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Infrared Spectra and Thermodynamic Functions of 5-Iodo-Uracil

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Abstract— The infrared (4000-600 cm–1) spectra in KBr matrix of title compound has been analyzed for the purpose of vibrational assignments. The tautomeric forms of the title compound have also been shown and discussed. Probable assignments to observe bands have been discussed. The thermodynamic functions have been computed, plotted and discussed.

I.   INTRODUCTION

The spectral interpretation of N-Hetrocyclics like Pyrimidine, cytosine, 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 and many workers1-10 have studied the vibrational and electronic spectra of such molecules. The vibrational spectra of these compounds may provide some evidence about outstanding structural problems. One of these concerns the tautomerism in some molecules which is possible with the involvement of functional groups like –OH, -NH and –SH and which may effect their function in the metabolism. A full understanding of the vibrational spectra of nucleic acid base is of great importance in biophysical research11-14 . The position of substituents their tautomeric behaviour and hydrogen bonding ability of C-O bond in substituted uracils will be considerable biological evidence. The spectral studies of nucleic acid bases and their derivatives which contain uracil moieties have been carried out both experimentally and theoretically.

In view of the above the present analysis reports the Infrared spectra and Thermodynamic Functions of Solid 5-Iodo-Uracil.

II.   EXPERIMENTAL

Spec-pure grade of 5-Iodo-Uracil (hereafter referred as 5-IU) was obtained. Its purity was confirmed by elemental analysis and melting point determination. Infrared spectrum was recorded with Perkin Elmer M-683 Spectrophotometer in the region 600-4000 cm–1 in KBr pallets.Vapour phase ultraviolet spectra were tried on medium Quartz spectrograph but under best experimental conditions no reportable bands were observed.

III.   RESULTS AND DISCUSSION

The structural diagram of the compound is given in the fig. 1. The infrared spectra are shown in fig. 2 and 3 and Vibrational Assignments are shown in table 1. Tautomeric forms of neutral, cationic and anionic forms of 5-IU are presented in fig. 4 & 5. The statistically computed thermodynamic function viz. enthalpy function, free energy function, entropy and heat capacity with absolute temperature are shown in table 2 for 5-IU. The variation of enthalpy function and heat capacity with absolute temperature is shown in the fig. 6, while the variation of free energy function and entropy with absolute temperature is shown in fig. 7. Also other values of thermal energy and potential barrier are given in the table 3 and their variation with absolute temperature is recorded in fig.8.
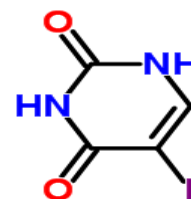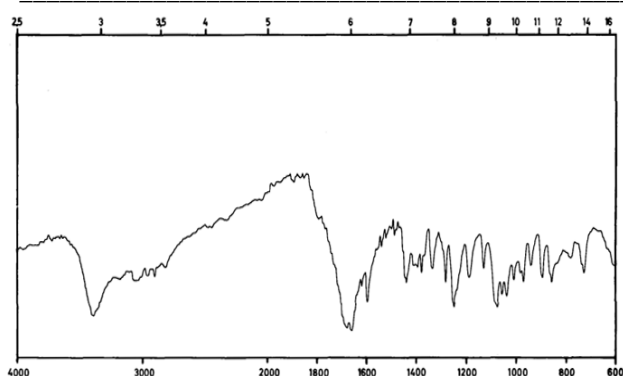

Fig. 1 5 – IU
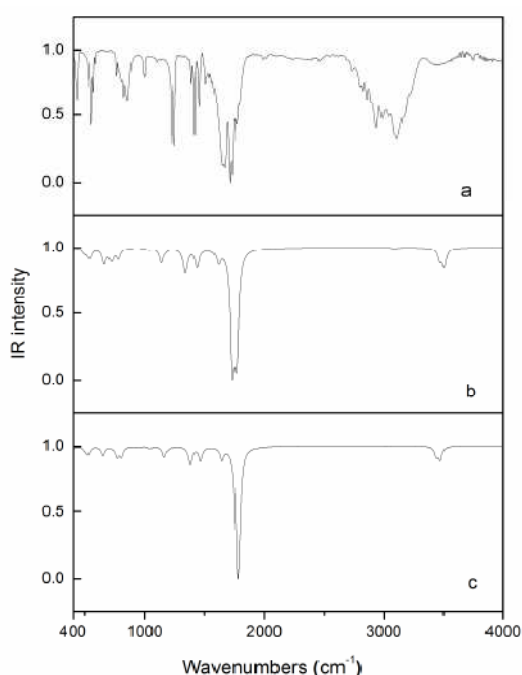
Fig. 2 Infrared spectrum of 5-iU

Fig.3. Comparison of normalized IR spectra, (a) experimental and scaled simulated spectrum obtained by using (b) DFT (scaling factor x 0.96) and (c) HF (scaling factor x 0.89), harmonic calculations for uracil.

In uracil, two C-H stretching frequencies are present. The molecule under investigation is tri-substituted pyrimidine. The aromatic structure of the ring compound shows the presence of C-H stretching vibration in the region 3100-3000 cm–1 15. These vibrations are characteristic of the aromatic ring itself and afford a ready identification for the structure. The bands are not appreciably affected by the nature of substituent. The C-H stretching frequencies in benzene derivatives arises from the mode of a18(3073 cm–1), e29 (3096 cm–1), b1u (3060 cm–1), and e1u(3080 cm–1) of benzene. In case of 5-IU only one hydrogen is attached with carbon atom of the ring, hence it will

involve one C-H valence oscillation in 3000-3100 cm–1 has been assigned to C-H stretching vibration, which in accordance with literature values16-19.

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 pair of absorption band at 1564 and 1568 cm–1 in pyrimidine were assigned as the C-C and C-N coupled vibrations20 analogous to the pair of bands originating from e1u (1485 cm–1) and e2g(1595 cm–1) modes of benzene. Under the present investigation these bands have been assigned at 1460, 1510, 1530 and 1555 cm–1 in infrared spectrum while at 1430, 1515 and 1530 cm–1 in Raman spectrum of the said molecule.

The frequency of ring breathing mode which corresponds to a1g (999 cm–1) mode of benzene, under reduced symmetry is lowered much because of the interaction of closely lying vibration b1u (1010 cm–1). Jakobsen and Brewer21 assigned the frequencies between 820-860 cm–1 to the a19 mode. Kartha22 reported this mode around at 820 cm–1 in methyl pyrimidines.

Table 1
Vibrational Assignment of 5-IODO-Uracil

I.R. Bands (cm–1)	Assignments
210 m	Lattice vibration
305 s	β (C-I)
330 m	γ(C-OH)
400 m	γ(O-H), γ(C=O)
420 m	γ ring
455 m	γ (C-I)
550 vs	β ring, β (C=O)
585 w	γ ring, β (C-H)
640 vs	β(C=O), β (C-H)
760 s	γ ring, ν(C-I)
810 vs	γ(N-H)
990 s	Ring breathing
1055 vs	β ring
1180 s	β (C-OH)
1245 s	ν(C-H), β(O-H)
1315 w	ν(C-OH)
1340 w	ν ring

I.R. Bands (cm–1)	Assignments
1460 m	ν ring
1510 ms	ν ring
1530 ms	ν ring
1550 ms	ν ring
1615 w	ν (C=C)
1645 m	ν (C=O4)
1690 m	ν (C=O2)
3010 w	ν (N-H)
3045 w	ν (C-H)
3180 m	ν (N-H)
3410 m	ν (O-H)
3540 m	ν (O-H)

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

The N-heterocyclic ring breathing vibrations occurs at 791, 779, 790 and 780 cm–1 in cytosine, cytosine-d3, 2-thiocytosine and 1-methyl-cytosine respectively18,23,24, In view of this the infrared band at 760 cm–1 in 5-IU has been assigned to ring breathing mode.

The components of vibration e2g (608 cm–1) and e2u (404 cm–1) which correspond to C-C in- plane and out-of plane deformation modes have been well identified in their respective regions in present study which find support from literature values15,25.

Susi and Ard26 assigned the N-H stretching mode at 3145 cm–1 in 1-methyl uracil and at 3146 cm–1 in 1- methyl thymine, Sanyal et al10 have assigned this mode at 3178 and 3098 cm–1 in 5-bromo-uracil, at 3188, 3128 cm–1 in 5-metyl uracil. In view of this, the bands at 3010 and 3180 cm–1 have been assigned to N-H stretching vibration in infrared spectrum of the present molecule.

The neutral form of uracil and its substituted derivatives have three double bands and their stretching vibrations are expected to given rise to three strong bands in region 1600-1700 cm–1. Susi and Ard27 have assigned the bands at 1695, 1662 and 1621 cm–1 to C=O2, C=O4 and C = C stretching vibrations respectively in 1-methyl uracil. Sanyal et al28 have assigned these vibrations at 1690, 1676 and 1614 cm–1 respectively in 5-metyl uracil. In view of this the bands observed at 1690, 1645 and 1615 cm–1 in infrared spectrum of the present molecule have

been assigned as C=O2, C=O4 and C-C respectively double bond stretching vibration.

Uracil due to the presence of two C=O at position 2 and 4 and two N-H group at 1 and 3 generally tautomerises to give a dihydroxy aromatic compound viz 2,4-dihydroxy-5-iodo-pyrimidine fig. 5.

It is well known that the substitution of –OH group in pyrimidine may change its aromatic structure to Ketonic one. Goel et al29 have observed strong bands at 3469 and 3569 cm–1 in case of 5,6-dimethyl uracil, to O-H stretching modes, which is well agreed with literature values30,31. In present molecule the infrared bands at 3540 and 3410 cm–1 may be assigned to O-H stretching modes. Kletz and Price32 have assigned C-OH stretching mode around 1300 cm–1 in substituted phenol while Sanyal et al35 assigned this mode at 1305 and 1332 cm–1 in dihydroxy methyl –pyrimidine. A weak C-OH stretching mode has been clearly identified at 1315 cm–1 in infrared spectrum of 5-IU, while the low frequency infrared at 1245 and 1180 cm–1 has been taken to represent the O-H in-plane bending mode, while only one Raman band at 1235 cm–1 has been assigned to this mode.

Money and other workers34-37 has assigned the C-I vibrations in the frequency interval the 1129-480 cm–1. The higher frequency bands have been assigned to C-I deformation mode. In few of this, the infrared band at 760 cm–1 has been assigned to c-I stretching vibration. While the infrared bands at 455 and 305 cm–1 has been assigned to in- plane bending and out- of plane bending vibrations respectively to C-I vibrations.

It is interested to note additional N-H stretching frequencies in the present studies. Sullivan and Sadler38 have suggested the occurrence of bands between 3120-2900 cm–1 in indole-3- aldehyde corresponding to N–H stretching frequencies due to strong intra-molecular hydrogen bonding. According to Szczsniak39 band observed in infrared spectra of 1-methyl uracil in the region 3100-2800 cm–1 are due to hydrogen bonded N-H stretching frequencies., Rao25 has suggested that N-H stretching frequencies in the region 3300-3510 cm–1 are due to intermolecular association through NH-O hydrogen bonding.
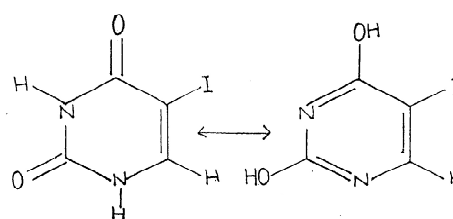
5- IODO URACIL   2,4-DIHYDROXY-5-IODO PYRIMIDINE

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Fig. 4 Tautomerism in 5-Iodo uracil

The band observed at 3010 cm–1 in 5-IU has been assigned to N-H stretching frequency.   Jakobsen40 has assigned at weak band at 190 cm–1 to stretching mode OH-O in P-Cresol. According to Mallic and Banerjee41 in substituted phenol a low frequency band at 138 cm-1 is assigned to OH-O stretching mode due to intermolecular hydrogen bonding presence of C-OH, C=O, stretching and bending fundamentals indicate that the molecule under study is in a state of tautomeric equilibria.

As suggested by Becker et al42 hydrogen bonding takes place between non-bonding electrons of solvent and solute. The non-bonding electros 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 center upon excitation, and a blue shift of the band will be observed relative to the band position in a non-hydrogen bonding solvent.
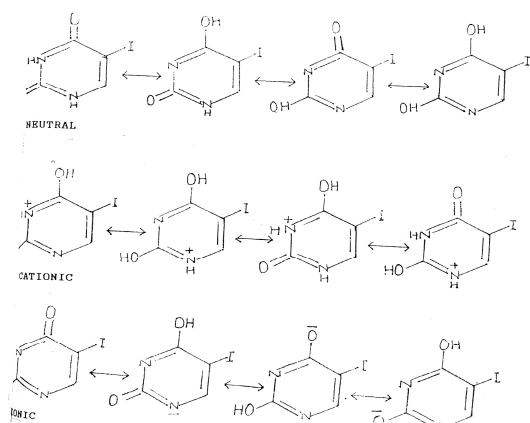

Fig. 5 Tautomeric form of 5-Iodo-Uracil (2,4- dihydroxy- 5- iodo-pyrimidine)

The unbonded or free hydroxyl group absorbs strongly in the region 3650-3580 cm–1. But intra-molecular hydrogen bonding or intermolecular hydrogen bonding usually, shifts the absorption to lower frequency, a broad extended band is characteristic of intra-molecular-hydrogen bonding while a splitted band suggests intermolecular hydrogen bonding. In the spectra of molecule under study we do not observe the same effect indicating the existence of hydrogen bonding in this molecule.

IV.   THERMODYNAMIC FUNCTIONS

Thermodynamic functions viz. enthalpy function (Ho-Eoo)/T, heat capacity C0p free energy function (Fo-

E0o)/T and entropy So of 5-idouracil have been computed using the standard expressions43,44, by taking Y-axis perpendicular to the molecular plane and Z-axis to pass through the para position. For determining rotational contribution, the following structural parameters were used45,46.

N_1 - C_2 = 1.31Å $\angle$ $N_2C_4O_2$ = 112°

C_2-N_2 = 1.34 Å $\angle$ $C_5C_4O_2$ = 129°

N_2-C_4 = 1.39 Å $\angle$ $N_1C_2O_1$ = 124°

C_4-C_5 = 1.32 Å $\angle$ $N_2C_2O_1$ = 120°

C_5-C_6 = 1.39 Å $\angle$ C_4C_5I = 118°

C_6-N_1 = 1.29 Å $\angle$ C_6C_5I = 124°

C_2-O_1 = 1.21 Å $\angle$ $C_2N_1C_6$ = 125°

$C4$-$O2$ = 1.24 Å $\angle$ $C_2N_2C_4$ = 120°

$C5$-I = 1.43 Å

All other angles were taken as 120° in the ring. The thermodynamic functions have been calculated at different temperatures between 200-1500 0K using fundamental frequencies and assuming rigid rotor harmonic oscillator approximation. The calculations were performed for 1 mole 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 moments of inertia were found to be 91.58, 116.63 and 25.05 gm × cm2 in this molecule while the reduced moment of inertia is 1.58 gm x cm2. The barrier height V is found to be 17.73 K cal/Mole.

The vibration of enthalpy function $\left(H^o - E_0^0\right)/T$ and heat capacity CoP with absolute temperature have been shown graphically in fig. 7. While those of free energy function $\left(F^o - E_0^0\right)/T$ and entropy So in fig. 8. Which are in agreement with the trend reported in literature47,48. The variation of thermal energy and potential barrier with absolute temperature has also been recorded in table 3.

Table 2

Thermodynamic Functions (In Cal/Deg. Mole) of 5-IODO Uracil

Temperature Deg. Kelvin	Enthalpy	Free Energy (–)	Entropy	Heat Capacity

Temperature Deg. Kelvin	Enthalpy	Free Energy (–)	Entropy	Heat Capacity
200	13.54	59.09	72.63	19.45
273	15.57	63.92	79.49	22.77
300	16.27	65.52	81.78	23.91
400	18.68	70.82	89.50	27.87
500	20.87	75.45	96.32	31.29
600	22.85	79.61	102.47	34.08
700	24.62	83.43	108.05	36.30
800	26.20	86.95	113.15	38.06
900	27.60	90.24	117.83	39.45
1000	28.84	93.31	122.15	40.59
1100	29.95	96.21	126.16	41.52
1200	30.95	98.95	129.90	42.28
1300	31.84	101.54	133.38	42.91
1400	32.66	104.00	136.38	43.45
1500	33.40	106.35	139.74	43.89

Table 3

Potential Barrier and Thermal Energy of 5-Iodo Uracil

Temperature Deg. Kalvin	Pot. Barrier	Thermal Energy
200	16.23	0.403
273	11.89	0.345
300	10.82	0.330
400	8.11	0.284
500	6.50	0.255
600	5.41	0.232
700	4.64	0.215
800	4.10	0.201
900	3.61	0.190
1000	3.25	0.180

Temperature Deg. Kalvin	Pot. Barrier	Thermal Energy
1100	2.95	0.172
1200	2.70	0.165
1300	2.50	0.158
1400	2.32	0.153
1500	2.16	0.147
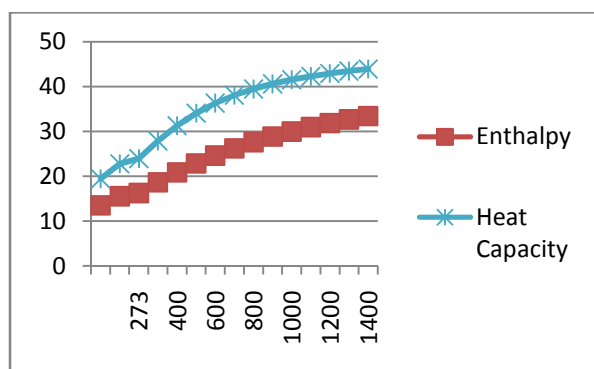
Fig. 6 Enthalpy / Heat Capacity
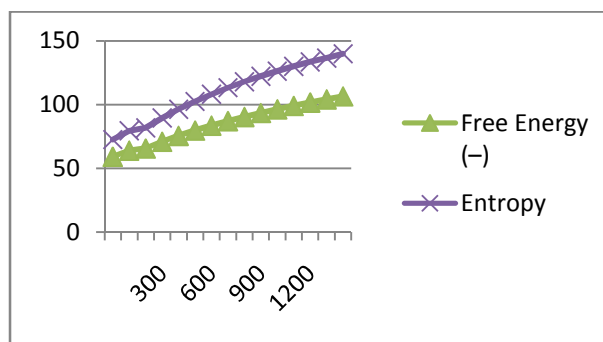
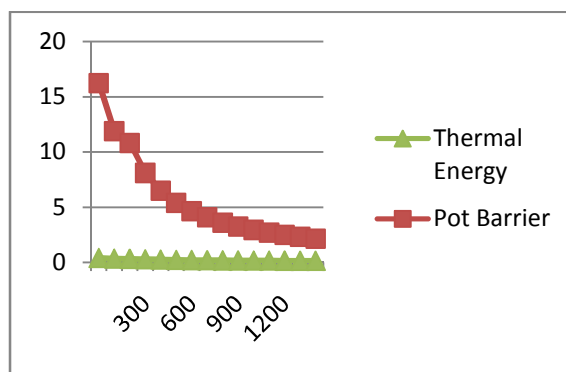*Fig. 7 Entropy / Free Energy*

Fig. 8 Thermal Energy / Potential Barrier

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