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Out-of-plane vibration modes of nucleic acid bases

II. Purine bases

R. Letellier, M. Ghomi, and E. Taillandier*

Laboratoire de Spectroscopie Biomoléculaire, U.F.R. Biomédicale de Bobigny, Université Paris XIII, 74, Rue Marcel Cachin, F-93012 Bobigny Cédex, France

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Abstract. The non-planar vibration modes of guanine and adenine, and their C8-deuterated, N-deuterated and perdeuterated analogs have been calculated using a valence force field and a set of non-redundant symmetrical coordinates. Moreover, the effect of ^{15}N isotopic substitution in both pyrimidic and imidazolic rings of guanine has been studied. The calculated wavenumbers are in agreement with the published Raman and infrared spectra. The extension of the force field to the N9-methylated derivatives of guanine and adenine bases has also been described. On the basis of these calculations one can assign the guanine and adenine residue out-of-plane modes observed in the $800-750\ cm^{-1}$ region in the infrared spectra of the mononucleotides and polynucleotides containing purine bases.

Key words: Guanine, adenine, vibration modes, nucleic acids, normal coordinate analysis

Introduction

As mentioned in our first paper devoted to the out-of-plane modes of pyrimidines (Letellier et al. 1986a), the $800-750\ cm^{-1}$ region in nucleic acid infrared spectra results from the non-planar vibrations of the base residues. In this work our aim is to assign the previously published data concerning the out-of-plane modes of guanine, adenine and their deuterated derivatives. This investigation allows us to obtain a reliable force field which will be extended to the N9-methylated derivatives. This final approach confirms the experimental assignment of the above-mentioned infrared bands to the base residue out-of-plane modes.

* To whom offprint requests should be sent

Theoretical considerations

Numbering of the out-of-plane modes of the bases and their methylated derivatives when the methyl group is considered as a rigid unit has been explained previously (Letellier et al. 1986a). Therefore, guanine as well as its deuterated and methylated analogs present 13 non-planar vibration modes, while one expects 12 similar modes for adenine and its corresponding derivatives. 18 non-planar internal coordinates (7 out-of-plane waggings (o.p.w.) and 11 torsions) are numbered in guanine and 17 similar ones (6 o.p.w. and 11 torsions) in adenine. The 5 superfluous internal coordinates in each of these bases have been removed by the numerical procedures described in our previous work (Ghomi et al. 1985; Letellier et al. 1986b).

It is not simple to propose a force field for the out-of-plane modes of purine bases because of their complex and non-symmetric structures (Fig. 1). This problem has been simplified by considering the fact that each purine base is formed by rings of pyrimidic and imidazolic nature. Therefore, a possible force field can be proposed as a superposition of pyrimidic and imidazolic force fields which have been studied previously (Letellier et al. 1986a; Cordes and Walter 1968). In fact, this procedure is only possible for the diagonal force constants. As can be seen in Table 1a, by adjusting a small number of cytosine and imidazolic force constants, a set of acceptable diagonal force constants can be proposed for pyrimidine bases. Unfortunately, this procedure does not give a good result for the interaction (off-diagonal) force constants which should be different in monocyclic and bicyclic bases because of their different distributions of ring electrons. The development procedure of the potential energy is similar to that proposed for the pyrimidine bases (Letellier et al. 1986a). The off-diagonal force constants obtained by a least-squares method are shown in Table 1b.

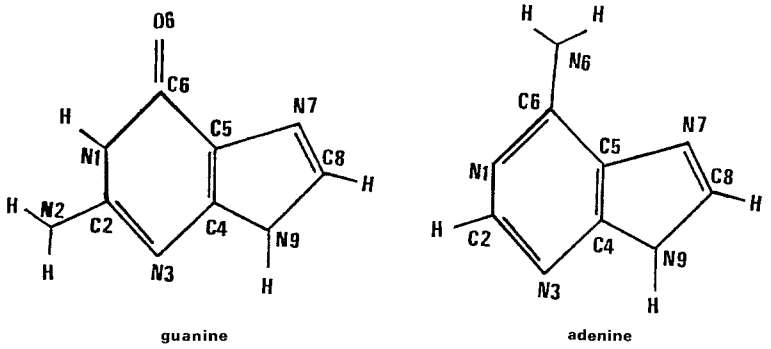

Fig. 1. Representation and atom numbering for guanine and adenine molecules

Table 1a

Coordinates	Values (mdyn.Å)			
	guanine (a)	adenine (a)	cytosine (b)	imidazole (c)
wagging				
W(C-H) (py.)		0.350	0.370	
W(N-H) (py.)	0.300		0.300	
W(C=O)	0.334		0.334	
W(C-NH2)	0.355	0.430	0.334	
W(NH2)	0.055	0.065	0.035	
W(N-Cm)	0.334	0.334	0.334	
W(C-H) (im.)	0.350	0.350		0.350
W(N-H) (im.)	0.330	0.330		0.330
torsions				
T(C-C)	0.520	0.520	0.520	
T(C-N) (py.)	0.255	0.255	0.255	
T(C=N) (py.)	0.629	0.629	0.629	
T(C-NH2)	0.100	0.100	0.112	
T(C=C)	0.520	0.520	0.520	0.520
T(C-N) (im.)	0.520	0.520		0.520
T(C=N) (im.)	0.570	0.570		0.570

Table 1a. Diagonal force constants for the out-of-plane vibration modes of purine bases and their N9-methylated derivatives. *W* designs an out-of-plane wagging coordinate and *T* a torsion coordinate. Cm: methyl group. im: imidazolic ring. py: pyrimidic ring. a: this work, b: cytosine force constants (Letellier et al. 1986a), c: imidazole force constants (Cordes and Walter 1968)

Table 1b

Interactions	adenine and its derivatives		guanine and its derivatives	
	values (mdyn.Å)	deviations	values (mdyn.Å)	deviations
wagging,torsion				
W(N9-H),T(N9-C8)	-0.137	(0.07)	-0.137	(0.01)
W(N9-H),T(C4-N9)	0.137		0.137	
W(C8-H),T(N9-C8)	0.153	(0.014)	0.153	(0.0)
W(C8-H),T(N7=C8)	-0.153		-0.153	
W(C2-H),T(N3=C2)	-0.123	(0.0)		
W(C2-H),T(N1-C2)	0.123			
W(C6-N6,T(N1=C6)	0.056	(0.0)		
W(C6-N6),T(C5-C6)	-0.056			
W(N9-Cm),T(N9-C8)	-0.056	(0.0)	-0.056	(0.0)
W(N9-Cm),T(C4-N9)	0.056		0.056	
W(C6=O6),T(N1-C6)			-0.056	(0.0)
W(C6=O6),T(C5-C6)			0.056	
W(N1-H),T(N1-C6)			-0.048	(0.022)
W(N1-H),T(N1-C2)			0.048	
W(C2-N2),T(N1-C2)			0.056	(0.0)
W(C2-N2),T(C2=N3)			-0.056	
torsion,torsion				
Ortho (py.)	0.014	(0.0)	-0.075	(0.0)
Ortho (im.)	-0.027	(0.0)	-0.029	(0.0)
wagging,wagging				
W(C8-H),W(N9-H)	0.018	(0.0)	0.006	(0.0)
W(NH2),W(C6-N6)	-0.041	(0.0)		
W(NH2),W(C2-N2)			0.028	(0.006)

Table 1b. Non-diagonal force constants for the out-of-plane modes of adenine, guanine and their N9-methylated derivatives. *W* designs an out-of-plane wagging coordinate and *T* a torsion coordinate. Cm: methyl group. im: imidazolic ring. py: pyrimidic ring

The Wilson GF-method (Wilson et al. 1955) has been used for the vibration mode calculations. The computational details have been explained elsewhere (Letellier et al. 1986a).

Results

A. Guanine and its deuterated derivatives

The calculations on guanine and its deuterated analogs are based on the geometrical data obtained from the X-ray diffraction patterns of guanine monohydrate crystals (Thewalt et al. 1971). Vibrational spectra of guanine (Table 2a) and its C8-deuterated, N-deuterated and perdeuterated analogs (Table 2b) have been studied previously (Delabar 1978; Delabar and Majoube 1978; Majoube 1984). The proposed non-planar wavenumbers observed in Raman and infrared spectra are compared to those obtained by calculation (Table 2a and b). The proposed force field accounts satisfactorily for the changes observed in the vibrational spectra upon C8- and N-deuteration. The calculated isotopic shifts of the guanine vibration wavenumbers upon ^{15}N substitution, as well as for the deuterated analogs, have also been reported in Tables 2a and b. The comparison between the experimental and calculated results (Majoube 1984) confirms the reliability of the proposed force field. However, it should be mentioned that the calculation on an isolated molecule would not be sufficient in order to explain all the experimental data arising from the crystalline samples. It is well known that the molecular vibration modes can be considerably altered by both hydrogen bonding and the crystalline field. Therefore, the present calculations should be considered as a first step in studying the phonon dispersion of the guanine crystals. Graphic representation of the calculated modes for guanine is given in Fig. 2.

B. Adenine and its deuterated analogs

X-ray data for adenine crystals is not available but the crystalline structure of 9-methyladenine has

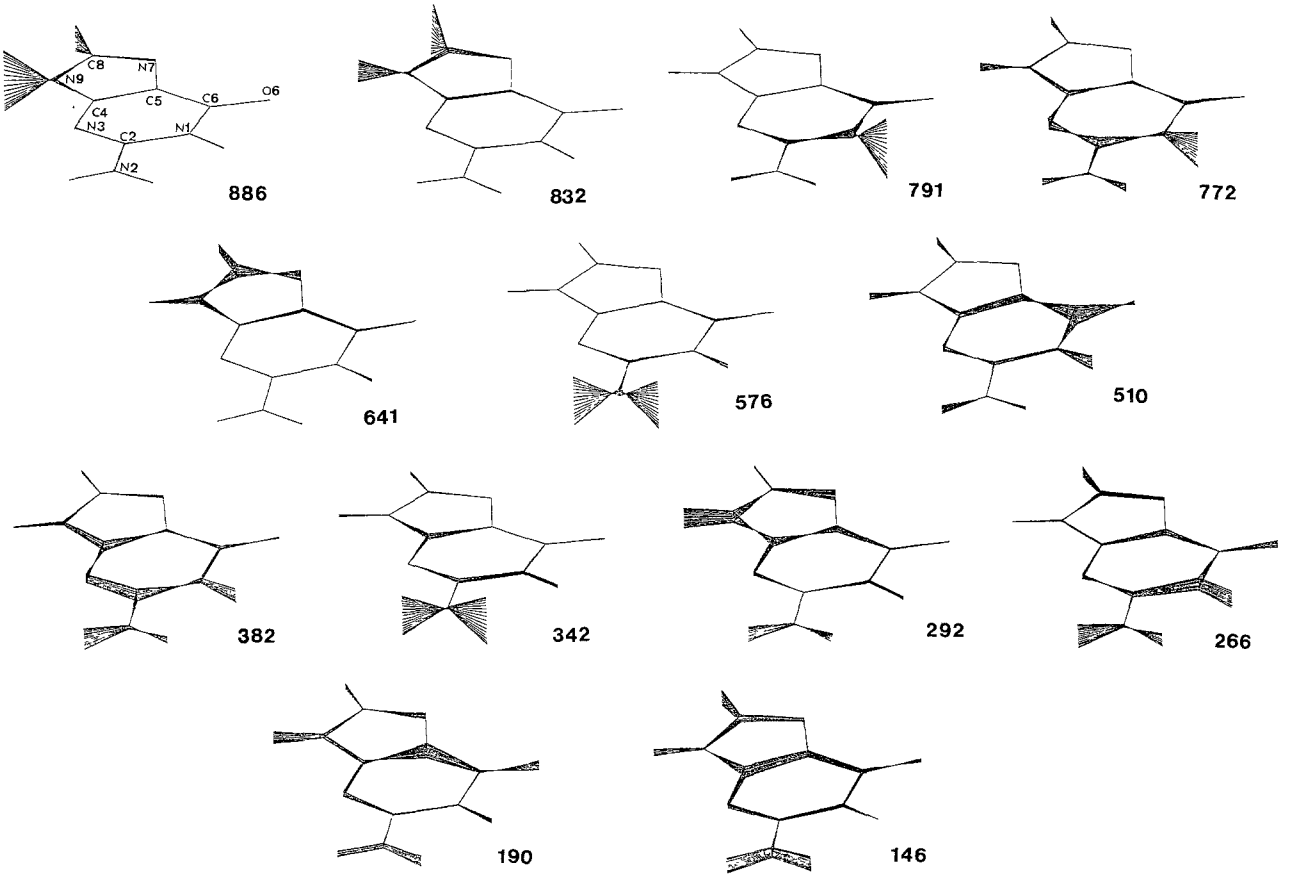

Fig. 2. Graphic representation of the 13 out-of-plane vibration modes for guanine obtained by the present calculation. The base plane initially perpendicular to the drawing plane has been titled about 10° in order to visualize the out-of-plane vibrations. All the situations of the base ring during a period of a given vibration mode have been drawn. The calculated wavenumber (cm^{-1}) of each mode is also noted. See also Table 2

been published (Steward and Jensen 1964). Supposing that the geometrical difference between adenine and its N9-methylated derivative can be neglected, the unknown structure has been obtained by replacing N−C by a standard N−H bond in the 9-position.

Raman and infrared spectra of crystalline and aqueous samples of adenine have been presented previously (Lautié and Novak 1974; Savoie and Jutier 1982; Majoube 1985a). In Table 3 the calculated and experimental wavenumbers have been compared. Adenine non-planar modes as well as their changes upon C8- and N-deuterations have been interpreted by the present calculation. The assignments based on the potential energy distribution (PED) are in good agreement with those suggested by Majoube (1985). Graphic representation of the calculated modes for adenine is given in Fig. 3.

C. 9-methyladenine and 9-methylguanine

The calculated results concerning 9-methyladenine and 9-methylguanine are shown in Table 4. The calculated wavenumbers of 9-methyladenine have been compared to previously published experimental data (Kyogoku et al. 1967; Savoie et al. 1981). A good agreement has been obtained. No experimental data is available for 9-methylguanine. However, the calculated results do allow us to follow the changes of adenine and guanine vibration modes upon N9-methylation.

Discussion

As in the case of pyrimidine bases, a considerable amount of theoretical work has been devoted to the study of the planar vibrations of purine bases (Tsuboi et al. 1973, 1986; Majoube 1984, 1985a, b; Ghomi et al. 1984, 1985; Letellier et al. 1986b, c). In contrast, the out-of-plane modes of these bases have not been studied so intensively and the published investigations are limited to the study of skeletal vibrations in which the hydrogen motions are entirely neglected (Eyster and Prohofsky 1974; Devi Prasad and Prohofsky 1984; Ghomi et al. 1984).

The present calculations follow our recent work on the non-planar modes of the pyrimidine bases (Letellier et al. 1986a) and propose a similarly extended force field for the purine bases. As it is detailed above, the quasi-whole diagonal force constants are transferable from guanine to adenine and are obtained by small corrections made on the previously published cytosine and imidazole out-of-plane force constants (Letellier et al. 1986a; Cordes and Walter 1968). However some alterations should be considered in the off-diagonal force constants when the N9-methylated bases are taken into consideration.

The present calculations take account of the spectral changes of guanine and adenine bases that occur upon selective deuterations and show the

Table 2a. Comparison between the calculated and experimental wavenumbers (cm^{-1}) for the out-of-plane modes of guanine. Assignments are based on the potential energy distribution (PED in %) described upon the internal coordinates. *Exp.* Experimental Raman (R) and infrared (I.R.) peak positions of polycrystalline samples (Majoube 1984). *Cal.* Calculated wavenumbers (this work). The vibration mode wavenumber shifts due to the ^{15}N-substitution are also reported in paranthesis. The first number indicates the isotopic displacement $\nu(^{14}N-^{15}N)$ when N1, N2 and N3 are substituted. The second concerns the analog displacement but upon the substitution on N7 and N9 atoms. *W* designs an out-of-plane wagging coordinate and *T* a torsion coordinate

Guanine				
Exp.		Cal.		Assignments (PED%)
885 R				
884 IR	(1,-)	886	(0,2)	W(N9-H)(39); T(N9-C8)(35) T(C4-N9)(14)
		832	(0,1)	W(C8-H)(51); T(C8=N7)(24)
790 IR		791	(6,0)	W(N1-H)(68); T(N1-C6)(12) T(C2-N1)(10)
778 IR	(2,-)	772	(10,0)	W(C2-N2)(24); T(C2-N1)(18)
775 R				T(C2=N3)(18); T(N3-C4)(14) T(N1-C6)(13)
		641	(1,11)	W(C8-H)(41); W(N9-H)(24) T(N7-C5)(16); T(C8=N7)(16)
578 IR		576	(4,0)	W(NH2)(88)
501 IR		510	(1,0)	W(C6=O)(66)
		382	(3,0)	W(C2-N2)(45); T(C2-N3)(14) T(N1-C6)(10); T(C2-N2)(10)
356 IR		342	(1,0)	T(C2-N2)(84)
		292	(0,5)	W(N9-H)(30); T(N7-C5)(19) T(C8=N7)(12)
243 IR	(3,-)	266	(4,0)	T(C5-C6)(28); T(N3-C4)(19) W(C2-N2)(12); W(N1-H)(10)
204 R		190	(0,1)	T(N1-C6)(19); T(C2-N1)(18)
		146	(1,0)	W(C2-N2)(20); T(N7-C5)(16) W(C6=O)(15)

Table 2b. Comparison between the calculated and experimental wavenumbers (cm^{-1}) of the guanine C8-deuterated, N-deuterated and perdeuterated (C8- and N-deuterated, analogs). Assignments are based on the potential energy distribution (PED in %) described upon the internal coordinates. *Exp.*: Experimental Raman (R) and infrared (I.R.) peak positions of polycrystalline samples (Majoube 1984). *Cal.*: Calculated wavenumbers (this work). The vibration mode wavenumbers shifts due to the ^{15}N-substitution are also reported in paranthesis. The first number indicates the isotopic displacement $\nu(^{14}N - {}^{15}N)$ when N1, N2 and N3 are substituted. The second concerns the analog displacement but upon the substitution on N7 and N9 atoms. *W* designs an out-of-plane wagging coordinate and *T* a torsion coordinate. D: Deuterium

Guanine C8-deuterated			Guanine N-deuterated			Guanine N,C8-deuterated		
Exp.	Cal.	Assignments(PED%)	Exp.	Cal.	Assignments(PED%)	Exp.	Cal.	Assignments(PED%)
890 IR (4,1)	877 (0,3)	W(N9-H)(54); T(N9-C8)(24) T(C4-N9)(21)						
				841 (0,1)	W(C8-H)(51); T(N9-C8)(25) T(C8=N7)(24)			
802 IR (8,-)	791 (6,0)	W(N1-H)(68); T(N1-C6)(12) T(C2-N1)(10)						
780 R						780 R		
775 IR (3,3)	773 (10,0)	W(C2-N2)(24); T(C2-N1)(19) T(C2=N3)(18); T(N3-C4)(14) T(N1-C6)(13)		780 (13,0)	W(C2-N2)(31); T(C2=N3)(20) W(N1-D)(20); T(N3-C4)(14)	778 IR (3,4)	781 (13,1)	W(C2-N2)(32); T(C2=N3)(21) W(N1-D)(20); T(N3-C4)(14)
	659 (0,3)	W(C8-D)(72); T(N9-C8)(10)				659 IR (5,0)	661 (1,3)	W(C8-D)(75); T(N7-C5)(10)
	614 (0,8)	T(C8=N7)(54); T(N9-C8)(21)	642 IR (3,4)	647 (1,4)	W(N9-D)(28); T(C4-N9)(21) T(N9-C8)(21); W(C8-H)(11)			
				638 (0,10)	W(N9-D)(58); W(C8-H)(14)	638 IR (2,1)	641 (0,6)	W(N9-D)(57); T(N9-C8)(21) T(C4-N9)(14)
							614 (0,7)	T(C8=N7)(51); T(N9-C8)(32)
	576 (4,0)	W(NH2)(89)	572 IR	577 (6,1)	W(N1-D)(59); T(N1-C6)(12) W(C6=O)(10); T(C2-N1)(10)	577 IR	576 (6,0)	W(N1-D)(59); T(N1-C6)(12) T(C2-N1)(10)
502 IR (-,4)	507 (2,0)	W(C6=O)(63)	506 IR (4,3)	491 (0,0)	W(C6=O)(49); T(C2-N1)(13) W(N1-D)(12)	503 IR (3,0)	489 (1,0)	W(C6=O)(49); T(C2-N1)(13) W(N1-D)(11)
			437 IR (5,2)	439 (5,0)	W(ND2)(79); W(C2-N2)(17)	429 IR (5,-)	439 (5,0)	W(ND2)(78); W(C2-N2)(17)
	382 (4,1)	W(C2-N2)(44); T(C2=N3)(14) T(C2-N2)(10); T(N1-C6)(10)						
358 IR (2,2)	342 (1,0)	T(C2-N2)(84)	356 IR (5,2)	369 (2,0)	W(C2-N2)(47); T(C2-N3)(16) T(N1-C6)(15)	345 IR	369 (3,1)	W(C2-N2)(46); T(C2=N3)(16) T(N1-C6)(15)
	292 (0,5)	W(N9-H)(29); T(N7-C5)(19) T(C8=N7)(12)		290 (2,2)	T(N7-C5)(17); T(C2-N2)(14) W(N9-D)(12); T(C8=N7)(11)		290 (2,3)	T(N7-C5)(17); T(C2-N2)(13) W(N9-D)(13); T(C8=N7)(11)
245 IR (7,1)	264 (4,1)	T(C5-C6)(29); T(N3-C4)(17) W(C2-N2)(13); W(N1-H)(11)		274 (2,2)	T(C5-C6)(25); T(C2-N2)(23) W(N9-D)(10)		272 (2,2)	T(C2-N2)(25); T(C5-C6)(24) W(N9-D)(9)
			240 IR	227 (0,0)	T(C2-N2)(79)	234 IR (0,-)	226 (0,0)	T(C2-N2)(78)
202 R	190 (1,1)	T(C2-N1)(19); T(N1-C6)(18)	202 R	186 (1,1)	T(C2-N1)(18); T(N1-C6)(17)		186 (1,1)	T(C2-N1)(19); T(N1-C6)(17)
	143 (1,0)	W(C2-N2)(19); T(N7-C5)(17) W(C6=O)(15)		142 (1,0)	W(C2-N2)(23); T(N7-C5)(16) W(C6=O)(15)		139 (1,0)	W(C2-N2)(22); T(N7-C5)(16) W(C6=O)(15)

Table 3. Comparison between the calculated and experimental wavenumbers (cm^{-1}) of the adenine C8-deuterated, N-deuterated and perdeuterated (C8- and N-deuterated) analogs. *Exp.*: Raman (R) and infrared (I.R.) data from polycrystalline samples (Majoube 1985). *Cal.*: Calculated wavenumbers (this work). *W* designs an out-of-plane wagging coordinate and *T* a torsion coordinate. D: Deuterium

Adenine			Adenine C8-deuterated			Adenine N-deuterated			Adenine N,C8-deuterated		
Exp.	Cal.	Assignments (PED%)	Exp.	Cal.	Assignments (PED%)	Exp.	Cal.	Assignments (PED%)	Exp.	Cal.	Assignments (PED%)
870 R	875	W(N9-H)(46); T(N9-C8)(33)	876 IR	873	W(N9-H)(53); T(N9-C8)(25)						
870 IR		T(C4-N9)(17)			T(C4-N9(20)						
848 R											
847 IR	844	W(C8-H)(52); T(C8=N7)(24)				852 IR	846	W(C8-H)(49); T(N9-C8)(26)			
		T(N9-C8)(18)						T(C8=N7)(24)			
797 R	797	T(C2-N1)(43); T(C2=N3)(27)	797 IR	797	T(C2-N1)(43); T(C2=N3)(27)	798 R	798	T(C2-N1)(42); T(C2=N3)(31)	798 R	798	T(C2-N1)(42); T(C2=N3)(31)
797 IR		W(C2-H)(15)			W(C2-H)(15)	797 IR		W(C2-H)(12)	798 IR		W(C2-H)(13)
771 IR	778	W(C2-H)(63); T(N1-C6)(16)	772 IR	778	W(C2-H)(63); T(N1-C6)(16)	768 IR	776	W(C2-H)(65); T(N1-C6)(14)	770 IR	776	W(C2-H)(65); T(N1-C6)(14)
		T(C2-N1)(12)			T(C2-N1)(12)			T(C2-N1)(14)			T(C2-N1)(14)
			685 IR	688	W(C8-D)(51); T(N9-C8)(20)						
									670 IR	687	W(C8-D)(23); W(N9-D)(22)
						665 IR	667	W(N9-D)(32); T(N9-C8)(19)			T(C4-N9)(16); W(C6-N6)(11)
660 IR	647	W(NH2)(31); T(C2=N3)(24)						T(C4-N9)(16); W(C6-N6)(11)			
		W(C6-N6)(22); W(C2-H)(11)						T(C2=N3)(10)			
650 IR	639	W(C8-H)(37); W(N9-H)(25)	650 IR	644	W(NH2)(39); W(C8-D)(20)	650 R	638	W(C8-H)(47); W(N9-D)(22)	650 IR	648	W(C8-D)(36); W(N9-D)(34)
		T(N7-C5)(17); T(C8=N7)(15)			W(C6-N6)(12); T(C2=N3)(12)	649 IR		T(C8=N7)(12); T(N7-C5)(11)			T(N9-C8)(22)
640 IR	630	W(NH2)(50); T(C2=N3)(16)									
		W(C6-N6)(13)	630 IR	630	W(NH2)(33); W(C8-D)(26)						
						624 IR	619	W(N9-D)(43); T(N9-C8)(15)	625 IR	630	T(N9-C8)(31); T(C8=N7)(14)
								T(C2=N3)(13); W(C6-N6)(10)			T(C2=N3)(12); W(N9-D)(11)
											W(C6-N6)(11)
			615 IR	610	T(C8=N7)(38); T(N9-C8)(11)				617 IR	604	T(C8=N7)(33); W(C8-D)(18)
					T(C2=N3)(11); W(N9-H)(10)						T(N9-C8)(12); T(C2=N3)(10)
						473 IR	475	W(ND2)(64); T(N1-C6)(15)	475 IR	475	W(ND2)(64); T(N1-C6)(15)
								W(C2-H)(14)			W(C2-H)(13)
	367	T(N1-C6)(47); T(C6-N6)(15)		367	T(N1-C6)(47); T(C6-N6)(16)						
		W(C2-H)(11)			W(C2-H)(10)						
327 IR	343	T(C6-N6)(88)	317 R	343	T(C6-N6)(87)		344	T(N1-C6)(44)		344	T(N1-C6)(45)
315 R			308 IR								
						297 R	285	T(C6-N6)(35); W(N9-D)(18)	297 R	282	T(C6-N6)(36); W(N9-D)(19)
	277	W(N9-H)(26); T(N7-C5)(13)		277	W(N9-H)(26); T(N7-C5)(14)						T(N9-C8)(10)
		T(N1-C6)(12); T(C5-C6)(10)			T(N1-C6)(12)	245 IR					
						238 R	240	T(C6-N6)(68)	237 R	240	T(C6-N6)(68)
									235 IR		
243 IR	220	T(C4=C5)(22); T(C5-C6)(18)	240 IR	220	T(C4=C5)(25); T(C5-C6)(15)						
240 R		T(C8=N7)(13); T(N9-C8)(13)			T(C8=N7)(14); T(N9-C8)(12)		216	T(C5-C6)(25); T(C4=C5)(14)		214	T(C5-C6)(23); T(C4=C5)(17)
		W(C6-N6)(12)			W(C6-N6)(11)			W(C6-N6)(14); T(N9-C8)(12)			W(C6-N6)(13); T(C8=N7)(11)
											T(N9-C8)(10)
	210	T(N3-C4)(31); T(N7-C5)(28)		205	T(N3-C4)(29); T(N7-C5)(28)		196	T(C6-N6)(26); T(N3-C4)(23)		193	T(N3-C4)(24); T(C6-N6)(22)
		T(C5-C6)(10)			T(C5-C6)(14)			T(N7-C5)(18)			T(N7-C5)(21)

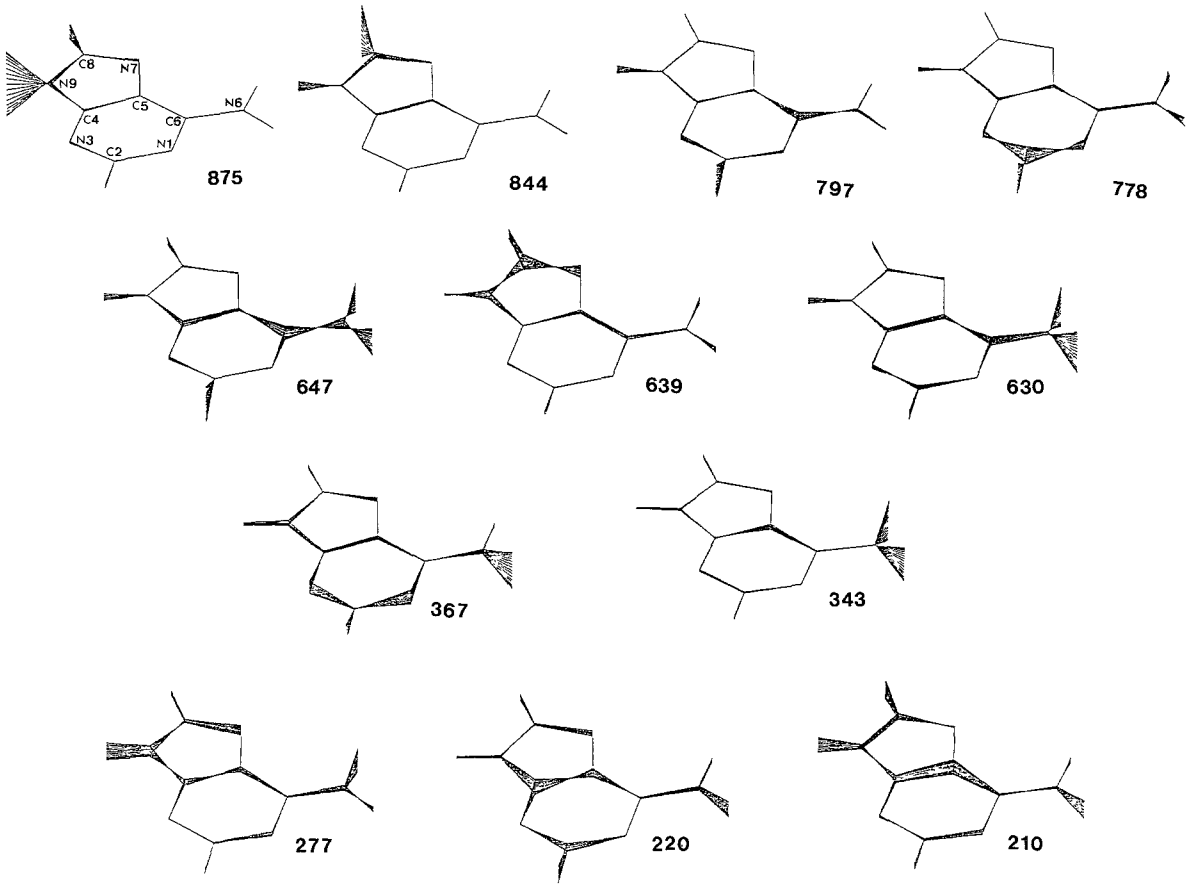

Fig. 3. Graphic representation of the 12 out-of-plane modes for adenine. The base plane initially perpendicular to the drawing plane has been titled about 10° in order to visualize the out-of-plane vibrations. All the situations of the base ring during a period of a given vibration mode have been drawn. The calculated wavenumber (cm^{-1}) of each mode is also noted. See also Table 3

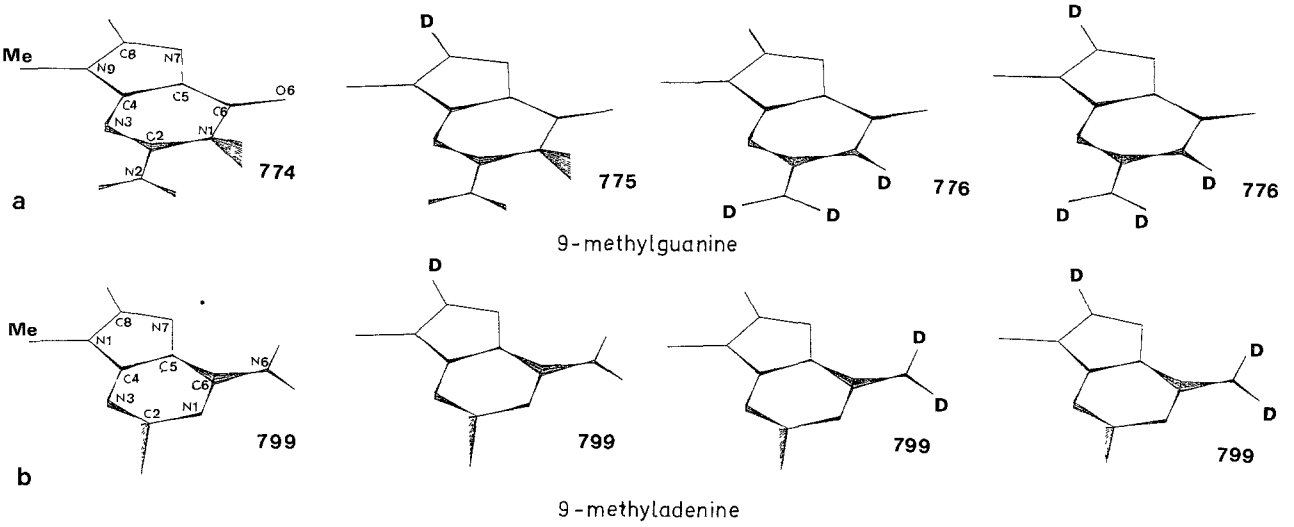

Fig. 4. Representation of the calculated vibration modes allowing us to assign the characteristic infrared bands observed in the 800–750 cm^{-1} spectral region and correlated with the out-of-plane modes of guanine and adenine residues involved in mononucleotides and polynucleotides. See also footnote of Fig. 2. *Me:* methyl group; *D:* deuterium. **a** Characteristic vibration modes calculated in 9-methylguanine and its C8-deuterated, N-deuterated and perdeuterated (C8- and N-deuterated) analogs. See also Table 5 a. **b** Characteristic vibration modes calculated in 9-methyladenine and its C8-deuterated, N-deuterated and perdeuterated (C8- and N-deuterated) analogs. See also Table 5 b

9-Methyladenine			9-Methylguanine	
Exp.	Cal.	Assignments (PEDX)	Cal.	Assignments (PEDX)
842(c)	848	W(C8-H)(52); T(N9-C8)(25)	844	W(C8-H)(54); T(N9-C8)(23)
841(b)		T(C8=N7)(22)		T(C8=N7)(22)
840(a)				
799(b)	799	T(C2-N1)(43); T(C2=N3)(30)		
796(c)		W(C2-H)(13)	791	W(N1-H)(68); T(N1-C6)(12)
795(a)				T(C2-N1)(10)
	779	W(C2-H)(63); T(N1=C6)(15)		
		T(C2-N1)(13)	774	W(C2-N2)(24); T(C2-N1)(19)
				T(C2=N3)(19); T(N3-C4)(14)
				T(N1-C6)(13)
	653	T(C2=N3)(28); W(C6-N6)(26)		
655(c)				
	637	W(C8-H)(29); T(C8=N7)(22)	638	W(C8-H)(31); T(C8=N7)(25)
		W(N9-Cm)(19); T(N7-C5)(16)		W(N9-Cm)(23); T(N7-C5)(16)
650(c)	634	W(NH2)(67)		
			576	W(NH2)(88)
			521	W(C6=O)(58)
	406	W(N9-Cm)(68)	403	W(N9-Cm)(61); W(C6=O)(10)
	365	T(N1=C6)(46); T(C6-N6)(22)	382	W(C2-N2)(44); T(C2=N3)(13)
355(b)		W(C2-H)(11)		T(C2-N2)(10); T(N1-C6)(10)
354(c)				
	340	T(C6-N6)(84)	340	T(C2-N2)(86)
245(b)	233	T(C5-C6)(22); T(C4-N9)(21)	265	T(C5-C6)(29); T(N3-C4)(17)
		T(N3-C4)(16); W(N9-Cm)(11)		W(C2-N2)(13); W(N1-H)(11)
205(b)	219	T(C4=C5)(20); T(N9-C8)(17)	219	T(C4-N9)(26); T(N9-C8)(22)
		T(C5-C6)(14); T(C8=N7)(14)		T(C8=N7)(16); T(N1-C6)(13)
		W(C6-N6)(12)		W(N9-Cm)(10)
			164	T(C2-N1)(22); T(C2=N3)(16)
				W(C2-N2)(15); T(C5-C6)(13)
				T(C4=C5)(12)
	142	T(N7-C5)(29); T(N9-C8)(19)	126	T(N7-C5)(26); W(C6=O6)(15)
		T(N3-C4)(14)		T(N9-C8)(11); T(N3-C4)(11)

Table 4. Out-of-plane mode wavenumbers (cm^{-1}) relative to 9-methyladenine and 9-methylguanine. Assignments based on the PED (in %) are also described. *Exp.* Experimental data. a: Infrared spectrum of oriented single crystals of 9-methyladenine (Kyogoku et al. 1967). b: Raman spectrum of polycrystalline 9-methyladenine (Savoie et al. 1981). c: Infrared spectrum of polycrystalline 9-methyladenine (Savoie et al. 1981). *Cal.* Calculated wavenumbers (this work). *W* designs an out-of-plane wagging coordinate and *T* a torsion coordinate. Cm: methyl group

Table 5a. Comparison between the experimental and calculated results for the characteristic infrared band located around 780 cm^{-1} and correlated to a guanine residue out-of-plane mode. 2'-deoxyguanosine 5'-monophosphate (5'-dGMP) infrared spectra (Ghomi and Taillandier 1985). poly d(G−C) · poly d(G−C) infrared spectra (Taboury et al. 1985). poly d(A−C) · d(G−T) infrared spectra (Taillandier et al. 1984). *A*: *A* form; *B*: *B* form; *Z*: *Z* form. The calculated wavenumbers of 9-methylguanine and its C8-deuterated, N-deuterated and perdeuterated analogs (this work) are also reported. For assignment see also Table 4

Table 5b. Comparison between the experimental and calculated results for the characteristic infrared band of the adenine residue located around 795 cm^{-1}. 2'-deoxyadenosine 5'-monophosphate (5'-dAMP) infrared spectra (Taillandier et al. 1985). poly d(A−T) · poly d(A−T) infrared spectra (Adam et al. 1985). poly d(A−C) · poly d(G−T) infrared spectra (Taillandier et al. 1984). *A*: *A* form; *B*: *B* form; *D*: *D* form; *Z*: *Z* form. The calculated wavenumbers of 9-methyladenine and its C8-, N- and perdeuterated are also reported. For assignments see also Table 4

Table 5a

Experimental				Calculated		Experimental		Calculated	
5'-dGMP		poly(dG-dC).poly(dG-dC)	poly(dA-dC).poly(dG-dT)	9-methylguanine		poly(dBG-dC).poly(dBG-dC)		9-methylguanine	C8-deuterated
in H2O	in D2O	in H2O	in D2O	in H2O	in D2O	pure	N1,N2-deuterated	in H2O	in D2O	pure	N1,N2-deuterated
778	778	778 (B)	778 (B)	780 (A)	782 (A)	774	776	778 (B)	778 (B)	775	776
		782 (Z)	784 (Z)	780 (B)	787 (B)			782 (Z)	782 (Z)		
				782 (Z)	784 (Z)						

Table 5b

Experimental				Calculated		Experimental		Calculated	
5'-dAMP		poly(dA-dT).poly(dA-dT)	poly(dA-dC).poly(dG-dT)	9-methyladenine		poly(dD8A-dT).poly(dD8A-dT)		9-methyladenine	C8-deuterated
in H2O	in D2O	in H2O	in D2O	in H2O	in D2O	pure	N6-deuterated	in H2O	in D2O	pure	N6-deuterated
795	795	795 (A)	795 (A)	796 (A)	796 (A)	799	799	798 (A)	795 (A)	799	799
		795 (B)	795 (B)	794 (B)	796 (B)			798 (B)	795 (B)		
		796 (D)	796 (D)	795 (Z)	795 (Z)						

ability of the force field to interpret the out-of-plane modes of the purine base residues involved in mononucleotides or polynucleotides.

Recent experimental results obtained by I.R. linear dichroism on polynucleotides showed that the bands around 780 cm^{-1} and 795 cm^{-1} arise mainly from the out-of-plane vibration modes of guanine and adenine residues respectively (Ghomi et al. 1984; Chinsky et al. 1984; Taboury et al. 1985; Taillandier et al. 1984, 1985; Adam et al. 1986). It should be mentioned that in the infrared spectrum of *B* form poly d(G−C) · poly d(G−C) the guanine and cytosine non-planar contributions are superimposed and give rise to a narrow and intense band at 778 cm^{-1}. In the *Z* form the guanine contribution is shifted to the high frequency region and makes its assignment easier.

Table 5a shows the position of the guanine non-planar mode observed simultaneously in 5′-dGMP, poly d(G−C) · poly d(G−C) and poly d(A−C) · poly d(G−T) infrared spectra. This mode is not sensitive to C8-deuteration and should, therefore, arise from the pyrimidic ring of the guanine residue. On an other hand, as the maximum shift upon N-deuteration is not larger than 2 cm^{-1}, the corresponding mode should not involve the N−H out-of-plane wagging contribution. Similar behaviour has been found for the adenine residue out-of-plane mode located around 795 cm^{-1} in the infrared spectra of 5′-dAMP, poly d(A−C) · poly d(G−T) and poly d(A−T) · poly d(A−T) (Table 5b).

These experimental results confirm the location of the above-mentioned vibration modes in guanine and adenine rings. 9-methylguanine and 9-methyladenine can therefore be considered as reasonable dynamic models for the interpretation of these out-of-plane modes observed in mononucleotides or polynucleotides containing guanine and adenine bases (Table 5a and b; Fig. 4a and b).

In conclusion, the validity of the base out-of-plane force field detailed here and in our recent paper (Letellier 1986a) has been demonstrated by assigning the non-planar modes of the pyrimidine and purine residues observed in the 800−750 cm^{-1} region of the infrared spectra of mononucleosides (tides) or polynucleotides. It will be interesting, in the future, to use this force field in the vibration mode calculations on the overall motions of oligo and polynucleotides.

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