Thermodynamic Functions

Thermodynamic functions *viz.* enthalpy $(H° - E_0^\circ)/T$, heat capacity C_p°, free energy $(H° - E_0^\circ)/T$, and entropy $S°$ of the title compound 4,2,6-ADHP have been computed using the standard expression[13, 14], by taking *y*-axis perpendicular to the molecular plane and *z*-axis to pass through the *para* positions.

Thermodynamic functions have been calculated at different temperatures between 100–1500 K using fundamental frequencies and assuming rigid rotor harmonic oscillator approximation. The principal moments of inertia were found to be 45.70, 76.36 and 30.66 $g \times cm^2$ in this molecule, while reduced moment of inertia is 9.88 $g \times 10\ cm^2$.

The variations of enthalpy function, heat capacity, free energy and entropy have been given in Table-2. which are in agreement with the trend reported in literature.[15–17] The variations of potential barrier and thermal energy with absolute temperature have been reported in Table-3 for the molecule 4,2,6-ADHP.

TABLE-2
THERMODYNAMIC FUNCTIONS (IN CAL/DEG. MOLE) OF 4-AMINO-2,6-DIHYDROXY PYRIMIDINE

Temperature (deg. kelvin)	Enthalpy	Free energy (—)	Entropy	Heat capacity
100	8.27	40.22	48.49	9.51
200	10.02	47.14	57.16	13.84
273	11.39	50.78	62.16	16.39
298	11.84	51.88	63.72	17.25
300	11.88	51.96	63.84	17.32
400	13.68	55.91	69.59	20.81
500	15.44	59.34	74.82	24.15
600	16.15	62.52	79.67	27.12
700	18.76	65.44	84.20	29.65
800	20.26	68.18	88.44	31.81
900	21.65	70.76	92.41	33.64
1000	22.93	73.22	96.14	35.22
1100	24.11	75.55	99.66	36.57
1200	25.19	77.78	102.98	37.74
1300	26.20	79.92	106.12	38.75
1400	27.13	81.97	109.10	36.63
1500	27.99	83.44	111.93	40.40

TABLE-3
POTENTIAL BARRIER AND THERMAL ENERGY OF 4-AMINO-2,6-DIHYDROXY PYRIMIDINE

Temperature (deg. kelvin)	Pot. barrier	Thermal energy
100	0.0120	22.77
200	0.0060	16.10
273	0.0043	13.78
298	0.0040	13.20
300	0.0039	13.15
400	0.0029	11.38
500	0.0024	10.18
600	0.0020	9.30
700	0.0017	8.60
800	0.0015	8.04
900	0.0013	7.59
1000	0.0012	7.00
1100	0.0011	6.86
1200	0.0010	6.57
1300	0.0009	6.31
1400	0.0008	6.08
1500	0.0007	5.88

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REFERENCES

1. F.M. Nejad and H.D. Stidham, *Spectrochim. Acta (GB)*, **31A**, 1433 (1975).
2. Y.A. Sharma, *Spectrochim., Acta* (*GB*), **30A**, 1801 (1974).
3. R.K. Goel, Nitish K. Sanyal and S.L. Srivastava, *Indian J. Pure Applied Phys.*, **18**, 842 (1976).
4. E. Allenstein, P. Kiemle, J. Weldin and W. Podszun, *Spectrochim., Acta* (*GB*), **33A**, 189 (1977).
5. S.P. Gupta, S.D. Sharma, Y.K. Gupta and Mrs. C. Gupta, *Acta Cienc. Indica*, **16**, 101, (1990).
6. Nitish K. Sanyal, R.K. Goel and S.N. Sharma, *Indian J. Phys.*, Part B (1980).
7. Nitish K. Sanyal, R.K. Goel and S.L. Srivastava, *Indian J. Phys.*, Part B, 103 (1977).
8. Smt. Vibha Sharma, S.D. Sharma, B.S. Yadav and Seema, *Orient. J. Chem.*, 10 (1994).
9. S.L. Srivastava and V.S. Pande, *Indian J. Phys.* (1979).
10. R.K. Goel, N.K. Sanyal and S.L. Srivastava, *Indian J. Pure Appl. Phys.*, **14**, 842 (1976).
11. R.C. Lord and G.L. Thomas (Jr.), *Spectrochim. Acta* (*GB*), **23A**, 2551 (1967).
12. T.A. Kletz and W.C. Price, *J. Chem. Soc.*, 644 (1947).
13. K.S. Pitzer and W.D. Cwinn, *J. Chem. Phys.* (*U.S.A.*), **10**, 428 (1942).
14. N.L. Owen and R.K. Hester, *Spectrochim. Acta*, **35A**, 343 (1979).
15. C.L. Chatterjee, P.P. Garg and R.M.P. Jaiswal, *Spectrochim. Acta*, **34A**, 943 (1978).
16. R.K. Goel and M.L. Agarwal, *Spectrochim. Acta*, **38A**, 583 (1982).
17. _____, *J. De. Chim. Phys.*, **79**, 765 (1982).

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