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F.T.-I.R. AND LASER-RAMAN SPECTRA OF CYTOSINE AND CYTIDINE*

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ABSTRACT

Fourier-transform infrared (F.t.-i.r.) and laser-Raman spectra of cytosine and cytidine in the solid state have been recorded and assignments of the frequencies made. Comparison of the observed frequencies for cytosine with those for cytidine permits identification of the bands characteristic of the sugar on the one hand, and of the pyrimidine base on the other.

INTRODUCTION

We have recently discussed[1–3] the Fourier-transform infrared (F.t.-i.r.) and Raman spectra of the two sugars of the nucleic acids, and of adenine, thymine, and their associated nucleosides, adenosine and thymidine. The interpretation of spectral data for constituents of nucleic acids is directed to its use as a basis for analysis of the vibrational spectra of polynucleotides and nucleic acids. Cytosine has been studied by i.r. and Raman spectroscopy[4–9]. Complete assignment of the vibrations observed in the spectra of such biomolecules as cytosine and cytidine is far from easy. However, isotopic substitution[4–9] or normal-coordinate analysis[4,9] help in assigning the most prominent vibrations. All other physical and structural information may be used[1–3] in supporting assignments of frequencies.

Molecular structural information that is "carved in stone" is given by crystallographic data. The crystallography of cytosine (**1**) and its derivatives have been actively studied by X-ray diffraction[10–14]. The hydrogen bonding[15] patterns and the single- or double-bond character[16,17] of the cytidine residue have been deduced from crystallographic data. This kind of information is essential for under-

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standing the shifts in frequencies and intensities of the vibrational spectra of cytosine, especially because of the resonant behavior of the pyrimidine ring. We now interpret the F.t.-i.r. and Raman spectra of cytosine and cytidine with particular reference to the different resonant forms of cytosine and the spectral differences between the sugar (D-ribose) and the base on the one hand, and the complete nucleoside, β-D-ribofuranosylcytosine[18], on the other.

EXPERIMENTAL

Materials and methods. — The F.t.-i.r. and Raman spectra of cytosine and cytidine were recorded by the techniques previously described[2]. The frequency ranges explored were 1700–200 and 3600–2700 cm^{-1}. Cytosine and cytidine were purchased from Sigma (St. Louis, MO) and used without further purification.

RESULTS AND DISCUSSION

A. Cytosine. — The F.t.-i.r. and laser-Raman spectra of cytosine (**1**) in the solid state are shown in Figs. 1 and 2, respectively. Observed frequencies and relative intensities are listed in Table I for F.t.-i.r. between 1800 and 600 cm^{-1} and laser-Raman in the region 1700–200 cm^{-1}. Analysis of the spectra is here conducted by reference to groups of frequencies of the same kind: 1800–1200 cm^{-1} for double bonds and local, symmetrical vibrations, 1200–800 cm^{-1} for out-of-ring vibrations,

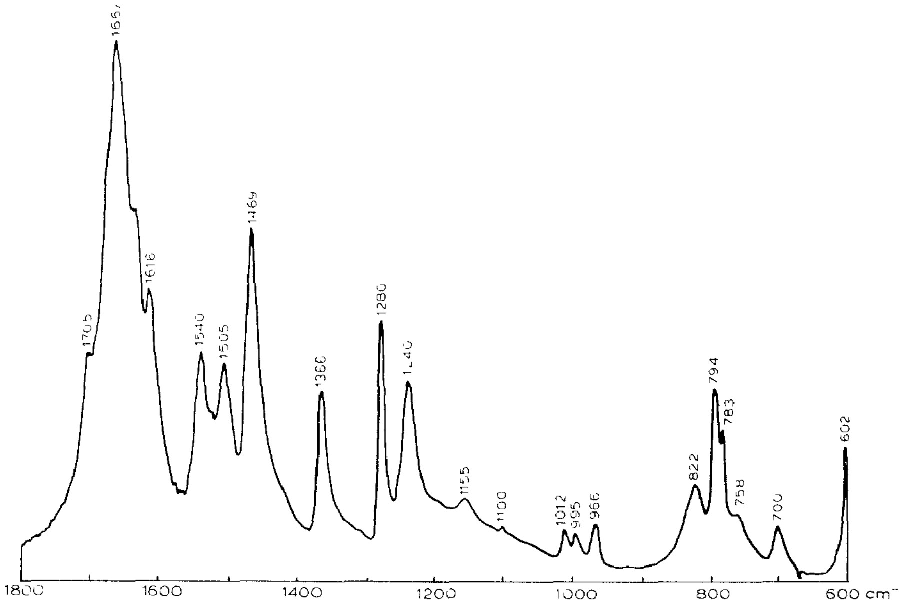


Fig. 1 F t -i r spectrum of cytosine (**1**)

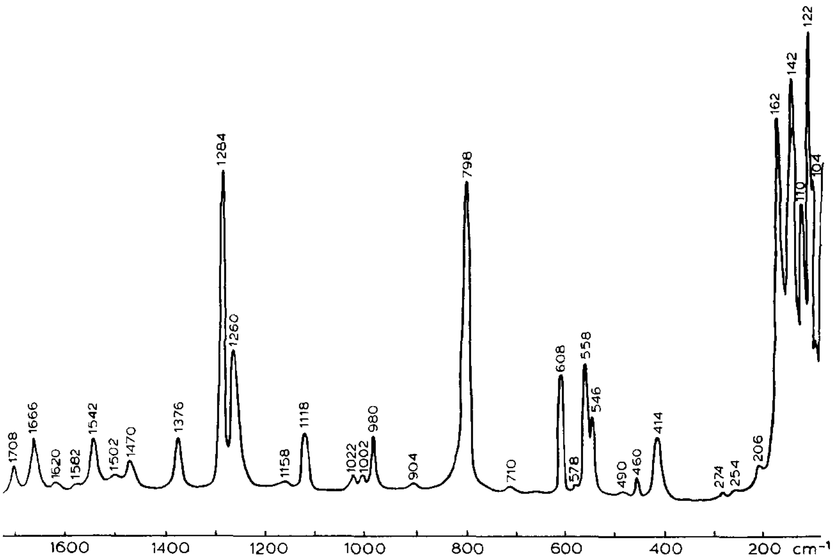


Fig. 2. Laser-Raman spectrum of cytosine (**1**).

and skeletal vibrations below 800 cm^{-1}. The 3600–2700 cm^{-1} region is then discussed.

Analysis of the bands observed. a. The 1800–1200 cm^{-1} region. Comparison of the general profile of the F.t.-i.r. (see Fig. 1) and laser-Raman (see Fig. 2) spectra of cytosine in this frequency region shows numerous intense i.r. absorptions, but only two Raman lines of high intensity, at 1284 and 1260 cm^{-1}. The i.r. spectrum shows a broad band at 1667 cm^{-1} with two shoulders at 1705 and 1616 cm^{-1}. The i.r. absorption at 1705 cm^{-1}, which corresponds to the Raman line at 1708 cm^{-1} (see Fig. 2), may originate from NH_2 bending. This assignment is in good agreement with previous results[4]. An intense band at 1705 cm^{-1} has been observed[5,19] in the i.r. spectrum of calf-thymus DNA, and was assigned to the secondary structure of DNA, with contribution from the A-T and G-C base-pairs. Isotopic substitution by ^{15}N enabled Tsuboi *et al.*[6] to ascertain that the 1705 cm^{-1} absorption originates from $\delta(NH_2)$. However, these authors[6] do not exclude a contribution to the 1705 cm^{-1} vibration by such other deformations as δ(NH) and such stretchings as ν(C-N) and ν(C=O). Theophanides[7] localized $\delta(NH_2)$ in the spectrum of adenine at 1650 cm^{-1}. We[2] assigned the 1675 cm^{-1} i.r. absorption of adenine to $\delta(NH_2)$. The double-bond stretchings ν(C=N), ν(C=C) were found[2] at lower frequencies. The carbonyl region is generally localized around 1700 cm^{-1}. The most intense i.r. band at 1667 cm^{-1} (see Fig. 1) and the corresponding Raman line at 1668 cm^{-1} (see Fig. 2) are assigned ν(C=O). Tsuboi *et al.*[6] attributed a band at 1676 cm^{-1} to the base pair G-C, while Theophanides[7] proposed assignment of the 1657 cm^{-1} band to ν(C-2=O). Susi *et al.*[4] observed an i.r. band at 1662 cm^{-1} and a Raman line at 1653 cm^{-1}, which were assigned to ν(C=O). However, it must

TABLE I

BANDS OBSERVED[a] IN LASER-RAMAN AND F.T.-I.R. SPECTRA OF CYTOSINE (**1**)

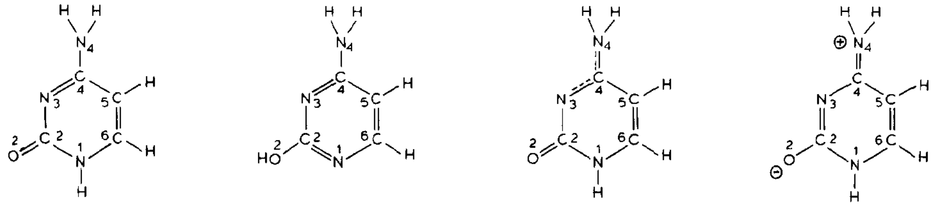
I.r.		*Raman*		*Assignments (modes)*
ν(cm^{-1})	*I*	*ν(cm^{-1})*	*I*	
		414	18.5	δ(N-3–C-2=O) and δ(N-1–C-2=O)
		460	5.8	δ(C-2–N-1–C-6) and δ(N-3=C-4–C-5)
		490	1.3	
		546	23.6	δ(C-C=C) and δ(N-3=C-4–N-4)
		558	40.3	δ(C-2–N-3=C-4) and δ(N-1–C-2–N-3)
		578	2.9	
602	24.8	608	35.8	ν(C=O) in phase
700	10.0	710	1.9	δ(C-5–C-4–N-4)
758	12.0			
783	27.9			ν(ring)
794	35.5	798	95.8	breathing mode
822	17.9			δ(N-H) out-of-plane
		904	1.9	
966	10.8	980	16.6	ν(C-4–C-5)
995	8.8	1002	4.8	δ(C-4–C-5-H) in plane
1012	9.3	1022	4.5	δ(N-1–C-6-H) in plane
1100	10.3	1118	17.9	r(NH_2)
1155	15.7	1158	2.6	ν(C-O)
1240	36.8	1260	42.8	ν(C-4–N-4)
1280	48.0	1284	100[b]	ν(C-2–N-1) and ν(C-6–N-1)
1366	35.3	1376	15.3	δ(C=C-H)
1469	65.2	1470	8.3	ν(C-4–N-3) and ν(C-2–N-3)
1505	40.4	1502	4.5	ν(C-4=N-3) and ν(C-4–N-4)
1540	42.2	1542	15.3	δ(N-H) in plane
		1582	1.3	
1616	53.9	1620	2.6	ν(C-5=C-6)
1667	100[b]	1666	17.3	ν(C-2=O)
1705	42.2	1708	8.9	δ(NH_2)

[a]Key: I = relative intensity, δ = bending mode; ν = stretching mode, r = rocking mode. [b]Taken as reference

be noted that the C-2=O-2 bond-length in crystalline β-cytidine at 124.6 pm, is significantly greater than the average value for a C=O bond distance[15]. The same observation was made by Jeffrey and Kinoshita[10], who found a C-2=O-2 distance of 126 pm in cytosine monohydrate. The fact that the carbonyl vibration occurs at a lower value than the usually accepted frequency 1720–1700 cm^{-1} is probably due to partial single-bond character (**1b**). Thus the 1667 cm^{-1} absorption is assigned to ν(C-2=O).

A shoulder is seen in Fig. 1 at 1616 cm^{-1} and a weak Raman line at 1620 cm^{-1} (see Fig. 2). This vibration should correspond to the ν(C=C) stretching mode, in agreement with the assignment proposed by Susi *et al.*[4] and Theophanides[7]. An i.r. absorption of moderate intensity at 1540 cm^{-1}, corresponding to the Raman line at 1542 cm^{-1}, has been mentioned in previous[4,6,20,21] studies and assigned to the G-C pair of bases[6] or to a contribution of guanine and cytosine residues[20,21]. Susi *et al.* [4] inferred from normal-coordinates analysis that the i.r. band at 1538 cm^{-1} and the Raman line at 1533 cm^{-1} correspond to a combination of ν(ring) and $\delta(NH_2)$. The contribution to this vibration of hydrogen is demonstrated by a deuteration study[4]. The 1540-cm^{-1} vibrations seem to be characteristic of cytosine[6,20,21] and, more precisely, of NH or NH_2 (ref. 4) in cytosine. We propose assignment of 1540 cm^{-1} (i.r.) and 1542 cm^{-1} (Raman) to δ(N-1-H).

Another i.r. band of almost the same intensity as that at 1540 cm^{-1} is observed at 1505 cm^{-1} (see Fig. 1). The Raman line at 1502 cm^{-1} originating from the same vibration is very weak (see Fig. 2). The stretching of C=N is expected in this frequency region. However, the weak Raman intensity of such a vibration could be explained by structural features peculiar to the cytosine molecule. The C-N and C=N bond lengths in cytosine obtained by averaging the values from crystallographic data of β-cytidine[11], cytosine monohydrate[10], 2′-deoxycytidine[12], α-cytidine[13], and cytosine residues in the protonated and the neutral forms[14] are: C-2–N-3 = 136.1; C-2–N-1 = 138.7; C-6–N-1 = 136.4; C-4–N-4 = 132.7, and C-4=N-3 = 134.0 pm. It should be emphasized that the C-4=N-3 double-bond distance is longer than the C-4–N-4 single bond. This probably arises from a resonance effect as shown in Scheme I. Moreover, the C-4–N-4 single bond was described[16,17] as having 30% double-bond character, whereas the C-4=N-3 double bond was shown to have 60% single-bond character. As observed by Susi *et al.*[4], the double-bond C=N stretching could not be separated from the single-bond vibration. The frequency of 1501 cm^{-1} has been found[6] as characteristic of cytosine. Accordingly, the vibration at 1505 cm^{-1} (i.r.) and 1502 cm^{-1} (Raman) is assigned to ν(C-4=N-3) with a contribution from C-4–N-4.



1a **1b** **1c** **1d**

Scheme I. Numbering of atoms in cytosine (**1**).

It may be observed in Fig. 1 that the 1469 cm^{-1} i.r. absorption is relatively strong. The corresponding Raman band at 1470 cm^{-1} (see Fig. 2) is very weak. The arguments derived from crystallographic data[11–14,16,17] support the existence of the resonant structures given in Scheme I. Usually[22] the C-N stretching is located in the 1300–1200 cm^{-1} frequency region. Assignment of 1469 cm^{-1} (i.r.) and 1470 cm^{-1} (Raman) to ν(C-4.N-3) and ν(C-2–N-3) is proposed. Such an attribution may be explained by the resonance effects (see Scheme I). Indeed, the resonance effect would lead[23] to the increase of the electric dipole-moment, and consequently to a more-intense i.r. absorption.

The band at 1366 cm^{-1} observed in the i.r. spectrum and the Raman line at 1366 cm^{-1} (see Fig. 2) could originate from deformation of the C=C-H angles. It was found[4] from normal-coordinate calculations that the modes at 1364 cm^{-1} (i.r.) and 1361 cm^{-1} (Raman) involve contributions from δ(C-N) and δ(C-H). The in-plane CH deformations in the vibrational spectra of cytosine were localized[8] in the 1400–1300 cm^{-1} frequency region. The strongest Raman line is observed at 1284 cm^{-1} (see Fig. 2). This frequency seems to be characteristic of the cytosine residue in polyC (ref. 20). On the other hand, the Raman line at 1260 cm^{-1} has approximately one-half the intensity of the vibration at 1284 cm^{-1}. Their coupling and the ratio of intensities lead us to assign 1284 cm^{-1} to endocyclic C-N stretchings around N-1, and 1260 cm^{-1} to exocyclic ν(C-N).

b. The 1200–800 cm^{-1} region. In general, neither the i.r. nor the Raman spectra in this frequency region exhibit strong bands. The vibrations given by the correlation charts[22] in the 1200–800 cm^{-1} region are ν(C-O), ν(C-C), δ(COH), δ(C-H), and the rocking mode of $\delta(NH_2)$. From the proposed structures (see Schemes Ib and Id), the weak i.r. absorption at 1155 cm^{-1} (see Fig. 1) and the Raman line at 1158 cm^{-1} (see Fig. 2) could arise from C-O stretching. This assignment may be supported by the single-bond character of C-2=O previously noted and the fact that an anionic cytosine residue was found to give rise to a Raman line in that region[8].

The wide Raman band at 1118 cm^{-1} probably originates from a combination of vibrations. The most important contribution may be due to $r(NH_2)$, which is in agreement with Theophanides[7]. Three weak i.r. absorptions, at 1012, 995, and 966 cm^{-1}, corresponding to Raman lines at 1022, 1002, and 980 cm^{-1}, are observed. We assign these frequencies to δ(N-1–C-6-H), δ(C-4–C-5-H), and ν(C-4–C-5), respectively (see Table I). This attribution is consistent with our previous suggestion[2] for δ(CH) and ν(C-C) in the sugars of nucleic acids.

c. Frequency region below 800 cm^{-1}. The most intense Raman line (see Fig. 2) appears at 798 cm^{-1}. Vibration at a similar frequency has been observed by different authors[5,7,11,16,20,24–27] in the vibrational spectra of cytosine. Both experimental and theoretical arguments were used to assign this frequency to a ring-stretching[5,25] or an in-phase, ring-breathing mode[7,24–27]. The i.r. absorption corresponding to this Raman line is observed at 794 cm^{-1}. It may be noted that this vibration is split into two bands at 794 and 783 cm^{-1}. The enhancement in Raman intensity of the vibration at 798 cm^{-1} (see Fig. 2) is certainly attributable to the resonant structure of the ring. Our proposed assignments listed in Table I are: 798 cm^{-1} (Raman), breathing mode, and 794–783 cm^{-1} (i.r.) for a combination of ring-stretching modes. The i.r. absorption at 822 cm^{-1} is broad (see Fig. 1). A deuteration study[5] indicates that this vibration involves a hydrogen atom. We propose assignment of the 822 cm^{-1} band to an out-of-plane, NH deformation.

Only the Raman spectrum is recorded below 600 cm^{-1}. In this frequency region, skeletal modes of vibration are generally expected. It was noted[8] that no frequency shifts occur for the deuterated cytosine in the regions 620–580 and 570–

530 cm^{-1}, but with increasing pH (or pD) these lines shift to higher frequencies with associated decreases in intensity. Similar behavior was found[8] for uracil derivatives in the same frequency region. These arguments led Lord and Thomas[8] to assign frequencies at 620–580 cm^{-1} and 570–530 cm^{-1} to C=O deformation modes. Accordingly, we propose assignment of 608 cm^{-1} (Raman) to in-phase δ(N-3–C-2=O) and δ(N-1–C-2=O). The out-of-phase C=O deformations could occur at 414 cm^{-1}.

The observed line at 558 cm^{-1} (see Fig. 2) probably corresponds to the vibration found by Susi *et al.*[4] at 568 cm^{-1} and assigned by them to a skeletal mode. The proposed assignments of 558 cm^{-1} to a contribution from C-2–N-3=C-4 and N-1–C-2–N-3 deformations, as listed in Table I, is supported by the double-bond character of C-2–N-3, as discussed earlier. This Raman line at 558 cm^{-1} is part of a doublet (558–546 cm^{-1}) which certainly originates from the same kind of vibrations. Thus we propose assignment of 546 cm^{-1} to δ(N-3=C-4–N-4) and δ(C-C=C). The ring deformations of C-2–N-1–C-6 and N-3=C-4–C-5 could occur at 460 cm^{-1}, in agreement with the assignments derived from normal-coordinate calculations[5].

d. Frequencies in the region between 3600 and 2400 cm^{-1}. The F.t.-i.r. spectrum of cytosine in the solid state is shown in Fig. 3. As expected, the NH and CH stretchings are found in this frequency region. Assignments of the observed frequencies are listed in Table II. Symmetrical and antisymmetrical NH_2 stretchings

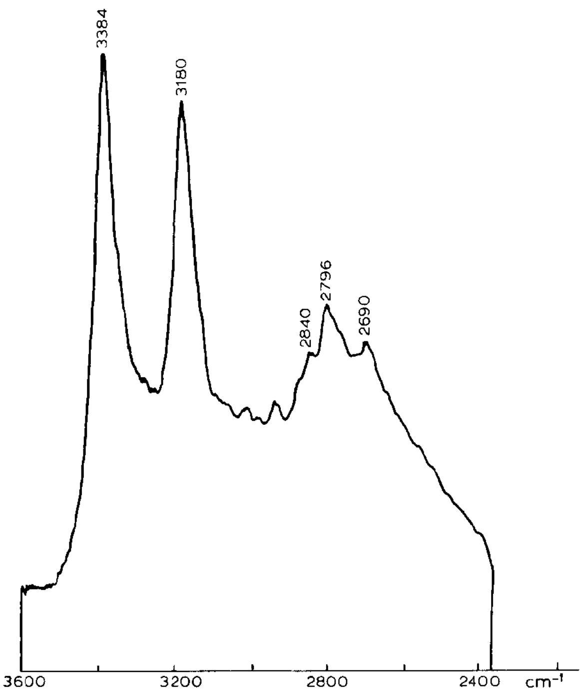


Fig. 3. F.t.-i.r. spectrum of cytosine (**1**) in the 3600–2400 cm^{-1} frequency region.

TABLE II

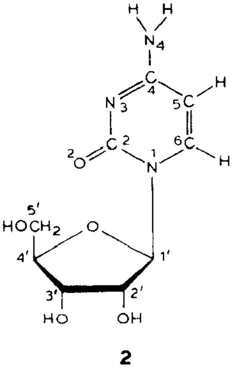
BANDS OBSERVED[a] IN THE F.T.-I.R. SPECTRUM OF CYTOSINE (THE 3600–2400 cm^{-1} REGION)

ν(cm^{-1})	I	Assignments
3384	100[b]	$\nu_a(NH_2)$
3180	92.2	$\nu_s(NH_2)$
2796	59.6	ν(C-H)
2690	53.4	ν(C-H)

[a]Key: I = relative intensity; ν = stretching mode (ν_a = antisymmetrical stretching and ν_s = symmetrical stretching). [b]Taken as reference.

are well defined and localized at 3180 and 3384 cm^{-1}, respectively. The vibrations at 2690 and 2796 cm^{-1} are assigned to ν(C-H).

B. Cytidine. — I.r. and Raman spectra of cytidine (**2**) are shown in Figs. 4 and 5. Comparison of the i.r. spectra of cytosine (see Fig. 1) and cytidine (see Fig. 4) reveals a richer spectrum for cytidine, especially in the 1200–800 cm^{-1} frequency region. The difference between the Raman spectra (see Figs. 2 and 5) is less obvious.



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Scheme II. Numbering of atoms in cytidine (**2**)

a. Observed bands identified from the spectra of cytosine and D*-ribose.* The strategy adopted in analyzing the spectra of cytidine is the same as that used for adenosine[3] and thymidine[1]. Assignments of the observed frequencies to the sugar (R) or the base residue (C) were derived from previous results (see ref. 2 and Table I) and are listed in Table III. It may be noted that the intensities are enhanced in the 1800–1500 cm^{-1} frequency region. This is probably due to stabilization of the cytidine ring: the resonant effect does not exist in the nucleoside, leading to well resolved and intense carbonyl and double-bond vibrations in the i.r. (see Fig. 4).

b. Observed bands differentiating cytidine from cytosine and D*-ribose.* The glycosylic bond in cytidine (**2**) is localized between C-1′ and N-1. Such an

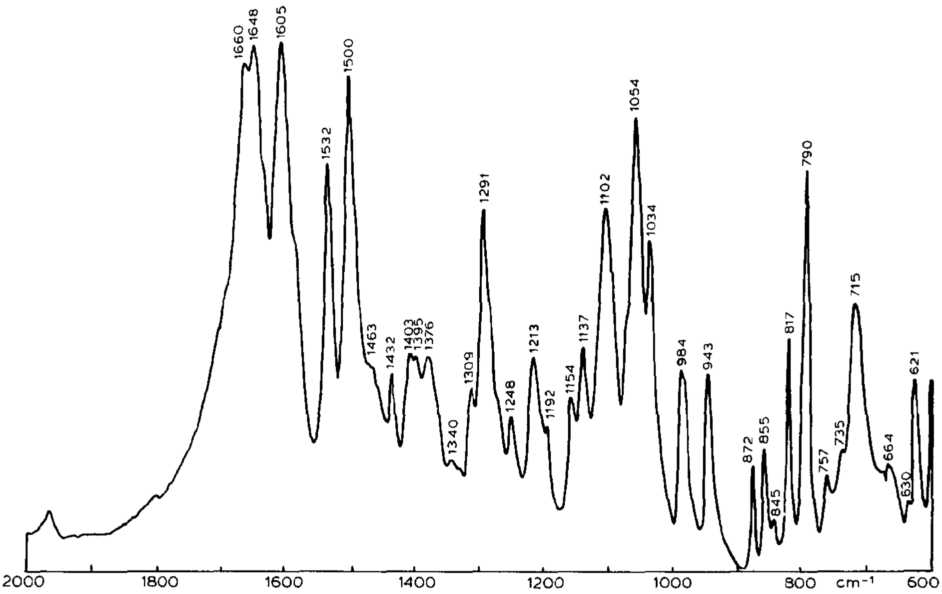

Fig. 4. F.t.-i.r. spectrum of cytidine (**2**).

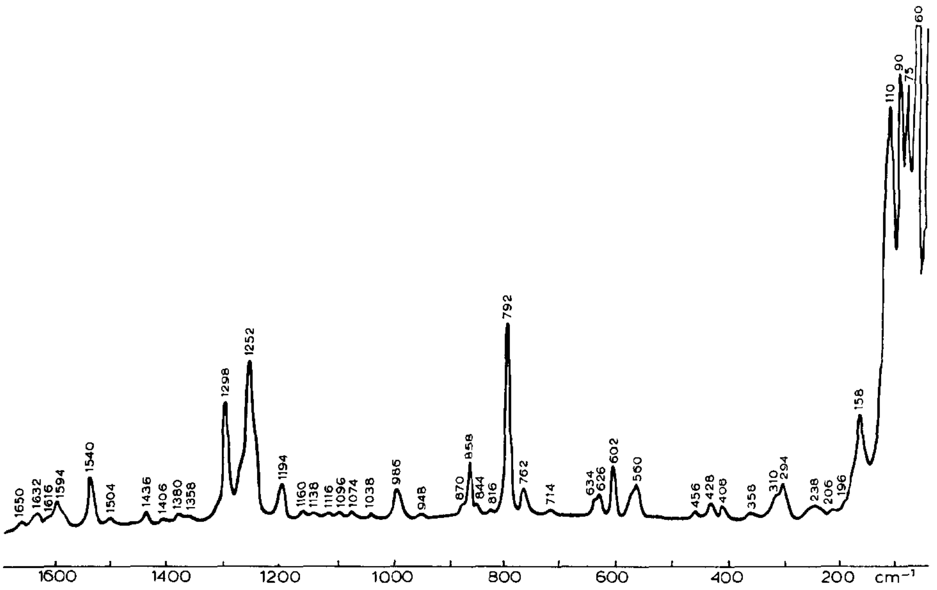

Fig. 5. Laser-Raman spectrum of cytidine (**2**).

association may induce hydrogen bonds that contribute to stabilize the syn or anti conformations. In nucleosides, the syn conformation, having an O-2 · · · O-5′ hydrogen bond, is favored[28]. However, in nucleotides, this hydrogen bonding is not possible because of the 5′-phosphate group. In that case, the O-2 · · · O-2′

TABLE III

BANDS OBSERVED^a IN THE F.T.-I.R. AND LASER-RAMAN SPECTRA OF CYTIDINE

I.r.		*Raman*		*Assignments (modes)*
ν(*cm*$^{-1}$)	*I*	ν(*cm*$^{-1}$)	*I*	
		158	32.5	C
		186	2.4	R
		208	2.4	C + R
		238	5.4	R
		294	18.1	R
		310	12.0	R
		358	3.6	R
		408	7.2	R
		428	8.4	R
		456	4.2	C + R
		560	16.9	C
		602	26.5	C + R
621	35.3	626	12.0	δ(N-1–C-1′–O-4′)
630	13.0	634	9.0	R
664	20.1			
715	50.0	714	3.6	C
735	22.8			δ(C-2′–C-1′–N-1)
757	18.1	762	14.5	C + R
790	75.5	792	100^b	C
817	43.6	818	3.6	C
845	9.8	844	7.2	δ(C-2′–C-1′–O-4′)
855	22.8	858	27.7	δ(C-N-1–C-1′)
872	19.2	870	7.2	R
943	37.3	948	2.4	R
984	37.5	986	15.7	C + R
1034	62.5	1038	3.0	R
1054	85.5			δ(N-1–C-1′-H)
		1074	3.0	R
		1096	3.0	R
1102	68.1			
		1116	2.4	C + R
1137	41.7	1138	3.0	R
1154	32.4	1160	4.8	C + R
1192	27.0	1194	19.3	ν(C-1′–N-1)
1213	40.0			R
1248	29.4	1252	81.9	C + R
1291	67.6	1296	61.4	C + R
1309	34.3			R
1340	21.3			R
		1358	3.0	R
1376	40.2	1380	4.2	C + R
1395	40.4			
1403	41.2	1406	1.0	R
1432	37.0	1436	6.0	R
1463	39.2			C + R
1500	94.1	1504	3.6	C
1532	76.7	1540	25.3	C
		1594	14.5	
1605	100^b			C

TABLE III *(continued)*

I.r.		*Raman*		*Assignments (modes)*
$\nu(cm^{-1})$	*I*	*$\nu(cm^{-1})$*	*I*	
		1616	6.0	C
		1632	8.4	R
1648	100[b]			C + R
1660	96.1	1660	4.8	C
1700	53.5			C

[a]Key: I = relative intensity; δ = bending mode; ν = stretching mode. C = cytosine (detailed assignments are given in Table I); R = D-ribose (detailed assignments are given in ref. 1). [b]Taken as reference.

hydrogen bond becomes particularly important as it limits the possible rotations $\chi_{C\text{-}N}$ around C-1′–N-1, and the base-pairing[28]. Besides these inter-residue interactions, Furberg *et al.*[11] reported that O-5′ is relatively close to C-6 in the cytidine molecule (O-5 · · · C-6 = 323.3 pm). The C-6-H bond is oriented in the same direction as C-5′–O-5′, which led the authors[11] to describe this interaction as a weak hydrogen bond (C-H · · · O). Other intramolecular interactions (in the sugar moiety) may take place because of the C-3′ endo puckering of D-ribose in cytidine[11]. The inter- and intra-molecular interactions provoke constraints that result in shifts in the observed frequencies and intensities.

The vibrations that differentiate the spectrum of the base from the spectrum of the nucleoside occur mainly around the C-1′–N-1 bond. The length of this bond is greater than other C-N distances derived from X-ray diffraction studies[11–13]. This particular bond-length allows assignment of a lower frequency to ν(C-1′–N-1), at 1192 cm^{-1} (i.r.) and 1194 cm^{-1} (Raman) (see Table III). Another i.r. band that differentiates the spectra observed in Fig. 1 and 4 is situated at 1054 cm^{-1}. This frequency is assigned to a C-H deformation with an important contribution from (N-1–C-1′-H).

Below 900 cm^{-1}, the differentiating vibrations are due to bond-angle deformations, including the C-1′–N-1 bond. The observed i.r. band at 855 cm^{-1} (see Fig. 4) and Raman line at 858 cm^{-1} (see Fig. 5) is assigned to δ(C-N-C), that is, δ(C-6–N-1–C-1′) and δ(C-2–N-1–C-1′). The i.r. absorptions at 735 and 630 cm^{-1} may originate from other angle-deformations around C-1′–N-1 and are assigned to δ(C-2′–C-1′–N-1) and δ(N-1–C-1′–O-4′) (see Table III). It may be noted that the C-3′ endo puckering of D-ribose in cytidine could be the origin of the vibration at 845 cm^{-1} (i.r.) and 844 cm^{-1} (Raman). We have previously[1] assigned 830 cm^{-1} (Raman) to δ(C-C-O) in β-D-ribofuranose. The observed shift in frequency could be attributable to the glycosylic linkage, and we propose assignment of 845 cm^{-1} (i.r.) and 844 cm^{-1} (Raman) to δ(C-2′–C-1′–O-4′).

c. Frequencies in the region between 3600 and 2600 cm^{-1} . The absorptions observed in this region are shown in Fig. 6 and their assignments are listed in Table IV. Comparison of the F.t.-i.r. spectra of cytosine (see Fig. 1) and cytidine (see Fig. 6) shows a new band at 3450 cm^{-1}, which certainly originates from ν(O-H) of the D-ribosyl residue. This vibration, as well as the vibration at 3087 cm^{-1} assigned to $\nu(CH_2)$ of the sugar moiety, shift towards higher values probably because of hydrogen bonding involving D-ribose, as previously discussed. The other vibrations expected in this frequency region are N-H and C-H stretchings. Assignments of the observed frequencies to these vibrations are proposed in Table IV.

TABLE IV

BANDS OBSERVED[a] IN THE F.T.-I.R. SPECTRUM OF CYTIDINE (THE 3600–2600 cm^{-1} REGION)

ν(cm^{-1})	*I*	*Assignments*
3450	91.1	ν(O-H)
3351	100[b]	$\nu_a(NH_2)$
3277	84.1	$\nu_s(NH_2)$
3234	86.5	
3087	51.0	$\nu(CH_2)$ from D-ribose
2963	42.6	
2953	46.6	
2920	51.5	ν(C-H)
2897	43.6	

[a] Key: I = relative intensity; ν = stretching mode (ν_a = antisymmetrical stretching and ν_s = symmetrical stretching). [b] Taken as reference.

Fig. 6. F.t.-i.r. spectrum of cytidine (**2**) in the 3600–2600 cm^{-1} frequency region.

CONCLUSION

X-Ray diffraction results recorded in the literature have been used in deriving arguments from bond distances and angles for assignments of observed F.t.-i.r. and Raman frequencies. The structure of the cytosine molecule with its delocalized π electrons, gives rise to some complexity because most of the observed frequencies originate from combinations of vibrations. The spectra of cytidine are interpreted on the basis of comparison of the spectra of both the sugar and the base. Reference is made to puckering of D-ribose in cytidine, which could be the origin of observed shifts in frequency and intensity.

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