Raman Spectra of a Compound under Inversion Motions. II. *N*-Methylpiperazine

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Raman spectra of *N*-methylpiperazine in proton donors and acceptors were measured. Forms of stable conformers in the donors and the acceptors were studied by comparison of the Raman spectra and normal vibration calculations. A conformational change of the molecule in the donors was found, suggesting the change of valence state of nitrogen atom, which is caused by hydrogen bonding.

One of the present authors reported[1] the conformational change of *N,N'*-dimethylpiperazine, which might be ascribed to suppression of inversion motion at nitrogen by hydrogen bonding. In the present study, the effect of hydrogen bonding on molecular conformation of *N*-methylpiperazine molecule, which has two nitrogen atoms, one bonded by a light atom and the other bonded by a heavier group, was investigated in order to compare the effect by hydrogen bonding on the valence state of nitrogen atoms in different situations.

Experimental

Commercial *N*-methylpiperazine (grade GR, Tokyo Kasei Chemicals Co., Ltd.) distilled under vacuum was used. Raman spectra were measured with a Model R-800T Raman Spectrophotometer (Japan Spectroscopic Co., Ltd.) under excitation with a Spectra Physics argon ion laser (model 165) using 514.5 nm line (300 mW). Depolarization ratio was measured by use of a system consisting of a half-wave plate, a lens and a polarizer. Measured depolarization ratio of the Raman bands of carbon tetrachloride at 459 $\mathrm{cm^{-1}}$ (A_1 species) and at 218 $\mathrm{cm^{-1}}$ (E species) were 0.007 ± 0.001 and 0.75 ± 0.01, respectively. Liquid samples at room temperature were measured with 0.3 ml Raman cells, while crystal at low temperature was measured with an Oxford-type cryostatt and liquid nitrogen. The experimental results are shown in Tables 1—2 and Figs. 1—2.

Results and Discussion

In the following discussion, refer to Tables 1—2 and Figs. 1—2.

Raman Spectrum Change Associated with Hydrogen Bonding. The three Raman bands of pure liquid at 615 $\mathrm{cm^{-1}}$, 608 $\mathrm{cm^{-1}}$, and 587 $\mathrm{cm^{-1}}$ reduce their frequencies by *N*-deuteration as shown in the spectrum of heavy water solution. On the other hand, the band at 339 $\mathrm{cm^{-1}}$ shifts to 330 $\mathrm{cm^{-1}}$ by an apparently small frequency decrease as the result of both decrease of frequency on *N*-deuteration and increase of frequency by hydration. On the basis of the frequency changes, they are ascribed to the vibrations of –NH– group. Among them, the band at 615 $\mathrm{cm^{-1}}$ reduces its intensity both in the benzene and the acetone solutions, where concentration of the species hydrogen-bonded to the nitrogen atom in the group decreases. Therefore, it is assigned to the species, which is hydrogen-bonded to the nitrogen atom, though which might be hydrogen-bonding to other molecule. On the other hand, the band at 587 $\mathrm{cm^{-1}}$ increases its intensity in the solutions, being assigned to the species, which is not hydrogen-bonded to the nitrogen atom.

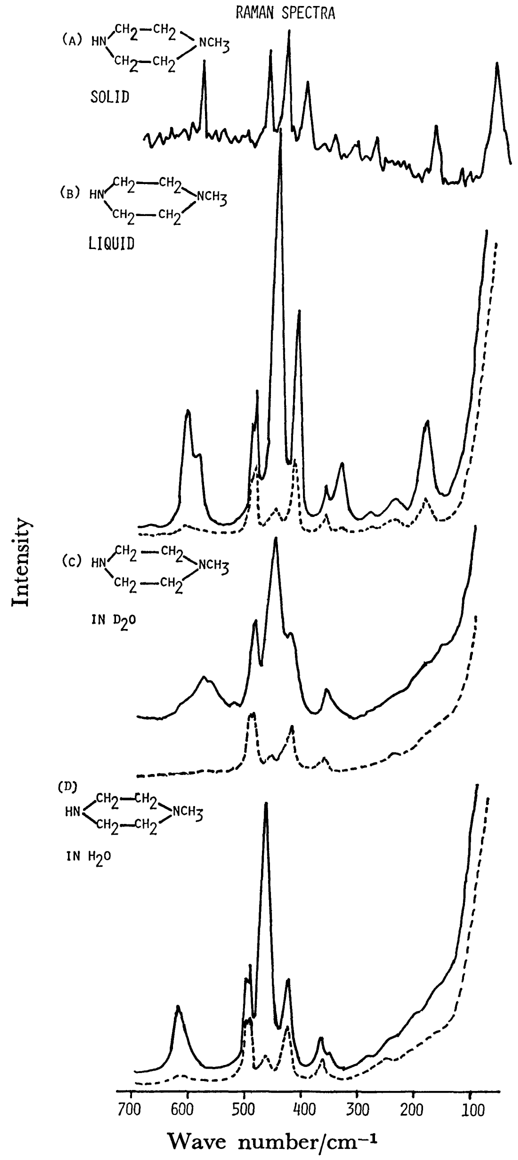

Fig. 1. Raman spectra of *N*-methylpiperazine. (A): Solid at −63 °C, (B): liquid at room temperature, (C): heavy water solution (mole fraction=0.335), (D): aqueous solution (mole fraction=0.335) Solid line: $I_{//}$, dotted line: $I_{\perp}$.

Intensity of the band at 608 $\mathrm{cm^{-1}}$ decreases in the acetone solution, in which the species hydrogen-bonding to acetone molecule but not hydrogen-bonded to its nitrogen atom increases. Therefore, it is assigned to the species which is hydrogen-bonded to its nitrogen, but is not hydrogen-bonding to other

TABLE 1. OBSERVED RAMAN SHIFT FREQUENCIES OF *N*-METHYLPIPERAZINE (in cm^{-1})

Liq			C_6H_6 soln		$(CH_3)_2CO$ soln		H_2O soln		CH_3OH soln		D_2O soln		Solid	
ν	I	ρ	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I
1467	34	0.60	1465	32			1472	25	1465	?*	1471	36	1463	32
1447	29	0.60	1442	28	1464	22	1453	22	1446	?*	1452	28	1460	44
1423	11	0.62	1423	sh	1420	13	1426	6	1422	sh	1426	9	1435	53
1397	3	0.54											1389	12
1377	4	0.50	1370	3	1365	4	1379	3	1376	15	1375	5	1370	6
1366	4	0.47	1366	sh									1366	sh
1345	4	0.57					1353	2	1348	5	1335	6	1345	9
1328	7	?	1330	sh	1318	8	1322	8	1317	11	1323	sh	1330	9
1316	11	0.61	1317	10			1307	20	1302	24	1307	27	1316	9
1303	30	0.44	1300	31	1300	17	1298	13	1292	16	1292	16		
													1292	88
1288	20	0.26	1286	19	1284	12	1284	sh						
1275	7	?	1275	sh	1270	4							1270	15
											1248	8		
1197	18	0.56	1194	21	1193	10	1202	13	1194	16	1198	17	1200	9
1187	10	?	1187	sh			1190	7	1183	11	1182	sh	1183	44
1178	9	?	1178	45	1176	6	1178	9					1172	15
							1165	10	1158	13	1160	14		
1155	13	0.52	1152	24			1152	10						
					1144	14			1147	sh	1143	15	1143	41
									1138	14				
1102	9	0.28	1102	sh			1107	8	1101	17*	1100	9	1102	6
1094	7	?	1096	9	1097	6							1094	12
1065	20	0.51	1061	23	1060	16*	1068	16			1063	8	1065	sh
									1058	25				
1053	9	?	1050	sh	1053	sh	1053	7			1050	15	1059	68
1037	11	0.61	1032	13	1030	7	1039	12	1034	?*	1035	15		
													1025	6
1018	9	0.52	*		1010	6	1018	5			1015	7		
1006	7	0.49	*		1000	4	1008	4			1005	5	1010	21
											983	6		
917	14	?	917	sh			910	8					925	29
					900	15								
897	26	0.04	896	41	895	17	895	sh	902	8			900	2
							867	8	872	sh	870	39		
853	10	0.41	850	15	850	5	855	9	857	sh			842	29
									846	9				
839	9	0.45	840	sh	832	6	839	9	830	8	830	sh		
825	7	?	820	sh					819	sh	827	13	825	12
783	100	0.18	780	100			782	100	775	100	780	100	773	100
					727	8								
615	20	0.08	612	sh			616	15	611	16				
608	21	0.07	608	86*	603	12	603	sh	603	sh				
587	13	0.11	585	26	593	13	593	sh	593	sh			592	38
											580	11		
495	19	0.59	490	sh	489	17	496	18	488	14	493	sh		
487	14	0.52	486	23	482	16	490	21	482	16	486	23	475	41
453	70	0.06	448	82	448	47	462	53	458	39	454	41		
440	sh	?	440	sh	439	38					440	sh	444	53
417	38	0.34	414	47	411	29	423	18	418	13	420	19		
													407	29
363	7	0.57	360	6	358	5	363	6	356	4	363	7	360	12
339	8	0.14	333	11	333	9	350	sh					323	9
											330	?		
285	1	0.56	284	1			283	?	278	?	285	?	286	13
244	2	0.75	240	3	252	7	245	?	235	?	245	?	244	6
							200	?						
185	15	0.30	178	10	177	5	190	?			190	?	182	26
													77	50

*: Overlapped by solvent band, ν: shift frequency, I: relative intensity, ρ: depolarization ratio.

Table 2. Calculated frequencies of non-hydrogen-bonded *N*-methylpiperazine compared with the observed frequencies (in cm^{-1})

Obsd	ee	e(CH_3)a(H)	aa	a(CH_3)e(H)	Description
			650(A′)	645(A′)	CH_2 rock, CCN def
587(P)	612(A′)	618(A′)			C(NH)C def
					CCN def
			528(A″)	529(A″)	CCN def
			518(A′)	525(A′)	CCN def
487(P, DP?)	503(A″)	501(A″)			CCN def
440(P)	454(A′)	450(A′)			CNC def, CCN def
			438(A′)	435(A′)	CNC def
417(P)	420(A′)	421(A′)			CNC def
			403(A″)	403(A″)	CNC def
363(P, DP?)	366(A″)	367(A″)			CNC def, CCN def
339(P)	322(A′)	326(A′)			CNC def, CN tors
			314(A′)	311(A′)	CNC def
244(DP)	257(A″)	256(A″)			CC tors, CCN def
			220(A″)	221(A″)	CCN def
185(P)	193(A″)	193(A″)	194(A″)	194(A″)	NC tors
	159(A′)	162(A′)			CNC def, CCN def
			133(A′)	131(A′)	CNC def, NC tors

P: Polarized, DP: depolarized, rock: rocking, def: deformation, tors: torsion, ee: diequatorial, aa: diaxial.

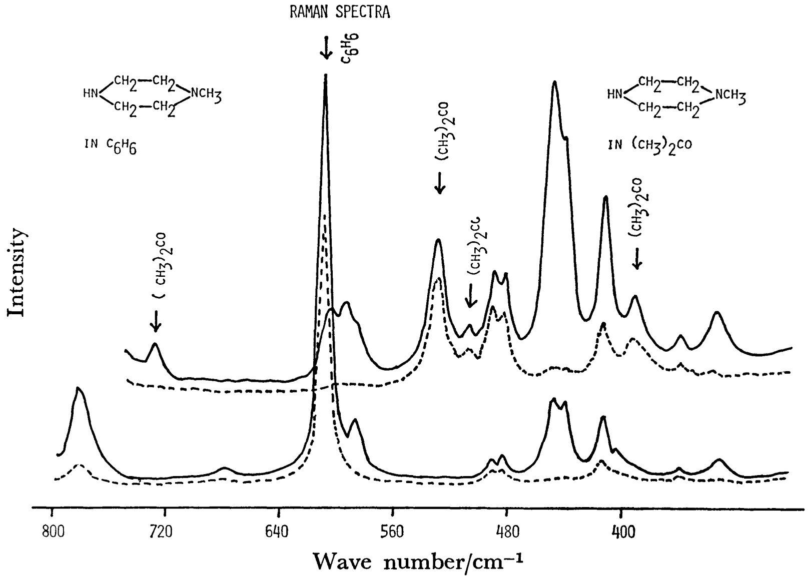

Fig. 2. Raman spectra of *N*-methylpiperazine.
Acetone solution (mole fraction=0.260), benzene solution (mole fraction=0.150).
Solid line: $I_{//}$, dotted line: $I_{\perp}$.

molecule. In the aqueous solution, the band at 587 cm^{-1} becomes weaker, and the band at 615 cm^{-1} becomes intense, so being the case for the methanol solution. Intensity of the band at 339 cm^{-1} increases in the benzene and the acetone solutions, while it decreases in the aqueous and the methanol solutions. So, the band is assigned to a vibration of –NH– group of the species, which is not hydrogen-bonded to nitrogen atom. In the latter solutions, frequency of the band increases to 363 cm^{-1} on hydrogen bonding to nitrogen atom.

These changes indicate that the bands at 587 cm^{-1} and 339 cm^{-1} arising from non-bonded –NH– group increase their frequencies to 615 cm^{-1} or 608 cm^{-1} and 363 cm^{-1} by being hydrogen-bonded to the nitrogen atom.

Frequencies of the bands of pure liquid at 453 cm^{-1}, 440 cm^{-1}, and 363 cm^{-1}, do not change much on *N*-deuteration. The band at 440 cm^{-1} increases its intensity in the benzene and the acetone solutions, while its intensity decreases in the aqueous and the methanol solutions. Therefore, it is attributed to the species which is not hydrogen-bonded to the nitrogen atom of –N(CH_3)– group. The other two bands at 453 cm^{-1} and 363 cm^{-1}, which are intense in the aqueous and the methanol solutions, are attributed to the species hydrogen bonded to the nitrogen atom of –N(CH_3)– group, although the latter band might be overlapped by a band of non-bonded species. Based on these changes, it is concluded that the band at 440 cm^{-1} of non-bonded –N(CH_3)– group increases its frequency to 453 cm^{-1} on the hydrogen bond for-

Table 3. Force constants of *N*-methylpiperazine (in mdyn/Å)

K(N-H)	5.900	H(HCN)(CH$_3$)	0.272	Y(NH-C)	0.058
K(C-N)	3.017	H(HCH)(CH$_3$)	0.513	Y(C-C)	0.107
K(C-C)	2.304	F(HNC)	0.313	Y(N(CH$_3$)-C)	0.062
K(C-H)(CH$_2$)	4.050	F(CNC)	0.195	Y(CH$_3$-N)	0·062
K(C-H)(CH$_3$)	4.437	F(NCC)	0.700	κ(CH$_2$)	0.030
H(HNC)	0.307	F(HCC)	0.482	κ(CH$_3$)	−0.010
H(CNC)	0.482	F(HCN)	0.664	t	0.107
H(NCC)	0.300	F(HCH)	0.069	g	−0.025
H(HCC)	0.217	F(HCN)(CH$_3$)	0.664		
H(HCN)	0.219	F(HCH)(CH$_3$)	0.173		
H(HCH)	0.363				

K: Stretching force constant, H: angle bending force constant, F: repulsive force constant, Y: internal rotation force constant, κ: intramolecular tension, t: trans coupling force constant, g: gauche coupling force constant.

mation.

Frequency change associated with hydrogen bonding to nitrogen atom in the case of –NH– group ((615−587)/587=0.048, (608−587)/587=0.036; (363−339)/339=0.071) is larger than that of –N(CH$_3$)– group ((453−440)/440=0.030).

Comparison of the Bands of Non-bonded Species with Normal Vibration Calculation and the Bands of the Solid. The results of normal vibration calculation according to Wilson's GF matrix method[2] by use of the modified Urey-Bradley force field and the force constants in Table 3 are shown in Table 2, compared with the observed frequencies of the non-bonded species. The observed frequencies agree well to the calculated frequencies of ee form or e(CH$_3$)a(H) (e: equatorial, a: axial), but they are not consistent with those of aa form or a(CH$_3$)e(H) form. Therefore, it is probable that molecular form of non-bonded species is close to ee form or e(CH$_3$)a(H) form. As valence state of nitrogen atom is almost sp^3 in the species hydrogen-bonded to the nitrogen atom, the observed frequencies in Table 2 are considered to be due to the molecular form, which is close to but not the same as the form having sp^3 valence state of nitrogen atom. In the solid state, species having similar molecular form persists as frequencies of the non-bonded species are somewhat close to those in the spectrum of the solid in the region below 700 cm^{-1}. From the above discussion, it is concluded that in the liquid state non-bonded *N*-methylpiperazine molecules are in one form close to ee or e(CH$_3$)a(H) form and that some of normal frequencies of –NH– or –N(CH$_3$)– group of the form are affected very much by hydrogen bonding to the nitrogen atom of –NH– or –N(CH$_3$)– group. The frequency changes on hydrogen bonding cannot be explained as the conformational change, ee or e(CH$_3$)a(H)→aa or a(CH$_3$)e(H), because the frequency of the polarized band at 339 cm^{-1} decreases and those of the bands at 363 cm^{-1}, 417 cm^{-1}, 440 cm^{-1}, and 587 cm^{-1} all increase in the case of the conformational change, while the observed change is contradictory to the change as shown in Table 2. Therefore, the change may be ascribed to change of valence state of nitrogen atom from the state for the ground state of the normal vibration associated with inversion coordinate to sp^3 type in hydrogen-bonded nitrogen atom.

Interpretation of the Spectrum Change Associated with Hydrogen Bonding. According to the normal vibration calculation, the Raman bands at 339 cm^{-1}, 440 cm^{-1}, and 587 cm^{-1}, which are affected much by hydrogen bonding, correspond to the vibrations to which the symmetrical skeletal deformation modes (A′ species) contribute to a great deal. These modes are related to the coordinates of inversions, ring inversion and inversion at nitrogen. It has been reported for 1,4-dimethylpiperazine and other compounds that rate of inversion at nitrogen is much faster than that of ring inversion and also that the activation energy for inversion at nitrogen of 1,4-dimethylpiperazine is a rather small value of 14 kJ mol^{-1}.[3] Therefore, the potential barrier for inversion at nitrogen is expected to be lower than that for ring inversion. When *N*-methylpiperazine is hydrogen-bonded, inversion at nitrogen may be suppressed and the molecule is likely to be primarily under ring inversion. In that situation, the potential is different from that of inversion motion including inversion at nitrogen especially in the height of potential barrier and the anharmonicity. The change of shape of the potential by hydrogen bonding necessarily accompanies the change of energy levels of normal vibrations associated with inversion coordinates as well as the change of molecular structure for the vibrational ground state. Thus, for the vibrations, to which inversion coordinates contribute, the energy difference between ground state (v=0) and the first excited state (v=1) become different between non-bonded molecule and hydrogen-bonded molecule. The Raman shift frequencies which we observe are related to the transition from the ground state to the first excited state, and therefore, they change considerably by the change of the energy difference of the energy levels.

Difference of frequency change associated with hydrogen bonding to nitrogen atom suggests that potential barrier of inversion at nitrogen of –NH– group is different from that of –N(CH$_3$)– group.

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