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Vibrational spectra of some molecules related to nucleic acids

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The infrared absorption spectra of 5 bromo-, 5 methyl- and 4(6) amino-Uracil, recorded in the region (350-4000 cm^{-1}) has been reported in this paper. Observed bands have been analysed in terms of fundamentals and their combinations in each molecule. Probable modes of vibration of the fundamentals have also been discussed.

1. INTRODUCTION

N-hetrocyclic compounds Adenine, Guanine, Cytosine, Thymine and Uracil are of great biological interest because they are basic constituents of DNA and RNA. In addition, DNA normally contains uncommon nucleotides usually in very small amount. 5-bromo-Uracil (1974) is one of the well known uncommon nucleotides base. As regards the spectroscopic studies of various nucleic acid constituents, the infrared (1961, 1964) and Raman (1967) spectra has been studied in detail. Inspite of the high complexity and low symmetry of such molecules, a normal coordinate analysis for Uracil is also available (1971) in literature Very little spectroscopic work has been done on the derivatives (1964) of N-hetrocyclic molecules. As a part of our programme on N-hetrocyclic molecules, the infrared absorption spectra 5-bromo, 5-methyl- and 4(6)- amino, -uracil was studied and is reported in this paper. In the absence of the Raman and vapour phase infrared spectra, the analysis of the fundamentals and their assignments to the probable modes of vibration is mainly based on the group frequency approach taking into account the spectra of molecules having similar structure.

2. EXPERIMENTAL

Pure chemicals obtained from M/S A. G. Fluka Switzerland were used without further purification. The infrared absorption spectra have been recorded on Perkin Elmer spectrophotometer in KBr phase. Observed bands have been caliberated by drawing an error graph. The accuracy for bands in the region (350-2000 cm^{-1}) is ± 10 cm^{-1} whereas for the region (2000-4000) it

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is upto ± 20 cm^{-1}. The position of the bands in cm^{-1} alongwith their intensities, their analysis and modal assignment is presented in table 1-3 for the three molecules, respectively. Table 4 contains the correlation of the fundamental vibrational frequencies associated with the double bonds in case of substituted Uracils.

Table 1. Analysis of the Infrared Spectra of 5-Bromo-Uracil

Position of the band in cm^{-1}	Assignment	Position of the band in cm^{-1}	Assignment	Position of the band in cm^{-1}	Assignment
3208 (w)	2×1609	1784 (w)	1235+545	872 (vsb)	γ(NH)
3178 (w)	ν NH	1721 (s)		783 (s)	ν β Ring
3098 (vs)	ν NH	1712 (s)	ν(2C=0)	763 (s)	γ(CH)
3058 (ms)	ν CH	1705 (s)		714 (ms)	—
2957 (wb)	1705+1235	1690 (s)	--	709 (m)	--
2927 (wb)	1294+1628	1681 (s)	ν(4C=0)	680 (ms)	—
2907 (m)	1676+1235	1676 (vs)		675 (ms)	--
2856 (m)	1628+1235	1628 (ms)	ν(C=C)	660 (vs)	—
2806 (ms)	—	1609 (m)	β(NH)	620 (m)	β-Ring
2604 (vw)	1609+1008	1550 (w)	783+763	560 (vs)	βC=0 in
2570 (vw)	1705+872	1496 (m)	872+620		Phase
2511 (w)	1628+872	1464 (w)	1064+390	545 (w)	ν(C-Br)
2481 (vw)	1609+872	1447 (s)	νRing	455 (vs)	—
2454 (ms)	1676+783	1427 (s)	β(NH)	445 (m)	-
2412 (vw)	1628+783	1407 (w)	783+620	435 (m)	-
2304 (vw)	1294+1008	1398 (w)	1008+390	425 (ms)	γ skeletal
2274 (mw)	1705+560	1376 (m)	763+620	390 (w)	βC=0 out
2245 (mw)	1628+620	1348 (ms)	783+560		of Phase
2230 (mw)	1609+620	1324 (mw)	763+560	380 (w)	-
2217 (vw)	1676+545	1315 (mw)	763+545	370 (w)	--
2166 (w)	872+1294	1294 (m)	β(CH)		
2107 (mw)	1235+872	1235 (vs)	ν Ring		
2078 (mw)	1294+783	1185 (vw)	620+560		
1979 (ms)	1427+560	1130 (m)	560×2		
1965 (w)	1427+545	1064 (m)	ν Ring		
1940 (w)	1064+872	1050 (w)	—		
1910 (w)	1294+620	1008 (ms)	ν-β Ring		
1890 (w)	1008+872	945 (w)	390+545		
1818 (m)	1427+390	881 (s)	--		

ν = Stretching, β = planar and γ nonplanar deformation
vs = very strong, s = strong, ms = medium strong, m = medium, w = weak, vw = very weak and b = broad.

Table 2. Analysis of the Infrared Spectra of 5-Methyl-Uracil

Position of the band in cm^{-1}	Assignment	Position of the band in cm^{-1}	Assignment
3672 (w)	2856+819	1388 (vs)	CH_3 sym. deformation
3651 (w)	3058+575	1383 (m)	985+396
3591 (w)	3188+395	1368 (w)	744+625
3470 (m)	—	1249 (vs)	β (CH)
3360 (w)	1690+1671	1220 (s)	ν Ring
3230 (w)	2856+370	1210 (sh)	ν (C-CH_3)
3209 (vw)	1614+1590	1030 (s)	ν Ring
3188 (w)	ν NH	985 (s)	ν β Ring
3128 (w)	ν NH	941 (s)	--
3058 (w)	ν CH	852 (vsb)	γ (NH)
2957 (w)	ν (C-H) Aliphatic asym	818 (vs)	γ (NH)
2927 (w)	1671+1249	763 (vs)	ν-β Ring
2896 (w)	1690+1210	749 (vs)	γ (CH)
2876 (sh)	—	744 (vs)	
2856 (w)	ν (C-H) Aliphatic asym.	680 (vs)	—
1989 (m)	1220+763	645 (w)	—
1863 (w)	1462+395	635 (w)	—
1805 (w)	985+818	625 (w)	β Rong
1738 (vsb)	--	757 (vs)	β C=0 in Phase
1690 (s)	ν (2C=0)	490 (vs)	—
1676 (vs)	ν (4C=0)	440 (s)	γ skeletal
1671 (vs)		430 (sh)	
1614 (w)	ν (C=C)	410 (m)	—
1590 (w)	β (NH)	395 (ms)	β C=0 out of phase
1486 (ms)	2×744	385 (ms)	—
1481 (sh)	—	380 (ms)	—
1462 (s)	ν Ring	370 (ms)	β (C-CH_3)
1452 (vs)	CH_3 asym. deform	365 (m)	—
1432 (s)	β (NH)	355 (m)	—

Symbols used in this table are the same as used in Table 1.

Table 3. Analysis of the Infrared Spectra of 4(6) Amino-Uracil

Position of the band in cm^{-1}	Assignment	Position of the band in cm^{-1}	Assignment	Position of the band in cm^{-1}	Assignment
3955 (m)	3430+530	1989 (ms)	1604+385	1442 (w)	882+560
3935 (m)	3178+763	1975 (w)	1599+385	1432 (w)	1046+385
3915 (m)	3107+808	1950 (m)	1427+530	1427 (w)	β NH
3895 (m)	2107+783	1930 (m)	1294+635	1398 (s)	—
3885 (ms)	3066+808	1925 (ms)	1289+635	1304 (m)	783+530
3864 (m)	3107+763	1890 (m)	1457+430	1294 (ms)	β (C-N) group
3844 (m)	3066+783	1864 (w)	986+882	1289 (m)	β (CH)
3834 (m)	3178+560	1849 (w)	1289+560	1240 (s)	ν Ring
3814 (w)	3178+635	1844 (ms)	1457+385	1046 (w)	NH_2 Twisting
3794 (w)	3400+395	1832 (w)	1025+808	1025 (w)	ν Ring
3773 (m)	3400+385	1827 (ms)	1046+783	986 (w)	ν-β Ring
3763 (m)	—	1822 (ms)	1427+395	882 (mb)	γ (NH)
3733 (m)	3178+560	1809 (w)	1025+783	808 (w)	γ (NH)
3703 (m)	3178+530	1800 (w)	1240+560	783 (ms)	ν-β Ring
3693 (m)	3066+635	1791 (w)	986+808	763 (w)	γ (CH)
3672 (m)	3107+560	1781 (w)	1025+763	724 (w)	—
3652 (m)	3107+530	1777 (w)	1240+530	690 (m)	—
3632 (m)	3066+560	1758 (m)	2×882	680 (ms)	—
3612 (m)	2178+430	1743 (m)	986+763	635 (m)	β Ring
3592 (m)	3066+530	1724 (w)	1294+430	570 (sh)	
3561 (w)	3178+385	1724 (w)	1289+430	560 (s)	β C=0 in phase
3430 (msb)	ν (NH) asym. gr.	1690 (w)	ν (2C=0)	530 (ms)	γ NH_2
3400 (mb)	ν (NH) sym. gr.	1662 (ms)	ν (6C—0)	485 (ms)	—
3178 (msb)	ν NH	1622 (ms)	ν (C=C)	470 (ms)	—
3107 (ms)	ν NH	1604 (s)	β NH_2	455 (ms)	—
3066 (w)	ν CH	1599 (w)	β NH	450 (ms)	—
2926 (ms)	1690+1240	1579 (w)	1046+530	430 (vs)	γ skeletal
2906 (sh)	—	1536 (w)	986+560	410 (vs)	—
2866 (sh)	—	1528 (w)	2×763	395 (vs)	β C=0 out of phase
2856 (ms)	1622+1240	1517 (w)	882+635		
2462 (ms)	1652+808	1467 (mb)	1046+430	380 (vs)	β (C-NH_2)
2393 (w)	1604+783	1457 (m)	ν Ring	365 (vs)	—
				350 (ms)	—

Symbols used in this table are the same as used in Table 1.

Table 4. Correlation of the Raman and Infrared Frequencies of the Uracil derivatives in the double bond region.** (All values are in cm^{-1}).

1,3-Dimethyl uracil[×]		1-Methyl uracil[+]		5-Bromo-uracil[×]	5-Methyl-uracil[×]	4 (6) amino-uracil	Assignment
Raman	IR	Raman	IR	IR	IR	IR	
1625 (m)	1625 (w)	1625 (m)	1620 (m)	1628 (ms)	1614 (w)	1622 (ms)	ν (C=C)
1663 (vs)	1663 (vs)*	1655 (vs)	1660 (vs)	1678 (vs)*	1673 (vs)*	1662 (ms)	ν (4C=0)
1700 (s)	1699 (s)*	1680 (vw)	1690 (s)	1708 (s)*	1690 (s)	1690 (w)	ν (2C=0)

* Centre of doublet.

** Symbols used in this table are similar to Table 1

\+ R.C. Lord and G.J Thomas (JR), Spectrochim acta **23A** (1967), 2551.

× Present work

3. DISCUSSION

From the structural point of view, the molecules of the present study belongs to C point group. Under this point group only two types of vibrations a′ (planar) and a″ (non-planar), which are active both in Raman and infrared, are permissible. In addition to these, vibrations associated with different groups will also appear.

(*i*) *3500-2800 cm^{-1} CH and NH Stretching Modes.*

All the three molecule of the present study containing only one hydrogen atom attached to the carbon atom of the ring involves a C-H valence oscillation which has been assigned at 3058, 3058 and 3066 cm^{-1} in the three molecules respectively. This assignment is in accordance to that proposed for Uracil (1971) and its derivatives (1967).

Two molecules, 5-methyl- and 4(6) -amino -Uracil contains one CH_3 and one NH_2 group attached to the carbon atom of the ring at 5 and 4(6) positions respectively. It is, therefore, expected to have the vibrations associated with these groups. The NH_2 vibration involves symmetric and asymmetric NH_2 stretchings. It has been suggested by Bellamy (1959) that two bands appear in the region (3300-3500 cm^{-1}) in case of nearly all the primary aromatic amines. Out of the two, the band observed around 3500 cm^{-1} has been assigned to asymmetric and the other appearing around 3400 cm^{-1} to symmetric NH_2 stretching vibration. In case of 4(6) amino-uracil two such bands at 3400 and 3430 cm^{-1} with considerable intensity has been deciphered which will represent the NH_2 symmetric and asymmetric stretching vibration.

Two N-H stretching vibration associated with ring in each molecule is expected to lie in this region also. In the infrared spectra of uracil (1971) a strong band at 3160 cm^{-1} which is in agreement with a weak Raman band at 3130 cm^{-1} has been assigned as N-H stretching vibration. Similar assignments have also been made in the spectra of 1-methyl uracil (1967). In the present study two bands at 3098 and 3178 cm^{-1} in 5-Bromo-, at 3128 and 3188 cm^{-1} in 5-methyl- and at 3107 and 3178 cm^{-1} in 4(6) -amino-, uracil have been identified as N-H stretching vibration The low value of this vibration is considered to be indicative of the strong hydrogen bonding in these compounds (1967).

Fox and Martin (1940) after analysing the spectra of large number of hydrocarbons containing methyl group, found that in all such molecules two bands appearing around 2962 and 2872 cm^{-1} represents the asymmetric and symmetric stretching vibration of the methyl group. In the spectra of 5-methyl-uracil these two vibrations have been assigned at 2957 cm^{-1} and 2856 cm^{-1}. Similar assignments have also been made by the authors in the spectra of 2-amino-4-methyl-pyrimidine and 5-methyl -cytosine (Unpublished Work).

(ii) 1710-1600 cm^{-1}. *Double bond stretching modes*

The neutral form of uracil and its substituted derivatives have three double bonds and their stretching vibrations are expected to give rise to three strong infrared bands in this region. Out of three, two strong bonds at 1678 and 1708 cm^{-1} in 5-Bromo-, at 1673 and 1690 cm^{-1} in 5-methyl- and at 1662 and 1690 cm^{-1} in 4(6) -amino-uracil are assumed to be primarily associated with the two C=O stretching fundamentals. The third vibration at 1628, 1614 and 1622 cm^{-1} in the three molecules respectively have been associated with C=C stretching vibration. Similar assignments are also available for Uracil (1971), 1-methyl- and 1,3-Dimethyl-Uracil (Table 4). In the spectra of 5-Bromo-uracil, the 1678 and 1708 cm^{-1} band and in 5-methyl-uracil the 1673 cm^{-1} band appears to be a closely spaced doublet. This splitting is probably due to crystal field effect.

(iii) 1600-1300 cm^{-1}. *Skeletal mode. CH$_3$ sym and asym. and NH in-plane deformation*

The analysis of the spectra of Uracil, substituted uracil and some of its deutrated analogues shows the presence of two NH in-plane deformation and one ring stretching mode. Bands observed at 1609 and 1427 cm^{-1} in 5-Bromo-, at 1590 and 1427 cm^{-1} in 5-methyl and at 1599 and 1427 cm^{-1} in 4(6)-amino-, uracil have been assigned as NH in-plane bending vibration. The ring stretching vibration has been assigned at 1447, 1462 and 1457 cm^{-1} in the three molecules respectively. These assignments are in close agreement with those made for similar molecules (1967, 1971). In addition to these, two strong bands at 1388 and 1452 cm^{-1} have also been observed in the spectra of 5-methyl-uracil. These vibrations have been associated with the symmetric and asymmetric deformation of the methyl group.

(iv) 1300-700 cm^{-1}. *C-X stretching, skeletal, CH planar and nonplanar and NH nonplanar deformation*

Spectra analysis of uracil and its derivatives by Susi and Ard (1971) reveals the intense bands lying in the region 790-1300 cm^{-1} to skeletal stretching and stretching bending modes and the band lying in the region 750-800 cm^{-1} to NH and CH out of plane deformation modes.

Further the analysis of the spectra of toluene, aniline and their derivatives shows the presence of C-CH$_3$ and C-NH$_2$ stretching vibration lying in this region. On the basis of these data, the bands in the above mentioned region are assigned in each case and they are given in tables 1-3.

Below 700 cm^{-}

In the shorter frequency region assignments could not be done due to non-availability of data. However some of the vibrations have been assigntd on the basis of the data available for similar molecules and also for those aromatic molecules which, contains CH_3 and NH_2 group as substituents.

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