

P-016: Molecular structure and vibrational spectra of 2-thiouracil: A comparison with uracil

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The effect of Uracil on the germination and growth of some leguminous plants has been studied by Turan and Konuk [1]. Also, the effect of uracil and 2-thiouracil (2TU)(Fig. 1) on flower initiation in rice and wheat plants grown under aseptic conditions has also been first studied by Jun Inouye and Jun-Ichiro [2]. It was found that uracil alone had a slight accelerating effect on flowering. It possesses several important biological properties, such as an anticarcinogenic agent, antifungal, antiprotozoal and antiviral activity [3]. To understand biochemically the mode of inhibitory or malforming actions of uracil and 2TU 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 2TU using vibrational spectroscopy as a technique.

The calculations were carried out by using several Density Functional methods (DFT), especially the B3LYP. This method appears implemented in the Gaussian09 program package [4]. The experimental IR spectra of 2TU in N₂ matrices [5], in Ar matrices [6] and in KBr [7], as well as the Raman spectra of polycrystalline samples [7] have been previously reported. It has been studied by us from the structural and spectroscopic point of view using DFT methods [8,9].

Compared to uracil, the sulfur atom in 2TU results mainly in a significant change of the bond-length at the substitution site: S=C ~1.66 Å, as compared to C=O ~1.22 Å, Table 1. This fact leads to a slight reduction in the neighboring bond lengths N1-C2 and N3-C2, with little influence on the N-H and C-H bonds. However, the great 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. The thio substitution also increases the polarizability of the nucleobases by a factor nearly of two.

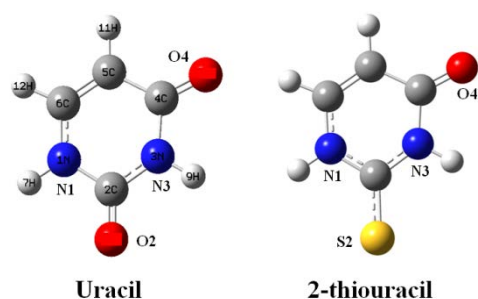


Fig 1. Structures of uracil and 2-thiouracil

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

Bond lengths	2TU	uracil	Bond angles	2TU	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-C4=O	120.0	120.3

An excellent concordance between the scaled value by two DFT methods and the experimental IR spectrum in Ar matrix [6] is obtained, Fig.2. It is noted that 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. 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 $\nu(\text{C=C})$ is little sensitive to sulphur substitution.

The strong band appearing at 1738 cm^{-1} is identified as C4=O stretching mode which is in good accordance with our predictions. The $\nu(\text{C=S})$ mode appears as a relatively strong band at 1148 cm^{-1} and is coupled with the vibrations of other groups as in the case of the C4=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 $\nu(\text{C2=O})$ mode decreases by a factor of ca. 5 when the oxygen atom is replaced by sulphur. The frequency of the in-plane deformation mode $\delta(\text{C=S})$ is shifted considerably, by ca. 100 cm^{-1} .

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

Modes	2TU		uracil	
	scaled ^a	Exp. ^b	scaled ^a	Exp. ^c
$\nu(\text{N1-H})$	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

^aWith scale equation: $\nu^{\text{scaled}} = 31.9 + 0.9512 \cdot \nu^{\text{calc}}$ [10].

^bExperimental IR values in Ar matrix [6].

^c Experimental in Ar matrix [11].

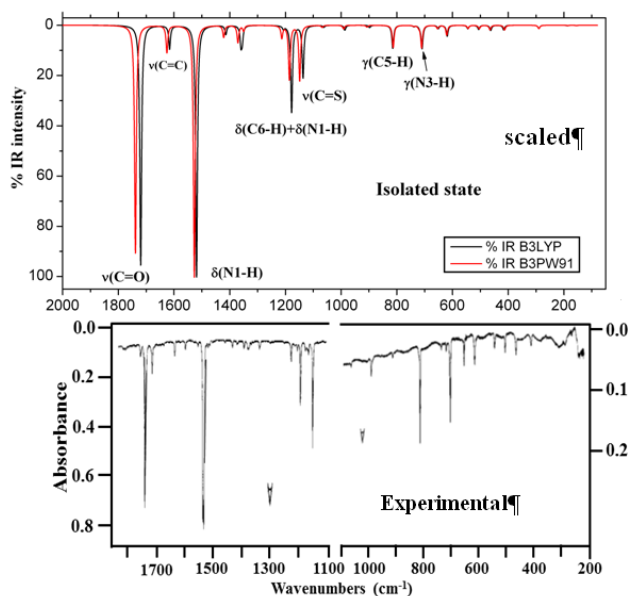


Fig. 2. Scaled and experimental IR spectrum of 2TU

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