

GEOMETRY AND VIBRATIONAL WAVENUMBERS OF BIOMOLECULE: 5-iodouracil

M Alcolea Palafox¹, V K Rastogi^{2*}, Piyush Garg² and Rekha Sharma³

¹Departamento de Quimica- Fisica I. Facultad de Ciencias Quimicas ,Universidad Complutense, Madrid 280 040. Spain

²Department of Physics, CCS University, Meerut , India 250 004

³Department of Physics, Meerut College, Meerut, India 250 001

Keywords : FTIR, Raman, 5-iodouracil, Geometry

Abstract: An IR and Raman study of 5-iodouracil(5-IU) was carried out . Semiempirical and ab initio quantum chemical calculations were performed to support the assignments of the bands. The geometry structure was determined at several theoretical levels .

5-halogenated uracils have been received special attention for their antitumor, antibacterial and antiviral properties [1]. As part of a project to study their vibrational spectra , the present work board the 5-IU. Although the FTIR and Raman spectra of 5-IU have been previously studied, some doubts appear in its assignment, which were clarified with the help of quantum chemical calculations.

The HF method was used ,together with DFT calculations at B3LYP level . For the iodine atom the largest standard basis set available in the most common chemical packages , like GAUSSIAN 98 [2], is the 3-21 G^{**}. Due to this small basis set , semiempirical values are of similar reliability than HF and B3LYP results , and thus they were performed to support the results . The AM1 and SAM1 semiempirical methods were selected as more appropriate.

Several selected optimized geometrical parameters are collected in Table 1. The last column shows the only x-ray data [3] reported, but due to packing forces and strong intermolecular H-bonds in the crystal , their values differ remarkably from our theoretical ones ;e.g the length for C2=O and C4=O bonds are different . The values determined by AM1 are in general smaller ~ 0.005 Å , than those by SAM1 , but higher than HF and B3LYP , which appear closest to the experimental data . Small differences ~2-4° are observed in the angles with the distinct methods used , being close between HF and B3LYP . The largest discrepancies correspond to the N-C-N and C-N-C angles.

TABLE 1. Optimized geometrical parameters . bond lengths in Å , angles in degrees

Parameters	AM1	SAM1	HF/3-21G ^{**}	B3LYP/3-21G ^{**}	x-ray
C5-I	2.008	2.132	2.1044	2.1132	2.11
C4-C5	1.472	1.488	1.4636	1.4650	1.44
C5=C6	1.366	1.371	1.3296	1.3504	1.32
N1-C2	1.418	1.412	1.3808	1.4048	1.36
N3-C4	1.411	1.415	1.3942	1.4171	1.38
C2=O	1.248	1.268	1.2093	1.2303	1.20
C4=O	1.240	1.255	1.2091	1.2332	1.24
C4-C5-I	120.5	119.1	117.72	116.62	116.4
C4-C5=C6	119.7	121.3	119.62	120.60	122.0
N3-C4-C5	116.2	114.0	113.38	112.67	113.0
N1-C2-N3	117.7	116.0	113.17	112.44	114.9

The vibrational bands computed in the stretching range of 5-IU are shown in Table 2. The last two columns shows the experimental IR and Raman wavenumbers reported in the solid state and in Ar matrix. To correct the theoretical values due to the deficiency of the methods were utilized three scaling procedures [4]. The best results were reached using specific scale factors for each mode determined from the uracil molecule [5], and thus they were included in Table 2. SAM1 leads to the worst scaled wavenumbers and therefore they were omitted in the Table. The large errors obtained by HF in the calculated wavenumbers were remarkably reduced with the scaling. Their values being of similar reliability to B3LYP. The scaling wavenumbers for the $\nu(\text{C-I})$ mode can be only determined with the scaling equation procedures, Table 2, although this procedure remarkably fails for semiempirical methods.

The agreement between scaled and experimental wavenumbers can be considered acceptable. Due to the small basis set used with HF and B3LYP methods, their scaled values are of similar accuracy (even worse) than AM1. HF and B3LYP seem to fail slightly in the scaled values of the $\nu(\text{C6-H})$ and $\nu(\text{NCN})$ modes, appearing very accurate by AM1 method.

TABLE 2. Calculated and scaled and experimental wavenumbers (cm^{-1}) in 5-iodouracil

Modes	Calculated AM1	HF	B3LYP	Scaled AM1	HF	B3LYP	Experimental IR	Raman
$\nu(\text{N1-H})$	3458	3977	3707	3473	3477	3478	3470	
$\nu(\text{N3-H})$	3438	3940	3668	3426	3431	3433	3426	
$\nu(\text{C6-H})$	3113	3489	3311	3054	3085	3086	3048	3060
$\nu(\text{C4=O})$	2039	1926	1742	1741	1733	1727	1723	1715
$\nu(\text{C2=O})$	1997	1954	1794	1768	1760	1758	1765	1765
$\nu(\text{C=C})$	1788	1808	1653	1624	1627	1622	1630	1640
$\nu(\text{NCN})$	1526	1500	1343	1412	1389	1373	1420	1410
$\nu(\text{C-I})$	263	260	243		236	260	235	245

The absence of a $\nu(\text{OH})$ band in the $3500\text{--}3700\text{ cm}^{-1}$ range and the appearance of $\nu(\text{C=O})$ modes as strong bands indicate that in the solid state the molecules exist in the keto form. Weak $\text{C6-H}\cdots\text{O=C}$ interatomic interactions in the solid state affect the vibrational wavenumbers of the $\nu(\text{C6-H})$ mode and cause the small discrepancies with the theoretical values. The low wavenumber determined for the $\nu(\text{C-I})$ mode in 5-IU appears as a contradiction with the spectral region observed [6] for this mode ($560 \pm 100\text{ cm}^{-1}$) in other compounds, like $\text{H}_2\text{NC(=O)CH}_2\text{I}$, CH_2I_2 and $\text{HOC(=O)CH}_2\text{I}$. It can be tentatively explained by the fact that when a halogen atom is directly attached to a ring, the C-X stretch vibration tends to interact with the ring vibrations and can lead to a remarkable reduction in its wavenumber, as in 5-IU.

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