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Polarized Raman and Infrared Spectra of 2,6-Dichloro-, 2,6-Dibromo-, 3,5-Dichloro-, and 3,5-Dibromopyridines

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Assignments of the normal vibrations of 2,6-dichloro-, 2,6-dibromo-, 3,5-dichloro-, and 3,5-dibromopyridines were made based on the polarization behavior of the Raman and infrared spectra in single crystals and the normal coordinate calculations. The effect of halo-substitution on the vibrational frequencies of the normal modes was discussed.

The Raman and infrared spectra of pyridine were studied by many workers.[1-4] Wong and Colson reviewed the previous works and reexamined the assignments of the normal vibrations of pyridine through the analysis of the high resolution FT-IR spectrum.[5] Very recently Ozono et al. reinvestigated the normal vibrations of pyridine based on the polarized Raman spectrum and gave new assignments for the out-of-plane vibrations.[6,7] Few investigations were made on the vibrational spectra of halo-substituted pyridines and reliable assignments of the normal vibrations, which are very important for the analyses of the fluorescence and phosphorescence spectra, have not been made yet.

In this paper, the assignments of the normal vibrations of 2,6- and 3,5-dihalopyridines will be discussed through the analyses of the polarized Raman and infrared spectra and normal coordinate calculations.

Experimental

Material. The samples, 2,6-dichloro- and 3,5-dichloropyridines (Nakarai Chemical Company), 2,6-dibromopyridine (Wako Chemical Company), and 3,5-dibromopyridine synthesized from pyridinium chloride were purified by repeated vacuum distillations.

Optical Measurements. The polarization measurements of the Raman spectrum were 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 the sample 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. Although the crystallographic analyses for these molecules were not reported yet, the crystal growth direction in the cleavage plane was found to be one of the extinction directions under the polarized light. The crystal growth direction was referred to as u axis and the direction perpendicular to this axis in the cleavage plane was to as v axis and the direction perpendicular to both the u and v axes to as w axis. The polarized Raman spectrum of the single crystal was denoted by two characters such as uv. The first letter refers to the direction of polarization of the excitation light and the latter to that of the scattering light. The method of measurement of the polarized Raman spectrum was exactly the same as that described previously.[8,9]

The infrared spectra were observed in vapor, CCl_4 and CS_2 solutions, and thin film obtained by sublimation, with a Hitachi Infrared Spectrophotometer Model 345. The polarized infrared spectra were observed in the thin film. The spectra measured with the incident lights polarized parallel and perpendicular to the crystal growth direction in the film plane are referred to as // and ⊥ spectra, respectively.

Normal Coordinate Calculation

The normal coordinate calculation was performed

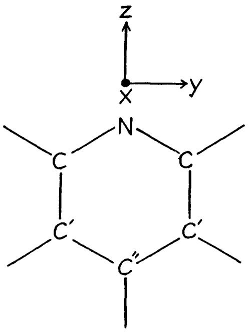

Fig. 1. Symbols for the atoms and internal coordinates.

Table 1. Force Constants for In-Plane Vibrations

$K_{N\text{-}C}$	5.6		$H_{CC'X}$	0.13[b)]	0.15[c)]
$K_{C\text{-}C'}$	4.8		$H_{C'CX}$	0.13[b)]	0.15[c)]
$K_{C'\text{-}C''}$	4.7		$H_{C''C'X}$	0.13[b)]	0.15[c)]
$K_{C\text{-}H}$	4.6		$F_{C\cdots C}$	0.9	
$K_{C'\text{-}H}$	4.6		$F_{N\cdots C'}$	0.5	
$K_{C''\text{-}H}$	4.6		$F_{C\cdots C''}$	0.6	
$K_{C\text{-}X}$[a)]	2.3[b)]	1.7[c)]	$F_{C'\cdots C'}$	0.6	
$K_{C'\text{-}X}$	2.3[b)]	1.7[c)]	$F_{N\cdots H}$	0.7	
H_{CNC}	0.2		$F_{C\cdots H}$	0.4	
$H_{NCC'}$	0.25[d)]	0.5[e)]	$F_{C'\cdots H}$	0.4	
$H_{CC'C''}$	0.45[d)]	0.2[e)]	$F_{C''\cdots H}$	0.4	
$H_{C'C''C'}$	0.45		$F_{N\cdots X}$	0.8	
H_{NCH}	0.17		$F_{C\cdots X}$	0.8	
$H_{C'CH}$	0.2		$F_{C'\cdots X}$	0.8	
$H_{CC'H}$	0.2		$F_{C''\cdots X}$	0.8	
$H_{C''C'H}$	0.2		ρ	0.38	
$H_{C'C''H}$	0.2		$k^{o}_{H,H}$	0.06	
H_{NCX}	0.13[b)]	0.15[c)]	$k^{m}_{H,H}$	−0.04	

Force constants are given in hNm^{-1} units. a) X refers to the Cl or Br atom. b) Values for dichloropyridines. c) Values for dibromopyridines. d) Values for 2,6-dihalopyridines. e) Values for 3,5-dihalopyridines.

Table 2. Force Constants for Out-of-Plane Vibrations

$Q_{\mathrm{N\text{-}C}}$	0.21	p^{o}	0.02
$Q_{\mathrm{C\text{-}C'}}$	0.20	$p^{\mathrm{m}}_{\mathrm{H,H}}$	−0.015
$Q_{\mathrm{C'\text{-}C''}}$	0.20	$p^{\mathrm{m}}_{\mathrm{H,X}}$	−0.01
P_{H}	0.31	$p^{\mathrm{m}}_{\mathrm{X,X}}$	−0.05
P_{X}[a)]	0.39[b)] 0.4[c)]	$t^{\mathrm{o}}_{\mathrm{H}}$	−0.02
q^{o}	−0.05	$t^{\mathrm{m}}_{\mathrm{H}}$	−0.01
q^{m}	0.01		

Force constants are given in aNmrad^{-2} units. a) X refers to the Cl or Br atom. b) Value for the Cl atom. c) Value for the Br atom.

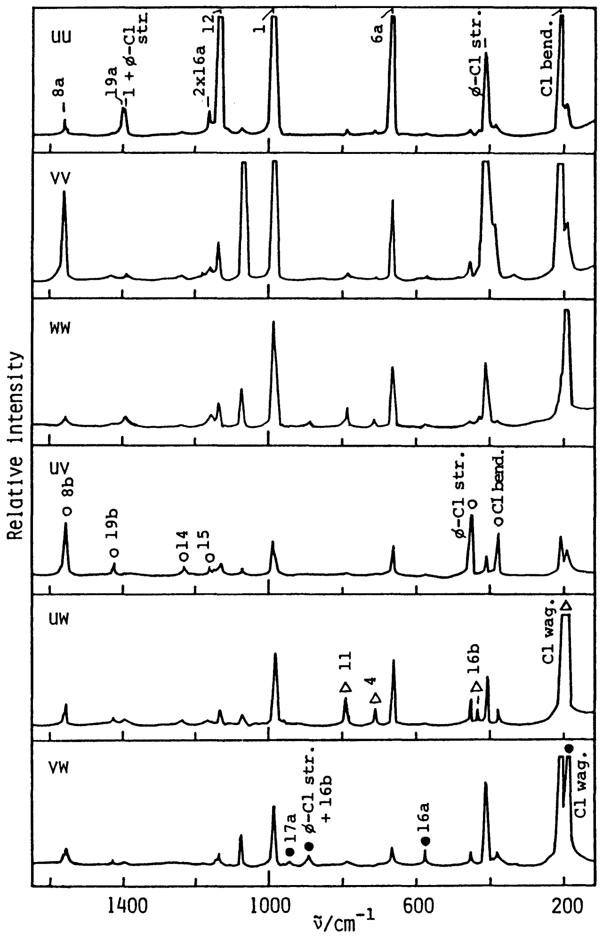

Fig. 2. Polarized Raman spectra of 2,6-dichloropyridine crystal.

through the standard GF matrix method with a FACOM M-380R computer at the Computer Center of Fukuoka University. The geometrical parameters of the molecules were assumed to be the same as those of pyridine except for the C-Cl and C-Br bonds, whose bond lengths were assumed to be 0.180 and 0.185 nm, respectively.

The F matrix elements for the in-plane and out-of-plane vibrations were evaluated with the potential fields of an improved modification of the Urey-Bradley and valence force fields, respectively, described previously.[9,10)] The symbols given for the atoms and the molecular axes are illustrated in Fig. 1. The force constants used for the normal coordinate calculations of the in-plane and out-of-plane vibrations are listed in Tables 1 and 2, respectively, and the calculated results of the vibrational modes and frequencies are given in Tables 3 and 4.

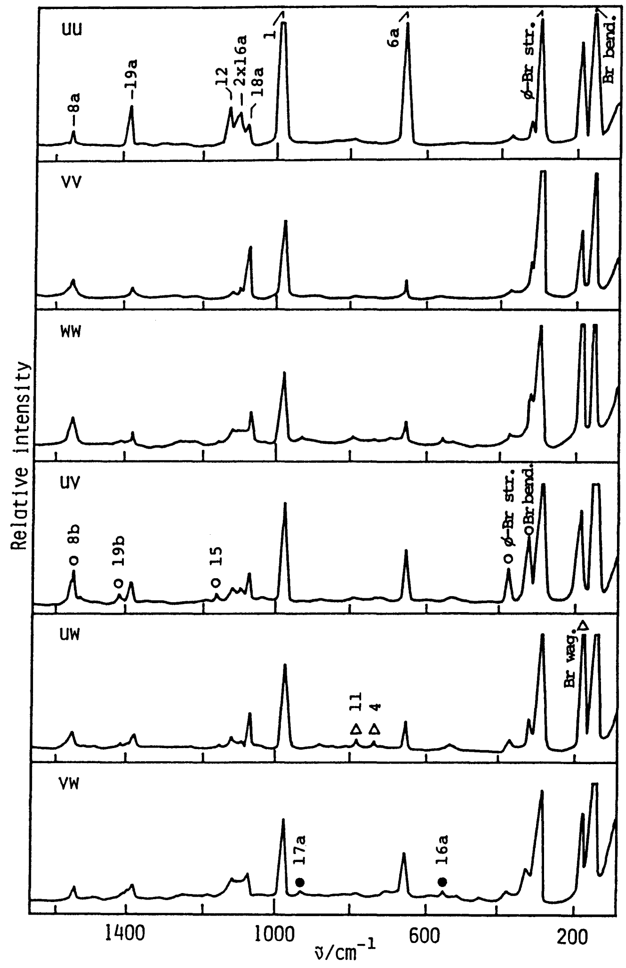

Fig. 3. Polarized Raman spectra of 2,6-dibromopyridine crystal.

Results and Discussion

The relative intensity of the Raman band in the polarized Raman spectra observed in the different orientations of the crystal is governed by the orientation of the molecule in the crystal in the oriented gas model approximation. If the crystal structure is known, the relative intensities of the Raman bands can be calculated from the direction cosines between the crystal and molecular axes and the assignments of the normal vibrations can be quantitatively made from the observed polarization behavior of the Raman bands. Even if the crystal structure is unknown, the polarization behavior of the Raman bands observed along and perpendicular to the crystal growth direction, which is one of the extinction directions, in the cleavage plane gives qualitative information on the classification of the Raman bands into certain symmetry species. This is because the molecular vibrations belonging to the same symmetry species should show the same polarization behavior. We analyzed the polarized Raman spectra and reasonable assignments of the normal vibrations were made for dichloromaleic anhydride[10] and 2-halosubstituted pyrimidines[11] whose crystal structures were unknown.

The polarized Raman spectra of 2,6-dichloro-, 2,6-dibromo-, 3,5-dichloro-, and 3,5-dibromopyridines are shown in Figs. 2, 3, 4, and 5, respectively. As can be seen in the figures, the depolarized Raman bands observed in a molten phase could be classified into three types of polarization behavior in the polarized Raman spectra observed in the crystal. The intensities of the Raman bands belonging to the first type are the strongest in the uv spectrum and decrease in the uw, vv, and vw spectra in order. The second type bands are strongest in the uw spectrum and their intensities decrease in the ww and uu spectra in order, and the third type bands could be observed clearly only in the vw spectrum. The first, second, and third type polarization behavior will be referred to as the uv, uw, and vw polarization, and the bands showing these types of polarization are marked with ○, △, and ● in the figures, respectively.

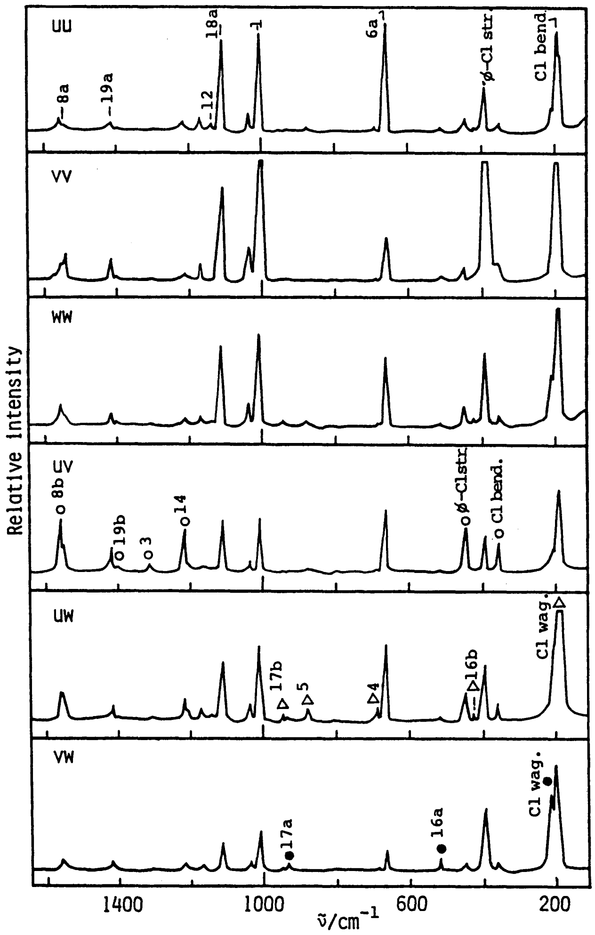

Fig. 4. Polarized Raman spectra of 3,5-dichloropyridine crystal.

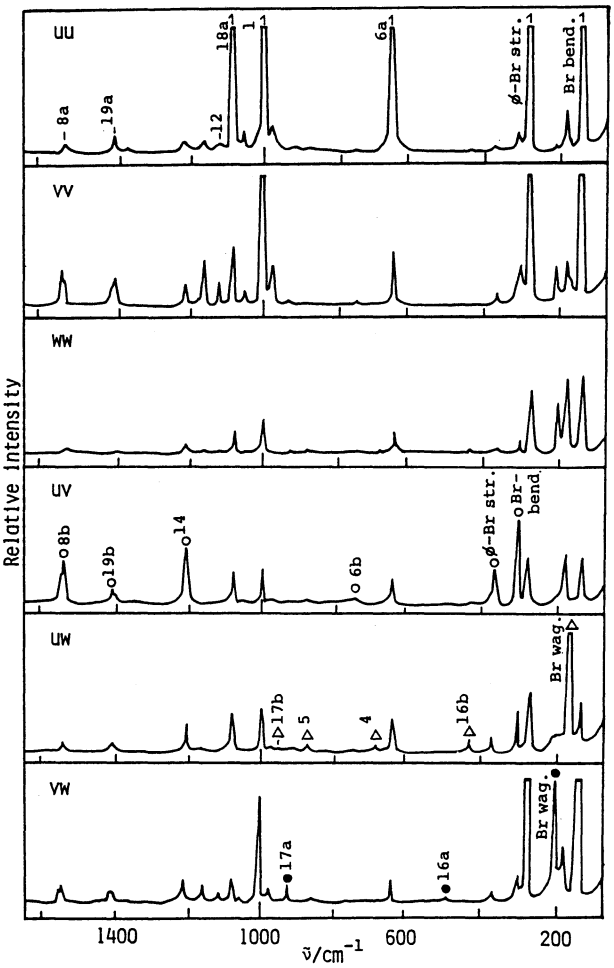

Fig. 5. Polarized Raman spectra of 3,5-dibromopyridine crystal.

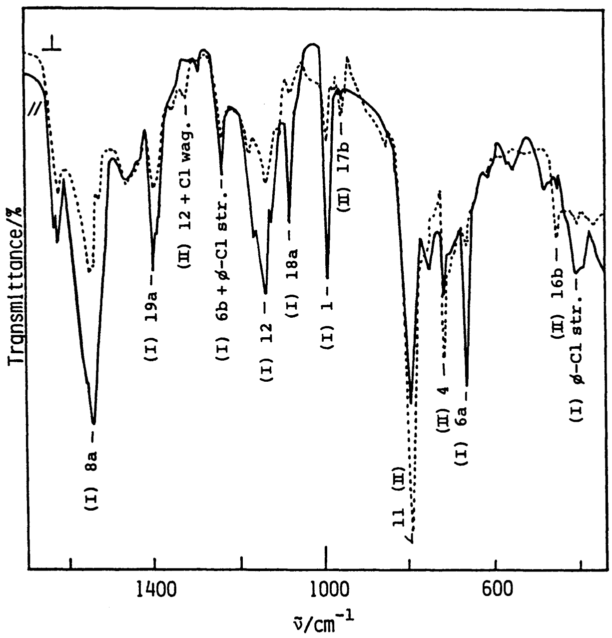

Fig. 6. Polarized infrared spectra of 2,6-dichloropyridine crystal.

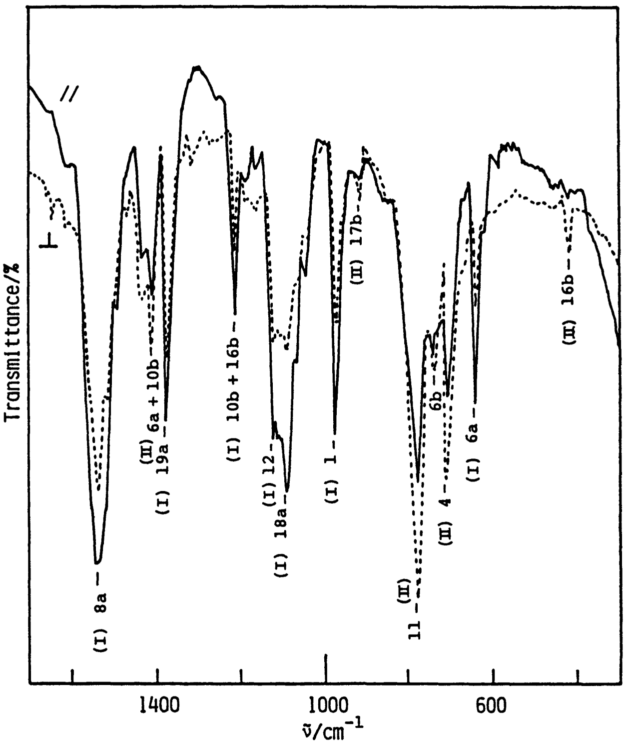

Fig. 7. Polarized infrared spectra of 2,6-dibromopyridine crystal.

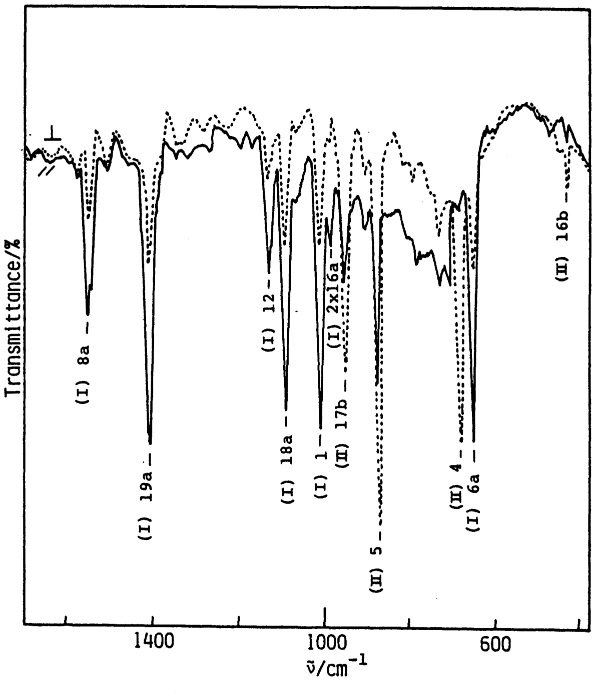

Fig. 9. Polarized infrared spectra of 3,5-dibromopyridine crystal.

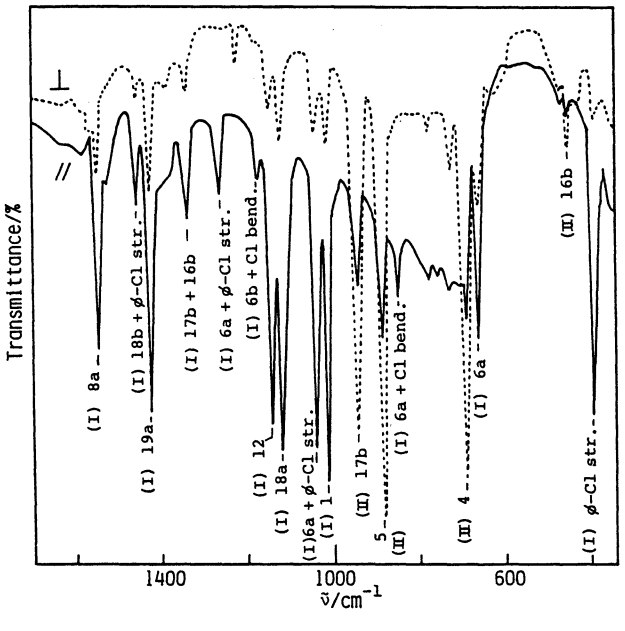

Fig. 8. Polarized infrared spectra of 3,5-dichloropyridine crystal.

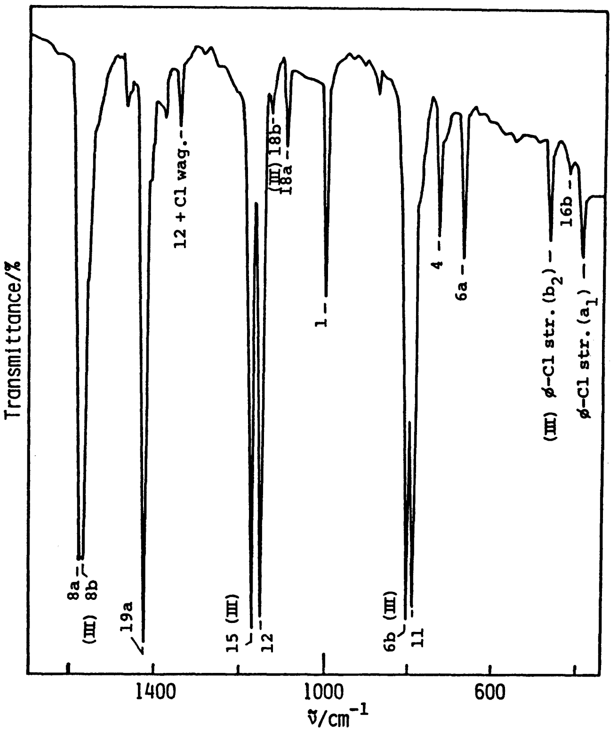

Fig. 10. Infrared spectrum of 2,6-dichloropyridine in solution.

The polarized infrared spectra of 2,6-dichloro-, 2,6-dibromo-, 3,5-dichloro-, and 3,5-dibromopyridines observed in the thin films are shown in Figs. 6, 7, 8, and 9, respectively, where the // and ⊥ spectra are drawn with the solid and dotted lines. The polarization behavior of the infrared bands could be classified into two types. The intensities of the bands belonging to the first type are stronger in the // spectrum than in the ⊥ spectrum while the intensities of the second type bands are weaker in the // spectrum than in the one. These two types of the bands will be referred to as types I and II, respectively as shown in the figures. Some infrared bands were observed strongly or clearly in the

CCl_4 and CS_2 solutions although observed very weakly or hardly in the thin film. This type of the bands will be referred to as type III. As an example, the infrared spectrum of 2,6-dichloropyridine observed in CCl_4 (1700—1000 cm^{-1}) and CS_2 (1000—350 cm^{-1}) is shown in Fig. 10, where these bands are marked with the symbol III. The very weak intensity of the type III bands in the thin film spectrum may be due to the polarization direction being nearly normal to the plane of the thin film.

Calculations of the principal moments of inertia of these molecules suggest that the infrared bands belonging to the a_1, b_2, and b_1 symmetry species show the B, A, and C rotational band contours, respectively. The vibrational modes were determined based on the normal coordinate calculation.

2,6-Dichloropyridine. **a_1 Species:** The strongly polarized Raman bands observed at 3078, 3030, 1400, 1133, 1072, 985, 664, and 409 cm^{-1} in molten phase could be straightforwardly assigned to the totally symmetric ν_2, ν_{7a}, ν_{19a}, ν_{12}, ν_{18a}, ν_1, ν_{6a}, and ϕ-Cl stretching vibrations, respectively, where ϕ refers to the pyridine ring. The corresponding infrared bands observed in vapor and the thin film showed the B band contour and the type I polarization, respectively. The infrared band observed at 1562 cm^{-1} was assigned to the ν_{8a} vibration because this band showed the type I polarization in the thin film, although the corresponding Raman band was depolarized in molten phase due to overlapping with the band assigned to the ν_{8b} vibration described later. The Raman band at 202 cm^{-1} was assigned to the Cl bending vibration of a_1 species because this band does not show any of the uv, uw, and vw polarization behavior.

b_2 Species: The infrared band observed at 1167 cm^{-1} showed the A band contour in vapor and therefore this band was assigned to the ν_{15} vibration of b_2 species. The corresponding infrared band in the thin film and the Raman bands in the crystal showed the type III and the uv polarization, respectively. The Raman bands observed at 1556, 1423, 1228, 452, and 374 cm^{-1} showed the uv polarization and thus were assigned to the ν_{8b}, ν_{19b}, ν_{14}, ϕ-Cl stretching, and Cl bending vibrations of b_2 species, respectively. The infrared bands observed at 1120 and 800 cm^{-1} showed the type III polarization and were assigned to the ν_{18b} and ν_{6b} vibrations, respectively.

b_1 Species: The infrared bands observed at 790 and

Table 3. Normal Vibrations of 2,6-Dichloro- and 2,6-Dibromopyridines

Sym spec	Mode	2,6-Dichloropyridine						2,6-Dibromopyridine				
		Raman			Infrared		Calcd	Raman			Infrared	Calcd
		$\tilde{\nu}$/cm^{-1}	pol		pol		$\tilde{\nu}$/cm^{-1}	$\tilde{\nu}$/cm^{-1}	pol		pol	$\tilde{\nu}$/cm^{-1}
			liq	cry	vap	cry			liq	cry	cry	
a_1	ν_2	3078	p				3064	3078	p			3064
	ν_{7a}	3030	p				3020	3040	p			3020
	ν_{8a}	1562	dp?			I	1561	1545	dp?		I	1560
	ν_{19a}	1400	p		B	I	1410	1387	p		I	1410
	ν_{12}	1133	p			I	1138	1123	p		I	1105
	ν_{18a}	1072	p			I	1070	1072	p		I	1068
	ν_1	985	p		B	I	998	987	p		I	998
	ν_{6a}	664	p			I	679	650	p		I	651
	ϕ-X str.$^{a)}$	409	p			I	400	290	p			297
	X bend.	202	dp				200	140	dp			145
b_2	ν_{7b}	3055	dp				3058					3058
	ν_{8b}	1556	dp	uv			1547	1543	dp	uv		1547
	ν_{19b}	1423	dp	uv			1407	1422	dp	uv		1403
	ν_{14}	1228		uv			1226	1222$^{b)}$				1226
	ν_{15}	1167	dp	uv	A	III	1161	1167		uv	III	1159
	ν_{18b}	1120$^{b)}$				III	1113	1111$^{b)}$			III	1106
	ν_{6b}	800$^{b)}$				III	808	747$^{b)}$			III	751
	ϕ-X str.	452	dp	uv		III	430	377	dp	uv		392
	X bend.	374	dp	uv			381	316	dp	uv		325
a_2	ν_{17a}	940	dp	vw			934	930		vw		934
	ν_{16a}	577	dp	vw			562	553		vw		562
	X wag.	185	dp	vw			181	190$^{c)}$				174
b_1	ν_{17b}	963	dp			II	963	970$^{b)}$			II	964
	ν_{11}	790	dp	uw	C	II	805	785		uw	II	808
	ν_4	716	dp	uw	C	II	729	720		uw	II	734
	ν_{16b}	430	dp	uw		II	407	418$^{b)}$			II	407
	X wag.	190	dp	uw			172	178	dp	uw		160

a) X refers to the Cl or Br atom. b) Observed in the infrared spectrum. c) Observed as a shoulder of the strong band at 178 cm^{-1}.

Table 4. Normal Vibrations of 3,5-Dichloro- and 3,5-Dibromopyridines

Sym spec	Mode	3,5-Dichloropyridine						3,5-Dibromopyridine				
		Raman			Infrared		Calcd	Raman			Infrared	Calcd
		$\tilde{\nu}/\mathrm{cm}^{-1}$	pol		pol		$\tilde{\nu}/\mathrm{cm}^{-1}$	$\tilde{\nu}/\mathrm{cm}^{-1}$	pol		pol	$\tilde{\nu}/\mathrm{cm}^{-1}$
			liq	cry	vap	cry			liq	cry	cry	
a_1	ν_2	3045	p				3041					3041
	ν_{7a}	3077	p				3080					3086
	ν_{8a}	1550	dp?			I	1556	1548	dp?		I	1566
	ν_{19a}	1417	p			I	1404	1407	p		I	1407
	ν_{12}	1141	p			I	1163	1120			I	1157
	ν_{18a}	1109	p			I	1110	1083	p		I	1079
	ν_1	1010	p		B	I	1020	1008	p		I	1021
	ν_{6a}	653	p		B	I	655	635	p		I	642
	ϕ-X str.[a]	393	p			I	395	275	p			289
	X bend.	197	dp				203	155	dp			151
b_2	ν_{7b}						3102					3102
	ν_{8b}	1557	dp	uv			1560	1539	dp	uv		1557
	ν_{19b}	1410	dp	uv			1392	1410	dp	uv		1392
	ν_3	1309		uv		III	1316	1300[b]			III	1316
	ν_{14}	1215	dp	uv		III	1207	1212	dp	uv	III	1208
	ν_{18b}	1103[b]			A	III	1073	1085[b]			III	1066
	ν_{6b}	820[b]				III	811	753	dp	uv	III	752
	ϕ-X str.	447	dp	uv		III	438	365	dp	uv		398
	X bend.	360	dp	uv			381	302	dp	uv		331
a_2	ν_{17a}	935	dp	vw			945	930	dp	vw		945
	ν_{16a}	512	dp	vw			526	492	dp	vw		525
	X wag.	209	dp	vw			199	200	dp	vw		191
b_1	ν_{17b}	945	dp	uw		II	922	950	dp	uw	II	922
	ν_5	878	dp	uw	C	II	870	875	dp	uw	II	870
	ν_4	687	dp	uw	C	II	704	685	dp	uw	II	706
	ν_{16b}	428	dp	uw		II	436	432	dp	uw	II	437
	X wag.	186	dp	uw			155	176	dp	uw		142

a) X refers to the Cl or Br atom. b) Observed in the infrared spectrum.

716 cm^{-1} showed the C band contour in vapor and the type II polarization in the thin film. Hence these bands were assigned to the ν_{11} and ν_4 vibrations of b_1 species, respectively. The corresponding Raman bands showed the uw polarization in crystal. The infrared band observed at 963 cm^{-1} showed the type II polarization and the Raman bands at 430 and 190 cm^{-1} showed the uw polarization. Therefore, these bands were assigned to the ν_{17b}, ν_{16b}, and Cl wagging vibrations of b_1 species, respectively.

a_2 Species: The Raman bands observed at 940, 577, and 185 cm^{-1} showed the vw polarization in crystal and were assigned to the ν_{17a}, ν_{16a}, and Cl wagging vibrations of a_2 species, respectively, because no corresponding bands could be observed in the infrared spectrum.

The polarization behavior of the Raman and the infrared bands of 2,6-dibromo-, 3,5-dichloro- and 3,5-dibromopyridines was exactly the same as that of 2,6-dichloropyridine except for the fact that the rotational band contours of the infrared bands were not resolved in the dibromopyridines. Assignments of the normal vibrations of these molecules were made based on the following polarization behavior.

a_1 Species: The polarized Raman bands in molten phase could be definitely assigned to the a_1 vibrations. The corresponding infrared bands showed the type I polarization in the thin films and some bands clearly showed the B band contour in vapor.

b_2 Species: The infrared bands showing the A band contour in vapor showed the type III polarization in the thin film and the corresponding Raman bands showed the uv polarization in crystal.

b_1 Species: The infrared bands showing the C band contour in vapor showed the type II polarization in the thin film and the corresponding Raman bands showed the uw polarization in crystal.

a_2 Species: The Raman bands showing the vw polarization were assigned to the a_2 vibration, because no corresponding infrared bands were observed.

The normal vibrations thus determined are given in Tables 3 and 4 and also shown in Figs. 2—10. The normal vibrations of the dihalopyridines show the following characteristic features. (1) The vibrational frequencies of the ν_{6a}, ν_{12}, ν_{6b}, ν_{18b}, ν_{16a}, and ν_{16b} vibrations increase markedly compared with those of pyridine. (2) The frequencies of the ϕ-Cl and ϕ-Br stretching vibrations decrease remarkably compared with the frequencies of the C-Cl and C-Br stretching vibrations of aliphatic compounds. These observations are well explained in terms of the normal coordinate calculation.

The normal coordinate calculation gave the following results. (1) The ν_{6a} vibration mixes with the ϕ-X (X=Cl or Br) stretching vibration of a_1 species in the dihalopyridines and its frequency increases compared with the corresponding frequency of pyridine (602 cm^{-1}). The ν_{6a} vibration also interacts with the ν_{12} vibration and the frequency of the ν_{12} vibration increases compared with the corresponding frequency of pyridine (1030 cm^{-1}). The mixing of the ϕ-X stretching, ν_{6a}, and ν_{12} vibrations is larger in the dichloropyridines than in the dibromopyridines and thus the frequencies of the ν_{6a} and ν_{12} vibrations increase more largely in the dichloropyridines than in the dibromopyridines. The difference of the mixing may be due to the fact that the energy separation between the C-Cl stretching and ν_{6a} vibrations is smaller than that between the C-Br stretching and ν_{6a} ones. (2) The ν_{6b} vibration interacts with the ϕ-X stretching vibration of b_2 species and the frequency of the ν_{6b} vibration increases compared with the corresponding frequency of pyridine (650 cm^{-1}). The ν_{6b} vibration also interacts with the ν_{18b} vibration and the frequency of the ν_{18b} vibration increases compared with the corresponding frequency of pyridine (1045 cm^{-1}). The mixing of the ϕ-X stretching, ν_{6b}, and ν_{18b} vibration is larger in the dichloropyridines than in the dibromopyridines and thus the frequencies of the ν_{16b} and ν_{18b} vibrations increase more largely in the dichloropyridines than in the dibromopyridines. This may be due to the smaller energy separation between the ν_{6b} and C-Cl stretching vibrations compared with that between the ν_{6b} and C-Br stretching vibrations. (3) The ν_{16b} and ν_{16a} vibrations mix with the Cl or Br wagging vibrations. Thus the frequencies of the ν_{16b} and ν_{16a} vibrations of dihalopyridines increase compared with those of pyridine (408 and 377 cm^{-1}) but the frequency increase of the ν_{16a} vibration is larger than that of the ν_{16b} vibration. This may be due to the difference of the energy separation between the two interacting vibrations as described above.

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