VIBRATIONAL SPECTROSCOPIC INVESTIGATION ON PROPYLTHIOURACIL

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ABSTRACT

The FTIR and FT Raman spectrum of propylthiouracil has been recorded in the regions $4000 - 400$ cm^{-1} and $3500 - 100$ cm^{-1}, respectively. The optimized geometry, wave number and intensity of the vibrational bands of propylthiouracil were obtained by ab initio and DFT levels of theory with complete relaxation in the potential energy surface using 6-31G (d,p) basis set. A complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed. The harmonic vibrational frequencies calculated have been compared with experimental FTIR and FT Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed bar type spectrograms.

INTRODUCTION

The increasing interest in the spectroscopic studies of N-heterocyclic molecules is due mainly to their biological and pharmaceutical importance. Among these compounds uracil and it derivatives have special attention [1-2]. 5-halogenated uracils have been found to exert profound effects in a variety of microbiological and mammalian systems, and they have been used as antitumour, antibacterial and antiviral drugs [3]. Some of 5-iodouracil derivatives also have antitumour activity and have been used in the treatment of hepatitis B infections [4]. 5-iodouracil has lethal and mutagenic effects on bacteriophage T4. 5-fluorouracil is widely recognized today as effective treatment modalities, especially with tumours of the head, neck and breast, and in combination drug regimens for cancer chemotherapy [5-7] 5-chlorouracil also has antitumour activity and forms complexes with some metal (II) ions [8]. Substitution of thymine with 5-bromouracil in DNA is known to change interaction between DNA and proteins (increases the cross-linking efficiency and reduce the direct damage), thereby inducing various biological phenomena [9].

Other 5-substituted uracils also play an important role in biochemistry and pharmacology, such as 5-methyl uracil, 5-aminouracil, and 5-nitrouracil. 5-methyluracil (thymine) is a natural constituent of DNA and its structure is of particular importance in understanding the mechanism of the biological functions of DNA. 5-aminouracil is a pyrimidine nucleobase analogue to thymine in which the methyl group is replaced by an amino group, adding therefore new hydrogen bonding sites. 5-aminouracil has been used as a starting material for the synthesis of other pyrimidines [10] and its compatibility has been recognized in the central position of a DNA triplex [11]. 5-nitrouracil is of prime interest to the non-linear optical community [12-13] and it is also of relevance to the biological and pharmaceutical sciences [14-15]. The 5- and 6-halouracils have also been investigated as a possible class of radio-sensitizers, which are used to control damage to healthy tissues in radiation therapy [16].

From the spectroscopic point of view the vibrational spectrum of uracil and its derivatives have been studied by several workers [17-24]. Although IR spectrum of propylthiouracil has been studied by Aruna and Shanmugam [25] and Raman and IR spectra by Jain *et al* [26], however there appears lack of consensus about certain assignments. On account of medicinal importance of propylthiouracil and lack of consensus between the spectral data on it reported in literature require supplementary studies on this molecular species. Therefore, we have reinvestigated the FT-IR and FT-Raman spectra of propylthiouracil and results of the vibrational analysis are being reported in the present work.

MATERIALS AND METHODS

The pure sample of propylthiouracil was obtained from M/s Sigma Chemical Co, USA and used as such without any further purification. A projection of propylthiouracil is shown in Fig. 1. The FT-IR spectrum was recorded in

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the region 400-4000 cm^{-1} on a Perkin Elmer FT-IR 1760 X instrument. Standard KBr technique with 1 mg sample per 300 mg KBr was used for the spectrum. 100 scans were collected. FT-Raman spectrum was obtained on a Bruker IFS 66 NIR-FT instrument equipped with a FRA 106 Raman Module. A Nd: YAG laser at 106 nm with an output of 300 mW was used as the exciting source and the spectrum was recorded over 500 scans at a fixed temperature. The detector was a Ge-diode cooled to liquid nitrogen temperature. The spectral resolution after iodization was 0.6 cm^{-1}. The upper limit for wave numbers was 3500 cm^{-1} due to the detector sensitivity and the lower wave number is around 100 cm^{-1} due to Rayleigh line cut off by a notch filter. The experimental FTIR and FT Raman spectra of propylthiouracil are presented in the Figures. 2 and 3. The spectral measurements were carried out at SAIF, IIT, Chennai, India.

COMPUTATIONAL DETAILS

The entire calculations conducted in the present work were performed at quantum chemical density functional calculations (DFT) using the Gaussian 03W package[27] program employing the Becke's three-parameter hybrid functional[28] combined with Lee-Yang-Parr correlation[29] functional (B3LYP) method together with the 6-31G(d,p) basis set utilizing gradient geometry optimization. The DFT partitions the electronic energy as E= E_T+E_V+E_J+E_{XC}, where E_T, E_V, and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC}, which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [30]. Molecular geometries were fully optimized using the Berny optimization algorithm using redundant internal coordinates. The optimized structural parameters were used in the vibrational wavenumber calculation at the DFT levels to characterize all stationary points as minima.

Then vibrationally averaged nuclear positions of propylthiouracil were used for harmonic vibrational wavenumber calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Thus according to the work of Rauhut and Pulay [31], a scaling factor of 0.963 has been uniformly applied to the B3LYP calculated wavenumbers. The atomic displacements corresponding to some selected modes of vibration are shown in the Figure 4. The transformation of force field, calculations of PED, IR and Raman intensities were done on a PC with a version V7.0-G77 of the MOLVIB program written by Sundius [32-33]. To achieve a close agreement between observed and calculated frequencies, the least square fit

refinement algorithm was used. For the plots of simulated IR and Raman spectrum, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1}.

Prediction of Raman intensities

The Raman activities (S_i), calculated by the Gaussian 03 programs, were converted to relative Raman intensities (I_i) using the following relationship [34]

$$I_i = \frac{f(\nu_o - \nu_i)^4 S_i}{\nu_i[1 - \exp(-hc\nu_i/kT)]}$$

where ν_o is the exciting frequency (in cm^{-1} units); ν_i is the vibrational wave number of the ith normal mode; h, c, k are the universal constants and f is the suitably chosen common scaling factor for all the peak intensities.

RESULTS AND DISCUSSION

Molecular geometry

The molecular structure of propylthiouracil having C_1 symmetry is shown in the Fig.1. The optimized structure parameters of propylthiouracil calculated by DFT-B3LYP level with the 6-31G (d,p) basis set are listed in the Table 1 in accordance with the atom numbering scheme given in Figure 1. Table 1 compares the calculated bond lengths and angles for propylthiouracil with those experimentally available from X-ray diffraction data [35]. From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating vibrational frequencies.
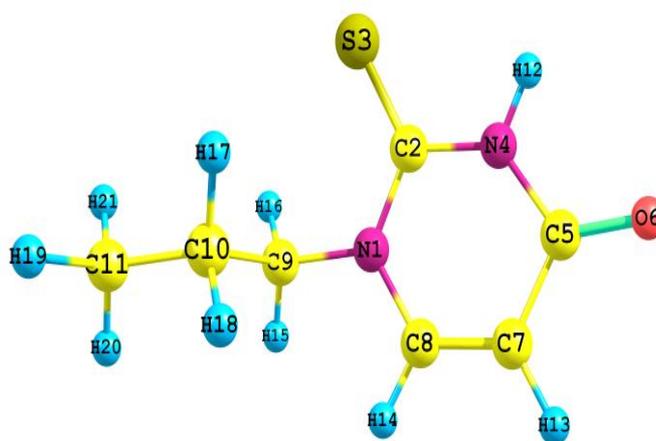

**Fig. 1** Numbering system of propylthiouracil *Vibrational assignments*

The vibrational analysis of propylthiouracil is performed on the basis of the characteristic vibrations of amide,

methyl, nitro and phenyl ring modes. The computed vibrational wavenumbers, their IR and Raman activities, depolarization ratios, force constants and the atomic

noted the calculated results are harmonic frequencies while the observed frequencies contain anharmonic contribution. The later is generally lower than the former due to anharmonicity. The reproductions of observed fundamental frequencies are more desirable because they are directly observable in a

**Table 1** Optimized geometrical parameters of propylthiouracil employing 6-31G (d,p) basic set

Parameters	Expt.	B3LPY
C_{11}-H_{21}	1.113	1.095
C_{11}-H_{20}	1.113	1.096
C_{11}-H_{19}	1.113	1.093
C_{10}-H_{18}	1.113	1.097
C_{10}-H_{17}	1.113	1.097
C_9-H_{16}	1.113	1.097
C_9-H_{15}	1.113	1.096
C_8-H_{14}	1.100	1.084
C_7-H_{13}	1.100	1.081
N_4-H_{12}	1.012	1.013
$1N_1$-C_9	1.470	1.47
C_{10}-C_{11}	1.523	1.531
C_9-C_{10}	1.523	1.531
N_1-C_8	1.466	1.381
C_7-C_8	1.337	1.352
C_5-C_7	1.351	1.453
C_5-O_6	1.208	1.209
N_4-C_5	1.369	1.412
C_2-N_4	1.367	1.372
C_2-S_3	1.576	1.573
N_1-C_2	1.466	1.385
H_{21}-C_{11}-H_{20}	109.5	107.9
H_{21}-C_{11}-H_{19}	109.4	107.6
H_{21}-C_{11}-C_{10}	109.4	111.3
H_{20}-C_{11}-H_{19}	109.4	107.7
H_{20}-C_{11}-C_{10}	109.4	111.5
H_{19}-C_{11}-C_{10}	109.5	110.8
H_{18}-C_{10}-H_{17}	109.5	107.8
H_{18}-C_{10}-C_{11}	109.4	110.8
H_{18}-C_{10}-C_9	109.4	109.9
H_{17}-C_{10}-C_{11}	109.4	110.1
H_{17}-C_{10}-C_9	109.4	107.9
C_{11}-C_{10}-C_9	109.5	111.5
H_{16}-C_9-H_{15}	109.5	108.3
H_{16}-C_9-N_1	109.4	107.3
H_{16}-C_9-C_{10}	109.4	110.5
H_{15}-C_9-N_1	109.4	108.6
H_{15}-C_9-C_{10}	109.4	110.8
N_1-C_9-C_{10}	109.5	110.8
H_{14}-C_8-N_1	119.5	117.4
H_{14}-C_8-C_7	120.0	121.7
N_1-C_8-C_7	120.0	121.5
H_{13}-C_7-C_8	121.2	121.7
H_{13}-C_7-C_5	121.2	121.3
C_8-C_7-C_5	117.6	119.1
C_7-C_5-O_6	123.6	122.2
C_7-C_5-N_4	112.7	112.5
O_6-C_5-N_4	123.6	122.3
H_{12}-N_4-C_5	115.5	115.4
H_{12}-N_4-C_2	115.5	115.3
C_5-N_4-C_2	128.8	129.1
N_4-C_2-S_3	121.5	121.2
N_4-C_2-N_1	116.8	114.7
S_3-C_2-N_1	121.5	122.7
C_9-N_1-C_8	118.0	118.4
C_9-N_1-C_2	118.0	118.6
C_8-N_1-C_2	124.0	112.9
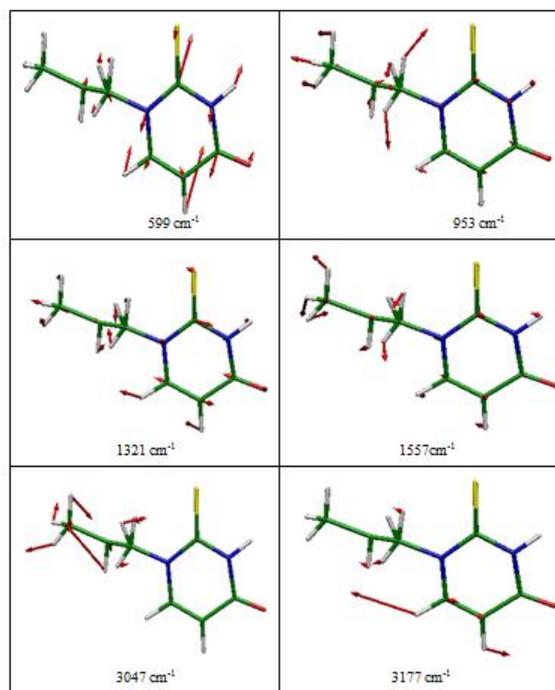
Fig. 2 Atomic displacements corresponding to selected vibrating modes of propylthiouracil
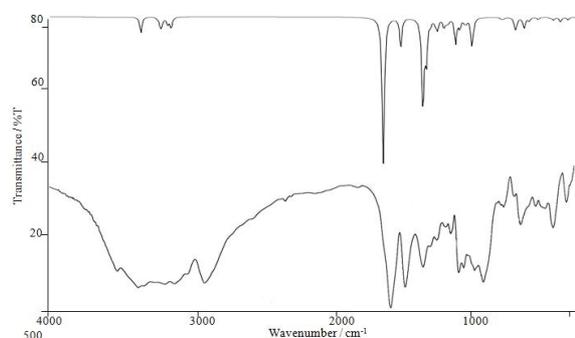
Fig. 3 FTIR spectra of propylthiouracil (a) calculated and (b) observed
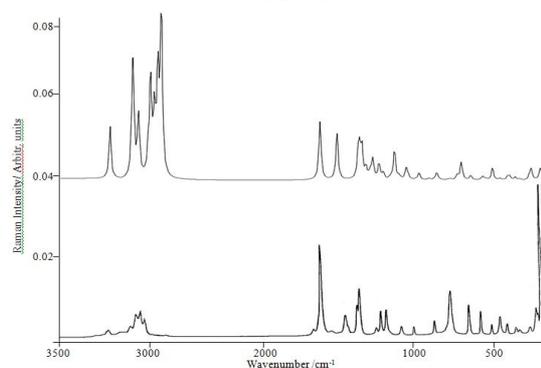
Fig. 4 FT Raman spectra of propylthiouracil (a) calculated and (b) observed

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vibrational spectrum. Comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features. The calculated vibrational wavenumbers, measured infrared and Raman band positions and their assignments are given in the Table 2. Comparison of the wavenumbers calculated at B3LYP

Table 2 Vibrational Wavenumbers obtained for propylthiouracil at B3LYP/ 6-31G(d,p)   [wavenumber (cm^{-1}) IR intensities (km mol^{-1}), Raman scattering activities (Å amu $^{-1}$), reduced mass (amu), force constants (m dyne Å $^{-1}$) and Raman depolarisation ratio]

Observed wavenumbers		Calculated Using B3LYP/6-31 G(d,p)						Characertization of normal modes with PED(%)
ν_{IR} cm^{-1}	ν_{Raman} cm^{-1}	ν_{cal} cm^{-1}	IR intensity	Raman activity	Reudced Mass	Force constant	ρ	
-	-	62	0.2889	1.8795	9.7586	0.1524	0.640	$\tau C_9H_{10}C_{11}(45)$
-	-	68	1.4386	1.8796	4.5763	0.0922	0.750	$\gamma NH(59), \tau C_{10}C_{11}(34)$
-	105	103	0.2235	0.2636	3.4924	0.0814	0.695	$\gamma C_9C_{10}(61)$
-	157	153	1.2969	0.0567	1.1388	0.0369	0.695	γ ring 3(29)
-	182	181	2.0216	0.5931	3.6860	0.2513	0.742	γ ring 1(35)
-	248	249	0.7823	0.3917	12.3344	1.0507	0.750	$\gamma CH_3(47)$
-	286	286	5.7733	1.3501	1.1994	0.1654	0.750	γ ring 1(51)
-	325	325	3.5039	2.8655	7.0624	1.1168	0.704	β CH(27)
-	369	367	2.8138	3.8074	8.3539	1.4038	0.665	$\gamma C_9C_{10}C_{11}(22)$
402	399	392	0.5796	3.2324	3.8672	0.8132	0.724	δ ring 2(46),γCH(25)
459	458	458	11.5948	1.8069	1.2542	0.2750	0.249	$\gamma C_2S_3(51), \beta CH(33)$
515	-	512	19.2341	11.8738	9.5865	2.3733	0.176	δ ring 1(39)
571	-	569	11.3085	1.3676	3.1735	0.8196	0.143	δ ring 4(47)
-	601	599	3.6923	3.7015	1.8218	0.5293	0.750	$\gamma C_9N_1(69)$
645	646	646	9.1259	4.3716	3.0323	1.0031	0.655	γ ring 4(53)
-	710	712	12.5636	3.5343	2.0104	0.7645	0.521	δ CO(59), γNH(61)
764	763	763	2.9932	15.3238	2.3560	0.9597	0.748	$\gamma C_8N_1(54), \gamma$ ring(46)
805	803	802	5.6058	1.9334	4.5174	2.5582	0.712	$\gamma C_2N_1(63), \gamma CH(41)$
832	-	835	40.8034	2.8083	2.7595	1.6287	0.296	$\nu C_2N_4(51), \delta C_9C_{10}(33)$
861	-	859	6.1577	0.8266	3.1680	2.1019	0.383	$\gamma C_2N_4(51), \gamma CH_2(35)$
913	910	912	55.4493	0.6917	1.4296	1.0444	0.407	$\gamma CH_3(57), \delta C_7C_8(44)$
954	953	953	0.8333	0.6117	3.3360	3.1028	0.356	$\delta C_5C_7(39)$
972	972	972	5.8443	7.0789	2.6566	2.6859	0.442	δ CH(50)
993	-	991	7.0114	0.9028	2.3840	2.7216	0.298	$\delta C_8H_{14}(14)$
1012	1010	1011	0.4613	1.7116	1.8422	2.1726	0.542	$\delta C_7H_{13}(43)$
1051	1050	1049	0.3267	6.7102	2.2452	2.7480	0.691	$\delta C_9N_1(39), \delta C_8H_{14}(52)$
1070	-	1068	0.3919	1.0531	4.1199	5.8099	0.617	$\delta C_7H_{13}(41)$
1129	1130	1129	12.7994	3.0162	2.9850	5.0235	0.447	$\delta CH_3(67)$
1147	1146	1147	120.3588	12.1549	1.5031	2.6166	0.226	$\nu C_9N_1(77), \nu C_9C_{10}(56)$
1191	-	1188	17.0756	0.6843	5.6567	10.0131	0.289	$\nu C_{10}C_{11}(69)$
1208	1208	1205	15.8894	3.2534	5.1539	9.4757	0.103	$\nu C_5C_7(81)$
1238	1238	1238	40.7933	29.8949	1.0927	6.8962	0.272	$\nu C_8N_1(65)$
1268	1266	1268	104.7054	2.1739	1.0770	8.3660	0.147	$\nu C_2N_1(72)$
1319	1317	1321	16.0165	6.2846	1.0516	8.2201	0.287	$\nu C_5N_4(78)$
1340	1340	1339	15.2013	0.9978	1.0720	8.3952	0.231	$\delta CH_2(63)$
1389	-	1387	37.4501	15.2624	1.1038	9.2290	0.750	$\delta CH_2(79)$
1405	1406	1405	45.9366	19.6604	1.8422	2.1726	0.298	$\delta_{sd}CH_3(86)$
1422	1421	1421	16.7301	4.5722	2.2452	2.7480	0.542	$\nu C_7C_8(83)$
1461	1460	1463	0.9794	3.1606	4.1199	5.8099	0.691	$\nu C_9C_{10}(89)$
1479	1478	1480	17.6781	10.6547	2.9850	5.0235	0.617	$\delta_{sd}CH_3(84)$
1501	-	1498	163.3196	29.6956	1.5031	2.6166	0.447	$\delta C_8H_{14}(78)$
1507	1505	1506	0.8377	19.3189	1.8422	2.1726	0.226	$\delta C_7H_{13}(81)$
1515	-	1514	238.8595	14.1864	2.2452	2.7480	0.289	$\delta C_{10}H_{17}(82)$
-	1523	1523	123.1515	7.7257	4.1199	5.8099	0.103	$\delta C_{10}H_{18}(78)$
1556	1556	1557	24.0488	6.1839	2.9850	5.0235	0.272	$\delta C_{11}H_{19}(77)$
1598	1597	1598	118.7482	46.9323	1.5031	2.6166	0.147	$\delta N_4H_{12}(63)$
1627	1626	1627	323.2176	60.1652	1.8422	2.1726	0.287	$\nu C_5O_6(82)$
3037	3036	3039	13.7531	107.1738	2.2452	2.7480	0.231	$\nu_s CH_2(88)$
3050	3050	3047	30.0826	60.2956	4.1199	5.8099	0.750	$\nu_s CH_3(93)$
3072	-	3076	28.9645	99.7677	2.9850	5.0235	0.617	$\nu_s CH_2(87)$
3101	3100	3100	2.2652	57.7352	1.5031	2.6166	0.447	$\nu_{as} CH_2(91)$
3123	3123	3120	34.2252	14.4245	5.6567	10.0131	0.226	$\nu_{as} CH_2(88)$
3132	-	3131	24.8835	89.7017	5.1539	9.4757	0.289	$\nu_{as} CH_3(89)$
3153	3151	3150	4.3046	18.5066	1.0927	6.8962	0.103	$\nu_{as} CH_3(97)$
3178	3179	3177	4.3059	65.1628	1.0770	8.3660	0.272	$\nu C_8H_{14}(94)$
3221	3221	3223	0.6243	132.3293	1.0516	8.2201	0.147	$\nu C_7H_{13}(91)$
3361	3361	3365	64.1561	51.7819	1.0720	8.3952	0.287	$\nu N_4H_{12}(91)$

ν-stretching; δ-in-plane bending; γ-out of plane bending; τ - torsion (out of plane); s-symmetry; as-asymmetry

with experimental values reveals the inclusion of electron correlation in density functional theory to a certain extend makes the wavenumber values in comparison with the experimental data.

C-H Vibrations

The hetero aromatic structure shows the presence of C-H stretching vibrations in the region 3250 - 3000 cm^{-1} which is characteristic region for the ready identification of C-H stretching vibrations [36]. Hetero cyclic compound C-H vibration absorption bands are usually weak, in many cases it

literature [39], while the theoretically observed values are at 1068, 1049 cm^{-1}.

Methyl group vibrations

The title molecule propylthiouracil under consideration possesses a CH$_3$ group in the side substitution chain. For the assignments of CH$_3$ group frequencies one can expect that nine fundamentals can be associated to each CH$_3$ group. The C-H stretchings are at lower frequencies than those of the aromatic ring. For CH$_3$ compound the mode appear in the region 3153 and 3050 cm^{-1} are assigned to CH$_3$ stretching mode of vibrations.

Table 3 Theoretically computed energies (a.u.), zero-point vibrational energies (kcal mol^{-1}), rotational constants (GHz), entropies (cal mol-1 K-1) and Dipole moment (D)

Parameters	propylthiouracil 6-31G(d,p)	
	HF	B3LYP
Total energy	-852.300157	-855.7277711
Zero point energy	104.49391	106.7453
Rotational constants	1.60817	1.60151
	0.63799	0.62561
	0.47956	0.47265
Entropy		
Total	100.270	103.009
Translational	41.301	41.301
Rotational	30.858	30.896
Vibrational	28.111	30.812
Dipole moment	5.9451	5.9671

Table 4 **Calculated Polarisibility for propylthiouracil**

Basis set	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$<\alpha>$
HF/6-31G(d,p)	128.205	-11.784	110.670	7.282	2.411	58.895	99.2967
B3LYP/6-31G(d,p)	142.451	-13.884	123.301	7.999	3.112	60.781	108.8443

Table 5 HOMO-LUMO and Energy gap calculation

Basis set	ε (HOMO) eV	ε (LUMO) eV	Energy gap (eV)	Ionisation potentia 1 eV	Electron Affinity (A)	Global Hardness $\eta = (I - A) / 2$ eV	Electronegativity $\chi = (I + A) / 2$ eV
HF/6-31G(d,p)	-8.8538	2.4991	11.3529	8.8538	-2.4991	5.6764	3.1773
B3LYP/6-31G(d,p)	-6.1411	-1.4922	4.6488	6.1411	1.4922	2.3244	3.8166

is too weak for detection. In this region, the bands are not affected, appreciably by the nature of substituents. In the present work, the FTIR and FT Raman bands observed at 3178 cm^{-1} and 3179 cm^{-1} have been assigned to C-H stretching vibration. The B3LYP level at 6-31G (d,p) gives the same frequency values at 3177 cm^{-1} as shown in Table 2. In general the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values [37] for trisubstituted benzene in the region 3250 - 3000 cm^{-1}. The title molecule propylthiouracil has out-of-plane and in-plane aromatic C-H bending vibrations. The out of plane bending mode of C-H is found well with experimentally predicted [38] in the region 900 - 800 cm^{-1} at B3LYP/6-31G (d,p). The observed FTIR value of 805 cm^{-1} is in excellent agreement with 802 cm^{-1} of B3LYP/6-31G (d,p) results. The C-H in plane bending vibrations assigned in the region 980-1260 cm^{-1} even though found to be contaminated by C-CH$_3$ stretch are found in

The theoretically computed value shows an excellent agreement with experimental results. The CH$_3$ deformations are found in both FTIR and FT Raman spectra are in good agreement with the calculated B3LYP results. The experimental observation at 248 cm-1 shows an excellent torsion vibrations are not observed in the FTIR spectrum because these appear at very low frequency. The FT Raman agreement with theoretical result. This assignment finds support with the frequency intervals given by Varsanyi [36].

C- O vibrations

The C O stretching vibration in propylthiouracil has a main contribution in the mode with B3LYP/6-31G (d,p) predicted frequency at 1627 cm^{-1}. This is in agreement with the very strong experimental frequencies at 1627 cm^{-1} and at 1626 cm^{-1} in FT Raman spectrum of propylthiouracil. The in-plane C-O bending vibration mode with the experimental frequency of 710 cm^{-1} is found to be in excellent agreement with the calculated

value at B3LYP level. The above conclusions are in agreement with the literature value [40].

C-S Vibrations

In general the assignment of the band due to C-S stretching vibrations in different compounds are difficult. Both aliphatic and aromatic sulphides have weak to medium band due to C-S stretching vibration in the region 850 - 510 cm^{-1} [41]. Double bond conjugation with the C-S band like vinyl or phenyl lowers the C-S stretching vibration and increases the intensity. In view of this the medium intensed bands present at 832 cm^{-1} in the FTIR spectrum of propylthiouracil is assigned to be due to C-S stretching modes of vibration. The calculated band at B3LYP level in the same region shows band position at 835 cm^{-1} for C-S stretching vibration and is in excellent agreement with experimental spectra.

C-C ring stretching

The C-C aromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1500 – 1300 cm^{-1}. The IR bands are 1461 and 1422 cm^{-1}; the Raman bands are 1460 and 1421 cm^{-1} has been assigned to C-C stretching vibrations. Of these bands, the bands at 1422 cm-1 have appeared characteristically strong in the IR and Raman spectra, respectively. The calculated bands at B3LYP levels in the same region are in excellent agreement with experimental observations of both in FTIR and FT Raman spectra of propylthiouracil [42]. The rings in plane vibrations have given rise to weak bands across the low frequency region, that is to say, below 1000 cm^{-1}. The bands at 954 cm^{-1} and at 832 cm^{-1} have been assigned to C-C in plane bending vibrations. As is seen from Table 2, the predicted frequencies by B3LYP agree well with the observed ones.

N-H vibrations

Primary aliphatic amines absorb in the region 3500–3250 cm^{-1} in solids or liquids and they are broad and of medium intensity. In solid and liquid phases, a band of medium intensity is observed at 3400–3300 cm^{-1} for secondary aromatic amines. In general the vibrational bands due to the N–H stretching are sharp and weak than those of O–H stretching vibrations by virtue of which they can be easily identified [43-44]. In the present case the compounds chosen for study is a hetero cyclic aromatic system of pyrimidine and has only one N-H stretching vibration. Hence, the band appear at 3361 cm^{-1} in the FTIR spectrum of propylthiouracil is assigned to N-H stretching mode of vibration.

C-N vibrations

The identification of C–N stretching vibration is a very difficult task since, the mixing of bands are possible in this region. The C–N stretching band is assigned at 1319 cm^{-1} in 2, 6-dibromo-4-nitroaniline by krishnakumar [45]. Hence in the present investigation, the FTIR bands observed at 1319 and 1268 cm^{-1} and the bands at 1317 and 1266 cm^{-1} in FT Raman spectrum of propylthiouracil are

assigned to C–N stretching mode of vibrations. The calculated value at 1321 and 1268 cm^{-1} are in excellent agreement with the observed value for the corresponding mode of vibration.

Other molecular properties

On the basis of vibrational analysis at B3LYP/ 6-31G (d,p) and HF/6-31G(d,p) levels, several thermodynamic parameters are calculated and are presented in Table 3 . The zero point vibrational energy (ZPVE) and the entropy, S_{vib} (T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in the total entropy of propylthiouracil at room temperature at different methods are only marginal. One of the objectives of the present investigation is to study the effect of the basis sets B3LYP/ 6-31G (d,p) and HF/6-31G (d,p) levels on molecular polarizability of propylthiouracil using the Gaussian 03W program. In this study, the computation of the molecular polarizability of propylthiouracil with different basis sets was reported. Here, α is a second-rank tensor property called the dipole polarizability and mean polarizability $< \alpha >$ is evaluated using Eqn. [46]

$$< \alpha >= 1/3 \ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The calculated polarizabilities using HF and DFT methods for the propylthiouracil molecule are summarized in Table 4. The largest polarizability was observed for B3LYP/6-31G (d,p) at 108.8443. Table 5 lists the calculated values of the first ionization potentials, HOMO & LUMO, energy gaps, Electron affinity (A), Ionisation potential (I), Electro negativity (χ) defined by Mulliken [47] and Global Hardness (η) of propylthiouracil. The hardness, defined as the second derivative of the total energy, together with the concept of electronegativity and the principle of quantization of electronegativities has been used to develop the principle of hard and soft acids and bases [48-49]. The lowest first ionization potential was obtained by HF/6-31G (d,p). The HOMO–LUMO energy gap is consistent for B3LYP methods and varies erotically to HF methods.

CONCLUSION

Attempts have been made in the present work for the proper wave number assignments for the compound propylthiouracil from the FTIR and FT Raman spectra. The equilibrium geometries and harmonic frequencies of propylthiouracil were determined and analyzed at DFT levels of theories utilizing 6-31G (d,p) basis set. The difference between observed and calculated wave number values of the most of the fundamental modes is very small. The experimental and the stimulated spectra of the title compound agree well. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignment made at higher levels of theory with only reasonable deviations from the experimental value seems to be correct. The potential energy distribution are made in this

study also confirms the assignments proposed for various modes of the title compound.

Acknowledgements

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