

Vibrational Raman spectra of some substituted uracils

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Abstract. Vibrational assignments of the frequencies of 6-azauracil, 5-fluorouracil, 5-bromouracil and 6-azathymine have been made with the help of their Raman and infrared spectra. Raman spectra of these molecules were recorded in the range $75\text{--}4000\text{ cm}^{-1}$. The near infrared spectra of these molecules were also recorded in the $400\text{--}4000\text{ cm}^{-1}$ range using the nujol mull technique. The vibrational frequencies have been noted and the vibrational assignments have been made on the basis of the group frequency approach. The assignments have also been facilitated by comparison with the frequencies of similar molecules.

Keywords. Vibrational Raman spectra; substituted uracils; group frequency approach.

1. Introduction

N-heterocyclic molecules are of great biological importance because they play a significant role in the structural problems of nucleic acids. These molecules are obtained by substituting an N atom for the CH group in aromatic cyclic compounds. Pyrimidine and substituted pyrimidines are important N-heterocyclic molecules. Some of the substituted pyrimidines have been studied spectroscopically. Austin (1934), Platt (1950), Marshall and Walker (1951), Brown *et al* (1955), and Mason (1959) have studied the absorption spectra of different pyrimidine substituents. The vibrational spectra of uracil (Lord and Thomas 1967; Susi and Ard 1971; Nishimura *et al* 1981), cytosine (Susi and Ard 1974), 6-azauracil and 5-fluorouracil (Rai 1983), dihydroxypyrimidine (Srivastava *et al* 1984) and dimethylpyrimidines (Srivastava *et al* 1985) have been studied in great detail. The present communication reports the vibrational spectra of 6-azauracil, 5-fluorouracil, 5-bromouracil and 6-azathymine molecules.

2. Experimental

The samples of these molecules were procured from Sigma Chemical Company and used without further purification. The infrared absorption spectra of the chemicals were recorded on a CZ Specord IR 75 double beam spectrophotometer using the nujol mull technique in the region $400\text{--}4000\text{ cm}^{-1}$. Raman spectra of these molecules were recorded on a Jobin-Yvon spectrophotometer coupled with an argon ion source (Coherent Innova 70 laser source) in the range $75\text{--}4000\text{ cm}^{-1}$ (figures 1–4). A correlation of the fundamental frequencies (cm^{-1}) of the four molecules along with their parent molecule uracil (Susi and Ard 1971) is given in table 1.

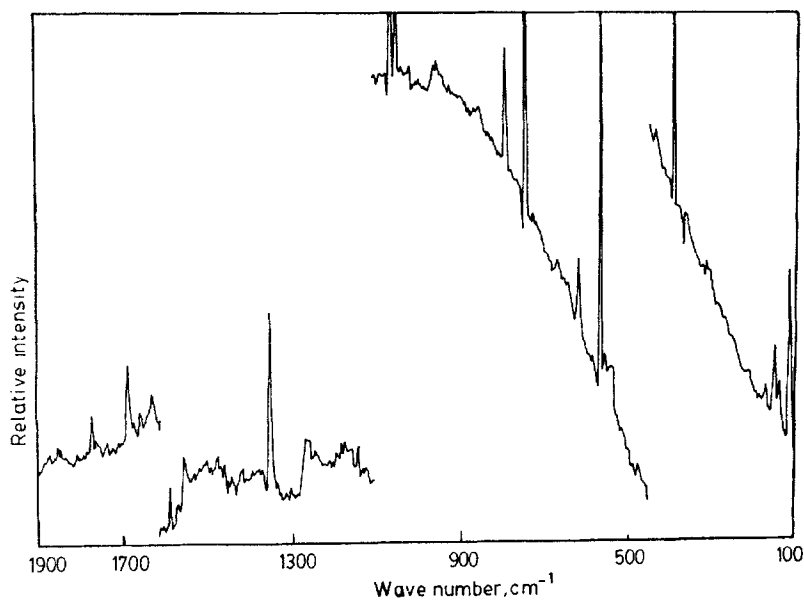


Figure 1. Raman spectrum of 5-bromouracil.

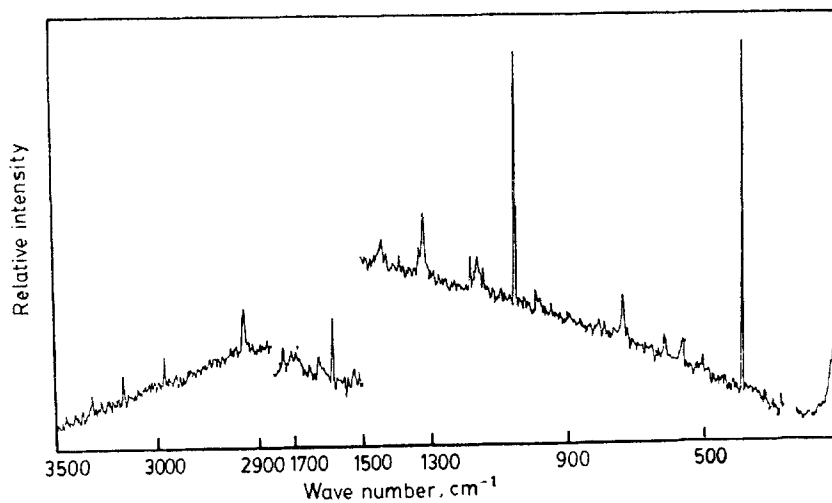


Figure 2. Raman spectrum of 6-azathymine.

3. Discussion

The molecules 6-azauracil, 5-fluorouracil, 5-bromouracil and 6-azathymine have only one element of symmetry each i.e. a plane of reflection. Thus, they belong to the C_s point group. They have only a' (totally symmetric vibrations and a'' (non-totally symmetric vibrations).

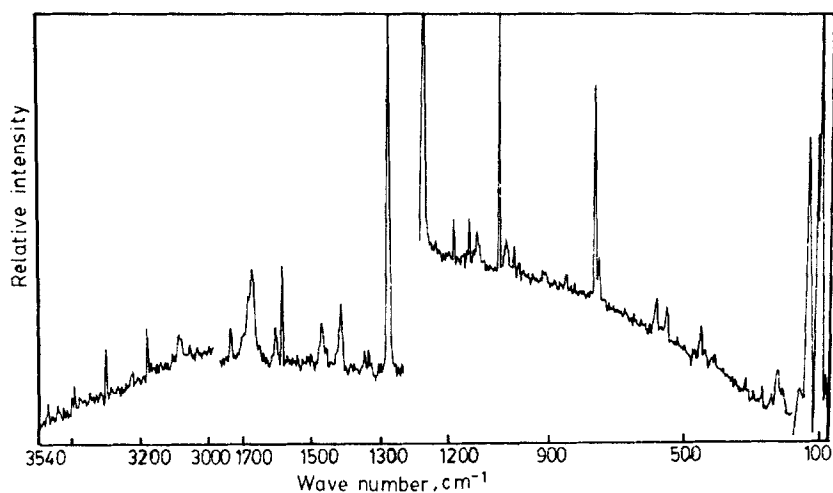


Figure 3. Raman spectrum of 6-azauracil.

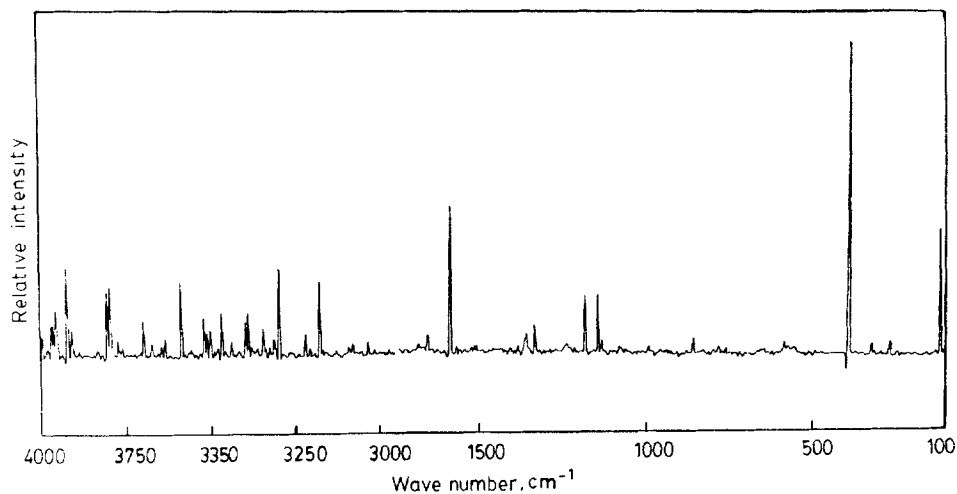


Figure 4. Raman spectrum of 5-fluorouracil.

The vibrational assignment of the observed frequencies of the molecules were made as per Lord and Thomas (1967) Susi and Ard (1971, 1974), Sanyal *et al* (1977), Durig and Little (1981) and Rai (1983). The assignments are based mainly on the concept of the characteristic frequencies associated with vibrations of groups of atomic nuclei with a molecule.

Investigations of the infrared spectra of compounds 6-azauracil, 5-fluorouracil, 5-bromouracil and 6-azathymine show very strong bands around 1500 cm^{-1} . These bands are due to the C=O, C=N, C=C and N=N stretching vibrations. The bands in the region $1500\text{--}1200\text{ cm}^{-1}$ correspond to various types of stretching motions involving C-C, C-N and N-N single bonds.

Table 1. Correlation of the fundamental vibrations (cm^{-1}) of uracil, 5-fluorouracil, 5-bromouracil, 6-azauracil and 6-azathymine.

Uracil	5-Fluoro- uracil	5-Bromo- uracil	6-Aza- uracil	6-Azathy- mine	Assignments
398	405	390	400	390	γ C=O
435	450	425	450	464	γ ring
550	—	—	540	535	δ ring
565	550	560	550	566	δ C=O
600	620	580	585	580	δ ring
760	750	750	740	737	γ CH
781	760	783	760	780	δ ring
822	—	—	—	—	γ CH
851	880	872	850	850	γ NH
993	950	1008	990	950	δ ring
1003	1000	1060	1010	1010	ν ring
1099	—	—	1105	1120	ν ring
1238	1260	1255	1260	1205	ν ring
1390	1380	1350	1370	—	δ CH
1417	1430	1427	1420	1410	δ NH
1453	1460	1447	1460	1450	ν ring
1508	1500	1496	1525	1525	δ NH
1611	—	—	1605	1590	ν C=N
1675	1660	1675	1650	1675	ν C=O
1760	1720	1770	1725	1720	ν C=O
3080	1250	545	3085	2872	ν CX
3100	3120	3058	3085	2965	ν CH
3160	3175	3098	3160	3140	ν NH
3160	3420	3178	3380	3175	ν NH

The molecule 6-azathymine possesses a methyl group. The infrared peaks can be picked up very easily as due to various methyl group vibrations. Bands at 2872 and 2965 cm^{-1} are due to symmetric and antisymmetric methyl C–H stretching vibrations, respectively. The bands at 1350 and 1450 cm^{-1} are due to CH_3 deformation modes. The CH_3 rocking mode appears at 950 cm^{-1} .

C–H and N–H stretching vibrations appear around 3000 cm^{-1} . Except for 6-azathymine, the three other molecules, viz. 6-azauracil, 5-fluorouracil and 5-bromouracil, have one C–H stretching vibration each. Similarly, all the four molecules possess two frequencies around 3200 cm^{-1} due to N–H stretching vibrations. In addition to these assignments, the other frequencies are also assigned and are listed in table 1.

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