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A Peculiar Conformation of Normal-Chain Dicarboxylic Acid Salts in Aqueous Solutions

Kunio FUKUSHIMA,* Koichi ADACHI, and Kiyohisa WATANABE
Department of Chemistry, Faculty of Science, Shizuoka University,
836, Oya, Shizuoka 422
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The Raman spectra of adipic acid, pimelic acid, and their salts were observed for various states. The spectra of the acids in aqueous sodium hydroxide solutions were found to be very different from those of the acids in organic solvents. The difference was interpreted, on the basis of normal vibration calculations, as being due to the helix formation of molecules in the former solutions. This tendency toward helical coiling is consistent with the same tendency found for the salts of azelaic acid and suberic acid in our previous study.

In our recent paper[1)] on the measurements of the Raman spectra of suberic acid ($HOOC(CH_2)_6COOH$), azelaic acid ($HOOC(CH_2)_7COOH$) and their salts in solutions, we reported a remarkable spectral difference between the acids and their salts, especially for the C–C stretching bands in the region of 850 to 1000 cm^{-1}. On the basis of the normal-vibration calculation of the molecules, we ascribed the difference to the helix formation of the molecular chains of the acid salts. However, these molecules are rather complicated for clear vibrational analyses; in addition, the spectral difference might be ascribed to other factors including the end group difference, COOH and COO^-. In the present study, smaller molecules, adipic acid ($HOOC(CH_2)_4COOH$), pimelic acid ($HOOC(CH_2)_5COOH$) and their salts, which are more suitable for clear vibrational analyses, were treated in order to ascertain if the tendency of forming a helix of molecular chain found in our previous study is also observed in these smaller molecules; the spectral change due to the end group change, COOH to COO^-, was studied.

Experimental

The samples, adipic acid and pimelic acid, were commercial products (GR grade) of the Tokyo Kasei Kogyo Co. The Raman spectra of these samples were recorded for a solid, for solutions of organic solvents, and for aqueous sodium hydroxide solutions. The spectra were obtained with an R-800T Raman Spectrometer (Japan Spectroscopic Co.), using a 514.5 nm line (250 mW) of an NEC argon ion laser. 0.3 ml liquid cells were used for the measurements. The results are shown in Tables 1 and 2 and in Fig. 1.

Normal-Vibration Calculation

The normal-vibration calculation was carried out for pimelic acid according to Wilson's GF matrix method.[2)] The following molecular parameters were used: C–C 1.53 Å, C–O 1.49 Å, C=O 1.25 Å, C–H 1.09 Å, O–H 1.07 Å, ∠CC=O=113°, ∠CCO=113°, ∠C–CO–C=124°, the other bond angles were equal to the tetrahedral angle. First, the normal-vibration calculation of a molecular model with an all-*ap* molecular chain (point group, C_{2v}) was calculated using the same force field as in the previous report[1)] for force constants transferred from related molecules (Set I in Table 3). The calculated frequencies were then fitted to the observed frequencies of the solid by the method of least squares.[3)] The results are shown for the region from 200 to 1700 cm^{-1} in Fig. 2. Then, using the refined force constants (Set II in Table 3),

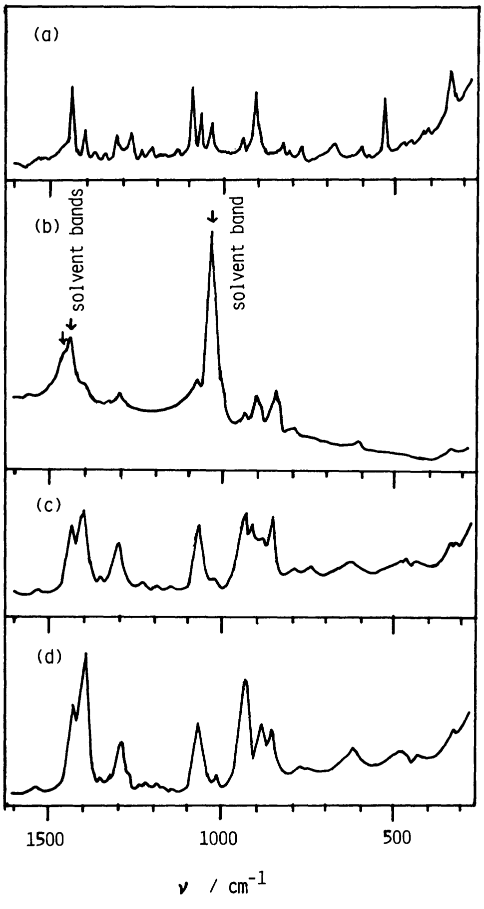

Fig. 1. Raman spectra of pimelic acid.
(a) Solid, (b) methanol solution (33.9 wt%), (c) aq. sodium hydroxide solution (mole ratio; NaOH: acid=1 : 1), (d) aq. sodium hydroxide solution (mole ratio; NaOH: acid=2.7 : 1).

normal-vibration calculations for various conformers were carried out. In Fig. 3, the results are compared with the observed C–C stretching bands.

Results and Discussion

Adipic acid was found to have an all-*ap* molecular chain in the crystalline state.[4] In addition, the infrared and Raman spectra were measured and analyzed based on the normal-vibration calculation by Suzuki and Shimanouchi.[5]

A pimelic acid is expected to assume an all-*ap* molecular chain in the solid state, a normal-vibration calculation was carried out for the model as has been described in the section of normal-vibration calculation. These calculations afford a basic information for the interpretation of the spectral difference of the solutions found in the present study; this information is shown in Tables 1 and 2 and in Fig. 1, in which the spectra of methanol solutions are shown as representatives of solutions of organic solvents (for adipic acid: methanol, pyridine, ethylacetate, 1,4-dioxane, dimethyl sulfoxide, acetic acid, formic acid; for pimelic acid: methanol, ethanol, pyridine, dimethyl sulfoxide, 1,4-dioxane).

The Spectra of Methanol Solutions. In Tables 1 and 2, the spectra in the regions from 1000 to 1080 cm^{-1} and from 1420 to 1500 cm^{-1} are not shown as the bands of the solvent overlap with the bands of the samples. Besides the bands corresponding to those of the solid conformer, new bands appear, showing that the conformer with an all-*ap* molecular chain and other conformer co-exist in methanol solutions. The prominent C–C stretching bands of pimelic acid at 807 and 854 cm^{-1} which are not ascribed to the all-*ap* conformation, correspond to the calculated frequencies of the TGTTGT, TTGGTT, TGGTGT conformers, as is shown in Fig. 3. Here, for example, TGTTGT represents the *ap-sc-ap-ap-sc-ap* conformation along the molecular chain of CO–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CH$_2$–CO.

The Spectra of Aqueous Sodium Hydroxide Solutions. Even after excluding the spectral change arising from the end group change, COOH to COO$^-$, from the spectral changes shown in Tables 1 and 2 with reference to Table 4, the following spectral change still remains. Bands with frequency values entirely different from those of methanol solutions appear at 384, 775, 930, 1193, 1235, 1255, and 1275 cm^{-1} (adipic acid) and at 332, 434, 779, 864, 896, 1143, and 1194 cm^{-1} (pimelic acid). At the same time, the bands observed for methanol solutions, 372, 735, 790, 829, 895, 1106, and 1154 cm^{-1} (adipic acid) and 339, 755, 807, 854, 904, and 1211 cm^{-1} (pimelic acid) decrease in intensity. Although Table 4 suggests that the stretching frequency of the CC bond attached to the COOH group increases upon the group change from COOH to COO$^-$, the above-mentioned spectral change cannot be explained by the frequency change alone. These facts show that a peculiar molecular conformation which differs from those in methanol solutions and also in a solid becomes abundant in aqueous sodium hydroxide solutions. Therefore, in

Table 1. Raman Spectra of Adipic Acid (<2000 cm^{-1})[a)]

Solid		CH$_3$OH soln			Aq. NaOH soln			Solid		CH$_3$OH soln			Aq. NaOH soln		
ν	I	ν	I	ρ	ν	I	ρ	ν	I	ν	I	ρ	ν	I	ρ
166	20							1051	46				1050	sh	?
246	9												1065	49	0.29
304	58												1080	sh	?
		372	8					1091	54						
					384	4	0.28			1106	33	0.69			
445	2	445	7	DP?						1154	15	0.75	1150	5	0.63
		475	8	DP									1193	8	0.50
					487	10	0.59	1224	4						
514	14												1235	8	?
575	11							1248	15						
		616	21	0.50									1255	8	?
					625	16	0.18			1265	8	P			
666	35	660	10	0.75	660	sh	?						1275	10	?
		735	13	P				1302	36	1307	19	0.75	1305	sh	?
					775	8	0.14						1315	38	0.38
		790	8	?									1360	16	0.21
800	3							1383	2						
		829	58	0.15				1413	76				1412	100	0.27
		850	sh	?	845	29	0.18	1436	33						
		895	100	0.15	890	38	0.13	1448	39				1443	48	0.54
		900	sh	?				1481	7						
920	100												1550	10	0.44
					930	95	0.09	1644	25				1635	7	0.50
					972	sh	?			1705	42	0.20			
					1020	sh	?								

a) ν, frequency in cm^{-1}; I, relative intensity; ρ, depolarization ratio; P, polarized; Dp, depolarized.

Table 2. Raman Spectra of Pimelic Acid ($<2000\,\mathrm{cm^{-1}}$)[a]

Solid		CH_3OH soln			Aq. NaOH soln (1 : 1)			Aq. NaOH soln (2.7 : 1)		
ν	I	ν	I	ρ	ν	I	ρ	ν	I	ρ
271	57									
328	43									
								332	8	0.67
		339	25	0.33	345	18	0.50			
					436	sh	?	434	8	?
					489	14	0.75	482	11	0.75
525	43									
598	29	600	8	?						
					628	18	P	623	16	0.5
670	29									
		755	17	0.50	755	17	P			
								779	8	?
					800	17	P			
810	14	807	25	P						
		854	100	0.33						
					863	77	0.24	864	32	0.38
					889	sh	?	896	39	0.27
906	86	904	83	P						
					917	sh	?			
945	29	942	sh	?	941	86	0.21	944	74	0.29
1036	43									
1068	57				1077	82	0.56	1074	47	0.56
1091	50									
								1143	3	?
		1165	20	?				1165	3	?
								1194	7	?
1214	13	1211	17	?						
								1256	7	?
1277	43									
1321	36	1314	33	0.75	1313	59	0.75	1315	39	0.75
		1393	17	?						
1412	43				1417	100	0.50	1413	100	0.50
1454	100				1450	86	0.75	1446	67	0.75
								1558	12	0.75
1645	43	1712	67	0.50	1703	32	P			

a) Figures in parentheses represent the mole ratio, NaOH: acid. ν, frequency in $\mathrm{cm^{-1}}$; I, relative intensity; ρ, depolarization ratio; P, polarized; DP, depolarized.

Table 3. Force Constants of Pimelic Acid (in mdyn/Å)

	Set I	Set II		Set I	Set II	
K(CH_2-CH_2)	2.137	2.134	H(CCO)	0.616	0.522	
K(CH)	4.026	4.229	F(CCO)	1.158	1.685	
K(C=O)	7.454	7.272	H(O=CO)	0.038	0.117	
K(C-O)	4.058	4.162	F(O=CO)	0.502	0.319	
K(OH)	4.994	4.945	H(COH)	0.450	0.401	
H(CH_2-CH_2-CH_2)	0.332	0.259	F(COH)	0.461	0.474	
F(CH_2-CH_2-CH_2)	0.353	0.336	π(C=O)	0.559	0.534	mdyn.Å
H(CCH)	0.198	0.191	Y(CH_2-CH_2)	0.08	0.154	mdyn.Å
F(CCH)	0.507	0.514	Y(CH_2-CO)	0.154	0.500	mdyn.Å
H(HCH)	0.412	0.389	Y(C-O)	0.087	0.087	mdyn.Å
F(HCH)	0.066	0.043	κ	0.056	0.034	mdyn.Å
H(CC=O)	1.168	1.368	t	0.159	0.180	mdyn.Å
F(CC=O)	0.970	0.833	g	−0.017	−0.059	mdyn.Å

aqueous sodium hydroxide solutions, most of the molecular chains have a conformation entirely different from those in methanol solutions.

Similarity of the Spectra of Adipic Acid and Pimelic Acid in Aqueous Sodium Hydroxide Solutions. As to the skeletal vibrations ($<1000\,\mathrm{cm^{-1}}$), which are sensitive to conformational changes, both acids have mutually corresponding observed frequencies: adipic acid (384, 775, 845, and $930\,\mathrm{cm^{-1}}$); pimelic acid(332, 779, 864, and $944\,\mathrm{cm^{-1}}$), although the increase of a

Table 4. Spectral Change Due to the Group Change, COOH to COO$^-$, for Acetic Acid and Its Salt

CH_3COOH Pure liquid	CH_3COONa Aq. soln (47.7%)	$CH_3COONa\ 3H_2O$ Solid	
453	480	490	CO_2 bend
610	621	635	CO_2 rock
627	655	670	CO_2 wag
900	922	935	CC str
1020	1018	1022	CH_3 rock
1280			CO str, COH bend
	1343	1360	CH_3 sym. def
1373		1377	CH_3 sym. def
	1409	1430	CO str
1425			COH bend, Co str
1435	1426	1450	CH_3asym. def
1673			C=O str (hydrogen-bonded)
1760			C=O str (free)

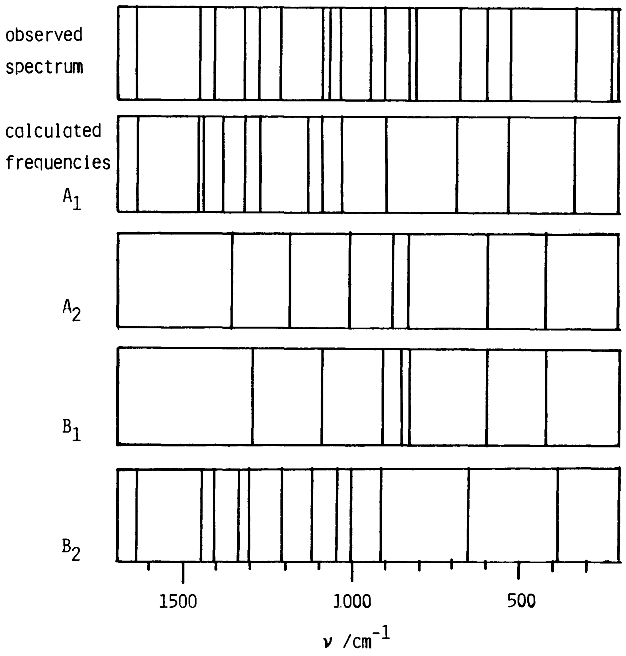

Fig. 2. Observed Raman spectrum of solid pimelic acid compared with calculated frequencies of the all-*ap* conformer.

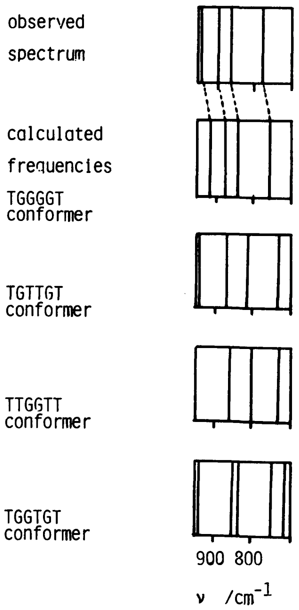

Fig. 3. Observed frequencies of C–C stretching bands of aq. hydroxide solution and calculated frequencies of various conformers for pimelic acid.

CH_2 group in pimelic acid compared with adipic acid shows an expected spectral difference between the acids. This correspondence suggests a similarity in the molecular conformations of the acids in aqueous sodium hydroxide solutions.

Molecular Conformation in Aqueous Sodium Hydroxide Solutions. Normal vibration calculations of various conformers were carried out using the refined force constants. For the C–C stretching vibrations, which give stronger bands in Raman spectra and which have remarkably different frequencies between methanol solutions and aqueous sodium hydroxide solutions, the calculated frequencies (Fig. 3) of various conformers are compared with the spectra of aqueous sodium hydroxide solutions. The bands of the spectrum of Fig. 1(c) correspond to the calculated frequencies of some conformers in Fig. 3; therefore, the solution corresponding to the figure might contain a mixture of those conformers. However, the pattern of the spectra (Fig. 1(d) and the top of Fig. 3) for a higher concentration of sodium hydroxide fits very well to the spectral pattern of the calculated frequencies of the TGGGGT conformer. Taking the similar situation found in the case of suberic acid and azelaic acid[1] into consideration, the conformer having the TGGGGT conformation of the skeleton is considerded to be abundant in aqueous sodium hydroxide solutions. This is in contrast to the case of some monocarboxylic acid salts, where the molecules may be supposed to gather to form micelles, taking an all-*ap* molecular chain.[6]

Interpretation of the Conformational Change. The remarkable conformational change from solutions of organic solvents to aqueous sodium hydroxide solutions may be interpreted as follows. In aqueous sodium hydroxide solutions, the carboxyl groups change to carboxylato groups, which are not capable of causing the intermolecular association of acid salt molecules. Therefore, the stabilization by hydrogen bonding, as in the case of the acids, is lost. Moreover, contact of the hydrophobic molecular chain of acid salt molecule with water molecules increases the instability of the molecular energy. In addition, the presence of a carboxylato group on each end of the molecular chain prevents the molecules from being stabilized by the formation of spherical micelles. These situations make the acid salt molecules take a conformation where the contact area of the hydrophobic molecular chain with water is minimized. The conformation with TGGGGT carbon-chain skeleton is a part of a helix in which the skeleton comes in contact with water molecules only at the outer surface of the helix; instability due to contact of the hydrophobic group and water is thus minimized. Therefore, this helical structure may be stable in aqueous solutions. This is consistent with the agreement of the observed frequencies for aqueous sodium hydroxide solutions with the calculated frequencies of the conformer with the helical structure.

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