Raman Spectra of a Compound under Inversion Motions: *N,N'*-Dimethylpiperazine

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Raman spectra of methanol and aqueous solutions of *N,N'*-dimethylpiperazine were measured. Forms of stable conformers in various states were studied by comparison of the spectra obtained under various conditions. It was found that hydrogen bonding to nitrogen atoms of *N,N'*-dimethylpiperazine causes a conformational change.

Many proofs of the inversion motion of the molecule have been given by NMR studies.[1-6] In order to study the conformation of molecules subjected to inversion motions, ring inversion and inversion at nitrogen, *N,N'*-dimethylpiperazine was studied by Raman spectroscopy because of its high molecular symmetry. Since suppression of inversion motion at nitrogen by hydrogen bonding was expected, effect of the suppression on molecular conformation was studied by measuring Raman spectra of solutions of the substance.

Experimental

Commercial *N,N'*-dimethylpiperazine (grade GR, Tokyo Kasei Chemical Co., Ltd.) was used without further purification. 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). 0.1 ml or 0.3 ml Raman cells were used. Infrared spectra of the liquid were recorded on a Hitachi EPI-G3 spectrophotometer and a Hitachi FIS-3 far infrared spectrometer. The results of the measurements are shown in Table 1 and Fig. 1.

Results and Discussion

Comparison of Raman Spectra of N,N'-*Dimethylpiperazine in Liquid State with Infrared Spectra.* Coincidence of Raman shift frequency with infrared absorption maximum frequency is observed only for 1420 cm^{-1} and 630 cm^{-1} (Table 1). The couples, 1450 cm^{-1} (Raman) and 1455 cm^{-1} (IR), 1020 cm^{-1} (Raman) and 1018 cm^{-1} (IR), are close, both being in the higher frequency region (>1000 cm^{-1}), and the difference in Raman shift frequency and infrared absorption maximum frequency is expected to be intrinsically small. For all the other couples, frequencies of Raman shift and infrared absorption maximum differ a great deal. This suggests that the mutual exclusion rule holds for the Raman spectra and infrared spectra. Thus, conformers in the liquid take molecular forms each having a center of symmetry, diaxial conformer (AA), diequatorial conformer (EE) or some other form. A Raman line and the corresponding infrared band are observed at *ca.* 630 cm^{-1}, their intensity or absorbance being very small. This can be interpreted as due to cis form (AE conformer), as confirmed by dipole moment measurement to exist in mole fraction of 0.103 for a benzene solution.[7]

Raman Spectrum Change Associated with the Change of State, Pure Liquid to Solutions. The Raman lines having shift frequencies (1313 cm^{-1}, 1173 cm^{-1}, 457 cm^{-1}, 277 cm^{-1}) higher than those of the pure liquid (1306 cm^{-1}, 1160 cm^{-1}, 440 cm^{-1}, 251 cm^{-1}) appear in the spectrum of aqueous solution A (Table 1 and Fig. 1), the weaker Raman lines corresponding to the latter coexisting with the former. In the case of aqueous solution B, where the fraction of water is smaller than that of aqueous solution A, shift frequency values of the

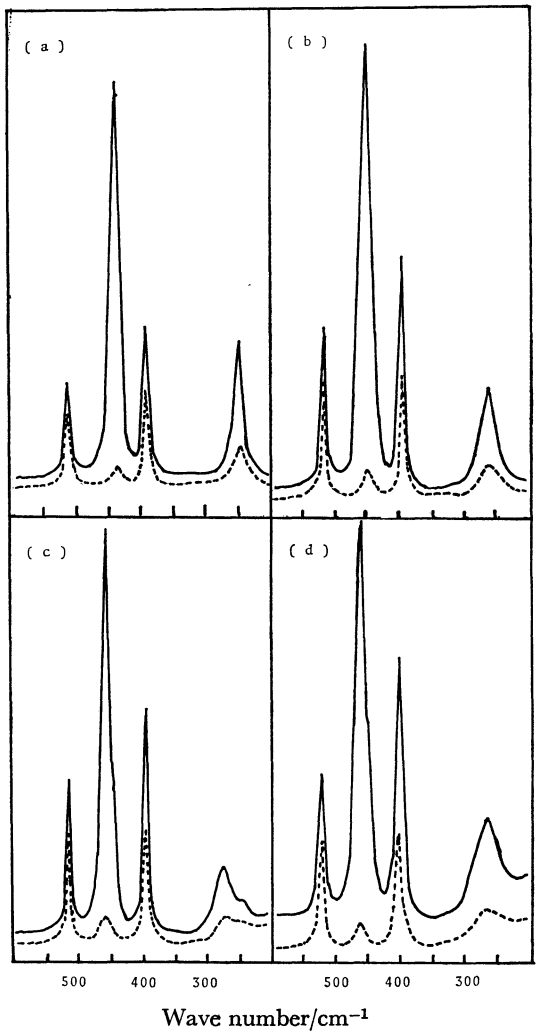

Fig. 1. Raman spectra of *N,N'*-dimethylpiperazine (*N,N'*-dmp) in lower shift frequency region.
(a) Liquid (b) aqueous solution B (mole fraction of *N,N'*-dmp, 0.433) (c) aqueous solution A (mole fraction of *N,N'*-dmp, 0.205) (d) methanol solution (mole fraction of *N,N'*-dmp, 0.197); solid line, $I_{\parallel}$; dotted line, $I_{\perp}$.

Table 1. Raman spectra of *N,N'*-dimethylpiperazine compared with infrared spectra of the pure liquid

IR Liquid ν[a]	Raman Liquid ν[a]	Liquid ρ[b]	Aqueous soln A ν[a]	Aqueous soln A ρ[b]	Methanol soln ν[a]	Methanol soln ρ[b]
	1467(32)	0.75	1473(45)	0.75	—[c]	—[c]
1455(s)						
	1450(?)[d]	?[d]	1455(?)[d]	?[d]	—[c]	—[c]
	1440(17)	0.75	1445(19)	0.75	—[c]	—[c]
1420(vw)	1420(12)	0.75	1427(21)	0.75	—[c]	—[c]
	1385(3)	0.75	1390(5)	0.75	1391(9)	0.75
1372(m)						
	1335(3)	0.75	1340(4)	0.75	1341(6)	0.75
			1313(38)	0.49	1314(43)	0.49
	1306(41)	0.47	1306(?)[d]	?[d]	1306(?)[d]	?[d]
1294(s)						
1283(sh)						
	1263(7)	0.75	1257(7)	0.75	1259(8)	0.75
	1196(11)	0.75	1202(16)	0.75	1203(17)	0.75
			1173(14)	0.64	—[c]	—[c]
1171(vs)						
	1160(22)	0.44	1160(?)[d]	?[d]	—[c]	—[c]
	1130(24)	0.75	1130(?)[d]	?[d]	—[c]	—[c]
			1116(31)	0.75	—[c]	—[c]
1122(m)						
1094(m)						
	1075(5)	0.35	1077(7)	0.38	1079(14)	0.42
1058(w)						
	1046(8)	0.75	1043(12)	0.75	—[c]	—[c]
	1020(13)	0.75	1019(10)	0.75	—[c]	—[c]
1018(m)						
977(vw)						
921(w)						
	856(5)	0.75	852(8)	0.75	854(8)	0.75
810(m)						
	780(100)	0.24	773(100)	0.18	774(100)	0.17
718(vvw)						
630(vvw)	630(1)	?[d]	630(1)	?[d]	630(1)	?[d]
	513(19)	0.75	514(27)	0.75	516(25)	0.75
			457(70)	0.06	456(67)	0.05
	440(78)	0.04	440(?)[d]	?[d]	440(?)[d]	?[d]
	393(30)	0.64	394(39)	0.49	396(44)	0.43
365(m)						
324(sh)						
278(w)						
			277(10)	0.34	264(17)	0.33
	251(26)	0.29	250(?)[d]	?[d]	250(?)[d]	?[d]
144(sh)						
	137(?)[d]	?[d]	140(?)[d]	?[d]	—[c]	—[c]
135(w)						

Figures in parentheses represent relative intensities, the maximum value being 100. a) Frequency in cm^{-1}. b) Degree of depolarization. c) Raman lines, the frequency, the intensity and ρ of which could not be determined because of overlapping with the Raman lines of methanol. d) Intensity and ρ could not be determined precisely.

four Raman lines have intermediate values between those for the pure liquid and those for aqueous solution A. For aqueous solution C (mole ratio, solute 1 : water 9.015) the four Raman lines corresponding to those of the pure liquid disappear. For a methanol solution, almost the same spectrum as that of aqueous solutions is observed.

Interpretation of Results. The spectrum change associated with the change of state, pure liquid to solution, is considered to be due to the conformational

TABLE 2. CALCULATED NORMAL FREQUENCIES (in cm^{-1})

Conformer	Symmetry species	Frequency	Description
EE	A_g	422	C–N(–CH_3)–C skeletal deformation
		369	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
		254	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
	B_g	457	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
		395	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
		186	N–CH_3 torsion
AA	A_g	496	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
		437	C–N(–CH_3)–C skeletal deformation
		173	C–N(–CH_3)–C skeletal deformation+N–C–C deformation+N–CH_3 torsion
	B_g	502	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
		356	C–N(–CH_3)–C skeletal deformation+N–C–C deformation
		183	N–CH_3 torsion

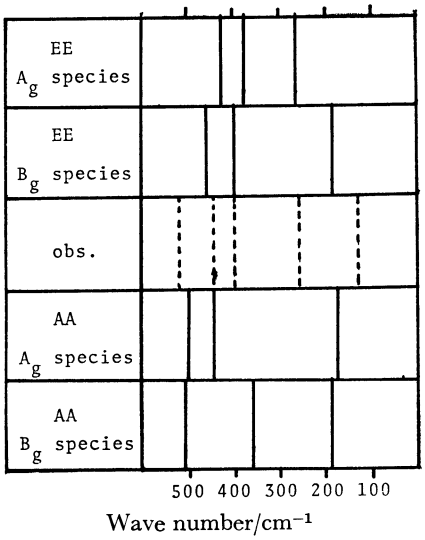

Fig. 2. Calculated frequencies of A_g and B_g species of *N,N'*-dimethylpiperazine compared with observed Raman shift frequencies.

change caused by hydrogen bonding or the change of nature of bonding in *N,N'*-dimethylpiperazine molecule. As the number of Raman lines arising from hydrogen bonded species is the same as that of the liquid, the species is also considered to have a center of symmetry. The molecular shape of species can be deduced as follows.

Normal vibration calculation of conformers (AA conformer and EE conformer belonging to C_{2h} point group) was carried out using force constants of related molecules.[8,9] The calculated frequencies of Raman active skeletal deformation vibrations (Table 2 and Fig. 2) are sensitive to conformational change. They are compared with the observed frequencies of the liquid in the table and the figure. Assigning polarized Raman lines ($0<\rho<0.75$) to calculated frequencies of A_g species and depolarized Raman lines ($\rho=0.75$) to those of B_g species, the calculated frequencies of EE conformer almost fit the observed Raman lines. However, those of AA conformer do not correspond exactly to the observed frequencies. The Raman lines of the pure liquid (440 cm^{-1}, 251 cm^{-1}), whose shift frequencies change with change of state, pure liquid to solution, are assigned to C–N(–CH_3)–C skeletal deformation vibrations.

The change can be interpreted as due to the conformational change arising from the change of valence state of nitrogen atoms. It can not be explained in terms of the conformational change of EE conformer to AA conformer for the following reason. Of the calculated frequencies of A_g species of EE conformer, both 422 cm^{-1} and 369 cm^{-1} increase and 254 cm^{-1} decreases by the conformational change. Thus, the observed frequency of polarized Raman line (251 cm^{-1}) of the pure liquid is expected to decrease if the change is caused by the conformational change. However, the frequency increases to 277 cm^{-1}. Of the calculated frequencies of B_g species of EE conformer, 457 cm^{-1} increases and 186 cm^{-1} does not change its frequency considerably, while 395 cm^{-1} decreases its frequency by the conformational change of EE conformer to AA conformer. Therefore, if the change is due to the conformational change, a depolarized Raman line is expected to appear in the region 300 cm^{-1}—400 cm^{-1}. However, this is not the case. It can thus be concluded that the conformer having a center of symmetry and a molecular shape similar to that of EE conformer exists in pure liquid in abundance and that another conformer, also having a center of symmetry and differing from the above conformer in the molecular conformation around nitrogen atoms, appears in aqueous solutions and in a methanol solution as a results of hydrogen bonding to nitrogen atoms.

Probable Conformers in Solutions and in Pure Liquid. Hydrogen-bonded species. By the formation of hydrogen bonding to nitrogen atoms of *N,N'*-dimethylpiperazine, valence orbitals of the nitrogen atoms may become similar to sp^3 hybrid orbitals, and the molecular conformation having bond angles close to tetrahedral angles would become abundant. Conformers in pure liquid. For trimethylamine, C–N–C angles have been found to be $108.7°\pm1°$, which is almost a tetrahedral angle corresponding to sp^3 hybrid orbitals.[10] Considering resemblace of the skeleton of C–N(–CH_3)–C of *N,N'*-dimethylpiperazine with trimethylamine, the valence orbitals of nitrogen atoms in *N,N'*-dimethylpiperazine are expected to be almost sp^3 orbitals, which do not seem to be affected much by hydrogen bonding to the

nitrogen atoms. However, a remarkable frequency change in the deformation vibrations of C–N(–CH_3)–C skeleton by hydrogen bonding is observed, suggesting the change in the valence state of nitrogen atoms. In pure liquid, therefore, time-averaged orbitals of the nitrogen atoms during inversion motions might be in sp^2 state. In accordance with the assumption, a simple calculation revealed that planar conformation around the nitrogen atoms can be realized by changing the azimuthal angle of N–CH_2–CH_2–N internal rotation axis from 60° to 46°34′ and all the C–N–C angles from at tetrahedral angle to 120° with no changes in all the bond lengths and other bond angles (tetrahedral angles), which require large energy. In the model, CH_2–CH_2 bond length is assumed to be the same as that of CH_2–N bond length on the basis of Rerat's work.[11]

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