

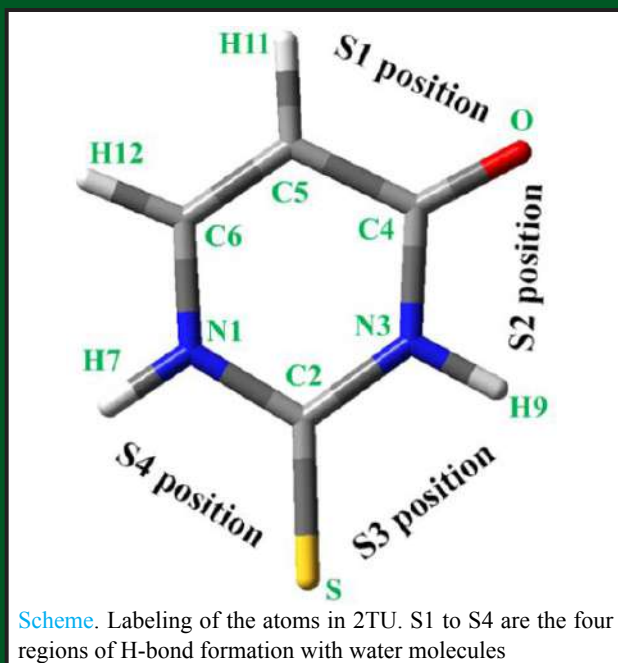
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Molecular structure and vibrational spectra of 2-thiouracil: A comparison with uracil

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Spectroscopic and structural studies of uracil and its derivatives have been reported both theoretically and as well experimentally by many authors. Uracil and its thio analogue 2-thiouracil (2-TU) affect the growth of plants. To understand biochemically the mode of inhibitory or malforming actions of uracil and 2-TU on the growth of rice and wheat plants, the knowledge of their structures is essential. Hence, in the present work an attempt has been made to study their spectra and structures using vibrational spectroscopy as technique. The replacement of an oxygen atom by sulphur leads to a shift of the experimental $\nu(\text{N-H})$ bands to lower wavenumbers, 27 cm^{-1} for the N1-H mode and 20 cm^{-1} for N3-H. The effect of sulphur substitution on $\nu(\text{N3-H})$ wavenumber and intensity reflects changes in proton abilities of this group as well as the hydrogen bonding in which they participate. Compared to uracil, the sulfur atom in 2-TU results mainly in a significant change of the bond-length at the substitution site: $\text{S}=\text{C} \sim 1.66\text{ \AA}$, as compared to $\text{C}=\text{O} \sim 1.22\text{ \AA}$. This fact leads to a slightly reduction in the neighboring bond lengths N1-C2 and N3-C2, but the N-H and C-H bonds are little affected. © Anita Publications. All rights reserved.

Keywords: Uracil, 2-Thiouracil, FT-IR, FT-Raman, Density Functional Theory (DFT).

1 Introduction

Spectroscopic studies of uracil and its derivatives have been reported both theoretically and as well experimentally by many authors [1-4]. 5-nitouracil (5-NU) is one of the substituted pyrimidines used in plants growth. The effects of uracil and its analogue 5-NU on growth and flowering of tomato have been studied and it was found that the treatments with uracil and 5-NU significantly increased the plant height and the fresh and dry weights of the shoot [5].

The effect of Uracil on the germination and growth of some leguminous plants has been studied by Turan and Konuk [6]. Also, the effect of uracil and 2-thiouracil (2-TU) (Fig 1) on flower initiation in rice and wheat plants grown under aseptic conditions was first studied by Jun Inouye and Jun-Ichiro [7]. It was found that uracil alone had a slight accelerating effect on flowering. It possess several important biological properties, such as an anticarcinogenic agent, antifungal, antiprotozoal and antiviral activity [8]. To understand

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biochemically the mode of inhibitory or malforming actions of uracil and 2-TU on the growth of rice and wheat plants, the study of their structures is essential. Hence, in the present work an attempt was made to study the structural differences between uracil and its derivative 2-TU using vibrational spectroscopy as technique.

The vibrational spectrum of uracil has been studied by several workers [9-11]. Structural studies of 2-TU have been reported using DFT methods [12]. Also, the vibrational spectra of thio-derivatives are of recent interest [13,14]. The experimental IR spectra of 2-TU have been previously reported in detail in N₂ [15,16] and in Ar [17,18] matrices, as well as in the solid state in KBr pellets [19]. Raman spectra of polycrystalline samples of 2-TU have been also recorded [19]. Palafox *et al* have studied this molecule in detail from the structural and spectroscopy points of view using DFT methods [3].

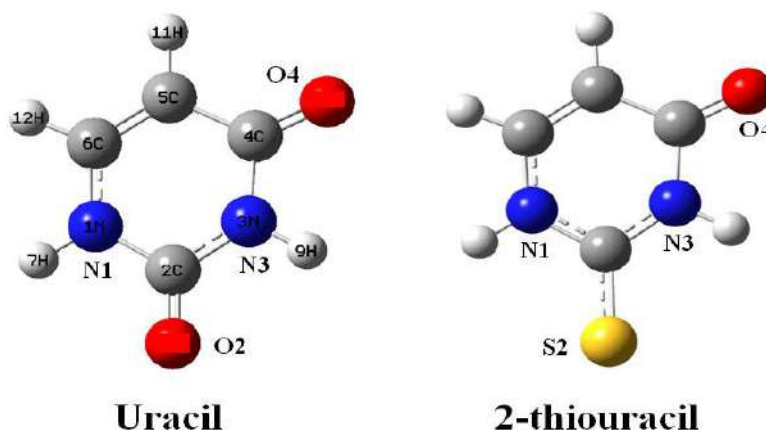


Fig 1. Structures of uracil and 2-thiouracil molecules.

The aims of the present work were the following:

- (i) To determine and compare the molecular structures of 2-thiouracil (2-TU) and uracil, and to establish the main analogies and differences.
- (ii) To predict the IR spectrum of Uracil in the monomer form, and to compare it with that reported in matrix isolation. A linear scaling procedure was used for this task.
- (iii) To establish the main spectroscopic differences between the spectra of uracil and 2-TU.

2 Calculations

All calculations were carried out using Density Functional theory (DFT) methods [20]. DFT methods give good vibrational wavenumbers and require low computational time. Furthermore, DFT methods have been applied most successfully in large number of studies. In the present study, as DFT method, the Becke's three-parameter exchange functional (B3) in combination with both the correlational functional of Lee, Yang and Parr (LYP) with basis set B3LYP/6-31G(d, p) and B3LYP/6-311++G(3df, pd) were selected. The procedure is implemented in the GAUSSIAN09 program package [21].

The characteristic calculated wavenumbers in U and 2-TU are collected in Table 2. To improve the computed wavenumbers two procedures were used: the linear scaling equation (LSE), and the specific scale factors for each mode. The LSE utilized the following equations:

$$\nu_{\text{scaled}} = 33.5 + 0.9391 \nu_{\text{calc.}} \quad \text{at B3LYP/6-31G (d, p)}$$

$$\nu_{\text{scaled}} = 31.9 + 0.9512 \nu_{\text{calc.}} \quad \text{at B3LYP/6-311++G(3df, pd)}$$

The corresponding scaled IR and Raman spectra are shown in Figs 2-4.

3 Results and Discussion

3.1 Geometry

The optimum geometry was determined with the key word OPT, by minimising the energy with respect to all geometrical parameters without imposing molecular symmetry constraints. The optimized bond lengths and bond angles of uracil (U) and 2-thiouracil (2-TU) at the B3LYP/6-31G(d, p) level are collected in Table 1, while the labeling of atoms is plotted in Fig 1.

Table 1. Calculated bond lengths and bond angles of uracil and 2-TU at the B3LYP/6-31G(d, p) level

| Bond lengths | 2-TU | uracil | Bond angles | 2-TU | uracil |
|--------------|-------|--------|-------------|-------|--------|
| N1-C2 | 1.378 | 1.396 | N-C2-N | 113.3 | 112.8 |
| C2-N3 | 1.368 | 1.384 | C-N3-C | 128.2 | 128.3 |
| N3-C4 | 1.419 | 1.414 | N-C4-C | 113.2 | 113.4 |
| C4-C5 | 1.458 | 1.460 | C-C5=C | 119.6 | 119.9 |
| C5=C6 | 1.351 | 1.350 | C2-N1-H | 115.1 | 114.8 |
| N1-C6 | 1.375 | 1.375 | C4-N3-H | 115.5 | 116.1 |
| C2=O/S | 1.665 | 1.217 | N1-C2=O/S | 122.3 | 122.7 |
| C4=O | 1.218 | 1.219 | N3-C=O | 120.0 | 120.3 |

3.2 Vibrational wavenumbers

All wavenumbers were determined under the harmonic approximation and at the same level of the corresponding optimisation process. The characteristic wavenumbers in U and 2-TU are given in Table 2. The assignments for several modes are self evident and has been discussed elsewhere [2,3], therefore, here we discuss only the characteristic vibrations, Table 2.

N-H modes

The N-H stretching modes are essentially pure group modes. In Uracil and its derivatives substitution only induces shifts of about 1% or less, therefore, the calculated and experimental wavenumbers appear little affected [3]. The stretching vibrations of N-H and C-H groups are expected to be in the region 2950-3500 cm^{-1} with the N-H stretching mode on the higher wavenumber side [22]. In the case of 2-TU, two vibrations due to stretching of N1-H and N3-H modes are predicted accurately at 3500 and 3465 cm^{-1} , whereas in U these vibrations are predicted at 3496 and 3454 cm^{-1} , respectively, Table 2.

The bending modes due to N1-H and N3-H groups are coupled vibrations [3]. In case of 2-TU they are more coupled than in uracil. Because the stretching of the N1-H group appears at a higher wavenumber than the N3-H group, the bending of N1-H appears at a higher value than the N3-H group, Table 2.

C=O group vibrations

The carbonyl group vibrations are the characteristic bands in the spectra of uracil and its derivatives and the intensity of these bands can change due to the formation of hydrogen bonds [2-4]. These vibrations in uracil and its derivatives are expected in the region 1600-1750 cm^{-1} . In uracil and substituted uracils, $\nu(\text{C2=O})$ is assigned at a higher wavenumber than the corresponding $\nu(\text{C4=O})$ normal mode, because the oxygen atom at C4 position is expected to be involved in the hydrogen bonds and therefore $\nu(\text{C2=O})$ mode is expected to appear at a higher wavenumber than $\nu(\text{C4=O})$ mode [22]. In the present study, the bands predicted at 1745 and 1713 cm^{-1} are assigned to $\nu(\text{C2=O})$ and $\nu(\text{C4=O})$ modes respectively in the case of Uracil and band predicted at 1738 cm^{-1} to $\nu(\text{C4=O})$ mode in 2-TU. In the case of 2-TU the band predicted at 1149 cm^{-1} is assigned to $\nu(\text{C2=S})$ in agreement with previous studies [2,3]. The $\nu(\text{C=C})$ stretching

mode in uracil molecule is sensitive to sulphur substitution at position 2, because it changes the electron distribution of the ring. The band predicted at 1626 cm^{-1} in uracil and at 1622 cm^{-1} in 2-TU is assigned to $\nu(\text{C}=\text{C})$ mode. All these assignments find wide support from literature values in related molecules [22-34].

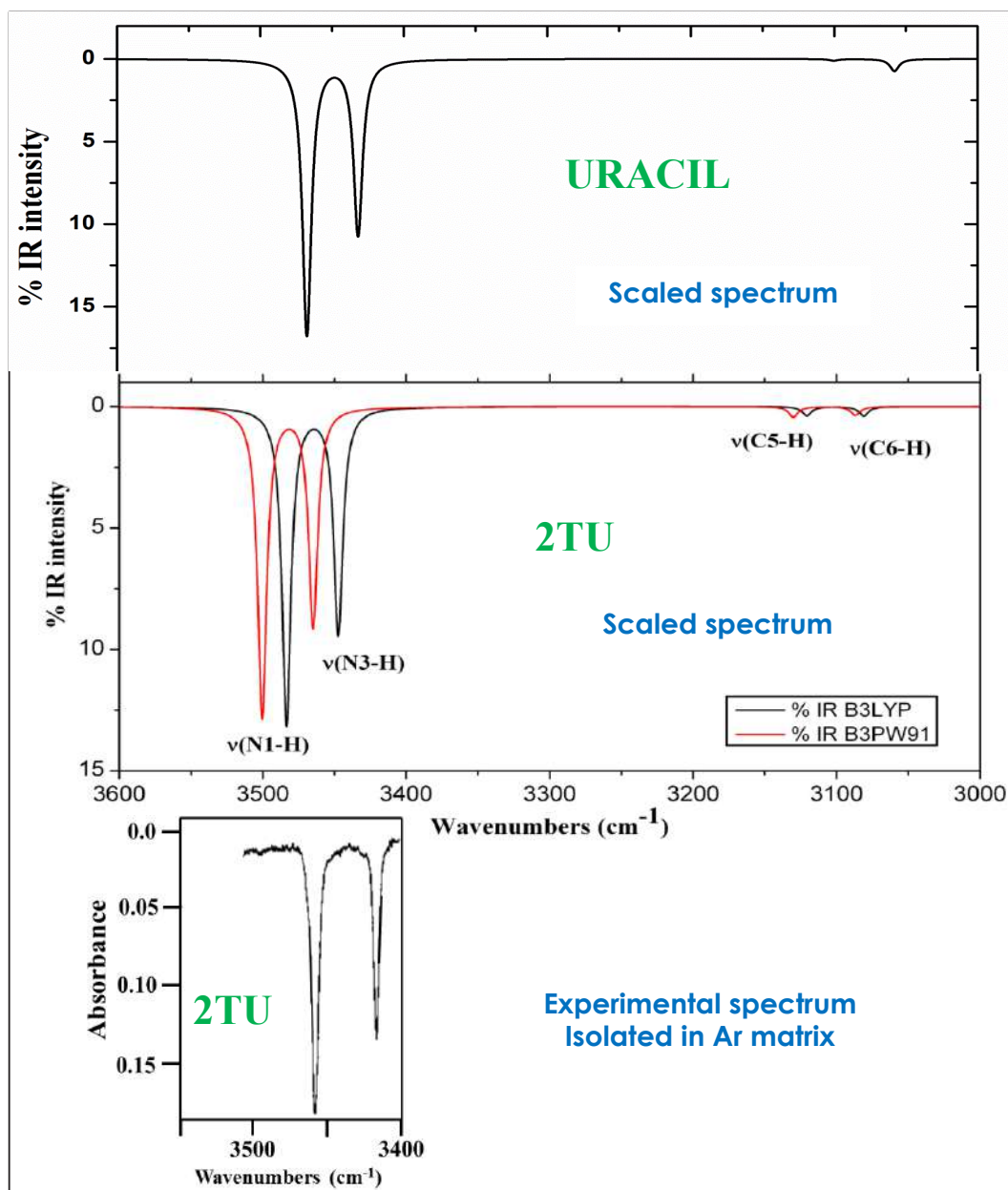


Fig 2. Theoretical scaled IR spectra of uracil and 2-TU with the B3LYP and B3PW91 methods in the 3600-3000 cm^{-1} range, together with that reported of 2-TU in Ar matrix [17,18].

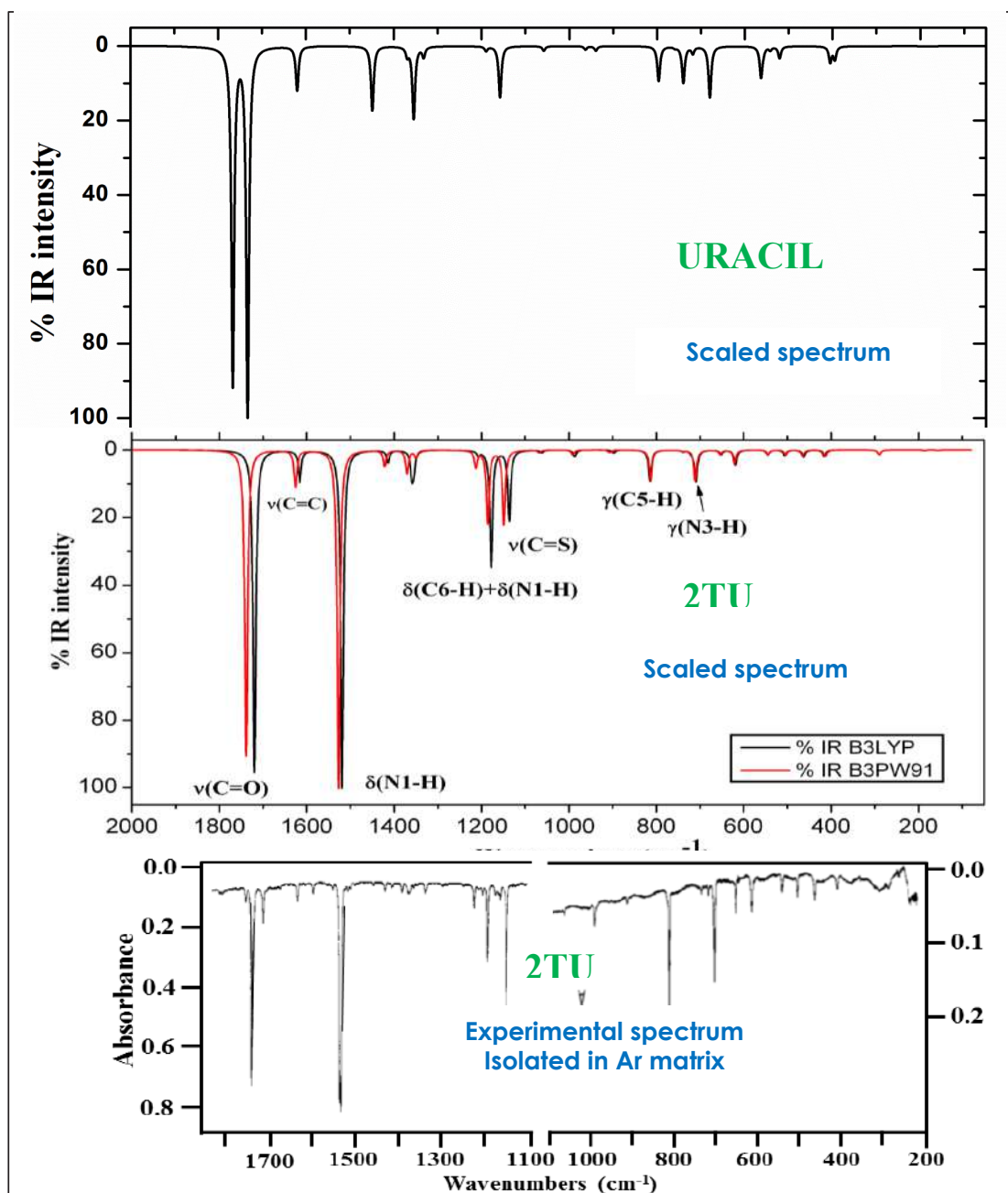


Fig 3. Theoretical scaled IR spectra of uracil and 2-TU with the B3LYP and B3PW91 methods in the 2000-50 cm^{-1} range, together with that reported of 2TU in Ar matrix [17,18].

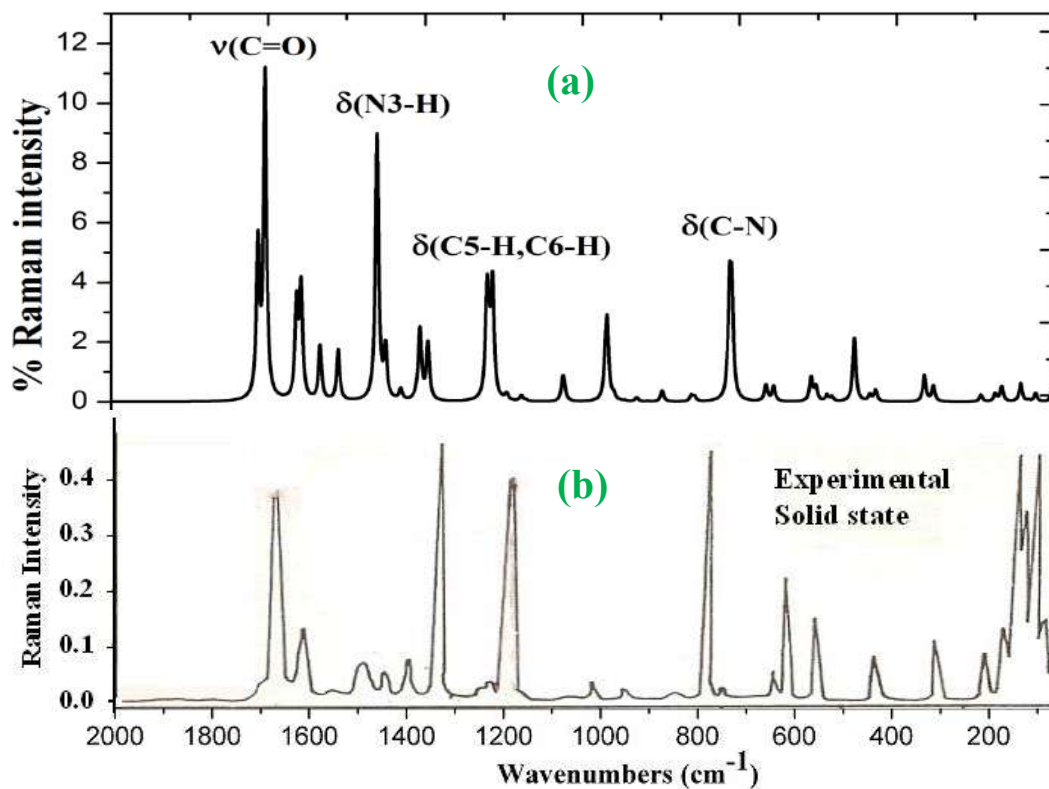


Fig 4. (a) Theoretical scaled Raman spectra in the 2000-50 cm^{-1} range of 2-TU. (b) Experimental Raman spectra in the solid state [19].

Table 2. Characteristic wavenumbers (cm^{-1}) of uracil and 2-TU by using the B3LYP/6-311++G(3df, pd) level and experimental ones.

| Modes | 2TU | | Uracil | |
|-----------------------|---------------------|-------------------|---------------------|-------------------|
| | scaled ^a | Exp. ^b | scaled ^a | Exp. ^b |
| $\nu(\text{N1-H})$ | 3500 | 3457 | 3496 | 3484.3 |
| $\nu(\text{N3-H})$ | 3465 | 3415 | 3454 | 3434.5 |
| $\nu(\text{C2=O/S})$ | 1149 | 1148 | 1745 | 1757.5 |
| $\nu(\text{C4=O})$ | 1738 | 1738 | 1713 | 1741 |
| $\nu(\text{C=C})$ | 1626 | 1634 | 1622 | 1644 |
| $\delta(\text{N1-H})$ | 1527 | 1534 | 1457 | 1472 |
| $\delta(\text{N3-H})$ | 1350 | 1363 | 1385 | 1388.7 |

5 Summary and Conclusions

The important findings of the present study are following:

- (1) Compared to uracil, the sulfur atom in 2-TU results mainly in a significant change of the bond-length at the substitution site: $\text{S=C} \sim 1.66 \text{ \AA}$, as compared to $\text{C=O} \sim 1.22 \text{ \AA}$, Table 1. This fact leads to a slightly reduction in the neighboring bond lengths N1-C2 and N3-C2 , but the N-H and C-H bonds are little affected.

- (2) The greatest impact of the 2-thio substitution is on the H-bond network. This is because the oxygen atom is more electronegative than the sulphur, and thus it creates stronger intermolecular H-bonds. The sulphur atom is a weaker Lewis base than the oxygen analogue, and it is a worse acceptor of H-bonds.
- (3) The thio substitution increases the polarizability of the nucleobases by a factor nearly of two.
- (4) The IR spectrum of 2-TU was simulated in the isolated state (monomer form), Figs 2-3, and it was compared with that reported in matrix isolation. An excellent agreement between the scaled value and the experimental IR spectrum [14] was obtained.
- (5) The calculated Raman spectrum was compared to the experimental ones in the solid state. In general a good correspondence was found between these spectra, Fig 4.
- (7) The replacement of an oxygen atom by sulphur leads to a shift of the experimental $\nu(\text{N-H})$ bands to lower wavenumbers, 27 cm^{-1} for the N1-H mode and 20 cm^{-1} for N3-H, Table 2. The effect of sulphur substitution on $\nu(\text{N3-H})$ wavenumber and intensity reflects changes in proton abilities of this group as well as the hydrogen bonding in which they participate.
- (8) The stretching and bending vibrations of the N1-H group appear at higher wavenumbers than the N3-H group, while in the out-of-plane vibrations the order is reverse. The $\nu(\text{C}=\text{C})$ is little sensitive to sulphur substitution.
- (9) The strong band appearing at 1738 cm^{-1} is identified as $\nu(\text{C4}=\text{O})$ in good accordance with our predictions. The $\nu(\text{C}=\text{S})$ mode appears as a relatively strong band at 1148 cm^{-1} and coupled with the vibrations of other groups as in the case of the $\text{C4}=\text{O}$ stretch. This is expected to affect the strength of hydrogen bonding in which they participate, particularly that formed by the biologically significant N3-H group. The IR intensity of $\nu(\text{C2}=\text{O})$ mode decreases by a factor of ca. 5, when the oxygen atom is replaced by sulphur. The frequency of the in-plane deformation mode ($\text{C}=\text{S}$) shifts considerably, Fig 2.

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