Nucleosides Conformations, XVIII *

Infrared and Raman Spectroscopic Study of Isocytosine

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Isocytosine, Vibrational Study

Isocytosine and isocytosine-d_3 crystals have been investigated at 300 K, 90 K, and 10 K by infrared spectroscopy; the Raman spectra of crystals and solutions in H_2O, D_2O have also been studied. Using these data and the frequency group approximation we propose assignments of the fundamental molecular frequencies. Eleven lattice vibration frequencies have been observed in absorption and nine in diffusion.

Introduction

In order to clarify some of the problems encountered in the study of guanosine[2–4], we have undertaken a vibrational study of this compound. Using an approach previously employed by Lautie and Novak[5] in the study of purine, we have begun this work by the study of isocytosine (Fig. 1) which represents the pyrimidine part of the base.

Several workers[6–9] have proposed group frequency assignments, particularly in the 1800 – 1500 cm^{-1} range for cytosine; after termination of this work a normal coordinate analysis of the in plane modes of cytosine and cytosine-d_3 appeared[10].

The present communication describes the infrared and Raman spectra of isocytosine and isocytosine-d_3. To interpret these spectra we have used alkyl derivatives, variations of temperature and solvents and polarized Raman spectra; finally, for the in plane ring we have made a comparison with the assignment published by Foglizzo and Novak[11, 12] on pyrimidine.

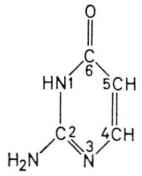

Fig. 1. 2-Amino-6-oxy pyrimidine.

Material and Methods

isoCyt was obtained from Cyclo Chemicals (Los Angeles). Recrystallization from water did not change its spectra. To study it by Raman diffusion it was necessary to purify it by sublimation. m^1-isoCyt[12] and m^3-isoCyt were synthesized by using the method described by Angier and Curran[13] and purified by paper chromatography. N^2-octyl-isoCyt was prepared by a simple reaction between N-methylthio-pyrimidinone and octylamine, followed by washing in different solvents. isoCyt-d_3 was prepared by recrystallization of commercial isoCyt from D_2O for IR spectra and of sublimed isoCyt from D_2O for Raman spectra. Deuteration on NH and NH_2 groups was checked by NMR on a Perkin Elmer 12, 60 MHz spectrometer.

IR spectra were recorded on Perkin Elmer 221, 225 and 180 spectrophotometers. Solid state spectra were obtained in nujol and voltaleff mulls and in KCl pellets containing 0.25 or 0.5% of isoCyt To take the spectra at 10 K we have used an Air Liquide cryostat. Raman spectra were obtained with a Coderg PHO apparatus equipped with an 80 mW HeNe laser and a 100 mW argon laser using the 4880 Å line.

Results and Discussion

Structural considerations

Molecule

Crystallographic[11] and solution work[15] had shown that there are two tautomers N_1H and N_3H-

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Abbreviations: Cyt, cytosine; isoCyt, isocytosine (Fig. 1) or 2-amino-6-oxy-pyrimidine; m^1-isoCyt; N_1-methyl-isocytosine; m^3-isoCyt, N_3-methyl-isocytosine; etc, isoCyt-d_3, isocytosine, where the three amino protons were deuterated, $d^1(d^2)_2$isoCyto.

isoCyt; in monocrystals cocrystallization in the ratio 1/1 is found[14]. Therefore, theoretically, one can expect twice as many vibrations as for one molecule; but, as shown by our spectra, a great number of the vibrations are not separated. For a molecule with C_S symmetry one expects 33 fundamental vibrations, 23 A′ in-plane vibrations and 10″ out-of-plane vibrations. The group frequency approximation provides for more or less pure 9 skeletal A′ ring modes and 3 skeletal A″ ring modes.

Table I. Counting of vibrations of isoCyt crystal[a].

	I	A	T′	R′	IR	R
Ag	33	0	3	3	in	a
Bg	33	0	3	3	in	a
Au	33	1	2	3	a	in
Bu	33	2	1	3	a	in

[a] I, Normal modes; A, acoustical modes; T′, translational modes; R′, rotational modes.

Crystal

For our counting of vibrations we shall not take into account the tautomeric forms. The crystal belongs to the monoclinic system, space groups $P2_{1/m}$ with four molecules in the unit cell. The are six hydrogen bonds of different lengths in the crystal. Every one of the 33 vibrations of the molecule will have four components, thus 132 internal vibrations will exist (Table I). Among them two are infrared active and two Raman active. In addition one expects 21 lattice vibrations which can be divided in 9 translational vibrations and 12 rotational vibrations.

Fundamental molecular vibrations

We have divided the analysis of the spectra into three parts: a. 4000 – 1800 cm^{-1} where we expect only vibrations which should accord well with the group frequency approximation, b. 1800 – 1000 cm^{-1} were only in plane vibrations occur, c. 1000 – 200 cm^{-1} where the remaining A′ vibrations and the A″ out of plane vibrations should be found. Only lattice vibrations are expected below 200 cm^{-1} [11, 16].

a. 4000 – 1800 cm^{-1} region: CH, NH, NH_2 stretching modes

In this region one expects two stretching modes, $\nu_s NH_2$ and $\nu_a NH_2$, which will overlap in the solid state[17]; two NH stretching modes for the tautomeric forms N^1H and N^3H; and two CH stretching modes, one for in-phase νCH and one for out-of-phase νCH.

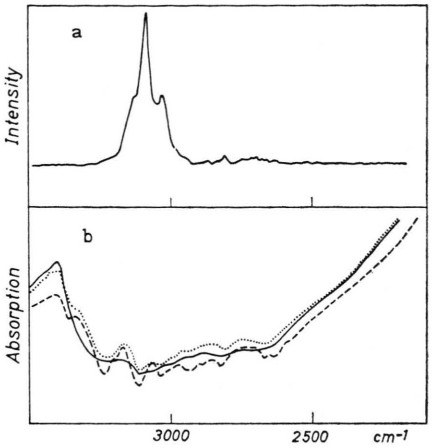


Fig. 2. a. Raman spectrum at 300 °K. b. Infrared spectra at 300 °K ———, 100 °K · · · ·, 10 °K – – –, of polycrystalline isoCyt.

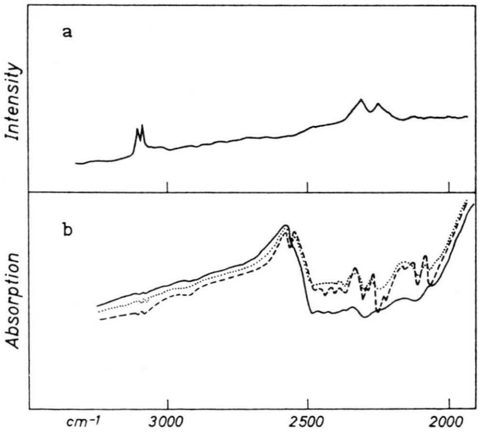


Fig. 3. a. Raman spectrum at 300 °K. b. Infrared spectra at 300 °K ———, 100 °K · · · ·, 10 °K – – –, of polycrystalline isoCyt-d_3.

It is not possible to assign precisely the νCH vibrations in non-deuterated compounds because they overlap those due to the stretching modes of NH and NH_2. In IR absorption spectra two very weak bands appear at 3100, 3085 cm^{-1} for isoCyt-d_3; in the Raman diffusion spectrum they appear at 3110 and 3079 cm^{-1} (Figs 2, 3) (Table II).

To differentiate the NH and NH_2 stretching modes we have compared two analogues without the NH group, m^1-isoCyt and 2-amino-pyrimidine (Fig. 4, b + c), and one with a substituent on the

Table II. Frequencies and assignments between 4000 and 2000 cm^{-1} for isoCyt and isoCyt-d$_3$.

IR isoCyt 300 °K	IR isoCyt 170 °K	IR isoCyt 10 °K	IR m^1-isoCyt 300 °K	Raman isoCyt 300 °K	Assignment
	3350	3360	3400		
3250	3230	3240	3345		νNH_2
		3200			
3140	3120	3118	3170	3130	νNH_2
3090				3092	νCH, νNH_2
	3040	3030	3050	3045	νCH
				3040	
2930	2930	2932			
2827	2815	2828		2815	νN_3H
2690	2670	2670		2700	νN_1H
		2640			
	isoCyt-d$_3$		m^1-isoCyt-d$_2$	isoCyt-d$_3$	
3100	3100	3100	3095	3110	νCH
3085	3080	3080	3050	3079	νCH
2550	2560	2564			νND_2
2470	2480	2473	2500		νND_2
2440	2440	2436			νND_2
2410	2400	2400			νND_2
2368	2369	2368	2320		νND_2
2300	2300	2300		2309	νN_3D
		2280			
2250	2245	2243		2240	νN_3D
	2140	2145			
2115	2105	2105		2129	νN_1D
2060	2065	2065			νN_1D
	2040	2045			

NH_2 group, N^2-octyl-isoCyt (Fig. 4 d), with isoCytosine (Fig. 4 a); for the two first compounds the absorption below 3000 cm^{-1} is strongly decreased (Fig. 4 b + c): We conclude that in isoCyt (Fig. 4 a) the two largest bands in this region, at 2827 and 2690 cm^{-1} can be assigned to νN^3H and νN^1H stretching vibrations.

In the octyl compound no bands above 3000 cm^{-1} are present except one at 3280 cm^{-1}, which we assign to the N^{2}H stretch; because of its frequency location this NH group near the octyl group is probably not strongly associated: Therefore one can assign the part between 3360 and 3100 cm^{-1} to the stretch of the amino group. To explain the submaxima, we can make two hypothesis: α. They may be due to the different hydrogen bonds in crystals: Crystallographic studies [14] have shown that there are four different hydrogen bonds involving the amino group, one of the NH . . . N type of length 2.98 Å and three of the NH . . . O type with lengths of 2.861, 2.904, 2.815 Å. By using the Pimentel relations [18] one can correlate the frequency shift of the hydrogen bonded νNH_2 vibrations with the bond lengths: We have calculated the shifts for the four different bonded N^{2}H; $\Delta\nu$ ranges from 170 to 420 cm^{-1}, in agreement with this hypothesis.

β. But they could also correspond to a multiple Fermi resonance between NH_2 stretch and overtones of vibrations around 1600 cm^{-1} [27] for isoCyt and around 1200 cm^{-1} for isoCyt-d$_3$.

Progressive deuteration does not allow a decision to be made between these two hypotheses.

b. 1800–1000 cm^{-1} region (Table II)

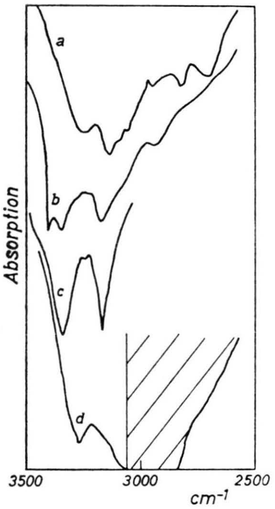


Fig. 4. Infrared spectra of a. isoCyt, b. m^1-isoCyt, c. 2-amino pyrimidine, d. N^2-octyl-isoCyt, in solid state (the hachured part corresponds to the stretching vibrations of the octyl group). (These spectra have been registered with a range different of that used for Fig. 2 and for Fig. 3.)

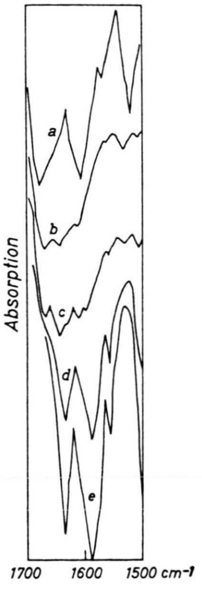


Fig. 5. Infrared spectra of isoCyt deuterated to a. 0%, b. 25%, c. 50%, d. 75%, e. 95%.

δNH_2, $\nu C = O$: The in-plane bending deformation of the NH_2 group is expected in the 1600 – 1700 cm^{-1} range. Progressive deuteration causes the strong band at 1689 cm^{-1} and the smaller one, only visible at liquid nitrogen temperature, to gradually disappear (Figs 5, 6 a). At 1250 cm^{-1} (Fig. 6 b) a new band appears which we assign to the δND_2 vibration. The N^1 met compound also shows a band at 1690 cm^{-1} which is sensitive to deuteration. Moreover the N^2-octyl compound shows only one band in this region, at 1660 cm^{-1}, assignable to $\nu C = O$ stretch. But for isoCyt the $C = O$ stretching vibration, also expected in this range, appears at 1645 cm^{-1} in the IR spectra.

The order of the frequencies of δNH_2 and $\nu C = O$ vibrations depends on the presence of hydrogen bonds in the solid or in solution: In a proton acceptor like dimethylsulfoxide we found the δNH_2 at 1640 cm^{-1} and the $\nu C = O$ at 1660 cm^{-1} (Fig. 7). For isoCyt-d_3 in the same solvent one can see a band at 1670 cm^{-1} with a shoulder at 1655 cm^{-1}: this latter visible only for the deuterated compound, is difficult to explain. We do not see a change of intensity if we vary the concentration; it may be due to the two tautomeric forms having two different carbonyl functions. In a proton donating solvent like hexafluoropropanol the order is inverted, 1640 cm^{-1} for $\nu C = O$, and 1665 cm^{-1} for δNH_2, the amino group being however, less free than in DMSO.

In Raman spectra we cannot distinguish between $\nu C = O$ and inplane ring stretching modes which overlap; but for isoCyt-d_3 they appear respectively at 1637 and 1622 cm^{-1}. $\nu C = O$ and νring vibration are not strongly coupled as is shown by their different behaviour in different solvents. Coupling between δNH_2 and one of the two ring vibrations at 1610 and 1580 cm^{-1} could also be proposed in this region: But deuteration has the same effect on these two highest ring vibrations for isoCyt and for uracil [19] where there is no NH_2 group.

δNH, δCH: These bending deformations are expected in the 1550, 1200 cm^{-1} range [20]. It seems difficult to make group frequency assignments in a region where there are also many ring vibrations. In the IR spectrum the d_3 compound shows two new bands, one at 1120 cm^{-1} and the other at 942 cm^{-1}; in non-deuterated compound two bands are complex: One at 1520 cm^{-1} with a shoulder at 1505 cm^{-1} and the other at 1475 cm^{-1} with a shoulder at 1464 cm^{-1}; after deuteration these shoulders disappear and the bands at 1520 and 1475 cm^{-1} become more symmetric; in Raman diffusion the 1528 and 1452 cm^{-1} band, visible in the isoCyt spectrum, are not visible in the spectrum of isoCyt-d_3; if one refers to uracil studies one can assign the first one to δN^1H and the second one to δN^3H. For the in-plane bending of the CH groups which should not show a frequency shift upon deuteration one can only refer to the literature [10, 20] to assign the 1410 cm^{-1} band to δCH in-phase and 1205 cm^{-1} to δCH out-of-phase movements, the latter being coupled with an in plane vibration of the ring.

$\nu C - N$: In aromatic compounds [21] this vibration appears between 1400 – 1240 cm^{-1}. Here the 1370 cm^{-1} band of the IR spectrum of isoCyt disappears in the d_3 compound where one notices a new band at 1280 cm^{-1}; the measured isotopic factor (1,07) corresponds quite well to the calculate isotopic factor (1,062).

rNH_2: By comparing with 2-amino-pyrimidine [17] where this vibration appears at 1100 cm^{-1} we can assign the 1154 cm^{-1} band, which increases upon

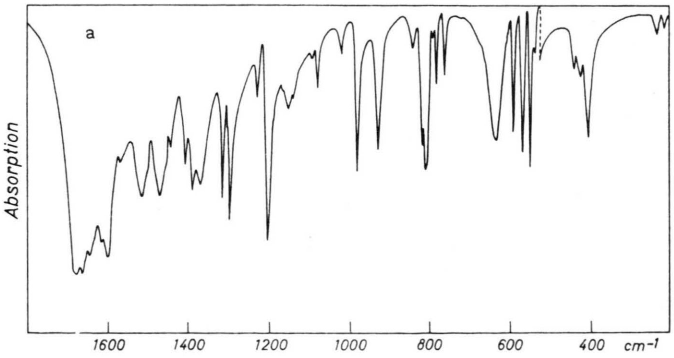


Fig. 6. a. Infrared spectrum at 90 °K of isoCyt. b. Raman spectrum at 300 °K of isoCyt, in solid state.

Table III. Frequencies and assignments between 2000 and 200 cm^{-1} for A/isoCyt, B/isoCyt-d_3.

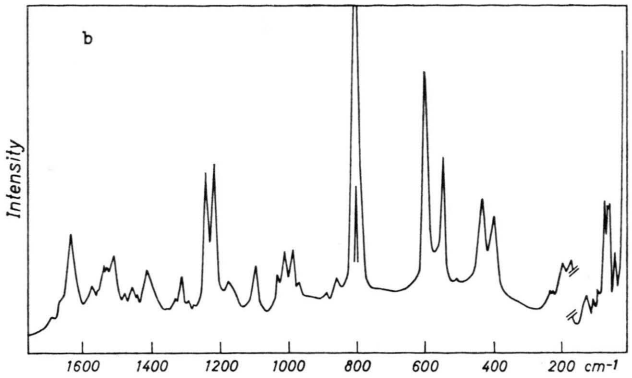
A: IsoCyt

IR	Raman		Assignment
Solid state	Solid state	Solution in H_2O	
1680 s (1680)	1685 (3)		NH_2
1665 w	1660 (3)		
1645 m (1645)			C=O
1605 s (1608)	1623 (24)	1630 ( ) p	ring i.p.
1560 w (1565)	1568 (8)	1570 (22) p	ring i.p.
	1540 (12)		
	1528 (4)	1530 (14) p	N^1H
1520 m (1520)	1507 (16)		ring i p
1475 m (1472)	1475 (4)	1490 (22) p	ring i p
1464 w	1452 (7)	1440 (5) p	N^3H
1450 w (1445)			
1410 m (1410)	1400 (11)	1410 (12) p	CH in phase, ring i.p.
1390 w (1394)			
1370 m (1373)	1370 (2)	1380 (8) p	C−N
1315 m (1317)	1321 (4)		
1300 s (1302)	1302 (9)	1315 (14) p	ring i.p.
1230 w (1230)	1235 (37)	1230 (55) p	ring i. p., CH out of phase
1205 w (1208)	1207 (39)		ring i. p., CH out of phase
1154 w (1157)	1162 (8)	1150 (1) p	NH_2
1085 w (1087)	1085 (12)	1080 (8) p	
1020 w (1022)	1018 (8)		
980 s (983)	1000 (15)	1000 (20) p	ring i.p.
	975 (15)		
920 m (925)	955 (7)		ring i.p.
850 w	870 (3)		N^1H
	847 (7)		
805 s (810)	797 (100)	790 (100) p	ring i.p., CH
780 w (785)	777 (2)		N^3H
760 w (763)			
630 m (630)			wNH_2
585 s (585)	580 (61)	585 (41) p	ring i. p.
565 s (565)			C−N
	554 (7)		C=O
548 s (548)	540 (40)	550 (28) d	ring o.p.
		500 (19) d	
440 w (440)			
430 w (427)	424 (27)	430 (27) d	ring o.p.
400 m (400)	390 (24)	400 (17) d	ring o.p.
235 w (236)			
215 m (215)	220 (9)		C=O

B: IsoCyt-d_3

IR	Raman		Assignment
Solid state	Solid state	Solution in H_2O	
1640 s (1640)	1637 (8)	1640 (22) p	ν C=O
1620 w (1620)	1622 (43)	1610 (13) p	ν ring i.p.
1590 m (1593)	1574 (18)	1580 (16) p	ν ring i.p.
1555 w (1555)	1542 (10)		
1500 m (1500)	1505 (21)	1525 (14) p	ν ring i.p.
1460 m (1462)	1490 (17)	1480 (13) p	ν ring i.p.
1410 m (1411)	1415 (14)	1425 (16) p	δ CH in phase, ring i. p.
1390 w (1390)	1393 (18)	1400 (10) p	
1330 m (1328)	1325 (5)	1325 (4) p	
1320 w (1318)			
1305 w (1307)			
1280 m (1280)	1280 (27)	1285 (25) p	ν C−N, ν ring i.p.
1250 s (1246)			δ ND_2
1205 m (1200)	1240 (25)	1240 p	ν ring i. p., δ CH out of phase
	1215 (23)		
1140 w (1145)	1150 (5)	1145 (13) p	
1120 m (1120)	1120 (22)	1100 (12) p	
1095 w (1097)	1090 (9)		δ N^1D
1040 w (1040)	1040 (6)		
1020 w			
988 w (985)	995 (7)	980 (13) p	
970 s (969)	965 (14)	960 (12) p	ν ring i.p.
942 m (940)	940 (4)		ν ring i.p.
933 m (931)	937 (5)		δ N^3D
894 m (893)	898 (10)	900 (7) p	
825 s (827)	822 (3)		ν ND_2
809 s (810)			
775 m (776)	774 (100)	776 (100) p	ν ring i.p., γ CH
760 m (764)			
718 w (720)	715 (2)		
680 m (680)	685 (1)		
620 m (621)			γ N^1D
582 s (583)	577 (57	580 (30) p	ν ring i.p.
575 w (576)			γ N^3D
566 m (566)			δ C=O
558 w (560)	548 (8)		
540 w (540)			
527 m (528)	521 (8)		δ C−N
480 m (480)			ν ring o.p.
468 m (467)		500 (10) d	wND_2
420 w (422)	415 (18)	430 (7) d	ν ring o. p.
380 m (380)	393 (6)	400 (6) d	ν ring o. p.
	365 (26)		
235 w (236)			
215 w (215)	215 (9)		γ C=O

[a] Infrared solid state spectra at 90 °K and at 300 °K in brackets: s, strong; m, medium; w, weak; Raman spectra at 300 °K: p, polarized; d, depolarized; assignment: i.p., in plane; o.p., out plane.



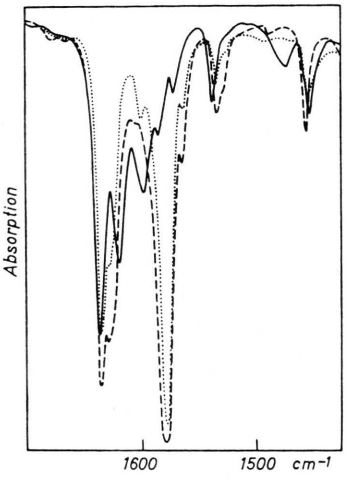


Fig. 7. Infrared spectra of a solution in DMSO-d_6 of: a. —— isoCyt (0.1 M/l). b. — — — isoCyt-d_3 (0.1 M/l). c. · · · · isoCyt-d_3 (0.01 M/l).

cooling, to the $r\mathrm{NH}_2$ vibration. With an isotopic factor identical to that for amino pyrimidine we found this vibration at 894 cm^{-1} in isoCyt-d_3.

In-plane skeletal modes: In the frequency group approximation and for each of the two tautomers one expects 5 or 6 in-plane ring vibrations above 1000 cm^{-1} [10, 11]. We found 8 intense bands in absorption and in diffusion, which did not vary very much in frequency, after deuteration.

Crystallographic data on pyrimidine and isoCyt may justify a comparison of their skeletal vibrations above 1000 cm^{-1} for the following reasons: Except for the C^5-C^6 bond and C^4-C^5 bond which differ by 4% and 6% from these in pyrimidine, the other bonds of the rings have quite comparable lengths. We can also justify the comparison by the behaviour of the 1605 and 1560 cm^{-1} band: Like the 8a and 8b vibrations of pyrimidine these two bands seem to be shifted to higher frequencies in the monochlorhydrate [22]. We have also observed a great increase of the 1560 cm^{-1} in the solid state or in solution in DMSO or in D_2O for isoCyt-d_3, but only in absorption. The two bands at 1410 and 1475 cm^{-1} found in pyrimidine and assigned to the 19a and 19b vibrations [11], correspond in isoCyt to two bands at 1410, 1475 cm^{-1}. In the same way we can explain the two bands at 1230 and 1205 cm^{-1}, very strong in Raman diffusion, which are assignable to an in-plane ring vibration coupled with a CH deformation.

1000 – 200 cm^{-1} region (Table III)

νring in plane, $\delta C=O$, $\delta C-N$: The infrared spectrum of isoCyt in the solid state shows four bands at 980, 930, 805 and 585 cm^{-1} to which correspond four intense Raman bands at 1000, 955, 797, 580 cm^{-1}. These four bands are polarized in aqueous solutions and, being little modified by deuteration, they are assigned to in-plane skeletal vibrations. In the 500 – 600 cm^{-1} region $\delta C=N$ and $\delta C=O$ vibrations are also expected [20, 23]; the great decrease of the 565 cm^{-1} band ($\delta C-NH_2$) after

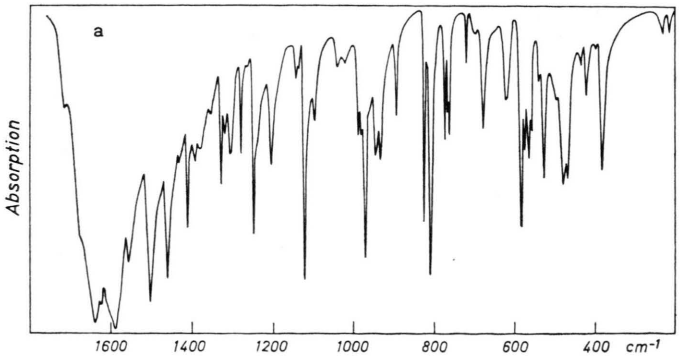
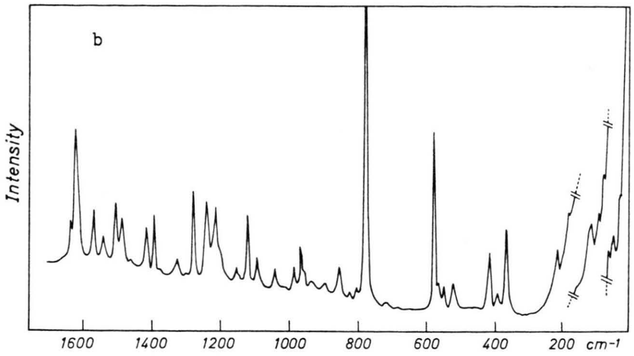


Fig. 8. a. Infrared spectrum at 90 °K of isoCyt-d_3. b. Raman spectrum at 300 °K of isoCyt-d_3, in solid state.



deuteration seems to correspond to the appearance of a 520 cm^{-1} band which could be assigned to $\delta C-ND_2$; therefore the remaining band in this region is assigned to $\delta C=O$ vibration, in Raman diffusion at 554 cm^{-1}.

γNH, γCH, WNH_2,tNH_2, $\gamma C=O$: The out-of-plane bendings of NH groups generally[24] appear between 950 and 750 cm^{-1}. Here we look for two γNH frequencies: One at 850 cm^{-1}, only visible at low temperature in absorption, the other at 788 cm^{-1} disappears in the isoCyt-d$_3$ infrared spectrum which however, shows two new bands at 620 and 575 cm^{-1} which we assign to γND. For the wagging of amino group the assignment is easier: The large 630 cm^{-1} band disappears, when one replaces the amino group with an octyl and also on deuteration. Moreover the WNH$_2$ and 630 cm^{-1} and WND$_2$ at 465 cm^{-1} bands greatly increase in intensity at liquid nitrogen temperature.

For the three other vibrations expected in this region we have no direct evidence. As in diazines[25] one can expect CH around 800 cm^{-1}: The strong band at 805 cm^{-1}, assigned to an in-plane ring vibration, is not completely polarized; we assume an overlapping between this band and a γCH vibration. The NH$_2$ (A″) twisting band is expected in a lower region and could be coupled with an out of plane ring vibration (A″) at 400 cm^{-1} which is shifted 5% by deuteration. According to Sing and Sing[23] the 215 cm^{-1} band which is also encountered in uracil, guanine, and cytosine[16] can be assigned to a $C=O$ vibration.

Out of plane skeletal modes: Three bands of medium intensity in the solid state, are also visible in solution at 550, 430, 400 cm^{-1} and are all depolarized. We assign them to the three out-of-plane ring vibrations expected in this region.

Table IV. Observed frequencies below 200 cm^{-1} for isoCyt and isoCyt-d$_3$.

Infrarouge		Raman	
IsoCyt	IsoCyt-d$_3$	IsoCyt	IsoCyt-d$_3$
204	197	190	184
175	175	164	160
166	163	124	123
153	154	116	116
139	135	97	96
120	118	83	81
95	92	73	64
76	77	49	49
68	68	34	32
60	58		
40	42		

Lattice vibrations: (Table IV)

As for the vibration of the molecule in the solid state neither the splitting due to the cristallinity nor that due to the presence of the two tautomers is observed. In absorpion, neglecting the tautomery, we would expect 12 vibrations (6 T′ + 6 R′) and we observe 11 bands between 200 and 33 cm^{-1}. In Raman diffusion, we would expect 9 vibrations (3 T′ + 6 R′) and we observe 9 bands between 200 and 20 cm^{-1}. In isoCyt-d$_3$ we do not find significant changes except a small shift to lower frequencies.

Conclusion

Crystallographic studies have shown[14, 26] that the hydrogen bonds in the isoCyt crystal are stronger than those in crystalline Cyt; this is evident from the frequencies shifts of the NH$_2$, NH, and $C=O$ groups. But even in D$_2$O solution there are differences between isoCyt and Cyt for the frequencies of these groups; we assume that they are due to the different location of substituents. For ring vibrations we found good agreement between isoCyt and Cyt in the solid state. With these data we have attempted to assign some of the intense bands of guanine above 1000 cm^{-1} to ring vibrations of the pyrimidine part of guanine; we hope to support these assignments by a vibrational study of ^{15}N guanine which we are synthesizing. With this information we intend to make a precise approach to the gel formation and polymorphisme of guanosine which imply modifications in substituent frequencies but also in ring vibrations[4].

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