August, 1987] © *1987 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 60, 2769—2774 (1987)* 2769

Polarized Raman and Infrared Spectra of 2-Amino- and 2-Amino-d_2-pyrimidines

Masayoshi MAEHARA, Sekiichiro NAKAMA,† Yoshinori NIBU, Hiroko SHIMADA,* and Ryoichi SHIMADA††
Department of Chemistry, Faculty of Science, Fukuoka University, Nanakuma, Jonan-ku, Fukuoka 814-01
†Department of Chemistry, Faculty of Liberal Arts, University of Yamaguchi, Yoshida, Yamaguchi 753
††Department of Chemistry, Faculty of Science, Kyushu University 33, Hakozaki, Higashi-ku, Fukuoka 812

(Received February 16, 1987)

An assignment of the normal vibrations of 2-aminopyrimidine was made through the vibrational analyses of the polarized Raman and infrared spectra and also through the normal coordinate calculation. The assignment was confirmed by the same study made on 2-amino-d_2-pyrimidine.

Lafaix and Lebas studied the infrared and Raman spectra of various amino-substituted pyrimidines and gave tentative assignments for some normal vibrations of these molecules.1) Kydd studied the amino inversion vibration of 2-aminopyrimidine through observation of the infrared spectrum in vapor and showed that the molecule is planar in the vibrational ground state.2) Scheinbeim and Schempp3) and Furberg et al.4) determined the crystal structure of 2-aminopyrimidine and pointed out that the molecules form hydrogen-bonded dimer-like pairs in crystal.

Since the orientation of the 2-aminopyrimidine molecule in crystal has been known, the vibrational analyses of the polarized Raman and infrared spectra in single crystals became possible. In this paper, the assignment of the normal vibrations of 2-aminopyrimidine is discussed based on polarization behavior of the Raman and infrared bands observed in single crystals and also the normal coordinate calculation. The same study is made on 2-amino-d_2-pyrimidine and the assignment is confirmed.

Experimental

Material. 2-Amino-d_2-pyrimidine was synthesized by the exchange reaction of 2-aminopyrimidine obtained from Tokyo Kasei Chemical Company with D_2O. Isotopic purity of the product was determined by the nuclear magnetic resonance measurement. The samples were purified by zone-refining of about 100 passages.

Optical Measurements. Polarization measurement of the Raman spectrum was made in molten and single crystal phases with a JEOL 400 T Laser Raman Spectrophotometer. The sample was excited with the 514.5 nm line from an Ar^+ ion laser. A well grown single crystal of 2-aminopyrimidine obtained by the Bridgman method was cut along the cleavage bc plane and then cut along the ab and ac planes. Samples with cubic shape of about 5 mm^3 were prepared. The crystal axes were determined by observing the birefringence under the polarization microscope. The crystal growth direction was found to be the c axis. 2-Amino-d_2-pyrimidine changes quite rapidly into 2-amino- and 2-amino-d_1-pyrimidines by the exchange reaction with moisture in atmosphere, and thus the polarized Raman spectrum of the 2-amino-d_2-pyrimidine crystal was observed for a single crystal grown in a capillary glass tube of about 50 mm in length and 3 mm in diameter. The method of measurement of the polarized Raman spectrum was exactly the same as that described previously.5,6)

The infrared spectrum of 2-aminopyrimidine was observed in vapor and single crystal phases with a Hitachi Infrared Spectrophotometer Model 345. The single crystal sample was grown between two KRS-5 plates in the same way as that described previously.7) A well grown single crystal portion of the crystal sample was selected under polarized light and other portion was covered with aluminum foil. The polarized infrared spectrum was measured with an AgBr wire-grid polarizer. The incident infrared light was polarized by the polarizer in such a way that the electric vector pointed in the direction of 45° from both the vertical and horizontal directions. The polarizer is rotatable by 90°. Although the spectrophotometer had some preferential sensitivity to vertically polarized light, the two components of the diagonally polarized light beam behaved equally concerning the intensity. The sample crystal sandwiched between two KRS-5 plates was held in a cell holder adjusting the orientation of the crystal, so that the spectrum showed the most remarkable polarization behavior by rotating the polarizer by 90°. The spectrum observed with polarized light which gives the maximum intensity for the strong and narrow band at 1210 cm^{-1} is referred to as the $\perp$ spectrum and that giving the minimum intensity is to as the // spectrum. In this orientation of the sample crystal, the crystal growth direction (c axis) was found to point roughly in the vertical direction. The infrared spectrum of the 2-amino-d_2-pyrimidine single crystal could not be observed because the deuterium atoms were replaced by the hydrogen atoms with moisture in atmosphere.

Normal Coordinate Calculation

A normal coordinate calculation was performed through the standard GF matrix methods with a FACOM M-200 computer at the Computer Center of Fukuoka University. The geometric parameters of the 2-aminopyrimidine molecule were taken from the data determined by Scheinbeim and Schempp.3) The F matrix elements for the in-plane vibrations were evaluated with the potential field of an improved modification of the Urey-Bradley force field described previously.5–7) For the out-of-plane vibrations the valence force field and ϕ type torsional coordinates were used. Values of the force constants used for the calculation of the in-plane and out-of-plane normal vibrations of 2-amino- and 2-amino-d_2-pyrimidines are listed in Table 1. The notation of the force constants are exactly the same as those used previously5–7) and the symbols given for atoms and internal coordinates are shown in Fig. 1. The calculated frequencies and modes of the normal vibrations are given in Table 4.

Table 1. Force Constants for the In-Plane and Out-of-Plane Vibrations of 2-Aminopyrimidine[a)]

$K_{C'-N}$[b)]	5.2 hNm^{-1}	$F_{N\cdots N}$	0.8 hNm^{-1}	$Q_{C'-N}$	0.17 $aNmrad^{-2}$
K_{C-N}	5.4	$F_{C'\cdots C}$	0.5	Q_{N-C}	0.18
K_{C-C}	4.5	$F_{N\cdots C}$	0.3	Q_{C-C}	0.2
$K_{N'-C'}$	4.3	$F_{C\cdots C}$	0.7	$Q_{N'-C'}$	0.1
K_{C-H}	4.4	$F_{N\cdots N}$	0.9	$P_{N'}$	0.13
$K_{N'-H'}$	5.9	$F_{H\cdots C'}$	0.5	P_H	0.32
$H_{N-C'-N}$	0.75	$F_{H\cdots H'}$	0.1	$q^{o}_{N'}$[c)]	−0.15
$H_{C'-N-C}$	0.5	$F_{N\cdots H}$	0.75	$q^{o}_{C'}$[c)]	−0.1
H_{N-C-C}	0.6	$F_{C\cdots H}$	0.45	q^{o}_{C}[c)]	−0.06
H_{C-C-C}	0.4	ρ	0.35	$q^{m}_{N'}$	0.04
$H_{N'-C'-N}$	0.4	k^{o}_{rr}	0.06	q^{m}	0.03
H_{N-C-H}	0.18	k^{m}_{rr}	−0.06	q^{p}	0.04
H_{C-C-H}	0.18	$h^{m}_{R\alpha}$	−0.7 $nNrad^{-1}$	p^{o}	0.02
$H_{H'-N'-H'}$	0.43	$h^{m}_{R\beta}$	0.5	$p^{m}_{H,H}$	0.02
$H_{H'-N'-C'}$	0.28			$t^{o}_{N'}$[d)]	−0.01
				t^{o}_{H}[d)]	−0.06
				t^{m}_{H}	0.02

a) The same values of the force constants were used for the calculation made on 2-amino-d_2-pyrimidine, where H′ atom of the amino group is replaced by D atom. b) See Fig. 1 for notation of atoms. c) Torsional vibration involving N′, C, or C′ atom. d) Wagging vibration involving N′ or H atom.

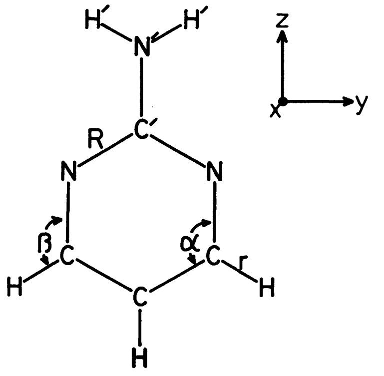

Fig. 1. Symbols for the atoms and internal coordinates.

Calculation of Relative Intensities of the Raman and Infrared Bands in Single Crystals

2-Aminopyrimidine crystallizes in orthorhombic space group D_{2h}^{15} with eight molecules in the unit cell, where the structure contains centrosymmetrically related hydrogen-bonded dimer-like pairs separated by hydrophobic regions and the dihedral angle between the planes of the amino group and pyrimidine ring is about 22°.[3,4)] The projection of the crystal structure on the bc plane is shown in Fig. 2. No factor group splitting was observed for the Raman bands due to molecular vibrations in crystal and thus the relationship between the Raman tensors for the free molecule and the crystal was derived based on the simple oriented gas model. Evaluation of the matrix elements of the Raman tensor of 2-aminopyrimidine was made in the same way as that made for maleic anhydride[5)] and tetramethylpyrazine.[6)] The direction cosines between the crystal and molecular axes were calculated using the crystal data given by Scheinbeim and Schempp.[3)] The squares of relative values of the elements of the Raman tensor, which are proportional to the relative intensities of the Raman bands, are given in Table 2, where the molecular structure of 2-aminopyrimidine is assumed to belong to point group C_{2v}.

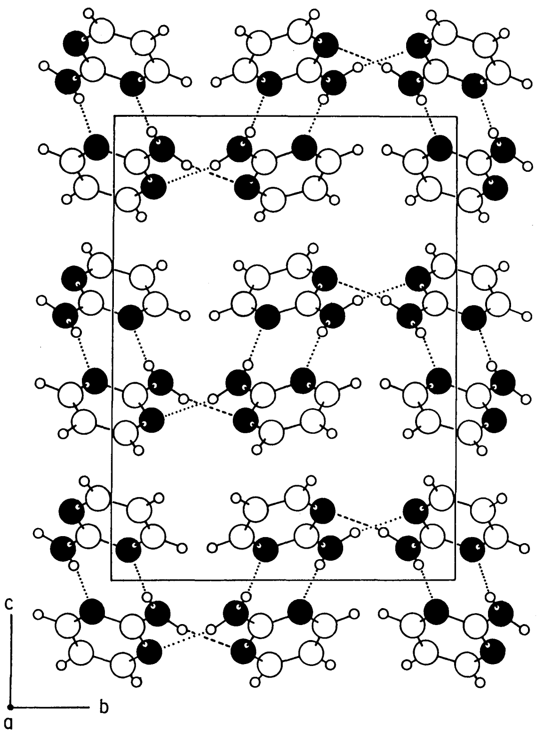

Fig. 2. Projection of the 2-aminopyrimidine crystal on the bc plane.

In order to carry out the vibrational analysis of the polarized infrared spectrum, the crystal axes in the sample crystal sandwiched between two KRS-5 plates have to be determined. Since the crystal growth direction (c axis) was found in a plane of the sample crystal,

Table 2. Squares of the Relative Values of Elements of the Raman Tensors for 2-Aminopyrimidine

	b_2	b_1	a_2
$(A_{aa})^2$	0.31	0.68	0.18
$(A_{bb})^2$	0.81	0.11	0.17
$(A_{cc})^2$	0.12	0.25	0.70
$(A_{ab})^2$	0.10	0.02	0.28
$(A_{ac})^2$	0.27	0.15	0.0
$(A_{bc})^2$	0.0	0.31	0.20

Table 3. Proportionality Factors of the Intensity of the Infrared Bands in the // and ⊥ Spectra

θ[a)]	Pol[b)]	a_1	b_2	b_1
0°	//	0.42	0.02	0.55
	⊥	0.04	0.83	0.13
10°	//	0.45	0.10	0.45
	⊥	0.01	0.76	0.23
20°	//	0.46	0.21	0.33
	⊥	0.00	0.65	0.35

a) θ is the angle between the c axis and the vertical line. The plane of the sample crystal was assumed to be the cleavage bc plane. b) For the definition of the // and ⊥ polarized spectra, see text.

the plane would be the cleavage bc or ac plane. Proportionality factors of the intensity of the infrared bands in the // and ⊥ spectra were calculated for the bands assigned to the vibrations belonging to symmetry species a_1, b_2, and b_1 assuming that the sample crystal plane is the bc or ac plane, in the same way as calculated for pyrazine.[9)] The calculation was made varying the angle between the c axis and the vertical line and the values obtained for the angles of 0, 10, and 20° for the bc plane are listed in Table 3.

Results and Discussion

2-Aminopyrimidine. The polarized Raman spectrum of 2-aminopyrimidine observed in single crystal is shown in Fig. 3. The polarized spectrum was denoted by two characters such as ab in the same manner as described previously.[5,6)] The first letter refers to the direction of polarization of the excitation light and the latter to that of the scattering light. It is expected from Table 2 that the relative intensity of the b_2 vibrations is strongest in the bb polarized spectrum, the b_1 vibrations in the aa spectrum and the a_2 vibrations in the cc spectrum.

The polarized infrared spectrum of 2-aminopyrimidine in single crystal is shown in Fig. 4, where the // and ⊥ spectra are drawn with the solid and dotted lines, respectively. As can be seen in the figure, polarization behavior of the infrared bands in crystal can be classified into three types. The bands showing the first type polarization are almost missing in the ⊥ spectrum, while the second type bands are observed much strongly in the ⊥ spectrum. The intensity of the third type bands observed in the // spectrum is about 1.5 times strong as that in the ⊥ spectrum. These three types of polarization behavior are referred to as the types I, II, and III, respectively. The proportionality factors of the intensity of the bands calculated for the bc plane, which is given in Table 3, indicate that the spectra can be well explained by the values calculated for the crystal orientation with the c axis pointing in the direction of 10° from the vertical line. This means

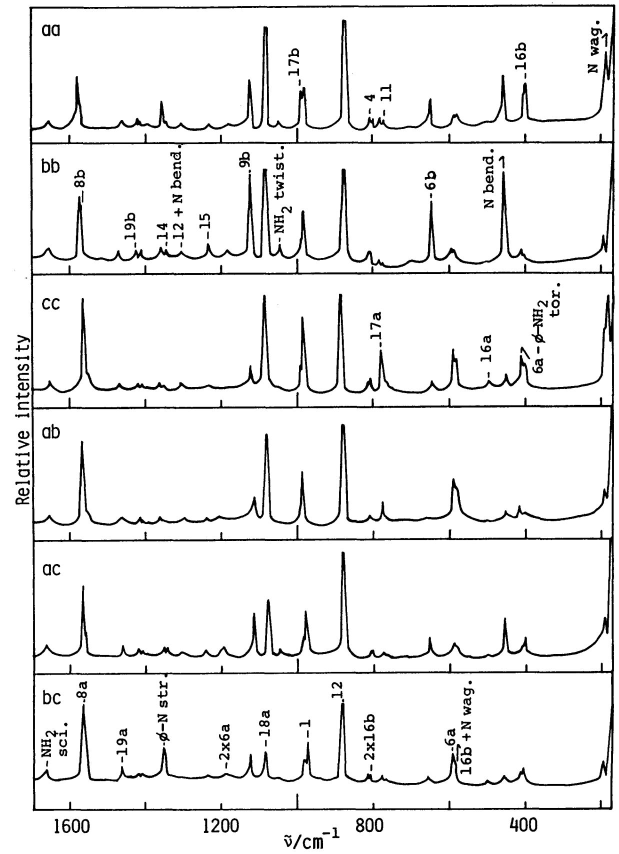

Fig. 3. Polarized Raman spectra of the 2-aminopyrimidine crystal. For the definition of the symbols of the spectra such as aa, see text.

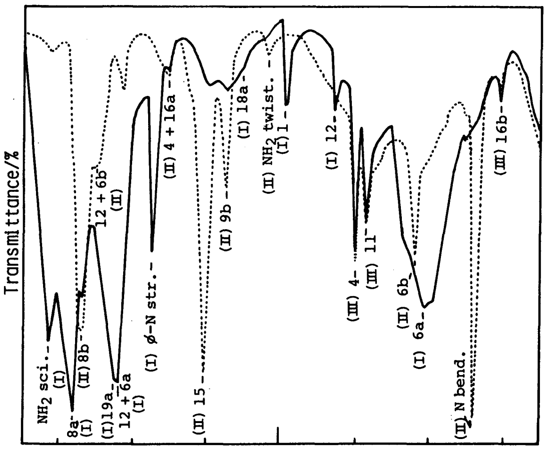

Fig. 4. Polarized infrared spectrum of the 2-aminopyrimidine crystal.

that the propagation direction of the incident light was along the a axis and the direction of the electric vector deviated from the c axis by 35° in our polarization measurement. The calculation was also made for the ac plane, but the result was not consistent with the observed polarization behavior even if the sample crystal assumes to be in any orientation. Thus the infrared bands showing the type I, II, and III polarization behavior could be assigned to the vibrations belonging to the symmetry species a$_1$, b$_2$, and b$_1$, respectively.

The vibrational modes were determined through the normal coordinate calculation. Since the 2-aminopyrimidine molecule forms hydrogen-bonded dimer-like pairs in crystal, the infrared bands whose frequencies largely shift in crystal from those in vapor could be assigned to the vibration involving the NH_2 group.

Species a$_1$: The strongly polarized Raman bands observed at 3330, 3025, 1580, 1448, 1360, 1080, 990, and 870 cm^{-1} in molten phase were directly ascribed to the a$_1$ vibrations and assigned to the N-H stretching, ν_2, ν_{8a}, ν_{19a}, ϕ-N stretching, ν_{18a}, ν_1, and ν_{12} vibrations, respectively. Where ϕ refers to the pyrimidine ring. The corresponding infrared bands showed the type I polarization as predicted. The Raman band observed at 1650 cm^{-1}, whose corresponding infrared band was observed strongly in crystal but was not in vapor and showed the type I polarization, was ascribed to the NH_2 scissoring vibration of the hydrogen-bonded molecule. The strong infrared band observed at 1597 cm^{-1} in vapor was assigned to the NH_2 scissoring vibration of the free molecule. The band at 605 cm^{-1} showing the type I polarization was assigned to the ν_{6a} vibrations, although the corresponding Raman band showed low depolarization factor in molten phase.

Species b$_2$: The relative intensities of the Raman bands observed at 1558, 1425, 1355, 1230, 1130, 1040, 642, and 457 cm^{-1} were strongest in the bb spectrum and decreased in the aa and ac spectra in order. This polarization behavior is consistent with the assignment to the b$_2$ vibrations and thus these bands were assigned to the ν_{8b}, ν_{19b}, ν_{14}, ν_{15}, ν_{9b}, NH_2 twisting, ν_{6b}, and N bending vibrations, respectively. The corresponding infrared bands showed the type II polarization.

Species b$_1$: The relative intensities of the Raman bands observed at 997, 802, 765, 410, and 187 cm^{-1} were strongest in the aa spectrum and medium in the bc and cc spectra. Thus these bands were assigned to the ν_{17b}, ν_4, ν_{11}, ν_{16b}, and N wagging vibrations belonging to the species b$_1$, respectively. The corresponding infrared bands showed the type III polarization. The NH_2 wagging vibration could not be resolved.

Species a$_2$: The relative intensities of the Raman bands observed at 782, 516, and 417 cm^{-1} were strongest in the cc spectrum and decreased in the ab, bc, aa, and bb spectra in order. Thus these bands were assigned to the ν_{17a}, ν_{16a}, ν_{6a}—ϕ-NH_2 torsional vibrations of the species a$_2$, respectively. The very weak infrared band observed at 514 cm^{-1} in crystal was assigned to the ν_{16a} vibration of the species a$_2$. An appearance of the infrared inactive a$_2$ band may be due to the distortion of the molecular structure in crystal.

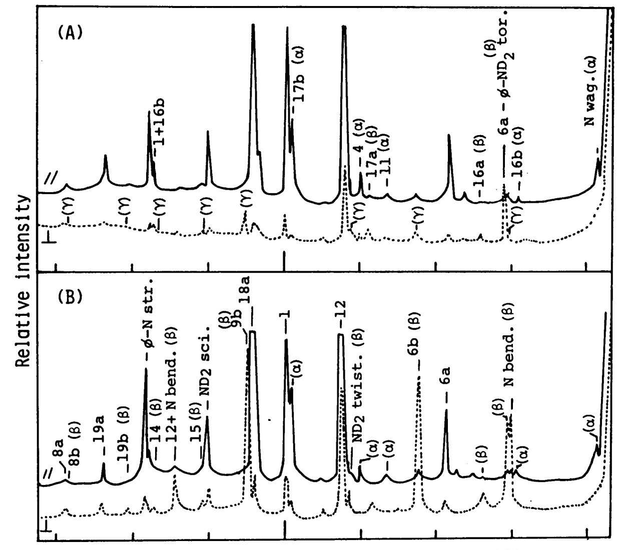

Fig. 5. Polarized Raman spectrum of the 2-amino-d_2-pyrimidine crystal. For the definition of the spectra of (A) and (B), see text.

2-Amino-d_2-pyrimidine. The polarized Raman spectrum of 2-amino-d_2-pyrimidine is given in Fig. 5. A single crystal of 2-amino-d_2-pyrimidine grown in a capillary tube was held in a cell holder in such a way that the crystal growth direction was along the polarization direction of the excitation light and the scattering light was observed at the direction perpendicular to the excitation light beam. The polarized Raman spectra were observed in two crystal orientations, in which the spectra showed drastically different polarization behaviors with each other. These crystal orientations are referred to as the orientations A and B. The narrow band at 648 cm^{-1} gave the minimum intensity in the orientation A and the maximum intensity in the orientation B.

The Raman spectra observed for the scattering lights polarized parallel and perpendicular to the crystal growth direction are referred to as the // and ⊥ spectra, respectively. The polarized Raman bands can be classified into three types α, β, and γ as indicated in Fig. 5. The type α refers to the band whose intensity is stronger in the // spectrum than in the ⊥ spectrum, the type β to the band whose intensity is stronger in the ⊥ spectrum than in the // spectrum, and the type γ to the band whose intensity is nearly equal in the // and ⊥ spectra. Polarization behavior of the Raman band is represented by two symbols such as $\gamma\beta$, where the first and second letters refer to the types of polarization behavior observed in the crystal orientations A and B, respectively. Observed polarization behavior of the non-totally symmetric Raman bands can be classi-

Table 4. Normal Vibrations of 2-Amino- and 2-Amino-d_2-pyrimidines

Sym	Mode	2-Aminopyrimidine							2-Amino-d_2-pyrimidine				
		L.L[a]	Raman			Infrared		Calcd	L.L[a]	Raman			Calcd
		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}	Pol Cry	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		$\tilde{\nu}$/cm^{-1}
				Liq	Cry						Liq	Cry	
a_1	N-H str.[b]		3330	p				3327		2410	p		2399
	ν_2		3025	p				3038		3027	p		3038
	ν_{13}							2993		2995			2993
	NH$_2$ sci.[b]		1650			1630	I	1650		1205			1209
	ν_{8a}	1576	1580	p		1560	I	1562	1597	1578	p		1563
	ν_{19a}	1440	1448	p		1460	I	1466	1421	1475	p		1470
	ϕ-N str.		1360	p		1348	I	1336		1363	p		1347
	ν_{18a}	1087[c]	1080	p		1090	I	1103	1081[c]	1078	p		1103
	ν_1	997	990	p		990	I	1008	997	983	p		1002
	ν_{12}	870	870	p		862	I	878	853	848	p		863
	ν_{6a}		587	p?		605	I	602		578	p?		585
b_2	N-H str.[b]		3395					3391		2520	dp	$\gamma\beta$	2512
	ν_{7b}		3050	dp				3058		3053	dp	$\gamma\beta$	3058
	ν_{8b}	1556	1558	dp	bb	1544	II	1563	1556	1557	dp	$\gamma\beta$	1550
	ν_{19b}	1472	1425	dp	bb			1415	1495	1420	dp	$\gamma\beta$	1415
	ν_{14}	1320	1355	dp	bb			1350	1290	1350	dp	$\gamma\beta$	1331
	ν_{15}	1224[c]	1230	dp	bb	1210	II	1225	1219[c]	1220	dp	$\gamma\beta$	1223
	ν_{9b}	1176[c]	1130	dp	bb	1155	II	1139	1168[c]	1102	dp	$\gamma\beta$	1122
	NH$_2$ twist.[b]		1040	dp	bb	1040	II	1039		823	dp	$\gamma\beta$	838
	ν_{6b}	644	642	dp	bb	640	II	655	643	648	dp	$\gamma\beta$	655
	N bend.		457	dp	bb	472	II	462		407	dp	$\gamma\beta$	423
b_1	ν_{17b}		997	dp	aa			990		975	dp	$\alpha\alpha$	990
	ν_4	804[c]	802	dp	aa	798	III	814	801[c]	798	dp	$\alpha\alpha$	824
	ν_{11}		765	dp	aa	768	III	730		745	dp	$\alpha\alpha$	737
	ν_{16b}	524	410	dp	aa	410	III	415	539	390	dp	$\alpha\alpha$	408
	NH$_2$ wag.[b]							377					315
	N wag.		187	dp	aa			187		173		$\alpha\alpha$	174
a_2	ν_{17a}	788[c]	782	dp	cc			781	788[c]	780	dp	$\beta\beta$	781
	ν_{16a}	411	516	dp	cc	514		526	405	480	dp	$\beta\beta$	480
	ϕ-NH$_2$ tor.[b]		172[d]					190		163[d]			149

a) See Ref. 1. b) H is replaced by D in 2-amino-d_2-pyrimidine. Vibrational modes for the NH$_2$ group are determined on referring to Ref. 8. c) Lafaix and Lebas presented the modes of H bending and H wagging vibrations instead of individual modes such as ν_{18a} and ν_{11} vibrations for these frequencies. d) Frequency obtained from difference band.

fied into three types $\gamma\beta$, $\alpha\alpha$, and $\beta\beta$ through which each Raman band can be experimentally assigned to the certain symmetry species.

Species a$_1$: The strongly polarized Raman bands observed at 3027, 2410, 1578, 1475, 1363, 1078, 983, and 848 cm^{-1} in molten phase were assigned to the ν_2, N–D stretching, ν_{8a}, ν_{19a}, ϕ–N stretching, ν_{18a}, ν_1, and ν_{12} vibrations, respectively. The Raman band observed at 578 cm^{-1} in molten with low depolarization factor and the band clearly observed at 1205 cm^{-1} in crystal were assigned to the ν_{6a} and ND$_2$ scissoring vibrations, respectively, because these bands showed no $\gamma\beta$, no $\alpha\alpha$, and no $\beta\beta$ polarization behavior in crystal.

Species b$_2$: The depolarized Raman bands observed at 3053, 2520, 1557, 1420, 1350, 1220, 1102, 823, 648, and 407 cm^{-1} in molten phase showed the type $\gamma\beta$ polarization in crystal and were assigned to the ν_{7b}, N–D stretching, ν_{8b}, ν_{19b}, ν_{14}, ν_{15}, ν_{9b}, ND$_2$ twisting, ν_{6b}, and N bending vibrations, respectively, because the frequencies of the out-of-plane vibrations are lower than 1000 cm^{-1} in pyrimidine derivatives.

Species b$_1$: The depolarized Raman bands observed at 975, 798, 745, 390, and 173 cm^{-1} in molten phase showed the type $\alpha\alpha$ polarization in crystal and were assigned to the ν_{17b}, ν_4, ν_{11}, ν_{16b}, and N wagging vibrations, respectively.

Species a$_2$: The depolarized Raman bands observed at 780, 480, and 415 cm^{-1} in molten phase showed the type $\beta\beta$ polarization in crystal and thus were assigned to the ν_{17a}, ν_{16a}, and ν_{6a}—ϕ–ND$_2$ torsional vibrations, respectively.

The normal vibrations thus assigned are summarized in Table 4. The table shows that the assignment of the normal vibrations given for 2-amino-d_2-pyrimidine is consistent with the assignment given for 2-aminopyrimidine, and this fact confirms the reasonability of the assignments.

The normal coordinate calculation indicates that the ν_{19a},ν_{12}, and ν_{6a} vibrations mix largely with the ϕ–N stretching vibration. This mixing is supported by the experimental fact that the ν_{19a} vibration increases in frequency and the ν_{12} and ν_{6a} vibrations decrease compared with the corresponding vibrations of pyrimidine (1402, 1068, and 677 cm^{-1}).[10] The normal coordinate calculation shows that the ν_{16b} and ν_{16a} vibrations mix with the N wagging and ϕ-NH$_2$ torsional vibrations, respectively. The fact that the ν_{16b} and ν_{16a} vibrations increase in frequency compared with the corresponding vibrations of pyrimidine (344 and 394 cm^{-1}) justifies the mixing. The ν_{17a} vibration decreases in frequency compared with the ν_{17a} vibration of pyrimidine (1004 cm^{-1}). This fact may be caused by the mixing of the ν_{17a} and NH$_2$ twisting vibrations as indicated by the normal coordinate calculation. The out-of-phase displacements of the H atoms of the NH$_2$ group from the plane of the pyrimidine ring are calculated to be fairly large in the NH$_2$ twisting vibration because of the nonplanality of the planes of the amino group and the ring. The same frequency shifts due to vibrational mixing were also found in the normal vibrations of 2-amino-d_2-pyrimidine. The vibrational analysis of the polarized sublevel phosphorescence spectra of 2-aminopyrimidine, which will be reported soon, also confirms the validity of the assignments made in this work.[11]

References

1) A. J. Lafaix and J. M. Lebas, *Spectrochim. Acta,* **26A**, 1243 (1970).

2) R. A. Kydd, *Chem. Phys. Lett.,* **61**, 183 (1979).

3) J. S. Scheinbeim and E. S. Schempp, *Acta. Cryst.,* **B32**, 607 (1976).

4) S. Furberg, J. Grφgaard, and B. Smedsrud, *Acta. Chem. Scand.,* **B33**, 715 (1979).

5) Y. Ishibashi, R. Shimada, and H. Shimada, *Bull. Chem. Soc. Jpn.,* **55**, 2765 (1982).

6) Y. Ishibashi, F. Arakawa, H. Shimada, and R. Shimada, *Bull. Chem. Soc. Jpn.,* **56**, 1327 (1983).

7) S. Kizuki, Y. Ishibashi, H. Shimada, and R. Shimada, *Mem. Fac. Sci. Kyushu Univ. Ser. C,* **13**, 7 (1981).

8) A. K. Kalkar and C. C. Ars, *Bull. Chem. Soc. Jpn.,* **59**, 3223 (1986).

9) S. Califano, G. Adembri, and G. Sbrana, *Spectrochim. Acta,* **20**, 385 (1964).

10) G. Sbrana, G. Adembri, and S. Califano, *Spectrochim. Acta,* **22**, 125 (1966).

11) M. Maehara, H. Shimada, and R. Shimada, Symposium on the Molecular Structure and Molecular Electronic Structure, Osaka, November 1986, Abstr. No. 1B08.