

TO STUDY THE INFRARED, LASER RAMAN AND ELECTRONIC SPECTRAL STUDIES AND THERMODYNAMIC FUNCTIONS OF 2-THIOURACIL

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ABSTRACT

The same kinds of absorption bands are seen in thiocarbonyl-containing compounds as in those that include carbonyl chromophores. However, compared to carbonyl compounds, the n-bands of thiocarbonyl compounds are red-shifted, with maximum values of 5990 for thiobenzophenone and 3300 for benzophenone. The higher energy of the non-bonding sulfur orbital and a lowering of the π^* orbital because sulfur has a lower electronegativity than oxygen are to blame for the red shift of the n-bands. Around 240 nm is about what pyrimidine absorbs, and this band exhibits some vibrational fine structure. Tautomerism is a potential when hydroxyl, thiol, or amino groups are added to the pyrimidine ring. The tautomers are equilibrium mixes in solution, albeit depending on the circumstances, the equilibrium may be quite much to one side. The inclusion of amino, carbonyl, nitro, and nitroso groups results in noticeable spectrum alterations. These groups' non-bonding electrons have the potential to couple with the ring structure, producing an n-band on the long wavelength side of the typical benzenoid absorption. The n- π^* band has a longer wavelength than the corresponding band of the unconjugated C=O chromophore because the excited electron in the n, state—i.e., the state in which one of the original lone pair of electrons stays in its n orbital and the other is excited into the system of the molecule—is not localized. When the solvent is changed from ethanol to methanol to water, the band with the greatest wavelength exhibits a noticeable blue shift. This characteristic shows that the band is the result of a non-bonding electron moving from a nitrogen atom's lone pair to a ring orbital.

KEY WORDS: Infrared, Laser Raman, Electronic, Spectral and Thermodynamic Functions.

INTRODUCTION

Because of their importance in biology and medicine, N-heterocyclic compounds, particularly purines and pyrimidine bases like cytosine, uracil, and their derivatives, have been the subject of much spectroscopic research during the past few decades. Blout and Fields, who characterized the spectra of a variety of nucleic acids, purines, and pyrimidines and

shown that it was likely that uracil existed in the keto form, are responsible for the first publications of pyrimidine spectra. Lacher, Campion, and Park, who looked at uracil, 5-chloro uracil, and thymine in the overtone region, validated this particular conclusion. Randall et al. have also gathered the spectra of a variety of pyrimidines and purines. Purines and pyrimidine bases are the fundamental building blocks of DNA and RNA, and they are crucial for both protein production and inheritance. The ability of nucleic acids and some of their analogues to undergo spontaneous and induced mutagenesis is exemplified by the tautomerism of heterocyclic bases, which plays a significant role in nucleic acid structure and is currently of additional significance in relation to the antimetabolic properties of some purine and pyrimidine analogs and nucleoside and nucleotide analogs.

The cytosine analog fluorocytosine is a popular antibiotic for bacterial infections. When a medicine enters bacterial cells, a short peptide attached chemically to the amino group of 5-fluorocytosine is released, releasing the active antifungal drug. Similar to thymidine, 1-D-2'-deoxyribofuranosyl-5-iodo-uracil functions as an antimetabolite and is a thymidine antagonist. The sulfur substituted pyrimidines have been shown to function as antimetabolites and potential inhibitors. The relevance of 6-amino-2-thiouracil in chemotherapy is well known. The vibrational modes of each base can interact with those of other bases over the full length of the macromolecule through hydrogen bonding and Vander Waals (stacking) interactions, which affects the ring vibrations. For biological processes, such as reproduction, the position at which sulfur is substituted in pyrimidines is crucial. In contrast to 4-Thiouracil, 2-Thiouracil possesses useful antithyroid action. Several of the bases found in natural nucleic acids were discovered to predominately occur in the keto or amino forms, as in the solution phase, in stark contrast to other heterocyclic systems. Particularly, the keto form is where uracils are most commonly found. According to theoretical calculations by Berthod et al., the ultraviolet absorption spectra of uracil and cytosine nucleosides are accurately anticipated. In the spectra of uracil and cytosine and related nucleosides, Miles et al. and Clark and Tinocoo discovered evidence of the existence of electronic transitions other than $\pi \rightarrow \pi^*$. Neither Kleinwachter et al., Brahms et al., nor Stewart and Jenson were able to identify any transition in the uracil derivatives' near ultraviolet spectral area. In order to prove the existence of $\pi \rightarrow \pi^*$ transitions, it is crucial to thoroughly analyze the electronic transitions of substituted uracil. Recent studies on the vibrational accounts of different substituted pyrimidines have been conducted by a number of researchers.

The current work includes a thorough description of the vibrational spectra of 2-thiouracil and the near ultraviolet absorption spectra of the chemical in various solvents, as well as a thermodynamic analysis of the same.

RESEARCH METHODOLOGY

2-Thiouracil (also known as 2-TU) was purchased from M/S Aldrich Chemie in West Germany as a spec-pure quality sample. By analyzing the elements and determining the melting point, the purity was verified. In KBr pellets, the compound's infrared spectrum was measured using a "Perkin Elmer" spectrophotometer model-52, and its laser Raman spectrum was measured using a "Spex-Rama Lab" spectrophotometer with an Ar-Ne laser beam that had a wavelength of 488 nm and a power of 200 mw. The "Beckmann" spectrophotometer type M-35 was used to record the electronic spectra of 2-TU in various solvents. In the current investigation, spectroscopic grade ethanol, methanol, and water were used as solvents. By comparing the spectra to those of empty cells as a reference and examining the cut off wavelengths, their purity was verified.

RESULTS AND DISCUSSION

The structural diagram of 2-TU with conventional atom numbering is shown in Fig. .1. The location of the substituents suggests that the 2-TU molecule has Cs point group symmetry. Table-.1 lists the molecular vibrational modes that were discovered, along with their intensities and likely assignments. The group frequencies, magnitudes, visual intensities of the band obtained, and the datum available for similar molecules were used to design the vibrational assignments in the current work.

Figure –.1 Molecular Structure of 2-Thiouracil

For the 2-TU molecule, Table-3 lists the statistically computed thermodynamic functions for enthalpy, free energy, entropy, and heat capacity at various absolute temperatures ranging from 200 to 1500°K.

VIBRATIONAL SPECTRA

Ring Vibrations

C–H, N–H, C–C and C–N vibrations

Due to the fact that the molecule under examination is a disubstituted pyrimidine, two C-H valence oscillations are anticipated. According to Bellamy, the C-H stretching vibration in pyrimidine and its derivatives produces an absorption band at 3100-3000 cm⁻¹. The type of substituents has little impact on these bands. Due to this, two C-H stretching vibrations in 2-TU have been attributed to the two weak infrared bands at 3089 and 3053 cm⁻¹, which are

likewise consistent with literature values. Most heterocyclic compounds display distinctive absorption bands in the range of 1250 to 1000 cm^{-1} .

These bands have been attributed to the ring breathing and C-H in-plane deformation modes. The direction and quantity of the isolated ring hydrogen atoms determine the location and the total number of C-H in-plane deformation modes. For the characterization and identification of molecules, these bands are irrelevant. Two prominent C-H in-plane deformation bands are seen in the current molecule at 1220 cm^{-1} in the infrared and 1200 cm^{-1} in the laser Raman spectrum, and at 1174 cm^{-1} in the infrared and 1180 cm^{-1} in the laser Raman spectrum, respectively. In the range of 900-700 cm^{-1} , the C-H out-of-plane deformation vibration occurs. The number of free hydrogen atoms nearby determines where these bands are located. Since there are two free hydrogen atoms next to each other in the current compound 2-TU, two medium-strong infrared bands are seen at 838 cm^{-1} and 759 cm^{-1} , respectively, with a faint laser Raman counterpart at 793 cm^{-1} . These bands signify out-of-plane deformation modes. These values align with those found in the literature.

Group Vibrations:

-SH (thio) group vibrations

The S-H stretch in mercaptans and thiophenols occur at 2590-2540 cm^{-1} . The band is weak in the infrared but strong in Raman spectrum. Lautie et al. suggested that pyridine-2-thione exists in tautomeric forms as they observed infrared band at 2510 cm^{-1} for this compound. Hussain et al. assigned the S-H stretching band at 2580 cm^{-1} in the infrared spectra of 2-thiopyridine.

The 4,6-dihydroxy-2-mercapto-pyrimidine S-H stretching band was assigned by Krishnakumar et al. to be at 2521 cm^{-1} . The faint band at 2617 cm^{-1} in the infrared spectra of 2-TU has been attributed to S-H stretching vibration in light of the explanation above. This figure is consistent with the value found in the literature.

While the S-H out-of-plane bending mode is observed at 457 cm^{-1} in infrared with laser Raman counterpart at 452 cm^{-1} in the spectrum of 2-TU, the S-H in-plane bending is observed as a moderately strong band at 710 cm^{-1} in infrared with laser Raman counterpart likewise at 710 cm^{-1} . These values are consistent with the value found in the literature .

TABLE – 1OBSERVED VIBRATIONAL FREQUENCIES AND THEIR PROBABLE ASSIGNMENT FOR 2–THIOURACIL
(all values are in cm^{-1})

FTIR	LASER RAMAN	ASSIGNMENTS
3644 w	—	\square (O–H)
3138 ms	—	\square (N–H)
3089 ms	—	\square (C–H), \square (N–H)
3053 ms	—	\square (C–H)
2617 w	—	\square (S–H)
1678 s	—	\square (C ₄ =O)
1627 ms	—	\square (C ₅ =C ₆)
1566 s	—	\square ring, β (N–H)
1451 ms	—	\square ring
1427 ms	—	\square ring
1394 ms	—	\square ring
1248 s	—	β (O–H)
1220 s	1200 ms	β (C–H), \square (C–OH)
1174 s	1180 w	β (C–H)
1166 s	1169 w	\square (C ₂ =S)
1011 ms	1045 w	β ring
889 ms	859 w	γ (N ₃ –H)
838 ms	—	γ (C–H), γ (N ₁ –H)
759 ms	793 w	Ring Breathing, γ (C–H)
716 ms	722 ms	γ ring
710 ms	710 w	β (S–H), \square (C–S)
653 w	673 w	β ring, β (C=S)
553 s	575 w	β ring, β (C–OH)
527 ms	509 w	β (C=O), γ (O–H)

457 ms	452 w	γ ring, OH torsion, γ (S-H), β (C-S)
—	282 w	Lattice Vibration
—	98 ms	Lattice Vibration

TABLE-2 : EFFECT OF SOLVENTS ON ELECTRONIC TRANSITIONS OF 2-THIOURACIL (all values are in nm)

SOLVENT	D.C.	R.I.	$n_{\square\square\square\square\square}$	-
Ethanol	25	1.3773	276	-
Methanol	32	1.3362	271	-
Water	80.5	1.3380	279	-

D.C-Dielectric Constant

R.I-Refractive Index

Hydrogen bonding and tautomeric behaviour

One significant type of molecular connection is hydrogen bonding. Both intramolecular and intermolecular hydrogen bonding have a noticeable impact on the group frequencies involved. With hydrogen bond energies of 3 to 5 Kcal mol⁻¹, it is possible to achieve frequency shifts of 100 cm⁻¹. The biggest shifts are produced by hydrogen bonding (association) involving OH groups, while NH groups exhibit smaller shifts. With SH and PH groups, only flimsy hydrogen bonds form. Unlike intermolecular bonds, intramolecular bonds are not disrupted by dilution. Alcohols or phenols exhibit a downward frequency shift and a very significant broadening and intensification of the absorption band as a result of intermolecular hydrogen bonding. Although the bands are widened and the frequency shift for intramolecular bonding is identical, the intensity increase is frequently much smaller. Cross asserts that intramolecular hydrogen bonding are restricted to a single molecule and that, with the exception of regions where chelation takes place, the associated absorption band is sharp. On the other hand, intermolecular hydrogen bonds can form between two molecules.

TABLE – 3

THERMODYNAMIC FUNCTIONS OF 2-THIOURACIL

(in cal K⁻¹ mol⁻¹)

Temperature (°K)	Enthalpy (H ^o – E _o ^o)/T	Heat capacity (C _P ^o)	Free Energy - (F ^o – E _o ^o)/T	Entropy (S ^o)
200	8.92	11.77	99.69	108.62
300	10.60	16.14	103.61	114.22
400	11.50	20.15	106.92	119.43
500	14.38	23.58	109.92	124.31
600	16.16	26.41	111.70	128.87
700	17.80	28.76	115.32	133.12
800	19.29	30.71	117.79	137.09
900	20.66	31.34	120.15	140.81
1000	21.90	33.72	121.39	144.29
1100	23.02	34.89	124.53	147.56
1200	24.06	35.88	126.58	150.64
1300	25.00	36.73	128.54	153.55
1400	25.86	37.46	130.43	156.30
1500	26.66	38.09	131.24	158.90

infrared absorption band becomes very sharp, or between several molecules (polymeric association) when an absorption band becomes broad. Several of the bases found in natural nucleic acids were discovered to predominately occur in the keto or amino forms, as in the solution phase, in stark contrast to other heterocyclic systems. Particularly, the keto form of uracils predominates [15]. For a very long time and even today, keto-enol and amino-imino tautomerism have been cited as the primary and even exclusive causes of spontaneous mutagenesis. Because the purine-pyrimidine association may also be stabilized by interactions other than H-bonding, such as dipole-dipole or dipole-induced dipole interactions, the self-dimerization of either the adenine or uracil derivative involves the formation of two H-bonds but is still significantly less stable than the heteroassociation [109].

Hydrogen bound N-H stretching frequencies have been attributed to bands in the area of 3100-2800 cm^{-1} in the spectra of 1-methyl uracil by Szczesniak et al. . According to Lautie et al. , significant (NH....S) hydrogen bond creation causes N-H stretching at 2870 cm^{-1} in the infrared spectra of 2-pyridine thione, 2950 cm^{-1} in 3-pyridazinethione, and 2940 cm^{-1} in 2,4-dithiouracil. According to Rao , the range 3300-3150 cm^{-1} is where N-H stretching mode, which is influenced by intermolecular hydrogen bonding of type (NH....N), occurs. Bellamy claims that secondary amines exhibit only a single N-H stretching absorption in diluted solution, however greater concentrations of these compounds occasionally exhibit a second band at low frequencies when hydrogen bonding processes take place. Although the shifts are modest, NH groups can also interact with alcohols and ketonic groups . This is consistent with the value found in the literature. When the OH group is close to a polar group or an electronegative element like F, O, Cl, or N, intramolecular hydrogen bonding occurs. Diols, o-nitro and o-halo phenols, nitro alcohols, 1,2 chlorohydrin, hydroxy and aminoketones, nitro alcohols, and nitro alcohols are examples of important molecules that exhibit intramolecular hydrogen bonding. Contrary to widely held beliefs, it is discovered that intramolecular OH....N hydrogen bonds are stronger than OH....O bonds. A generalization might be made that the ortho-substitution of phenol by halogen, amino, ether, thioether, allyl, hydroxyl, benzyl, modified benzyl, or phenyl groups results in one sort of intramolecular hydrogen bond or another.

ELECTRONIC SPECTRA

Pyrimidine bases' spectra exhibit three or four bands of absorption between 180 and 300 nm[88]. These bands are also observed in various pyrimidine bases and maybe in the long wavelength n- transition. The correlations demonstrate that the pyrimidine spectrum, whose electronic states are derived from those of benzene, is simply related to the spectrum of each base. Thus, all pyrimidine bases use benzene as their parent absorbing chromophore. Additionally, Mason interpreted the first "-" band of a few substituted pyrimidines as the benzene band at 260 nm. When the symmetry is lowered from D_{6h} or C_{2v} , the $A_1 B_2$ transition of benzene, which corresponds to the ultraviolet bands observed in pyrimidine bases about 240 nm, occurs. According to Clark and Tinocoo , the benzene $A_{1g} E_{1u}$ and $A_{1g} B_{1u}$ transitions correspond to the 200 nm and 210 nm bands of pyrimidine. The benzene $A_{1g} B_{1u}$ and $A_{1g} B_{2u}$ transitions are associated with the 221 nm and 279 nm systems, respectively, in 2-TU. Hug and Tinocoo assert that n- transitions in pyrimidine bases correspond to out-of-plane transitions and n-* transitions to in-plane transitions. This is consistent with the literature that was read. It has been discovered that bands at 266 nm for 6-amino-1-methyl uracil and around 267 nm for 6-amino-1,3-dimethyl uracil have been taken

to represent n-, or out-of-plane transitions, while bands around 225 and 194 nm for 6-amino-1-methyl uracil and around 227 and 195 nm for 6-amino-1,3-dimethyl ura. As a result, the band around 279 nm represents an n-transition or out-of-plane transition in the current molecule, 2-TU, while the band around 221 nm represents an in-plane transition. On carbonyl substitution, which is analogous to what is generated by vinyl substitution, the 260 nm band of benzene is redshifted. Since the orbital on oxygen has a higher electronegativity than the orbital on carbon, preventing maximal contact between the carbonyl molecular orbitals and the benzene orbitals, the shift is not as dramatic as in styrene. Since this is the case, the red (bathochromic) shift for the n- transition from methanol to water may be described in 2-TU.

Solvent Effect

In the case of azaaromatics, the non-bonding orbitals are located at an energy higher than the highest filled molecular orbital, hence the longest wavelength n transitions are anticipated. The n-band distance from the long wavelength band increases with the number of aza substituents, and it frequently exhibits a clearly defined vibrational structure. The n-absorption band of 1,2,4,5-tetrazine enters the visible spectral area. In the range 3000-3410, the n- transitions of diaza benzenes manifest as separate bands.

THERMODYNAMIC FUNCTIONS

The total of a molecule's translational, rotational, vibrational, and electronic energies makes up its total energy. These four energy contributions can be handled independently for a first estimate. When the vibrational frequencies of a molecule are known, the vibrational energy's share of the molecule's total energy can be determined. Similar calculations can be made for the rotational energy contribution if the molecule's moment of inertia is known. Therefore, the measured frequencies and the moments of inertia are crucial inputs when computing the thermodynamic functions of the compound 2-TU, such as the enthalpy function, heat capacity (C_P), free energy function, and entropy (S₀). Direct experimental measurements of the vibrational contribution of a molecule's thermodynamic properties are challenging and occasionally impossible. However, by employing the molecule's fundamental wavenumbers, thermodynamic quantities of a molecule can be estimated with greater accuracy than they can be measured.

Atomic masses, molecular weights, molecular structural characteristics, complete fundamental vibrational frequencies (3n-6), and the symmetry number are needed for the statistical mechanical computation of thermodynamic properties for the 2-TU molecule. The following structural characteristics were utilized to calculate rotational contributions.

Bond Length (Å)	Bond Angle (°)
N ₁ C ₂ =1.37	N ₁ C ₂ N ₃ =120
C ₂ N ₃ =1.38	C ₂ N ₃ C ₄ =120
N ₃ C ₄ =1.40	N ₃ C ₄ C ₅ =120
C ₄ C ₅ = 1.34	C ₄ C ₅ C ₆ =120
C ₅ C ₆ =1.35	C ₅ C ₆ N ₁ =120
C ₆ N ₁ =1.33	C ₆ N ₁ C ₂ =120
C ₂ S ₇ =1.72	N ₁ C ₂ S ₇ =120
C ₄ O ₈ =1.28	N ₃ C ₂ S ₇ =120
	N ₃ C ₄ O ₈ =110
	C ₅ C ₄ O ₈ =130

The molecule is planar, sitting in the XY plane with the Y axis passing through the para position and the Z axis going through the molecular plane since it is aromatic. The entire rotation symmetry number is 1. The following were identified as the main moments of inertia:

$$I_x = 4.40 \times 10^{-38} \text{ gm cm}^2$$

$$I_y = 5.03 \times 10^{-38} \text{ gm cm}^2$$

$$I_z = 9.44 \times 10^{-38} \text{ gm cm}^2$$

Table- displays the various thermodynamic functions estimated for 2-TU.

CONCLUSION

The thermodynamic functions were estimated using the compound's 18 fundamental frequencies between (200 and 1500 oK) while adopting the stiff rotor harmonic oscillator approximation. One mole of an ideal gas was used in the calculations, which were done at one atmosphere of pressure. The entire amount of energy held in a system is represented by enthalpy functions. Enthalpy increases as a system transitions from solid to liquid to vapour.

As the temperature varies between 200 and 1500 oK, a similar variation, or an increase in enthalpy values for the 2-TU molecule, is seen.

Entropy (So) is thought of as the system's measure of unpredictability. Entropy of the system grows as temperature rises. Similar to this, the free energy for the molecule in the title increases as the temperature rises from 200 to 1500 oK.

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