Molecular Deformation Caused by Hydrogen Bonding and Resonance. 1,3-Dimethyl-2-imidazolidinone

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The Raman spectra of 1,3-dimethyl-2-imidazolidinone were found to change due to a hydrogen bonding to its nitrogen atoms, especially at low temperatures. The change in the spectra included the unusual change for CH_2 bending vibrations, suggesting that the deformation of the ring of the molecule takes place by hydrogen bonding.

In a preceding paper,[1] one of the present authors reported a remarkable change in the spectra of *N,N'*-dimethylurea in hydrogen-bonding solvents. This change was attributed to the molecular deformation by hydrogen bonding to nitrogen atoms. Further measurements regarding the temperature dependence of the spectra of the substance and an estimation of the enthalpy change of hydrogen bonding supported the idea of molecular deformation.[2] However, in this substance, other probable cause for the change (existence of cis and trans conformers due to an internal rotation around its CO–N axes) is present. In the present study, 1,3-dimethyl-2-imidazolidinone, which has no possibility of cis or trans conformations with respect to its CO–N axes, was adopted. Thus, measurements of Raman spectra were made in the hope of finding some change of the spectra (due to a molecular deformation caused by hydrogen bonding to nitrogen atoms).

Experimental

1,3-Dimethyl-2-imidazolidinone was a commercial product from Tokyo Kasei Co. (grade GR). The Raman

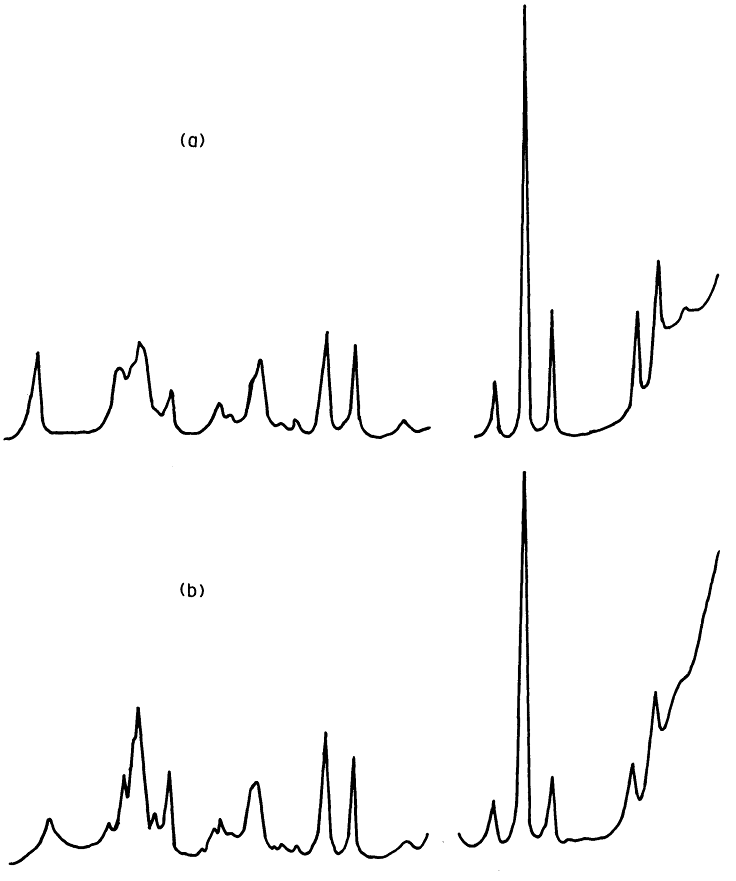

Fig. 1. Raman spectra of 1,3-dimethyl-2-imidazolidinone: (a) pure liquid; (b) aq soln(mixing mol ratio of solute to solvent: 1 : 8.75).

TABLE 1. RAMAN SPECTRA OF 1,3-DIMETHYL-2-IMIDAZOLIDINONE IN SOLUTIONS

Solid		Pure liq			Aq soln*			CCl_4 soln			CH_3CN soln		
$\tilde{\nu}$	I	$\tilde{\nu}$	I	ρ	$\tilde{\nu}$	I	ρ	$\tilde{\nu}$	I	ρ	$\tilde{\nu}$	I	ρ
100	10												
123	46												
153	6												
198	14												
213	10												
235	10												
283	17	283	6		284	4	P				281	4	0.75
329	19	330	4	0.75	338	2	0.75				329	3	0.75
520	28	523	6	0.75	521	3	0.75	520	5	0.75	520	5	0.75
577	40	584	20	0.24	584	21	0.25	580	17	0.17	581	21	0.24
648	21	652	2	0.75	658	3	0.75	651	2	0.59	650	2	0.75
763	100	764	100	0.09	772	100	0.08				764	100	0.11
856	13	858	1	0.75	853	1	0.75				858	1	0.75
963	16	965	5	0.23	972	6	0.24	962	5	0.15	965	6	0.26
					981	sh	?						
986	6	986	1	0.66				984	1	?	984	sh	?
1028	21	1031	5	0.30				1030	4	0.19	1032	6	0.37
					1040	9	0.29						
1070	3												
1093	6	1096	1	0.61	1098	1	0.67	1095	1	0.36	1098	1	0.75
1127	6	1129	1	0.75	1129	1	0.75	1128	1	0.43	1132	1	0.75
1170	44												
1186	7	1184	4	0.35				1180	4	0.18	1184	5	0.38
					1195	sh	?	1195	sh	?	1200	sh	?
		1201	sh	?	1203	6	0.50						
1239	7	1248	1	0.57	1250	1	?	1242	sh	?	1250	sh	?
1266	5	1269	2	0.37	1275	3	P	1269	2	0.16	1274	2	?
1280	7				1293	sh	?				1287	sh	?
1377	8	1384	2	0.31	1384	sh	?	1383	2	?			
					1394	5	0.29						
1406	6												
					1420	1	0.62						
1440	29	1446	sh	?	1446	sh	?	1441	sh	?			
1453	21	1451	5	0.75	1460	12	0.75	1449	5	?			
1465	18	1470	sh	?	1470	sh	?	1463	sh	?			
1473	sh												
1490	19	1494	3	0.67	1491	2	0.65	1488	5	?			
1513	21				1537	sh	?						
1675	24	1684	4	?	1641	6	0.25						
		1695	sh	?				1696	sh	?			

$\tilde{\nu}$: Shift frequency. I: Intensity. ρ: Depolarization ratio. P: Polarized. *: Mixing ratio(solute 1 mol : solvent 71 mols).

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

Results and Discussion

An 1,3-dimethyl-2-imidazolidinone molecule is expected to undergo a molecular deformation due to a deformation of its five-membered ring or the internal rotation of its methyl groups around the N–C axes. The vibrational frequencies of conformers (arising from the internal rotation of methyl groups) do not show any remarkable dependence on the

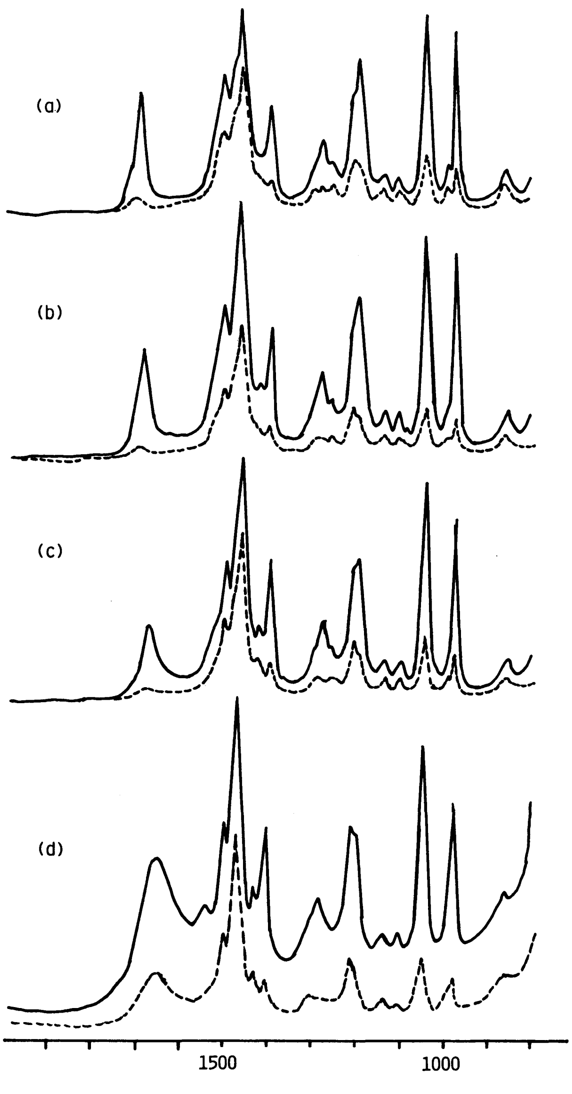

Fig. 2. Raman spectra of aqueous solutions of 1,3-dimethyl-2-imidazolidinone: mixing mol ratio of solute to solvent: (a) 1 : 0.21 (b) 1 : 0.99 (c) 1 : 3.00 (d) 1 : 71.

conformation of the methyl groups. Therefore, a difference among the spectra of the conformers is not expected. On the other hand, the effects of the deformation of the five-membered ring on the vibrational spectra are expected to be very remarkable. The probable causes of the deformation of the ring are the conformational changes due to the internal rotation around the bonds in the ring and that due to a change in the valence angle around the nitrogen atoms. Assuming the above-mentioned conformational change arising from a deformation of the ring, the observed spectral change associated with the state change was interpreted.

(a) Comparison of Liquid Spectra with Those of Solid: As shown in Table 1, there are two groups of bands. One group (1070 cm^{-1}, 1170 cm^{-1}, 1280 cm^{-1}, 1406 cm^{-1}, 1473 cm^{-1}, 1513 cm^{-1}, bands below 235 cm^{-1}) exists in the solid spectra but does not in the liquid spectra. The other (1201 cm^{-1}, 1695 cm^{-1}) exists in the liquid spectra but does not in the solid spectra. In the case of the former, although those below 235 cm^{-1} can be interpreted as due to lattice modes, which are characteristic to crystalline state, the existence of others suggests that a conformation of molecules in the solid state is a little different from that of molecules in a liquid state. The existence of bands of the latter group also supports this interpretation.

(b) Comparison of Liquid Spectra with Those of Solutions of Hydrogen-bonding Solvents: The following frequency shifts were observed to be associated with state changes from pure liquids to aqueous solutions (refer to Table 1 and Fig. 1); 1031 cm^{-1}→1040 cm^{-1}, 1184 cm^{-1}→1195 cm^{-1}, 1384 cm^{-1}→1394 cm^{-1}. The concentration dependency of relative intensities was determined (refer to Fig. 2). In addition, there are Raman bands of pure liquid (1201 cm^{-1} and 1451 cm^{-1}) which increase in intensity in the spectra of aqueous solutions. The 1420-cm^{-1} band appears only for aqueous solutions and the band for a pure liquid (523 cm^{-1}) decreases in intensity for the spectra of aqueous solutions. Similar changes are observed for methanol solutions. The above-mentioned changes do not occur for solutions of non-hydrogen-bonding solvents, of which a few examples (acetonitrile and carbon tetrachloride) are shown in Table 1. The changes are, therefore, considered to be characteristic of solutions of hydrogen-bonding solvents and are interpreted to be caused by the generation of hydrogen-bonded conformers. These arise from the deformation of the conformer which is stable in pure liquid as a result of hydrogen bonding. The Raman bands which appear at the higher frequency side of the pure-liquid bands for solutions of hydrogen-bonding solvents and the bands which appear only in the spectra of solutions of hydrogen-bonding solvents are due to the above-mentioned deformed conformers.

There are two types of hydrogen bonding to 1,3-dimethyl-2-imidazolidinone: Hydrogen bonding to its oxygen atom and that to its nitrogen atoms. In the former, the planarity of the $CH_2(CH_3)NCON$ skeleton by an increase of the double-bond character of the NC bond is expected, while in the latter, a tetrahedral configuration around the nitrogen atom is probable. In solutions of 1,3-dimethyl-2-imidazolidinone dissolved in hydrogen-bonding solvents, the latter situation is considered to be present because the spectra of 1,3-dimethyl-2-imidazolidinone in a hydrochloric acid solution, in which a species having a hydrogen ion attached to its nitrogen and having a tetrahedral configuration around the nitrogen atom is expected to occur, are almost similar to those of 1,3-dimethyl-2-imidazolidinone in an aqueous solution, as shown in Table 2. In connection with this, the remarkable increase in the intensity

TABLE 2. RAMAN SPECTRA OF 1,3-DIMETHYL-2-IMIDAZOLIDINONE IN ACIDS

Pure liq			Aq soln			HCl soln			$DCl-D_2O$ soln		
$\tilde{\nu}$	I	ρ	$\tilde{\nu}$	I	ρ	$\tilde{\nu}$	I	ρ	$\tilde{\nu}$	I	ρ
283	6	?	284	4	P	286	4	P	283	6	P
330	4	0.75	336	2	0.75	338	2	0.75	330	4	0.75
523	6	0.75	520	3	0.75	520	4	0.75	519	6	0.75
584	20	0.24	585	20	0.25	586	23	0.19	583	25	0.23
652	2	0.75	655	2	0.75	656	3	0.75	652	3	0.75
764	100	0.09	767	100	0.08	770	100	0.10	768	100	0.12
858	1	0.75	853	1	0.75	852	1	0.42	851	1	0.66
965	5	0.23	968	6	0.24	969	6	0.24	967	6	0.26
986	1	0.66									
1031	5	0.30									
			1037	7	0.29	1038	8	0.27	1034	6	0.30
1096	1	0.61	1097	1	0.67	1097	w	DP?	1098	w	DP?
1129	1	0.75	1129	1	0.75	1129	w	DP?	1128	w	DP?
1184	4	0.35							1185	4	0.33
			1190	4	?	1192	sh	?			
1201	sh	?	1202	sh	0.50	1201	5	0.47	1200	sh	?
1248	1	0.57	1250	1	?	1243	sh	?	1248	w	DP?
1269	2	0.37	1270	2	P	1273	3	?	1273	2	0.24
			1291	sh	?	1287	sh	?	1287	1	0.61
1384	2	0.31	1384	sh	?	1390	4	0.16	1386	3	0.20
			1392	5	0.29						
			1417	1	0.62	1418	w	?			
1446	sh	?	1446	sh	?				1448	7	0.75
1451	5	0.75	1454	9	0.75	1455	9	0.45	1454	7	0.75
1470	sh	?	1470	sh	?						
1494	3	0.67	1491	5	0.65	1490	2	0.52	1491	4	?
1684	4	?	1658	3	0.25	1661	2	0.26	1673	3	0.23
1695	sh	?									

$\tilde{\nu}$: Shift frequency. I: Intensity. ρ: Depolarization ratio. P: Polarized. DP: Depolarized. sh: Shoulder. w: weak. *: Mixing ratio(solute 1 mol : solvent 7 mols).

of the band at 1460 cm^{-1} (CH_2 bending vibration band) in the spectra of aqueous solutions, (whose frequency is different from those of conformers in pure liquid), is interpreted to be due to a valence change of the CH_2 group due to a deformation of the molecular ring caused by a configuration change around the nitrogen atom due to hydrogen bonding.

(c) Spectrum Change Due to Temperature Change: The change in the relative intensity of the bands of a methanol solution at 1195 and 1203 cm^{-1} were observed in a temperature range between −65 °C and room temperature. The former band increased in intensity, while the intensity of the latter decreased. Assuming a Lorentzian curve for the two bands, the overlapping bands were decomposed into two bands by a computer calculation. The enthalpy stabilization about 2 KJ mol^{-1}, of a hydrogen-bonded conformer relative to a non-hydrogen-bonded conformer was obtained. The obtained lower stabilization-enthalpy suggests that the stabilization enthalpy regarding hydrogen bonding is somewhat cancelled by the enthalpy loss due to a deformation around the nitrogern atom.

References

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2) K. Fukushima and T. Kawai, *J. Mol. Struct.*, **112**, 51 (1984).