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Vibrational Spectral Studies and Thermodynamic Functions of Solid 2, 4-Dihydroxy-5-Fluro Pyrimidine

Dr. Sunil Sharma[1], Dr. Nitin Singh[2]

[1]Associate Professor, Department of Physics, N. A. S. College, Meerut

[2]Associate Professor, Department of Physics, Neelkanth Institute of Technology, Meerut

Abstract: ***The infrared, and laser Raman spectra of solid 2,4-Dihydroxy-5-Fluoropyrimidine are reported. Assignments of various fundamentals are proposed. The hydrogen bonding and tautomerism are also discussed. Thermodynamic functions have been computed and discussed.***

1. Introduction

The spectral interpretation of N-heterocyclic like pyrimidine, cytosin, thymine, uracil and their derivatives is difficult because of their high complexity and low symmetry. Since these molecules are of considerable biological interest, their detailed spectral investigations are of great importance .One of these concerns the tautomerism in some molecules which is possible with the involvement of functional groups like and -OH,-NH_2, -SH which may affect their function in the metabolism.

2. Experimental

Spec-pure grade of 2,4-Dihydroxy-5- Fluor pyrimidine (hereafter referred to as 2,4,5 DHFP) was obtained from Sigma Aldrich chemie U.S.A. Its purity was confirmed by elemental analysis and melting point (282°C) determination. Infrared spectrum was recorded with Perkin Elmer M-683 spectrophotometer in the region 200–4000cm^{-1} by KBr pallet technique. The laser Raman spectrum in the region 25-4000 cm^{-1} has been recorded on a spexrama spectrophotometer using argon laser source with exciting radiations 5145 Å.

3. Result and Discussion

The structural diagram of the compound is given in Fig.1.

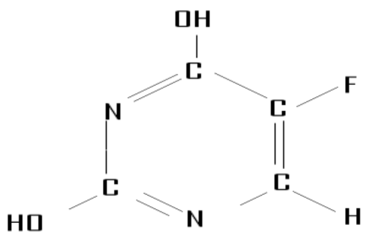


Fig I : 2,4-Dihydroxy-5-Fluoropyrimidine

The vibrational spectra (infrared, Raman) are shown in Fig. 2, 3 in Table 1, Fig.4 shows the intermolecular and intramolecular hydrogen bonding in the compound. Hydrogen bonding by the solvent in 2,4,5 DHFP is shown in Fig.5. The tautomeric forms of 2,4,5 DHFP, showing migration of H^+ is shown in Fig.6. Tautomeric forms of neutral, cationic and anionic forms of 2, 4, 5 DHFP are presented in Fig. 7.The statistically computed thermodynamic function viz. enthalpy function, free energy function, entropy and heat capacity with absolute temperature are shown in Table 2.while the variation of free energy function and entropy with absolute temperature is shown in Fig.8.The variation of enthalpy & heat capacity with absolute temperature is shown in figure 9. Also other values of thermal energy and potential barrier are given in Table 3 and their variation with absolute temperature is shown in fig.10.

Vibrational Spectra

C–H Vibration: In Pyrimidine there are three C–H stretching vibrations belonging to $a_1$species and one belonging to b_2 species.In Uracil, two C–H stretching vibrations are present. The molecule under investigation in tri-substituted pyrimidine. The aromatic structure of the ring compound shows the presence of C–H stretching vibration in the region 3100–3000cm^{-1}.The C–H stretching frequencies in benzene derivatives arises from the mode of υa_{1g} (3073), υe_{2g} (3096) υb_{1u}(3060) and υe_{1u} (3080) $cm^{-1}$of benzene. In case of 2, 4, 5 DHFP only one hydrogen is attached with the carbon atom of the ring, hence it will involve one C–H valence oscillation in 3000–3100 cm^{-1} regions. A weak band at 3040 cm^{-1} in 2, 4, 5 DHFP has been assigned to C_5H stretching vibration, which is in accordance with the literature values[2,3,4,5]. However, Raman band at 650 cm^{-1} and infrared active band at 640 cm^{-1} have been well assigned to C–H in-plane bending vibration.

C–C and C–N Vibration: Pyrimidine and the tautomers of uracil have the usual four bands corresponding to coupled C–C, C–N stretching vibrations in the region 1600–1400 cm^{-1}. The pairs of absorption band at 1564 cm^{-1} and 1568 cm^{-1} in pyrimidine were assigned as the C–C and C–N coupled vibrations[6] analogous to the pair of bands originating form e_{1u}(1485) and e_{2g} (1595) modes of benzene. In the present case the vibrations have been assigned at 1450, 1515, 1530, 1550 cm^{-1} in 2, 4, 5 DHFP which correspond to Raman values 1435, 1515 and 1535 cm^{-1} . The bands at 1340 cm^{-1} in 2,4,5 DHFP has been identified as the ring stretching vibration mode of benzene.

The frequency of ring breathing mode which corresponds to

$\upsilon_1 a_{1g}$999 cm^{-1} mode of benzene, under reduced symmetry is lowered much because of the interaction of closely lying vibration b_{1u} 1010cm^{-1}. Jakobsen and Brewer[7] assigned the frequencies between 820-860 cm^{-1} to the mode. Kartha reported this mode around 820 cm^{-1} in methyl pyrimidines. The N-heterocyclic ring breathing vibration occurs at 791, 779, 790 and 780 cm^{-1} in cytosine, cytosine-d, 2-thiocytosine and 1-methyl-cytosine respectively. In view of the above the infrared band at 750 cm^{-1} in 2,4,5 DHFP has been assigned to ring breathing mode.

The components of vibration υ_6(e_{2g}608 cm^{-1}) and υ_6(e_{2u} 404 cm^{-1})which correspond to C–C in-plane and out-of-plane deformation modes have been well identified in their respective regions (Table 1) which find support from the literature values. The out-of-plane non-degenerate vibration υ_4(b_{2g} 703 cm^{-1}) is identified at 750 cm^{-1} in 2,4,5 DHFP.

C–X Vibrations: Susi and Ard[11] assigned the N–H stretching mode at 3145 cm^{-1} in 1-methyl uracil and at 3146 cm^{-1} in 1-methylthymine, sanyl et al[12] have assigned this mode at 3178 cm^{-1} and 3098 cm^{-1} in 5-bromo-uracil, at 3188 cm^{-1} and 3128 cm^{-1} in 5-methyl uracil. Infrared band at 3110 cm^{-1} and 3190 cm^{-1} have been assigned to this mode.

The neutral form of uracil and its substituted derivatives have three double bonds and their stretching vibrations are expected to give rise to three strong bands in the region 1600-1700 cm^{-1} . In 1-methyl uracil Susi and Ard[11] have assigned the bands at 1695, 1662 and 1621 cm^{-1} to C=O_2, C=O_2 and C=C stretching vibrations respectively. Sanyal et al[12]have assigned these vibrations at 1690, 1676 and 1614 cm^{-1} respectively in 5-methyl uracil. The bands observed at 1690, 1640 and 1610 cm^{-1} in 2,4,5 DHFP have been assigned to these double bond stretching vibrations.

Uracil due to the presence of two C=O groups at position 2 and 4 and two N–H groups at 1 and 3 generally tautomerises to give a dihydroxy aromatic compound viz 5-Fluoro-2, 4-Dihydroxy pyrimidine Fig. 6.

It is well known that the substitution of –OH group in pyrimidine may change its aromatic structure to ketonic one. But Goel et al[14] have observed strong band at 3469 cm^{-1} and 3569 cm^{-1} in case of 5,6-dimethyluracil, which in view of the literature values[15-16] may be assigned to O–H stretching modes. The bands observed at 3550 cm^{-1} and 3420 cm^{-1} in 2,4,5 DHFP may be assigned to O–H stretching modes.

Kletz and Price[17] have assigned C–OH stretching mode around 1300 cm^{-1} in substituted phenol, while sanyal et al[18]. assigned this mode at 1305 and 1332 cm^{-1} in dyhydroxy methylpyrimidine. A weak C–OH stretching mode has been clearly identified at 1310 cm^{-1} in 2,4,5 DHFP, while the low frequency band at 1240 cm^{-1} and 1180 cm^{-1} has been taken to represent the OH in-plane-bending mode.

Bellamy[1] and Rao[10] have suggested that the C–F stretching frequency usually appears in the region 1300-1000 cm^{-1}. The C–F bond, containing a strongly electronegative atom such as F, is expected to be Polar and to give rise to very strong infrared absorption. Goel et al.[19] assigned this mode at 1250 cm^{-1} in substituted toluences. In view of these observations, the medium strong band at 1280cm^{-1} in 2, 4, 5 DHFP has been assigned to C–F stretching mode . During the present study the bands observed at 550 cm^{-1} and 400 cm^{-1} in the compound have been taken to represent in-plane-bending and out-of-plane deformation modes respectively. However, the Raman bands at 555 cm^{-1} and 390 cm^{-1} have been taken to represent this mode in 2,4,5 DHFP.

Hydrogen Bonding and Tautomeric Behaviour

Sullivan and Sadler[20] have suggested occurence of bands between 3120-2900 cm^{-1} in indole-3-aldehyde corresponding to N–H stretching frequencies due to strong intramolecular hydrogen bonding. According to Szczesniak et al.[21] bands observed in the infrared spectra of 1-methyluracil in the region 3100-2800 cm^{-1} are due to hydrogen bonded N–H stretching frequencies.

Rao[10] has suggested that N–H stretching frequencies in the range 3300-3150 cm^{-1} are due to intermolecular association through NH- - -O hydrogen bonding. The band observed at 3010 cm^{-1} in 2,4,5 DHFP has been assigned to hydrogen bonded N–H stretching frequency due to intramolecular and intermolecular hydrogen bonding in the compound as shown in fig.4.

Jakobsen [22]has assigned a weak band at 190 cm^{-1} to (OH–O) mode in *p*-cresol. According to Mallick and Banerjee[23] in substituted phenols a low frequency band at 138 cm^{-1} is assigned to (OH–O) mode due to intermolecular hydrogen bonding. Presence of C–H, C=O, stretching and bending fundamentals indicate that the molecule under study is in a state of tautomeric equilibria.

The existence of C=O stretching shows the migration of H atom from the OH group at position 2 to the N_1 atom of the ring in 2, 4, 5 DHFP. However, at the same time the presence of a weak OH stretching further suggests that the OH group is involved in hydrogen bonding.

The C=O stretching mode has been assigned to a medium band at 1640 cm^{-1} in 2,4,5 DHFP which shows the possibility of intramolecular and intermolecular hydrogen bonding. As suggested by Becker et al.[24], hydrogen bonding takes place between non-bonding electrons of solvent and solute. The non-bonding electrons are localized upon more electronegative atoms of Polar group. The hydrogen bonding which stabilizes the ground state will be weakened by the shift of electron density away from the non-bonding centre upon excitation, and a blue shift of the band will be observed relative to the band position in a non-hydrogen bonding solvent.

The unbonded or `free' hydroxyl group absorbs strongly in the region 3650-3580 cm^{-1}. But, chelation (Infra-molecular hydrogen bonding) or association (Intermolecular hydrogen-bonding) usually, shifts the absorption to lower frequencies, a broad extended band is characteristic of chelation while a splitted band suggests association. In the spectra of molecule under study we do observe shifting, splitting and broadening of the same band indicating the existence of hydrogen bonding in this molecule. The same is also indicated by the appearance of N–H stretching, N–H bending, C=O stretching C=O bending and C–OH bending modes in the spectra.

4. Thermodynamic Functions

Thermodynamic functions viz. enthalpy function $\left(\frac{H^o - E_o^o}{T}\right)$ heat capacity $\left(C_p^o\right)$ free energy function $\left(\frac{F^o - E_o^o}{T}\right)$ and entropy $\left(S^o\right)$ of 2,4-Dihydroxy-5-Fluoropyrimidine have been computed using the standard expressions, by taking y-axis perpendicular to the molecular plane and z-axis to pass through the para positions. For determining rotational contribution, the following structural parameters were used.

Bond Length	Bond Angle
N_1-C_2=1.37A^o	$C_2N_1C_6$=123^o
C_2-N_3=1.38A^o	$C_2N_3C_4$=120^o
N_3-C_4=1.40A^o	$C_4C_5C_6$=119^o
C_4-C_5=1.34A^o	$N_3C_4O_5$=120^o
C_5-C_6=1.35A^o	$N_3C_2N_1$=116^o
C_6-N_1=1.33A^o	C_4C_5F=121^o
C_2-O_2=1.23A^o	C_6C_5F=115^o
C_4-O_4=1.28A^o	$N_3C_4O_4$=110^o
C_5-F_5=1.35A^o	$C_5C_4O_4$=130^o
	$N_3C_2O_2$=120^o
	$N_1C_2O_2$=124^o

All other angles were taken as 120^o in the ring.

The thermodynamic functions have been calculated at different temperatures between 200-1500K using 21 fundamental frequencies and assuming rigid rotor harmonic oscillator approximation. The calculations were performed for 1 mol of an ideal gas at 1 atmospheric pressure. The symmetry number for overall rotation has been taken as 2 and internal rotation as 2. the principal moment of intertia were found to be 48.32, 69.71 and 21.38 X 10^{-39}gm in this molecule. While the reduced moment of inertia is 1.129 cm^{-1}. The barrier height (Vo) is found to be 4.618 K Cal/mol.

The variation of enthalpy function $\left(\frac{H^o - E_o^o}{T}\right)$ and heat capacity $\left(C_p^o\right)$ with absolute temperature have been shown graphically in Fig. 8. While those of free energy function $\left(\frac{F^o - E_o^o}{T}\right)$ and entropy $\left(S^o\right)$ in Fig. 9. Which are in agreements with the trend reported in literature[25-27]. The variations of thermal energy and potential barrier with absolute temperature have also been shown in Fig. 10.

Table 1: Assignments of Vibrational Frequencies of 2, 4-Dihydroxy-5-Fluoropyrimidine [All values in]

IR Bands	Raman Bands	Assignments
110*m	115*Vs	Lattice Vibration
150*m	–	Lattice Vibration
330 m	340 m	λ(C–OH)
400 m	390 vs	γ(O-H) γ(C=O) γ(C-F)
420 m	425 m	γ ring
550 vs	555 m	β ring, β(C-O) β(C-F)
590 w	–	γ ring, β(C–H)
640 vs	650 m	β(C=O), β(C–H)
750 s	–	γ ring
810 vs	–	γ (N–H)
990 s	–	ring breathing
1060 vs	1065 vs	β ring
1180 s	1175 m	β (C–OH)
1240 s	1235 vs	ν (C–H), β (O–H)
1280 ms	–	ν (C–F)
1310 w	–	ν (C–OH)
1340 w	–	ν ring
1450 m	1435 vs	ν ring
1515 ms	1515 w	ν ring
1530 ms	1535 m	ν ring
1550 ms	–	ν ring
1640 m	–	ν (C=O)
1690 m	1680 vs	ν (C=O)
3010 w	–	ν (N–H)
3040 w	–	ν (C–H)
3190 m	–	ν (N–H)
3420 m	–	ν (O–H)
3550 m	–	ν (O–H)

* Far infrared values

s = Strong
ν = Stretching
vs = Very Strong
β = In-plane-bending
ms = Medium strong
γ = Out-of-plane-bending
m = Medium
w = Weak
mw = Medium weak
vw = Very weak

Table 2: Thermodynamic Functions (in Cal/mole-K) 2,4-Dihydroxy-5-Fluoropyrimidine

Temperature (K)	$\left(\frac{H^o - E_o^o}{T}\right)$	$\left(\frac{F^o - E_o^o}{T}\right)$	$\left(S^o\right)$	$\left(C_p^o\right)$
200	13.53	56.84	70.37	19.45
273	15.57	61.67	77.24	22.76
300	16.27	63.26	79.53	23.91
400	18.68	68.56	87.25	27.87
500	20.87	73.19	94.07	31.29
600	22.85	77.36	100.21	34.08
700	24.62	81.17	105.79	36.30
800	26.19	84.70	110.89	38.06
900	27.59	87.98	115.58	39.46
1000	28.84	91.06	119.90	40.59
1100	29.95	93.95	123.91	41.51
1200	30.94	96.69	127.64	42.27
1300	31.84	99.28	131.13	42.91
1400	32.65	101.75	134.40	43.44
1500	33.38	104.09	137.48	43.89

Table 3: Potential Barrier and Thermal Energy with Temperature of 2, 4-Dihydroxy-5-Fluoropyrimidine

Temperature (K)	Potential Barrier	Thermal Energy
200	11.62	0.4761
273	8.512	0.4075
300	7.746	0.3887
400	5.81	0.3366
500	4.648	0.3011
600	3.873	0.2749
700	3.32	0.2545
800	2.905	0.238
900	2.582	0.2244
1000	2.324	0.2129
1100	2.112	0.203
1200	1.936	0.1943
1300	1.787	0.1867
1400	1.66	0.1799
1500	1.549	0.1738

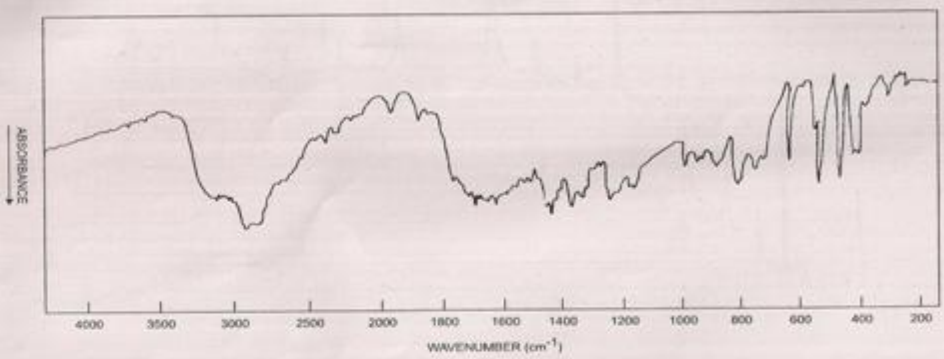


Fig. 2 : Infrared Absorption Spectrum of 2,4-Dihydroxy-5-Fluoropyrimidine

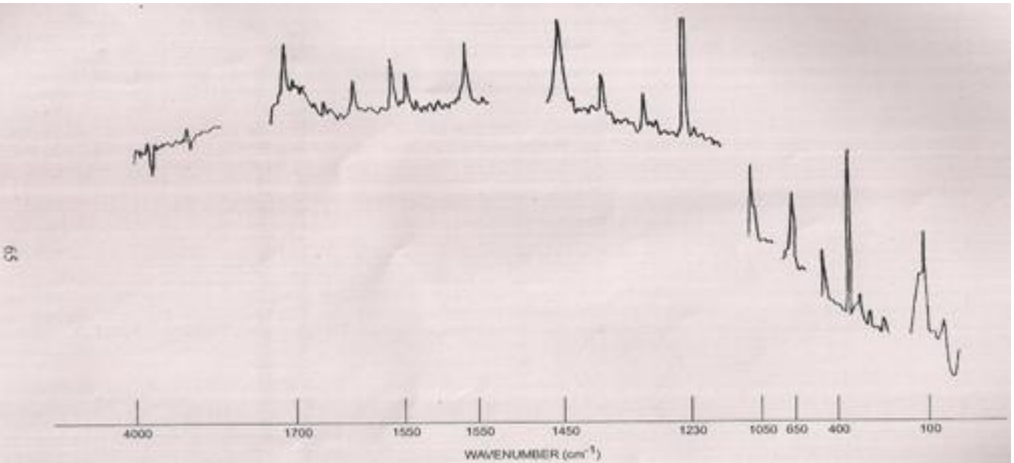


Fig. 3 : Laser Spectrum of 2,4-Dihydroxy-5-Fluoropyrimidine

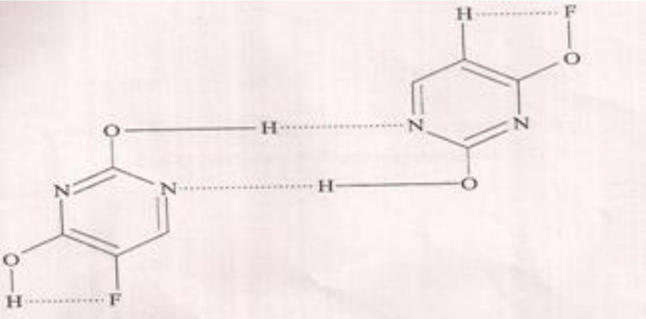


Fig. 4 : Intermolecular and Intramolecular Hydrogen Bonding in 2,4-Dihydroxy-5-Fluoropyrimidine

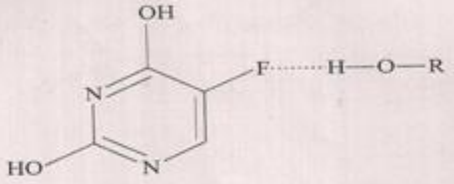


Fig. 5 : Hydrogen Bonding by the Solvent in 2,4-Dihydroxy-5-Fluoropyrimidine

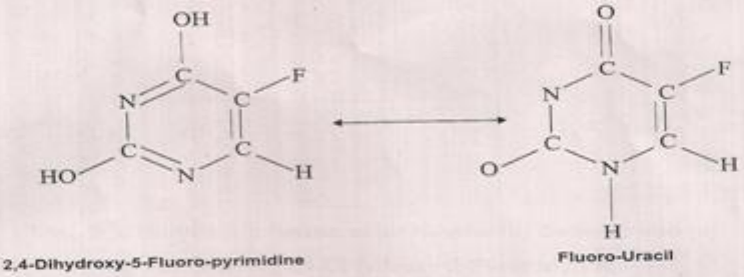


Fig. 6 : Tautomerism in 2,4-Dihydroxy-5-Fluoropyrimidine

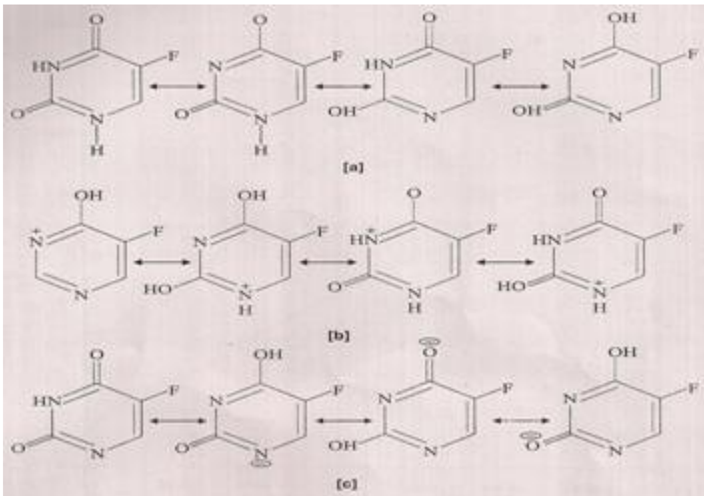


Fig. 7 : Tautomeric Forms of (a) Neutral (b) Cationic and (c) Anionic Forms of 2,4-Dihydroxy-5-Fluoropyrimidine

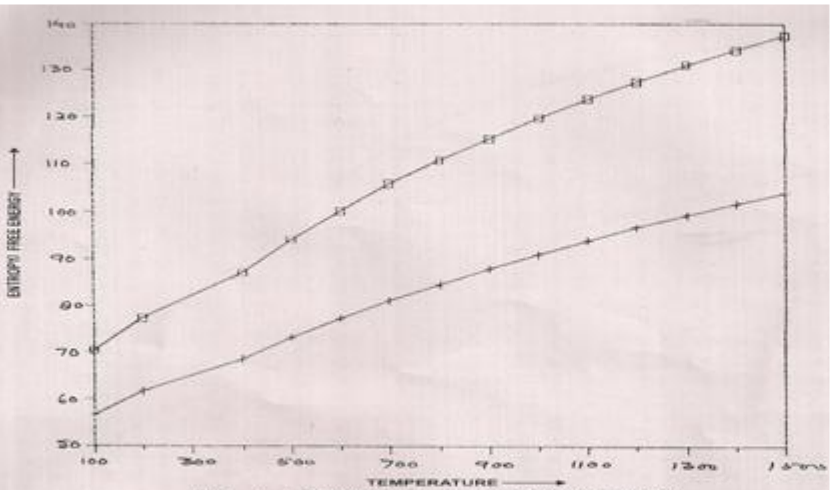


Fig. 8 : Temperature Vs Entropy/Free Energy 2,4-Dihydroxy-5-Fluoropyrimidine

□ Entropy
+ Free Energy

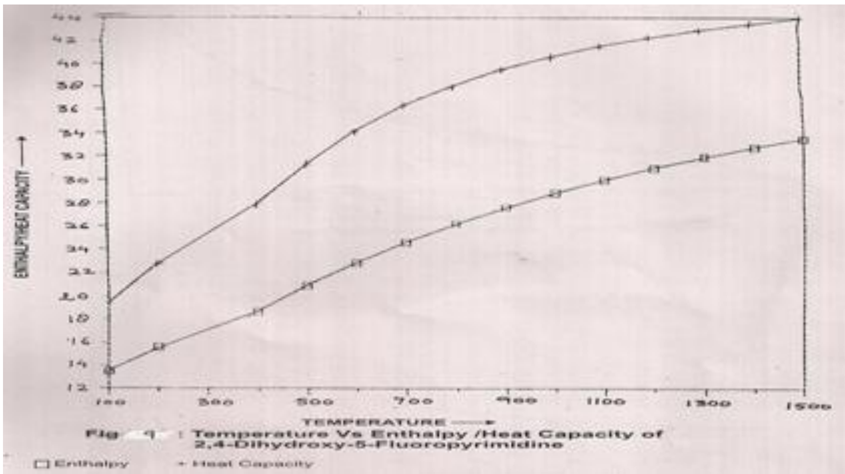
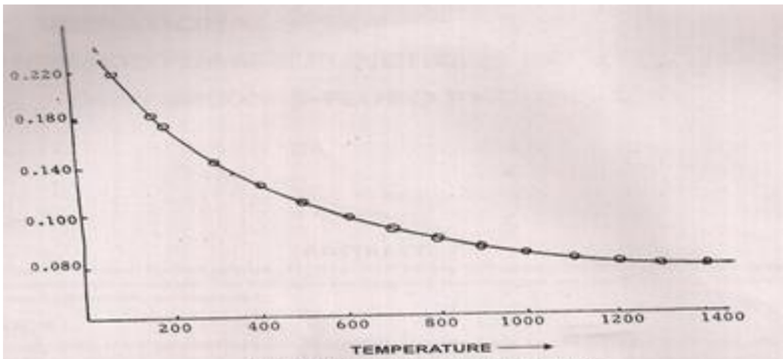
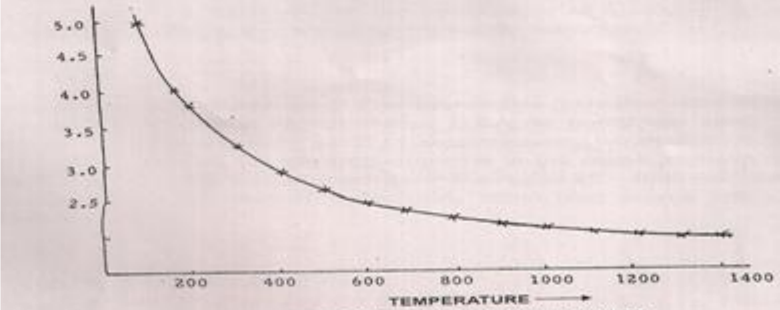


Fig 9 : Temperature Vs Enthalpy /Heat Capacity of 2,4-Dihydroxy-5-Fluoropyrimidine



TEMPERATURE VS THERMAL ENERGY



TEMPERATURE VS POTENTIAL BARRIER

Fig. 10 : 2,4-Dihydroxy-5-Fluoropyrimidine

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