# P-014: Molecular structure and vibrational spectra of 5-nitrouracil: A comparision with uracil

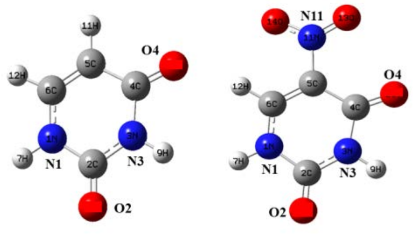
Alcolea M. Palafox[1], Vinod K. Rastogi[2], Manoj Kumar[2], Surendra Pratap Singh[3]

*[1]Departamento de Química-Física. Facultad de C. Químicas. Universidad Complutense. Madrid - 28040, Spain, E-mail: alcolea@ucm.es*
*[2]Indian Spectroscopy Society, KC 68/1, Old Kavinagar, Ghaziabad-201 002, India, e-mail: v_krastogi@rediffmail.com*
*[3]Department of Physics, Dr B R Ambedkar Govt Degree College, Mainpuri, India*

The nitro radical is one of the strongest electron-accepting groups in the aromatic molecules. The first thoroughly studied aromatic nitro compound has been 5-Nitrouracil (5-NU, Fig. 1) discovered by Jerphagnon et al. [1] in 1971. 5-NU is currently of prime interest to the non-linear optical community [2] and to the biological and pharmaceutical sciences [3-5]. It is also one of the few substituted pyrimidines, reported to be active as chemotherapeutic and mutagenic agents [3,4], and it is also used in Plant Growth. The effects of uracil and its analogue 5-nitrouracil on growth and flowering of tomato have been studied and it was found that the treatments with uracil and 5-nitrouracil significantly increased the plant height and the fresh and dry weights of the shoot [6]. In order to understand how uracil and its substituted derivative 5-NU affect the growth of plants, we investigate their molecular structures and some molecular properties, including the effect of $NO_2$ group on the spectra and structure of uracil.

Table 1. Calculated bond lengths and bond angles of uracil and 5-NU at the B3LYP/6-31G(d,p) level

| Bond lenghts | 5-NU | uracil | Bond angles | 5-NU | uracil |
|---|---|---|---|---|---|
| N1-C2 | 1.407 | 1.396 | N-C2-N | 112.4 | 112.8 |
| C2-N3 | 1.380 | 1.384 | C-N3-C | 129.8 | 128.3 |
| N3-C4 | 1.420 | 1.414 | N-C4-C | 111.4 | 113.4 |
| C4-C5 | 1.474 | 1.460 | C-C5=C | 120.7 | 119.9 |
| C5=C6 | 1.360 | 1.350 | C2-N1-H | 115.1 | 114.8 |
| N1-C6 | 1.354 | 1.375 | C2-N3-H | 115.5 | 115.5 |
| C2=O | 1.212 | 1.217 | N1-C2=O | 122.1 | 122.7 |
| C4=O | 1.211 | 1.219 | N3-C4=O | 119.7 | 120.3 |



**Uracil** **5-nitrouracil**

Fig 1. Structures of Uracil and 5-nitrouracil

Although the cyclic structure of 5-NU is considered nonaromatic, however, some interactions are expected to occur between the $\pi$ electrons of the C=C double bond and the nonbonding electrons of the out-of-plane $p_z$ orbital of the $sp^2$ hybridized nitrogen atoms belonging to the N-H groups. The nitro group may also interact with the electrons of the uracil ring. This $NO_2$

group appears remarkably rotated, -27.7° by MP2 theoretical method. It is due to the repulsion between the oxygen atoms of $NO_2$ group that leads to a lengthening of the C4-C5 and C5-N bonds and opening of the C4-C5-N angle. This fact also produces a slight shortening of C2=O and C4=O bonds (Table 1) and the low negative charge on their oxygen atoms (in O2 −0.469*e* vs −0.619*e* in uracil, and in O4 −0.443*e* vs −0.586*e* in uracil molecule) that leads to a lower reactivity of this molecule through these oxygen atoms, i.e. 5-NU can worse H-bonded to the complementary base pair in the RNA formation and it can be one of the reasons of the chemotherapeutic plant growth activity of this molecule. The lower positive charge (ca. 0.15*e*) on the amino hydrogen H9(N3) in 5-NU than in uracil molecule also contributes to this fact.

One of the goal of the present investigation is to compare the spectra of 5-NU with that of uracil, and to identify and correct the assignments of various normal modes. The calculations were carried out by using the B3LYP/6-311++G(3df,pd) level implemented in the Gaussian 09 program package [7], Table 2 and Fig. 2.

Table 2. Characterstic wavenumbers ($cm^{-1}$) of uracil and 5-nitrouracil.

| Modes | 5-NU | | uracil | |
|---|---|---|---|---|
| | scaled[a] | Exp.[b] | scaled[a] | Exp.[c] |
| $\nu$(N1-H) | 3478 | 3456 | 3496 | 3484.3 |
| $\nu$(N3-H) | 3446 | 3419 | 3454 | 3434.5 |
| $\nu$(C2=O) | 1762 | 1773 | 1745 | 1757.5 |
| $\nu$(C4=O) | 1744 | 1752 | 1713 | 1741 |
| $\nu$(C=C) | 1614 | 1640 | 1622 | 1644 |
| $\delta$(N1-H) | 1466 | 1475 | 1457 | 1472 |
| $\delta$(N3-H) | 1379 | 1393 | 1385 | 1388.7 |

[a] With scale equation: $\nu^{scaled} = 31.9 + 0.9512\cdot\nu^{calc}$ [8].

[b] Experimental IR values in Ar matrix [9].

[c] Experimental in Ar matrix [10].

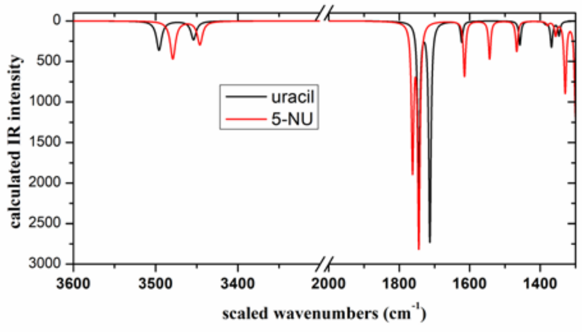


Fig. 2. Scaled IR spectrum of uracil and 5-nitrouracil.

Compared to uracil, the nitro group leads to a red-shift of 19 $cm^{-1}$ in the $\nu$(N1-H) band [11], and 8 $cm^{-1}$ for $\nu$(N3-H). The slightly larger shift in N1-H stretch than in N3-H is in accordance to the larger shortening in N1-H than in N3-H bond. The bending vibrations $\delta$(N1-H) appear at higher wavenumbers than $\delta$(N3-H), while in the out-of-plane vibrations the order is reverse.

The carbonyl stretching motions couple significantly with the N-H bending motions, as observed previously in other uracil derivatives [12-14]. The C2=O stretching (mode 26 [11]) is predicted at 1769 cm$^{-1}$, in excellent accordance to the experimental IR band at 1773 cm$^{-1}$. It is calculated with very strong IR intensity, the second highest of the spectrum. The C4=O stretching (mode 25) is predicted at 1765 cm$^{-1}$ with the highest IR intensity, in accordance with the experimental band with the strongest intensity at 1752 cm$^{-1}$. The C5=C6 stretching (mode 24) is predicted at 1630 cm$^{1}$ in good accordance to the experimental band at 1640 cm$^{-1}$. This mode is assigned in uracil molecule to the IR band in Ar matrix at 1644 cm$^{-1}$, which confirms our assignment and it indicates the weak effect of the -NO$_2$ substituent on the C=C stretching band. According to our calculations, other substituents in the 5th position of the uracil ring also slightly affect the frequency of this mode.

**References**

[1] Jerphagnon, J., 1971: IEEE J. Quantum Electron, **QE 7**, 42.
[2] Gopalan, R.S., Kulkarni, G.U., and C.N.R. Rao, 2000: Chem. Phys. Chem, **1**, 127.
[3] Singh, U.P., Singh, B.N., Sastry, S., and A.K. Ghose, 1995: Cryst. Res. Techn, **30**, K13.
[4] Li, X., Zhu, B., Gao, X. et al., 2017: Pest Management Sci, **73,** 1402.
[5] Kita, T., Takahashi, H., and Y. Hashimoto, 2001: Bio. Pharm. Bull., 860.
[6] Mathur, S. N., and R. A. Sharma, 1968: Physiology Plantarum, **21**, 911.
[7] Frisch, M.J. et al, 2009: Gaussian 09, Revision D.01, Gaussian, Inc., Wallingford CT.
[8] Alcolea Palafox, M., and V.K. Rastogi, 2011: Asian J. Phys, **20**, 103.
[9] Stepan'yan, S.G., Radchenko, Y.D., Sheina, G.G., and Y.P. Blagoi, 1989: Biophys, **34**, 814.
[10] Alcolea Palafox, MIza, N., and M. Gil, 2002: J. Mol. Struct. (Theochem), **585**, 69.
[11] Kattan, D., Palafox, M.A., Rathor, S.K., and V.K. Rastogi, 2016: J. Mol. Struct., **1106**, 300.
[12] Palafox, M.A., Nielsen, O.F., Lang, K., and V.K. Rastogi, 2004: Asian Chem. Lett, **8**, 81.
[13] Rastogi, V.K., Palafox, M.A., and L. Mittal, et al, 2007: J. Raman Spectrosc, **38**, 1227.
[14] Palafox, M.A., Rastogi, V.K., and H. Kumar, et al., 2011: Spectrosc. Letts, **44**, 300.