Raman Spectra of Compounds under Inversion Motions. III. *N*-Methylpyrrolidine

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Raman spectra of *N*-methylpyrrolidine were measured in various states and a normal vibration calculation was carried out on its conformers. Results of the measurement and calculation indicate that the Raman band of the inversion vibrational mode is caused to shift remarkably by the formation of hydrogen bond to the nitrogen atom. This phenomenon, along with the enthalpy of hydrogen bond formation obtained from measurements at various temperatures, suggests that the conformer predominant in pure liquid corresponds to one minimum in the potential for the inversion motion, which has a low potential barrier and high anharmonicity.

Some Raman bands of 1,4-dimethylpiperazine and 1-methylpiperazine are caused to shift remarkably by formation of hydrogen bonds to their nitrogen atoms, and this phenomenon has been interpreted as being due to a suppression of the motion of inversion at the nitrogen by the hydrogen bonding.[1,2] The present study is concerned with a five-membered heterocyclic compound, *N*-methylpyrrolidine. Existence of an inversion motion at the nitrogen in this compound was concluded by NMR studies,[3-5] and a value of 33.5 kJ/mol was obtained for the free energy of activation.[5] In addition, dipole moment studies also suggested the existence of the motion.[6,7] An effect of a hydrogen bonding between this compound and chloroform was found in NMR spectral measurements, and a report[8] was made on shifts of its Raman bands of CH stretching vibrations caused by dissolution in water. In the present study, Raman spectra of *N*-methylpyrrolidine in various states were measured, and band shifts found in association with hydrogen bonding are discussed from many points of view.

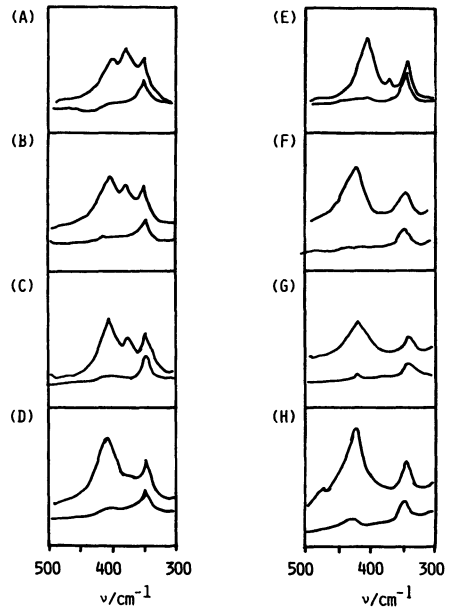

Fig. 1. Raman spectra (350—450 cm^{-1}, $I_{//}$ and $I_{\perp}$) of aqueous solutions of *N*-methylpyrrolidine at room temperature.
(A): x=0.658, (B): x=0.549, (C): x=0.488, (D): x=0.405, (E): x=0.272, (F): x=0.037, (G): x=0.022, (H): x=0.019.
x: Mole fraction of *N*-methylpyrrolidine.

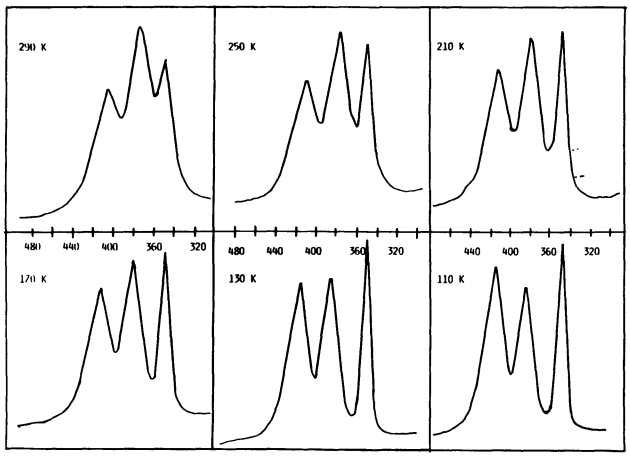

Fig. 2. Raman spectra (350—450 cm^{-1}) of a methanol solution of *N*-methylpyrrolidine (a mixture of *N*-methylpyrrolidine and methanol in mole ratio of 1 to 0.80) at various temperatures.

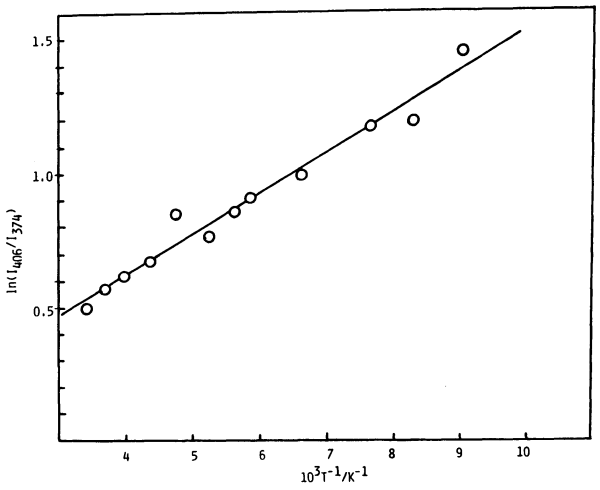

Fig. 3. Relation between $\ln(I_{406}/I_{374})$ and $1/T$. T in K.

Experimental

Sample *N*-methylpyrrolidine was a commercial product from Tokyo Kasei Co. (grade GR). Raman spectra were

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Table 1. Raman spectra of *N*-methylpyrrolidine[a)]

Pure liquid			Solid		Aq soln (1 : 1.1)			CH_3OH soln (1 : 1.0)			C_6H_6 soln (1 : 1.0)			Dioxane soln (1 : 1.0)			Acetone soln (1 : 1.0)		
ν	I	ρ	ν	I	ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ	ν	I	ρ
			120	7															
230	5	0.39	232	6	230	3	0.37	223	3	0.40				223	3	0.31	225	23	0.23
?			292	5															
348	9	0.62	354	15	348	9	0.69	346	9	0.66	342	9	0.55	344	7	0.62	350	9	0.55
											366	14	0.08						
375	15	0.11	388	20	374	8	0.17	372	10	0.13	375	14	0.12	371	12	0.06	376	17	0.09
					406	12	0.13	405	7	0.13									
570	41	0.18	574	56	570	41	0.20	568	43	0.17	565	41	0.12	569	37	0.14	572	43	0.16
?			642	8															
?			734	8							797	4	0.20						
			852	11															
873	23	0.21	876	78	874	33	0.17	870	29	0.18	869	28	0.17	871	28	0.18	874	27	0.21
895	100	0.03	896	100	896	100	0.03	895	100	0.03	890	100	0.03	893	100	0.02	897	100	0.03
941	2	0.75	940	8	940	2	0.75	940	1	0.75							941	1	0.75
961	2	0.75	965	10	960	3	0.64	960	2	0.75							965	2	0.20
1030	9	0.56	1033	27	1032	12	0.71	1030	16	0.48	1027	13	0.46	1027	12	0.24	1032	9	0.52
1040	6	0.75	1044	19				1037	17	0.37									
			1083	6															
1112	4	0.35	1118	7	1117	4	0.55	1110	4	0.55	1108	5	0.32	1105	10	0.58	1112	4	0.24
1148	5	0.75	1148	19	1144	6	0.61	1141	5	0.60	1143	9	0.43	1144	6	0.43	1149	4	0.65
			1177	6															
1201	3	0.40	1201	11	1215	4	0.75	1215	4	0.66	1195	2	0.35				1218	6	0.68
1217	2	0.75	1215	12															
1238	5	0.33	1244	17	1240	6	0.47	1238	5	0.50	1235	5	0.19	1239	6	0.34	1240	6	0.47
1278	3	0.56	1258	12															
1285	3	0.68	1288	22	1285	5	0.67	1280	5	0.50	1280	4	0.41	?		sh	1280	4	0.54
1330	2	0.75	1334	9	1350	4	0.59	1331	2	0.59	1325	2	0.62	1330	6	0.64	1330	2	0.75
1349	3	0.42	1353	13				1347	3	0.56	1345	5	0.32	1344	4	0.29	1350	5	0.41
											1398	3	0.26	1390	3	0.58			
1414	4	0.75	1417	13	1417	4	0.75	1414	5	0.57	1411	4	0.48	1411	6	0.66	1419	4	0.56
1446	10	0.75	1449	29	1449	12	0.75	1447	15	0.75	1443	16	0.74	1440	27	0.71	1447	14	0.72
1467	9	0.75	1465	26	1465	11	0.75	1460	12	0.75	1474	11	0.58						
1480	7	0.75	1483	15													1482	9	0.34

a) ν, frequency in cm^{-1}; I, intensity; ρ, polarization ratio. The ratios in parentheses represent the mole ratio of *N*-methylpyrrolidine to solvent.

recorded on a Model R-800T Raman spe trometer (Japan Spectroscopic Co.) with an excitation effected by use of a Spectra Physics argon ion laser (Model 165) at 514.5 nm (300 mW). Depolarization ratio was measured with a system consisting of a half-wave plate, a lens, and a polarizer. Liquid samples at room temperatures were measured with 0.3 ml Raman cells, while crystals, solutions, and pure liquids at lower temperatures were measured with an Oxford-type cryostat and liquid nitrogen. Experimental results are shown in Table 1 and 2 and Figs. 1, 2, and 3.

Normal Vibration Calculation

Normal vibration calculations on conformers of *N*-methylpyrrolidine (the axial and equatorial conformers and other molecular models) were carried out according to Wilson's GF matrix method[9)] by use of the Computation Center, University of Tokyo and library programs BGLZ and LSMB. The molecular parameters used are: bond lengths, $r(N-CH_3)=1.49$ Å, $r(NCH_2-CH_2)=1.53$ Å, $r(CH_2-CH_2)=1.54$ Å, and $r(C-H)=1.09$ Å; bond angles, $\alpha(N-CH_2-CH_2)=105°$, $\alpha(CH_2-CH_2-CH_2)=104°$, and $\alpha(H-C-H)$(CH_2 group) = bond abgles of CH_3 group = bond angles around nitrogen atoms = tetrahedral angle. For the molecular models, an envelope structure for the five-membered ring was used on the basis of the existence of depolarized bands in the observed Raman spectra of *N*-methylpyrrolidine in the liquid state. Force constants and results of calculation are shown in Table 3 and Fig. 4, respectively.

Results and Discussion

Spectral Change with State Change from Liquid to Solid. As shown in Table 1, no bands are caused to disappear by the state change from liquid to solid. Therefore, it may reasonably be concluded that one conformer prevails in the pure liquid and that this persists in the solid state. The intensity change of the bands at 1238, 873 and 348 cm^{-1} may be due to a change in their associated polarizabilities.

Spectra of N-*Methylpyrrolidine in Hydrogen-bonding Solvents.* A change in the spectrum of *N*-methylpyrrolidine with

Table 2. Raman spectra of *N*-methylpyrrolidine in acids[a)]

Pure liquid			HCOOH soln (1 : 2.1)		CH_3COOH soln (1 : 1.0)		HCl soln (1 : 1.5)		DCl soln (1 : 1.0)	
ν	I	ρ	ν	I	ν	I	ν	I	ν	I
230		50.39			216	5				
			335	5			330	6	330	7
348	9	0.62			354	6				
375	15	0.11			375	8				
			450	30	430	9	455	30	443	37
					477	9				
			555	40			552	38	546	42
					571	26				
570	41	0.18								
					662	6				
			697	21						
			790	29			788	26		
873	23	0.21	860	77	880	48	855	69	853	75
895	100	0.03	905	100	900	100	905	100	900	100
			955	9			953	9		
							1006	21	1010	13
1030	9	0.56	1010	21	1036	16	1035	17	1035	17
1040	6	0.75								
							1070	15		
1112	4	0.35			1114	5	1105	18	1100	10
1148	5	0.71								
1201	3	0.40							1190	18
1217	2	0.75								
1238	5	0.33			1240	12	1230	14		
1278	3	0.56								
1285	3	0.68								
1285	3	0.68							1285	19
1330	2	0.75			1333	9				
1349	3	0.42	1348	77			1350	11	1355	14
			1375	45	1380	11				
									1400	8
1414	4	0.75			1413	17				
									1428	
1446	10	0.75	1456	45	1449	30				
1467	9	0.75					1462	39	1458	52
1480	7	0.75								

a) ν, frequency in cm^{-1}; I, intensity; ρ, polarization ratio. The ratios in parentheses represent the mole ratio of *N*-methylpyrrolidine to solvent.

dissolution in water was reported by Hirokawa *et al.*[8)] in a spectal region above 2600 cm^{-1}. In a region below 2600 cm^{-1}, a change has been found, as shown in Table 1, that the band at 375 cm^{-1} (pure liquid) remarkably shifts to higher frequencies in aqueous solutions. Relative intensity changes in this band and its shifted band are shown in Fig. 1. With increasing mol fraction of water, the band at 375 cm^{-1} decreases its intensity, while a band appears in the higher frequency side of the band with increasing intensity. In the case of the lowest concentration in the figure, the former disappears and only the latter remains at 424 cm^{-1}. The frequency increase 375 $cm^{-1} \rightarrow 424$ cm^{-1} is a remarkably large one. No other bands in the region below 2600 cm^{-1} show such a remarkable change, although some of them experience smaller frequency change. The valence state of the nitrogen atom of *N*-methylpyrrolidine is expected to resemble an sp^3 state when it is hydrogen-bonded. The observed frequencies for hydrogen-bonded species in Table 1 correspond well to the frequencies calculated for the equatorial conformer by using the first-guess force constants, but not satisfactorily to the axial conformer. The calculated frequencies for the equatorial conformer were made to fit to the observed frequencies so as to give the final force constant set by the method of least squares.[10)] The set is shown in Table 3. The calculated frequencies for the skeletal vibrations of the axial conformer for the set of force constants are shown in Fig. 4. They are very different from those of the equatorial conformer included in the figure, which agree well with the observed frequencies. Therefore, it is reasonable to consider that most of hydrogen-bonded species assume equatorial conformations.

Spectral Change with Temperature Change. As discussed in the preceding section, two bands (one at 375 cm^{-1} and the other at the higher frequency side) appear

TABLE 3. FORCE CONSTANTS(mdyn Å^{-1}, 1 dyn$=10^{-5}$ N) OF *N*-METHYLPYRROLIDINE FOR THE MODIFIED UREY-BRADLEY FORCE FIELD

K(N–CH_3)	2.515	F(C–C–C)	0.652	
K(N–C)	3.117	F(H–C–CH_2N)	0.614	
K(NC–C)	1.371	F(H–C–CH_2CH_2N)	0.447	
K(C–C)	1.570	Y(N–CH_3)	0.028	mdyn Å
K(C–H)(CH_3)	4.307	Y(N–CH_2)	0.246	mdyn Å
K(C–H)(CH_2)	3.921	Y(NC–CH_2)	0.157	mdyn Å
H(N–C–H)(CH_3)	0.303	Y(NCH_2CH_2–CH_2)	0.110	mdyn Å
H(H–C–H)(CH_3)	0.363	κ(CH_3)	−0.022	mdyn Å
H(C–N–C)	0.685	κ(N–CH_2–C)	0.090	mdyn Å
H(C–N–CH_3)	0.432	κ(CH_2–CH_2–CH_2)	0.057	mdyn Å
H(N–C–C)	0.106	g	0.067	mdyn Å
H(H–C–N)	0.127	t	−0.040	mdyn Å
H(H–C–$CH_2CH_2CH_2$)	0.261	c	−0.050	mdyn Å
H(H–C–H)(CH_2)	0.376			
H(C–C–C)	0.218			
H(H–C–CH_2N)	0.280			
H(H–C–CH_2CH_2N)	0.222			
F(N–C–H)(CH_3)	0.657			
F(H–C–H)(CH_3)	0.144			
F(C–N–C)	0.466			
F(C–N–CH_3)	0.183			
F(N–C–C)	0.761			
F(H–C–N)	0.633			
F(H–C–$CH_2CH_2CH_2$)	0.623			
F(H–C–H)(CH_2)	0.000			

Y: internal rotation force constant
κ : intramolecular tension force constant
g: gauche-type interaction force constant
t: trans-type interaction force constant
c: cis-type interaction force constant

These force constants are expressed in the unit of mdyn Å.

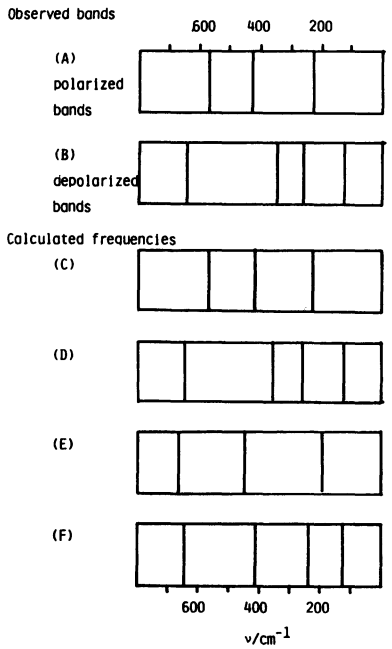

Fig. 4. Observed frequencies of liquid *N*-methylpyrrolidine ((A) and (B)) compared with the calculated frequencies ((C): equatorial form, A′ species, (D): quatorial form, A species, (E): axial form, A′ species, (F): axial form, A″ species).

in the spectra of *N*-methylpyrrolidine solutions in hydrogen-bonding solvents, suggesting two conformers (a hydrogen-bonded equatorial conformer and a conformer having a different conformation) to exist in the solutions. In order to evaluate the energy difference between these two conformers, spectra of a methanol solution were measured at various temperatures between 298 and 110 K. At equilibrium, *N*-methylpyrrolidine $(b-a$ mol$)+CH_3OH(a-a$ mol$)\rightleftarrows$ hydrogen-bonded complex (a mol), hence the equilibrium constant $K=a/(b-a)(a-a)$, where a and b are the initial quantities in mol of CH_3OH and *N*-methylpyrrolidine, respectively. On the assumption that $b-a$ and a are proportional to the band intensities of the band at 375 cm^{-1} and the one in the higher frequency side, respectively, K was obtained at various temperatures. Plots of ln K *vs.* $1/T$ are shown in Fig. 3. From the figure and the equation $\ln K=-\Delta H/(RT)+$ const, the enthalpy difference for the above reaction is estimated as $\Delta H=-1.3\pm0.2$ kJ/mol.

Spectra of N-*Methylpyrrolidine in Non-hydrogen-bonding Solvents.* Benzene (nonpolar), dioxane (polar), and acetone (polar) were used. They give spectra almost the same as the spectrum of pure liquid. This indicates that the shift of Raman band mentioned above under the second heading is due to hydrogen bonding to the nitrogen atom of the compound.

Spectra of N-*Methylpyrrolidine in Carboxylic Acids and Aqueous Hydrochloric Acid Solutions.* A band corresponding to the band of liquid *N*-methylpyrrolidine at 375 cm^{-1} is observed for each of the solutions shown in Table 2 (HCOOH soln, 450 cm^{-1}; CH_3COOH, 430 cm^{-1}; aqueous hydrochloric acid solution, 455 cm^{-1}). For *N*-methylpyrrolidine in a deuterium chloride–heavy water mixture, the corresponding band appears at 443 cm^{-1}, close to 455 cm^{-1} for the band of aqueous hydrochloric acid solution, indicating that this band is not due to the NH deformation mode but to the skeletal deformation mode. Between these frequency values and 375

cm^{-1} (*N*-methylpyrrolidine, liquid) there lie frequency values for bands of the inversion mode of *N*-methylpyrrolidine in hydrogen-bonding solvents, in agreement with the change in valence state of the nitrogen atom to the sp^3 type with hydrogen bonding.

Concluding Remarks. In liquid *N*-methylpyrrolidine, almost all the molecules are in one conformation different from that for the hydrogen-bonded equatorial conformer.

These two conformers give rise to bands at different frequencies 375 and 424 cm^{-1} for the vibrational mode of inversion at the nitrogen. This may be explained as follows. The hydrogen bonding to the nitrogen atom increases the potential barrier for the inversion motion at the nitrogen and changes the shape of potential for the motion. As a result, for the inversion mode the energy level separation between the ground state ($v=0$) and the first excited state ($v=1$) increases, and the $0\rightarrow1$ transition frequency increases to give the above-mentioned shift of band. On the other hand, the observed enthalpy difference, -1.3 kJ mol, between the hydrogen-bonded equatorial conformer and the abundant conformer in the pure liquid is very small compared with ordinary hydrogen-bond energy values. Therefore, the instability of the non-hydrogen-bonded equatorial form having a nitrogen atom in the sp^3 state may be considered to be compensated by the stabilization energy due to hydrogen bonding. Thus, the potential for the inversion vibrational mode of the conformer in the pure liquid is a low barrier potential with high anharmonicity, one of whose potential minima corresponds to the abundant conformer in the pure liquid. The conformer is stabler than the non-hydrogen-bonded equatorial conformer having a nitrogen atom in the sp^3 state, and the structure around the nitrogen atom is intermediate between the planar and tetrahedral structures.

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