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Normal Vibrations of 5-Chloro-, 5-Bromo-, 5-Methyl-, and 2-Methylpyrimidines

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Assignment of the normal vibrations of 5-chloro-, 5-bromo-, 5-methyl-, and 2-methylpyrimidines was made through the vibrational analyses of the polarized Raman and infrared spectra and also through the normal coordinate calculation. The normal vibrations of 5-halo- and 5-methylpyrimidines were compared with those of 2-halo- and 2-methylpyrimidines, and a substitutional effect on the vibrational frequencies and modes of the hydrogen bending and wagging vibrations was studied.

Very recently the assignment of the normal vibrations of aromatic compounds containing three hydrogen atoms such as dihalopyridines, dimethylpyridines, and trihalobenzenes was studied and a characteristic substitutional effect on the hydrogen bending and wagging vibrations was discussed.[1,2] The hydrogen bending and wagging vibrations of 1,2,3-trihalobenzenes, 2,6-dihalopyridines, and 2,6-dimethylpyridine are of the ν_{18a}, ν_{18b}, and ν_{15} modes, and the ν_{17a}, ν_{17b}, and ν_{11} modes, respectively, while in 1,3,5-trihalobenzenes, 3,5-dihalopyridines, and 3,5-dimethylpyridine the bending ν_{15} and wagging ν_{11} modes are altered to the ν_3 and ν_5 modes having higher frequencies than those of the ν_{15} and ν_{11} modes, respectively. The frequency separations between the ν_{18a} and ν_{18b} vibrations and between the ν_{17a} and ν_{17b} vibrations become very narrow in 3,5-dihalo- and dimethylpyridines as if the molecular symmetry belongs to the pseudo D_{3h} point group for the hydrogen bending and wagging vibrations. The study of the normal vibrations of 2-halo-, 2-methyl-, 5-halo-, and 5-methylpyrimidines is interesting in order to ascertain the substitutional effect on the hydrogen bending and wagging vibrations, because the C–H bonds are located on the 4, 5, and 6 positions of the pyrimidine ring in 2-halo- and 2-methylpyrimidines and on the 2, 4, and 6 positions in 5-halo- and 5-methylpyrimidines.

The phosphorescence and fluorescence spectra of 2-methylpyrimidine have essentially the same spectral structure as those of 5-methylpyrimidine, while those of 2-halopyrimidines show different spectral structure from those of 5-halopyrimidines.[3] For the vibrational analysis of the emission spectra of these molecules the normal vibrations have to be determined.

The normal vibrations of 2-chloro- and 2-bromopyrimidines (2-CP and 2-BP) have been studied by several workers,[4–8] while a few studies have been made on 5-methylpyrimidine (5-MP).[9–11] The assignment of the normal vibrations of 5-chloro-, 5-bromo-, and 2-methylpyrimidines (5-CP, 5-BP, and 2-MP) has not been published. The crystal structure of 5-MP molecule has been determined[12] and thus the vibrational analysis of the polarized Raman and infrared spectra of 5-MP in single crystal can be made quantitatively.

In this paper, the assignment of the normal vibrations of 5-CP, 5-BP, 2-MP, and 5-MP is discussed first on the basis of the polarization behavior of the Raman and infrared bands observed in single crystal and the normal coordinate calculation, and then the substitutional effect on the normal vibrations is discussed. The modes of the normal vibrations of 2-CP and 2-BP given previously are also reexamined.

Experimental

Material. 5-CP and 2-MP were synthesized from (*Z*)-2,3-dichloro-4-oxo-2-butenoic acid and formamide, and acetamidine hydrochloride and diethyl malonate, respectively, following the methods reported by Kress and Szymanski,[13] and Henze et al.[14] and Smith and Christensen.[15] 5-BP and 5-MP were obtained from Nakarai Chemical Company and Aldrich Chemical Company, respectively. The samples were purified by repeated vacuum distillations.

Optical Measurements. The polarized Raman spectra were observed in liquid and single crystal phases with a JEOL 400 T Laser Raman Spectrophotometer exciting the sample with the 514.5 nm line from an Ar ion laser. Single crystals of 5-CP, 2-MP, and 5-MP were grown in a capillary glass tube in the same way as described previously[16] because these samples are very volatile. The direction of crystal growth which was along the capillary tube was found to be one of the extinction directions under the polarized light. The coordinate u axis was taken in this direction. Another extinction direction was determined by rotating the capillary tube around the crystal growth direction and this direction was taken to the v axis. The w axis was taken to be perpendicular to both the u and v axes. The single crystal sample kept at 20, −15, and −5 °C for 5-CP, 2-MP, and 5-MP, respectively, was held in a Raman cell in such a way that the u axis pointed in the polarization direction of the excitation laser beam. The capillary tube could be rotated about the u axis so that the v and w axes were directed to the propagation direction of the excitation beam. The Raman scattering was observed at right angles to the excitation beam. Thus the uu, uv, and uw polarized Raman spectra

Table 1. Force Constants for the In-Plane and Out-of-Plane Vibrations of Halo- and Methylpyrimidines

	Halo-	Methyl-		Halo-	Methyl-
$K_{\text{C-N}}$	5.6	5.6 hN m^{-1}	$K_{\text{C}'\text{-H}'}$[a]		4.7 hN m^{-1}
$K_{\text{C-C}}$	5.4	5.4	$H_{\text{CC}'\text{H}'}$		0.18
$K_{\text{C-H}}$	4.4	4.4	$H_{\text{H}'\text{C}'\text{H}'}$		0.44
$K_{\text{C-X}}$[b]	2.1 (1.9)	3.0	$F_{\text{N}\cdots\text{C}'}$		0.5
H_{NCN}	0.6	0.6	$F_{\text{H}'\cdots\text{H}'}$		0.05
H_{CNC}	0.4	0.4	$F_{\text{C}\cdots\text{H}'}$		0.25
H_{NCC}	0.3	0.4	$Q_{\text{C-N}}$	0.16	0.16 aN m rad^{-2}
H_{CCC}	0.2	0.4	$Q_{\text{C-C}}$	0.26	0.25
H_{HCN}	0.15	0.15	$Q_{\text{C-C}'}$		0.10
H_{HCC}	0.15	0.15	P_{X}	0.34	0.30
H_{CCX}	0.07 (0.06)	0.22	P_{H}	0.31	0.31
$H_{\text{NCC}'}$		0.22	q^{o}	−0.06	−0.06
$H_{\text{C}\cdots\text{C}}$	0.8	0.8	q^{m}	0.04	0.03
$F_{\text{H}\cdots\text{N}}$	0.7	0.7	q^{p}	0.01	0.01
$F_{\text{H}\cdots\text{C}}$	0.5	0.55	p^{o}	0.05	0.07
$F_{\text{N}\cdots\text{C}}$	0.6	0.6	p^{m}	−0.05	−0.06
$F_{\text{N}\cdots\text{N}}$	0.7	0.75	t_{X}^{o}	0.02	
$F_{\text{C}\cdots\text{X}}$	0.9 (0.7)	0.5	t_{H}^{o}	−0.04	−0.04
ρ	0.26	0.26	t_{H}^{m}	0.03	0.03
$f_{R\alpha}^{\text{m}}$[c]	−0.05	−0.05 nN rad^{-1}			

a) C′ and H′ atoms refer to the C and H atoms in the methyl group. b) X refers to the Cl, Br or C′ atom. The first value is for chloropyrimidine and the value in parentheses for bromopyrimidine. c) R and α refer to the bonds and angles in the pyrimidine ring.

Table 2. Normal Vibrations of 5-Halo- and 2-Halopyrimidines

Sym Spec	Mode	5-Cl-pyrimidine					5-Br-pyrimidine						2-Cl-pyrimidine		2-Br-pyrimidine	
		Raman			IR	Calcd	Raman			IR		Calcd	Obsd[a]	Calcd	Obsd[a]	Calcd
		$\tilde{\nu}$/cm^{-1}	Pol		Pol	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		Pol		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}
			liq	cry	vap			liq	cry	vap	cry					
a_1	ν_2	3062	p			3063	3058	p				3063	3045	3059	3050	3059
	ν_{20a}	3043	p			3036	3035	p				3036	3010	2993	3013	2993
	ν_{8a}	1553	dp[b]			1559	1546	p			I	1550	1561	1560	1559	1560
	ν_{19a}	1400	p		A	1402	1400	p			I	1397	1380	1391	1381	1390
	ν_{18a}	1158	p		A	1168	1151	p			I	1163	1163	1163	1157	1153
	ν_1	1089	p		A	1074	1085	p			I	1070	1078	1091	1074	1089
	ν_{12}	1025	p		A	1032	1014	p		A	I	1029	990	1002	998	1002
	ϕ-X str[c]	433	p			413	321	p				316	437	436	330	344
	ν_{6a}	755	p			751	736	p				722	754	751	734	732
b_2	ν_{7b}	3037	dp			3050	3030	dp	uu			3050	3080	3085	3080	3085
	ν_{8b}	1553	dp			1564	1553	dp	uu		I	1561	1540	1551	1539	1551
	ν_{19b}	1430	dp	uu		1434	1430	dp	uu		I	1433	1425	1431	1432	1431
	$\nu_3(\nu_{15})$[b]	1370				1376						1375	1277	1264	1270	1264
	ν_{14}	1340	dp	uu	B	1360	1340		uu		I	1356	1384	1355	1367	1355
	ν_{18b}	1186	dp	uu	B	1183	1187	dp	uu		I	1178	1154	1132	1170	1132
	ν_{6b}	620	dp	uu	B	619	620	dp	uu	B	I	615	626	622	630	622
	X bend	290	dp	uu		304	246	dp	uu			251	332	323	276	290
b_1	ν_{17b}	990	dp			987						986	960	968	960	969
	$\nu_5(\nu_{11})$[d]	905	dp	uv(I)	C	902	902	dp	vw	C	II	902	815	794	826	792
	ν_4	717	dp	uv(I)	C	731	719	dp	vw	C	II	731	767	744	766	742
	ν_{16b}	423		uv(I)		434	420	dp	vw		II	430	477	460	465	460
	X wag	197	dp	uv(I)		207	187	dp	vw			192	178	177	158	166
a_2	ν_{17a}					965						963		929		929
	ν_{16a}	403	dp	uv(II)		406	401	dp	uv			405	405	397	400	397

a) Taken from Ref. 8. b) The 8a band is overlapped with the 8b band. c) X refers to the Cl or Br atom. d) The first mode is for 5-halopyrimidines and the mode in parentheses for 2-halopyrimidines.

could be obtained, where the first letter refers to the polarization direction of the excitation laser beam and the latter to that of the scattering light. A well grown single crystal of 5-BP was obtained by the Bridgman method and a cubic sample of about (5 mm)^3 was cut off, where the cleavage plane was selected as one of the planes of the cube. The crystal growth direction on the cleavage plane was taken to the u axis and the direction perpendicular to the u axis on the cleavage plane was taken to the v axes. The w axis was taken to be perpendicular to both the u and v axs. The polarized uu, vv, ww, uv, uw, vw spectra were obtained for 5-BP in the same way as described previously.[17]

The infrared spectra were observed in vapor and single crystal phases with a Hitachi Infrared Spectrophotometer Model 345 in the same way as described previously.[2,18] The infrared spectra measured with the incident light polarized parallel and perpendicular to the crystal growth direction in the sample plane are referred to as the // and ⊥ spectra and are drawn with the solid and dotted lines in the figures, respectively. The polarized infrared spectrum of the 5-CP could not be observed because this sample is quite volatile.

Normal Coordinate Calculation

The normal coordinate calculation was performed through the standard GF matrix method with a FACOM M-780/10S computer at the Computer Center of Fukuoka University. The geometric parameters of the 5-MP molecule were taken from the data determined by Furberg et al.[12] The geometric parameters

Table 3. Normal Vibrations of 2-Methyl- and 5-Methylpyrimidines

Sym Spec	mode	2-Methylpyrimidine						5-Methylpyrimidine						
		This work						Kartha[a]	This work					
		Raman			IR		Calcd		Raman			IR		Calcd
		$\tilde{\nu}$/cm^{-1}	Pol		Pol		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	Pol		Pol		$\tilde{\nu}$/cm^{-1}
		liq	liq	cry	vap	cry			liq	liq	cry	vap	cry	
a_1	ν_2	3046	p				3031	3050	3053	p				3063
	ν_{20a}	3077	p				3049	3025	3026	p				3046
	ν_{8a}	1583	p			I	1584	1582	1584	p			I	1600
	ν_{19a}	1435	p			I	1438	1408	1410				I	1410
	ν_{18a}	1280	p			I	1265	1163	1245	p		A	I	1260
	ν_1	1083	p		A	I	1126	815	1105	p		A	I	1098
	ν_{12}	1000	p		A	I	1029	1046	1049	p		A	I	1068
	ϕ-CH_3 str	826	p				821	1242	820	p				840
	ν_{6a}	580	p		A	I	553	558	558	p				549
b_2	ν_{7b}						3044		3032	dp	uw			3043
	ν_{8b}	1567	dp	uu		II	1579	1563	1567	dp	uw	B	II	1579
	ν_{19b}	1460	dp	uu		II	1460	1424	1450	dp	uw		II	1457
	$\nu_{15}(\nu_3)$[b]	1313[c]					1298	1312	1380	dp	uw			1396
	ν_{14}	1355	dp	uu			1357	1197	1355	dp	uw		II	1361
	ν_{18b}	1180[d]			B	II	1163	1124	1200	dp	uw	B	II	1188
	ν_{6b}	642	dp	uu	B	II	631	635	635	dp	uw	B		626
	CH_3 bend	373	dp	uu	B	II	339	330	332	dp	uw			354
b_1	ν_{17b}	990	dp	uv		III	1031	965	995	dp	uu		III	1013
	$\nu_{11}(\nu_5)$[b]	810[d]			C	III	848	884	888	dp	uu	C	III	880
	ν_4	752	dp	uv	C	III	702	728	728	dp	uu	C	III	720
	ν_{16b}	469	dp	uv	C	III	453	426	425	dp	uu	C	III	423
	CH_3 wag	196	dp	uv			197	216	217	dp	uu			217
a_2	ν_{17a}	930	dp	uu(uv)			974	878	990	dp	uw			989
	ν_{16a}	400	dp	uu(uv)			415	400	402	dp	uw			416
	ϕ-CH_3 tor						239							226
Characteristic vibrations of CH_3 group														
a_1	C–H str						2990	2980	2982	p				2990
	C–H str	2930	p				2925	2940	2930	p				2925
	CH_3 sym def	1377	p				1405	1392	1390	p				1418
b_2	C–H str						2991	2863	2995	dp	uw			2991
	CH_3 deg def	1425	dp	uu			1439		1425	dp	uw			1437
	CH_3 rock	855	dp	uu			857		860[e]				II	858
b_1	CH_3 deg def						1439		1429	dp	uu			1437
	CH_3 rock	905		uv			892							870

a) Taken from Ref. 11. b) The first mode is for 2-methylpyrimidine and the mode in parentheses for 5-methylpyrimidine. c) Observed in crystal. d) Taken from the infrared spectrum in vapor. e) Taken from the infrared spectrum in crystal.

of 5-CP and 5-BP and those of 2-MP were assumed to be the same as those of 5-MP and 2-CP,[8] respectively, where the lengths of the C–Cl, C–Br, and C–CH_3 bonds were assumed to be 0.172, 0.185, and 0.150 nm, respectively. The F matrix elements for the in-plane and out-of-plane vibrations were evaluated with the improved modification of the Urey-Bradley force field and the valence force field described previously,[18,19] respectively. Values of the force constants used for the calculation are listed in Table 1. The notations of the force constants are exactly the same as those used previously.[18,19] The calculated frequencies and modes of the normal vibrations are given in Tables 2 and 3.

Results and Discussion

5-Chloro- and 5-Bromopyrimidines. The infrared spectra of 5-CP in vapor and 5-BP in single crystal are shown in Fig. 1. The moments of inertia calculated from the molecular structure suggest that the infrared bands belonging to symmetry species a_1, b_2, and b_1 show the A, B, and C band contours, respectively, in both molecules. The polarization behavior of the infrared bands of 5-BP can be classified into two types. In the first type (type I) the intensity of the // band is weaker than that of the ⊥ band and in the second type (type II) the // band is stronger than the ⊥ bands.

The polarized Raman spectra of 5-CP and 5-BP in single crystal are shown in Figs. 2 and 3. The depolarized Raman bands in molten phase show three types of polarization behavior in single crystal. The intensity relationship among the bands observed in the uu, uv, and uw polarized Raman spectra of 5-CP is $I_{uu}>I_{uw}>I_{uv}$, $I_{uv}>I_{uu}\approx I_{uw}$, and $I_{uv}>I_{uu}>I_{uw}$ for the first, second, and third type polarization behavior, respectively, where I_{uu} means the intensity of a band in problem observed in the uu spectrum and I_{uw} the intensity of the same band in the uw spectrum, and so

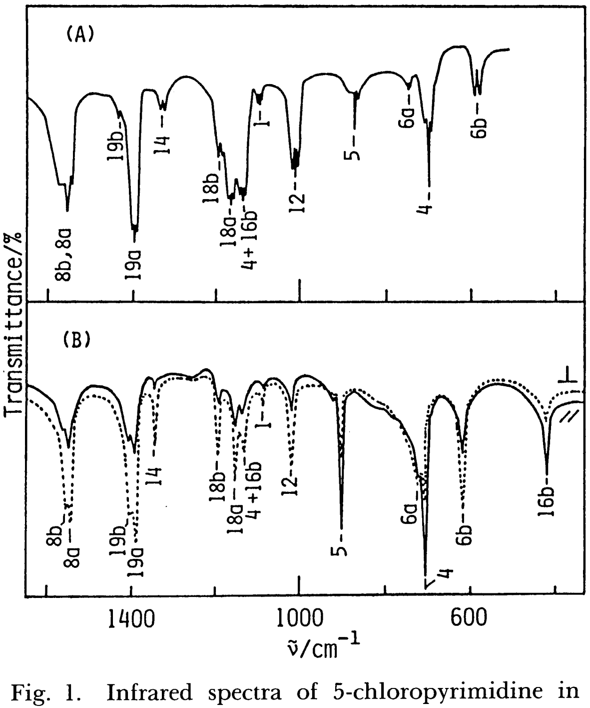

Fig. 1. Infrared spectra of 5-chloropyrimidine in vapor (A) and 5-bromopyrimidine in crystal (B).

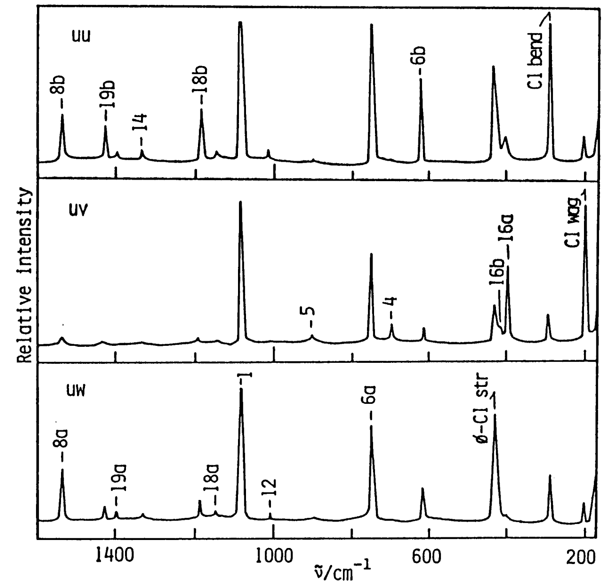

Fig. 2. Polarized Raman spectrum of 5-chloropyrimidine crystal.

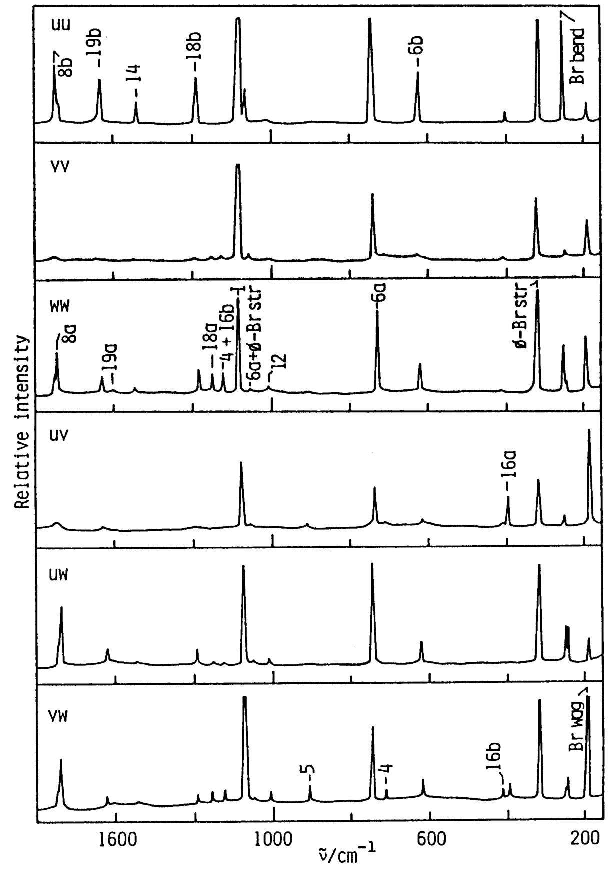

Fig. 3. Polarized Raman spectrum of 5-bromopyrimidine crystal.

on. These types of polarization behavior are denoted by uu, uv(I), and uv(II), respectively. In 5-BP the intensity relationship for the bands belonging to the first, second, and third types is $I_{uu}>I_{ww}>I_{uw}>I_{vw}$, $I_{vw}>I_{uv}>I_{ww}$, and $I_{uv}>I_{uu}\approx I_{vw}$, respectively. These types of polarization behavior are denoted by uu, vw, and uv, respectively. The vibrational analyses of the Raman and infrared bands were carried out on the basis of the polarization behavior.

Species a_1: The highly polarized Raman bands in molten phase and the infrared bands showing the A band contour in vapor were straightforwardly assigned to the a_1 vibrations. The corresponding infrared bands in crystal show the type I polarization in 5-BP.

Species b_2: The infrared bands showing the B band contour in vapor were assigned definitely to the b_2 vibrations. The corresponding infrared and Raman bands show the type I and uu polarization in crystal, respectively, in 5-CP and 5-BP.

Species b_1: The infrared bands showing the C band contour in vapor were assigned to the b_1 vibrations. The corresponding Raman bands in crystal show the uv(I) and vw polarization in 5-CP and 5-BP, respectively. Although the vw spectrum of 5-CP could not be observed in our experimental conditions, the bands showing the vw polarization in 5-BP could be observed clearly in the uv spectrum. This observation indicates that the polarization behavior of the Raman bands of 5-CP may be the same as that of 5-BP. The corresponding infrared bands show the type II polarization in 5-BP.

Species a_2: The Raman bands showing the uv(II) and uv polarization in 5-CP and 5-BP, respectively, could be assigned to the a_2 vibrations since none of the corresponding infrared bands could be observed.

The normal vibrations of 5-CP and 5-BP thus determined are given in Table 2 and Figs. 1—3. The normal coordinate calculation indicates that the C-Cl stretching vibration mixes considerably with the ν_1 and ν_{6a} vibrations and slightly with the ν_{18a} vibration. This mixing is proved by the experimental fact that the frequencies of the ν_1 and ν_{6a} vibrations increase largely and that of the ν_{18a} vibration slightly from the corresponding frequencies in pyrimidine (986, 676, and 1135 cm^{-1}). The calculation also shows that the ν_{16b} vibration mixes largely with the Cl wagging vibration and the frequency of the ν_{16b} vibration largely increases from the corresponding frequency in pyrimidine (345 cm^{-1}). The same frequency shifts due to the vibrational mixing were found in the normal vibrations of 5-BP.

5-Methyl- and 2-Methylpyrimidines. 5-MP crystallizes in monoclinic space group $P2_1/c$ with eight molecules in the unit cell.[12] The relationship between the Raman tensor for the free molecule and that for the crystal was derived based on the simple oriented gas model, and the matrix elements of the Raman tensor were evaluated in the same way as described previously.[17] The direction cosines between the crystal and molecular axes were calculated using the crystal data.[12] The squares of relative values of the elements of the Raman tensor, which are proportional to the relative intensity of the Raman bands, are given in Table 4 for 5-MP.

The polarized Raman spectra of the 5-MP and 2-MP single crystals are shown in Figs. 4 and 5. The polarization behavior of the Raman bands to be assigned to the nontotally symmetric vibrations can be classified into two types in 5-MP. The relative intensity of the Raman bands belonging to the first type polarization observed in the uw spectrum is about four times stronger than that observed in the uv spectrum and the bands are hardly detected in the uu spectrum. The Raman bands belonging to the second type are detected clearly only in the uu spectrum. These types of the polarization behavior are referred to as uw and uu polarization, respectively. The depolarized Raman bands of 2-MP in liquid can be classified into three types on the basis of the polarization behavior in crystal. The intensity relationship between the

Table 4. Squared Values of the Elements of the Derived Polarizability Tensor for 5-Methylpyrimidine

	b_1	a_2	b_2
$(a\ a)^2$	1.20	0.68	0.65
$(b\ b)^2$	1.94	0.002	0.002
$(c'\ c')^2$	0.10	0.61	0.73
$(a\ b)^2$	0.04	0.20	0.23
$(a\ c')^2$	0.33	0.38	0.28
$(b\ c')^2$	0.01	0.77	0.80

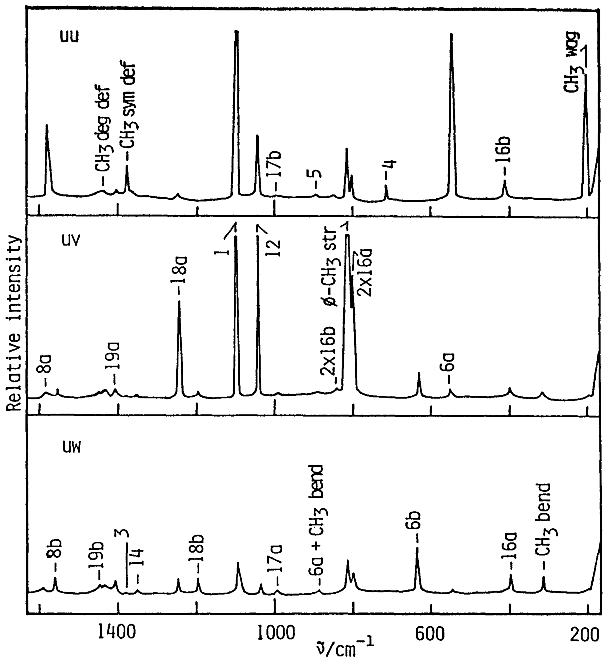

Fig. 4. Polarized Raman spectrum of 5-methylpyrimidine crystal.

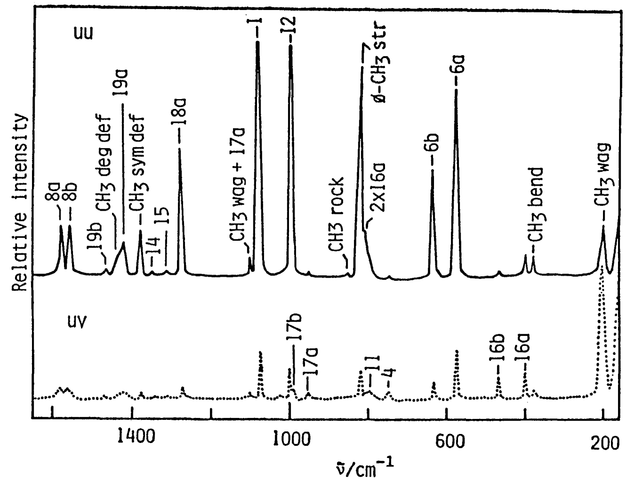

Fig. 5. Polarized Raman spectrum of 2-methyl-pyrimidine crystal.

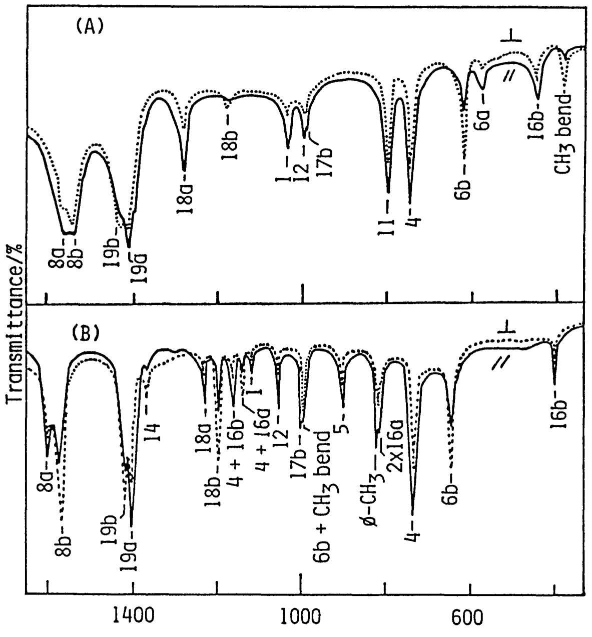

Fig. 6. Polarized infrared spectra of 2-methyl- (A) and 5-methylpyrimidine (B) crystals.

bands observed in the uu and uv polarized spectra is $I_{uu}>I_{uv}$, $I_{uu}<I_{uv}$, and $I_{uu}\gtrapprox I_{uv}$, for the first, second, and third type polarization, respectively. These types of polarization behavior are referred to as uu, uv, uu(uv) polarization, respectively.

The moments of inertia calculated from the molecular structure suggest that the infrared bands belonging to a_1, b_2, and b_1 symmetry species show the A, B, and C band contours, respectively, in both 2-MP and 5-MP. The polarized infrared spectra of the 2-MP and 5-MP single crystals are shown in Fig. 6. As can be seen in Fig. 6, the polarization behavior of the infrared bands can be classified into three types. The relative intensity of the bands showing the first type polarization observed in the // spectrum is stronger than that in the ⊥ spectrum, while the second type bands are observed more strongly in the ⊥ spectrum than in the // spectrum. The third type bands are observed with almost equal intensity in the // and ⊥ spectra. These three types of polarization behavior are referred to as the type I, II, and III, respectively. The relative intensity of the infrared bands polarized along the a, b, and c crystal axes of the 5-MP crystal were calculated and the results are listed in Table 5. The sample plane might be the ab or bc plane because two extinction directions on the sample plane are perpendicular to each other.

Table 5. Relative Intensity of Infrared Bands of 5-Methylpyrimidine

	a_1	b_2	b_1
//a	0.73	0.43	0.83
//b	1.02	0.18	0.97
//c	0.73	0.55	0.72

5-Methylpyrimidine: Species a_1: The highly polarized Raman bands in liquid and the infrared bands showing the A band contour in vapor were assigned straightforwardly to the a_1 vibrations. The corresponding infrared bands in crystal show the type I polarization.

Species b_2: The infrared bands showing the B band contour in vapor were assigned to the b_2 vibrations. The corresponding infrared and Raman bands in single crystal show the the type II and uw polarization, respectively.

Species b_1: The infrared bands showing the C band contour in vapor were assigned to the b_1 vibrations. The corresponding infrared and Raman bands in single crystal show the type III and uu polarization, respectively.

Species a_2: The Raman bands showing the uw polarization in crystal were assigned to the a_2 vibrations, because the corresponding infrared bands could not be observed.

Comparison of the observed polarization behavior with the calculated intensity relationship among the b_2, b_1, and a_2 Raman bands and among the a_1, b_2, and b_1 infrared bands given in Tables 4 and 5, respectively, suggests that (1) the u, v, and w axes correspond to the b, a, and c′ crystal axes, respectively, and (2) the sample plane measured in the polarized infrared spectra corresponds to the ab plane.

The assignment made in this work is different from that given by Kartha for the ν_{18a}, ν_1, ϕ-CH_3 stretching, ν_3, ν_{14}, ν_{18b}, ν_{17b}, and ν_{17a} vibrations, as can be seen in Table 3. Kartha assigned the infrared band at 1163 cm^{-1} to the ν_{18a} vibration but this band can not be ascribed to a fundamental vibration because this band was observed strongly only in the crystal with the type I polarization but hardly detected in vapor. Kartha assigned the highly polarized Raman band at 1105 cm^{-1} in molten state to the methyl bending vibration but this vibration belongs to the b_2 or b_1 species in 5-MP. In this work the strong and highly polarized Raman bands at 1245, 1105, 1049, and 820 cm^{-1} in molten phase were assigned to the ν_{18a}, ν_1, ν_{12}, and ϕ-CH$_3$ stretching vibrations on the basis of the normal coordinate calculation. Kartha assigned the 1312 and 1124 cm^{-1} infrared bands to the ν_3 and ν_{18b} vibrations, respectively, but the former band should be assigned to the b_1 vibration because this band shows the C band contour in vapor and the latter may not be ascribed to a fundamental vibration because this band was observed strongly only in crystal with the type II polarization but hardly detected in vapor. The infrared band at 1197 cm^{-1}, which was assigned to the ν_{14} vibration by Kartha, was assigned to the ν_{18b} vibration and the Raman band at 1355 cm^{-1} was assigned to the ν_{14} vibration in this work because the normal coordinate calculation indicates that the ν_{14} vibration is hardly affected by methyl substitution and hence the vibrational frequency of this mode is to be nearly equal to that of pyrimidine (1367 cm^{-1}). The Raman band at 888 cm^{-1} assigned to the ν_{10b} vibration by Kartha was assigned to the ν_5 vibration in this work. Although Kartha assigned the infrared band at 965 cm^{-1} to the ν_{17b} vibration from the band contour, this band does not show clear C band contour but shows the type I polarization in crystal. The Raman band at 995 cm^{-1} was assigned to the ν_{17b} vibration on the basis of the polarization behavior of the infrared and Raman bands in this work. The polarization behavior suggests that the 1163, 1312, 1124, and 965 cm^{-1} bands described above may be assigned to the $\nu_4+\nu_{16b}$, ν_1+CH$_3$ wagging, $\nu_4+\nu_{16a}$, and ν_{6b}+CH$_3$ bending vibrations, respectively.

2-Methylpyrimidine: The infrared bands having the A, B, and C band contours show the type I, II and III polarization in crystal, respectively. The Raman bands, whose corresponding infrared bands show the type II and III polarization, show the uu and uv polarization, respectively, in crystal. Therefore the infrared bands showing the type II and III polarization and the Raman bands showing the uu and uv polarization were assigned to the b_2 and b_1 vibrations, respectively. The infrared and Raman bands showing the type I and uu(uv) polarization, respectively, were assigned to the a_1 and a_2 vibrations, respectively.

Normal vibrations of 5-MP and 2-MP thus determined are summarized in Table 3 and Figs. 4—6. The normal coordinate calculation indicates that the ν_{18a} and ν_1 vibrations mix largely with the ϕ-CH$_3$ stretching vibration and the ν_{16b} vibration mixes with the CH$_3$ wagging vibration. These mixings are proved by the experimental facts that the frequencies of the ν_{18a}, ν_1, and ν_{16b} vibrations increase largely in 2-MP and 5-MP compared with those of pyrimidine (1135, 986, and 345 cm^{-1}).

Correlation diagram of the hydrogen bending and wagging vibrations of 5-CP, 5-MP, and 2-MP is shown in Fig. 7 together with those of trichlorobenzenes, dihchloropyridines, dimethylpyridine, methylpyrimidine, and 2-CP. The hydrogen bending and wagging vibrations are ν_{18a}, ν_{18b}, and ν_{15} modes, and

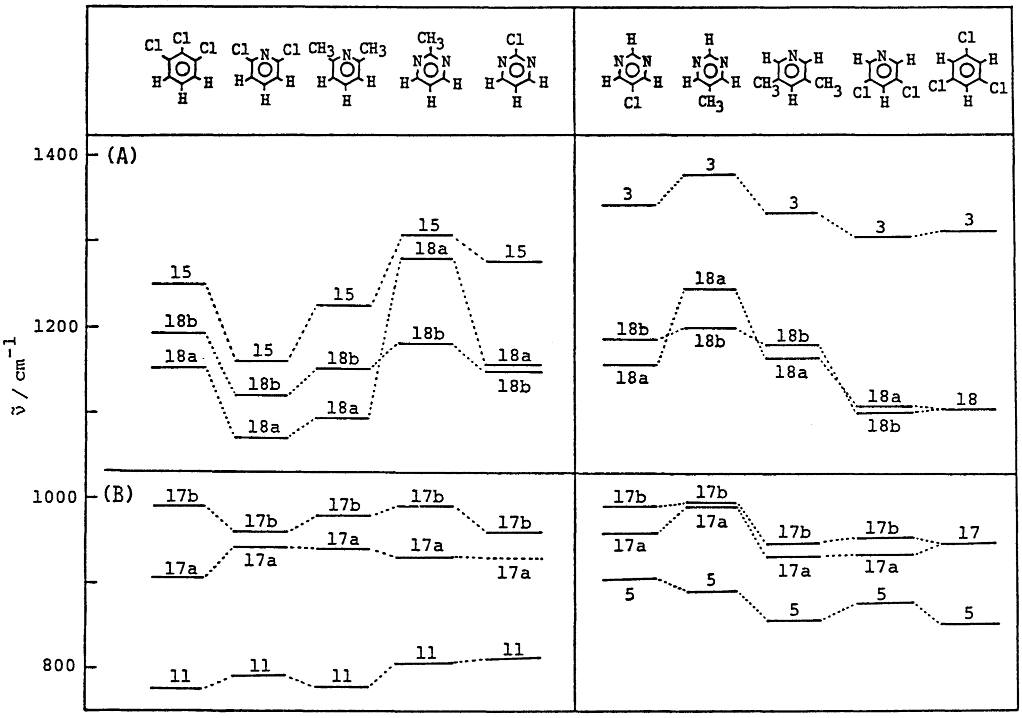

Fig. 7. Correlation diagram for the H bending (A) and H wagging (B) vibrations of 1,2,3- and 1,3,5-trichlorobenzenes, 2,6- and 3,5-dichloropyridines, 2,6- and 3,5-dimethylpyridines, 2- and 5-methylpyrimidines, and 2- and 5-chloropyrimidines.

ν_{17a}, ν_{17b}, and ν_{11} modes, respectively, in 2-MP, while these modes are altered to the ν_{18a}, ν_{18b}, and ν_3 modes and ν_{17a}, ν_{17b}, and ν_5 modes, respectively, in 5-CP and 5-MP. This fact supports the substitutional effect caused by the difference of the substituted positions discussed in detail previously[1,2] except for the fact that the frequency of the ν_{18a} vibration in 5-MP and 2-MP increases largely compared with trihalobenzenes and dihalopyridines due to the large mixing with the ϕ-CH_3 stretching vibration as described above. Substitutional effect suggests that the assignment given for 5-MP in this work is preferable to that given by earlier workers.

Reexamination of the normal vibrations of 2-CP and 2-BP made through the substitutional effect and the normal coordinate calculation carried out with the refined force constants suggests that (1) the assignment of the ν_{9a}, ν_3, and ν_{15} modes given for the hydrogen bending vibrations and that of the ν_{10b} mode given for the hydrogen wagging vibration are preferably altered to the ν_{18a}, ν_{15}, ν_{18b}, and ν_{11} modes, respectively, (2) the frequency of the ν_{17a} vibration is expected to be about 930 cm^{-1} and therefore, the assignment given previously for the very weak Raman band at 1005 cm^{-1} to the ν_{17a} vibration should be reexamined, that is, this band might be assigned to the ν_{11}+Cl wagging vibration because the polarization behavior of this band corresponds to either symmetry a_1 or a_2 vibration, and (3) the assignment given for the ν_1 and ν_{12} vibrations should be altered to the ν_{12} and ν_1 vibrations, respectively, because the frequency of the ν_1 mode increases owing to the mixing with the ν_{6a} and C–Cl stretching modes as described in the normal coordinate calculation. These results are summarized in Table 2.

We believe that the assignment given in this work is quite reliable and useful for the reasonable vibrational analyses of the phosphorescence and fluorescence spectra of these molecules.

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