

[CONTRIBUTION FROM THE BIOLOGICAL LABORATORIES, HARVARD UNIVERSITY, CAMBRIDGE 38, MASS.]

Raman Spectra of Diamines and Diammonium Ions: Effects of Ionization on Carbon-Hydrogen Stretching Frequencies¹

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RECEIVED OCTOBER 2, 1963

Raman spectra are reported for ethylenediamine, 1,3-propanediamine, 1,4-butanediamine, cadaverine, ethanolamine, and their hydrochlorides, and for malonic acid and its disodium salt, in aqueous solution. All the amines except 1,4-butanediamine were also studied as pure liquids, and 1,3-propanediamine was also studied in D₂O-DCl solution after nearly complete conversion of the -NH₂ to -ND₂ groups. When one of these diamines dissolves in water the C-H stretching frequencies near 2900 cm.⁻¹ generally increase by 15-25 cm.⁻¹. On addition of hydrochloric acid, with the protonation of the amino groups, there is a further and considerably larger increase in these frequencies, by 35-70 cm.⁻¹ above that of the basic amine in water solution. This change is much less marked in ethanolamine, which contains only one amino group. It is relatively small in cadaverine, in which only two of the five methylene groups immediately adjoin amino groups. The upward displacement of the methylene C-H stretching frequencies when a neighboring amino group acquires a positive charge is in accord with earlier observations on glycine, β -alanine, and cysteine. The methylene stretching frequencies of malonic acid are displaced downward by 20-25 cm.⁻¹ when the two carboxyl groups lose their protons, although no such effect has been noted in chloroacetic acid when its carboxyl group ionizes. Complete deuteration of an -NH₂ or -NH₃⁺ group has almost no influence on the C-H frequencies of an adjoining methylene group; it is the state of charge of the amino group, not the mass of the attached atoms, that is important. Addition of 3 M sodium chloride has no significant effect on the Raman spectrum of ethylenediamine in aqueous solution; therefore the observed frequency shifts on protonation of the amino group are not dependent on the large increase in ionic strength that accompanies the addition of acid. The C-H deformation frequencies are in general little affected by ionization or deuteration of the amino group, although many frequencies below 1400 cm.⁻¹ are of course greatly altered.

Introduction

Garfinkel,³ in this Laboratory, was the first to note that the carbon-hydrogen stretching frequencies of methylene groups in certain amino acids increased by 40-60 cm.⁻¹ on protonation of a neighboring amino group. These effects are clearly visible in glycine and in β -alanine; on the other hand, α -alanine, which contains no methylene group but does contain a hydrogen atom and a methyl group on the α -carbon atom, shows no marked change in the C-H stretching frequencies on ionization of either the carboxyl or the amino group.⁴ In the present study we have extended these observations to ethanolamine and several aliphatic diamines and have found much further evidence for the marked influence of the ionization of the amino group on the C-H stretching frequencies of an adjoining methylene group. We also report a study of the ionization of the two carboxyl groups in malonic acid and its effect on the methylene frequencies in this compound. The present studies, unlike the earlier ones, were carried out with photoelectric recording of the Raman spectra, so that the relative intensities of the Raman bands can be evaluated with fairly high accuracy.

Experimental Methods and Materials

The Raman spectra were recorded on a Cary Model 81 Raman spectrophotometer (Applied Physics Corp., Monrovia, Calif.). Intensities and depolarization factors were measured as described by Elson and Edsall,⁵ except that the intensities reported were determined by measuring the areas rather than the heights of the Raman bands. Some of the depolarization factors (ρ), recorded in Tables I-VI below, are higher than the theoretical limiting value of 0.87. Such values are simply to be taken as an indication that the lines in question are depolarized; we make no claim to high absolute accuracy in these values, although they are reported to two significant figures, since comparative values of ρ are often important.

Ethylenediamine was obtained from Fisher Scientific Co., and purified by distillation in a glass distilling apparatus, all contact with rubber being avoided. 1,4-Butanediamine HCl (Eastman Organic Chemicals) was clarified by filtration after treatment with Norit. Malonic acid was obtained from Matheson Coleman and Bell and clarified by treatment with Norit.

(1) This work was supported by grants from the National Science Foundation (G-9116) and the United States Public Health Service (H-03169).

(2) To whom correspondence concerning this paper and requests for reprints should be sent.

(3) D. Garfinkel, Thesis, Harvard University, 1955.

(4) M. Takeda, R. E. S. Iavazzo, D. Garfinkel, I. H. Scheinberg, and J. T. Edsall, *J. Am. Chem. Soc.*, **80**, 3813 (1958).

(5) E. L. Elson and J. T. Edsall, *Biochem.*, **1**, 1 (1962).

TABLE I

RAMAN SPECTRA OF ETHYLENEDIAMINE IN THE PURE STATE, IN AQUEOUS SOLUTION, AND IN WATER AS HYDROCHLORIDE

NH ₂ CH ₂ CH ₂ NH ₂ —pure base—			NH ₂ CH ₂ CH ₂ NH ₂ —in H ₂ O—			NH ₃ ⁺ CH ₂ CH ₂ NH ₃ ⁺ —in H ₂ O—		
$\Delta\nu^a$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ
475	5	0.37	477	10	0.53	462	13	0.77
841	21	0.42	844	13	0.53	820	12	.56
			950 (b)	3		920	11	.34
1058 (S)	5	0.87	1013 (b)	4		985	5	(1.0)
1098	19	0.46	1090	23	0.68	1055	16	0.77
						1221	6	.57
1306	8	0.87	1320	13	(1.0)	1339	18	.91
1360	10	.87	1362	10	(1.0)	1421 (S)	2	
1459	19	.80	1464	23	(1.0)	1460	21	0.93
1604	7	.87	1602	38	(1.0)	1625	57	0.97
						2839	6	
2863	110	0.18	2885	60	0.34	2920 (S)	47	0.23
2925	140	.41	2950	170	.57	2990	125	0.28
3306	103	.16	3316	50	.22			
3368	60	.73	3377	27	.88			

^a Values of $\Delta\nu$ in cm.⁻¹; *I* denotes integrated intensity; (b) denotes an unusually broad Raman band; (S) denotes a shoulder on a higher peak; ρ is depolarization factor.

1,3-Propanediamine and cadaverine (1,5-pentamethylenediamine) were obtained from K. and K. Laboratories, Inc. They were distilled under reduced pressure in glass, the middle fraction of the distillate being used to obtain the Raman spectra of the anhydrous amines. Aqueous solutions (4 M) were then prepared and their spectra determined. The solutions were then acidified with concentrated hydrochloric acid to pH < 1 and the spectra determined again.

N-Deuterated 1,3-propanediamine [D₂N(CH₂)₃N⁺D₂] was prepared by dissolving the diamine in 99.5% in D₂O, removing most of the water (D₂O, HDO, and H₂O) by evaporation in a desiccator over sodium hydroxide under reduced pressure, and evaporating the remaining water by gentle heating under mild vacuum. After this procedure had been repeated four times, more than 95% of the amino hydrogens had been replaced by deuterium as evidenced by the relative intensity of N-H and N-D stretching frequencies. After the Raman spectrum of this compound in D₂O had been recorded, DCl gas was passed into the solution until it was distinctly acid (pD < 1). The DCl was generated from the interaction of D₂O with benzoyl chloride as described by Brown and Groot.⁶ The spectrum of the N-deuterated ion [D₃N(CH₂)₃ND₃⁺] was then recorded.

Ethanolamine (2-aminoethanol, from Eastman Organic Chemicals) was purified by vacuum distillation. The Raman spectra of the anhydrous liquid and of its 4 M aqueous solution were recorded. It was then acidified to pH < 1 with hydrochloric acid and the Raman spectrum of the hydrochloride was determined. Butanediamine solution was made by addition of concentrated NaOH to the solution of the hydrochloride until the pH was greater than 13. A concentrated solution of malonic

(6) H. C. Brown and C. Groot, *J. Am. Chem. Soc.*, **64**, 2223 (1942).

TABLE II

RAMAN SPECTRA OF 1,3-PROPANEDIAMINE AND ITS N-DEUTERATED DERIVATIVE IN DIFFERENT IONIC FORMS IN WATER AND DEUTERIUM OXIDE

$\text{H}_2\text{N}(\text{CH}_2)_3\text{NH}_2$ pure base			$\text{NH}_2(\text{CH}_2)_3\text{NH}_2$ in H_2O			$\text{ND}_2(\text{CH}_2)_3\text{ND}_2$ in D_2O			$\text{NH}_3^+(\text{CH}_2)_3\text{NH}_3^+$ in H_2O			$\text{ND}_3^+(\text{CH}_2)_3\text{ND}_3^+$ in D_2O		
$\Delta\nu^a$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ
283	1	0.44												
383	4	.25				393	3	0.15	406	5	0.26	387	1	0.73
414	6	.30	410	6	0.39	487	2	0.41				462	2	0.46
515	3	.4	508	4	0.29				492	3				
						775 (b)	5	0.38				740 (S)	2	
819	6	0.05	825	10	0.27	830 (S)	2	.40	827	6	0.26	786	5	0.52
910	6	0.19	902	7	0.44	914	5	.25	887	4	.31			
942 (S)						980	1	.51	953	12	.59	938	3	0.73
1000 (b)			975	12	0.39	1022	2	.47	1008	5	.56	998	3	.44
1075	20	0.53	1067	29	0.57	1066	5	.93	1044	11	(1.0)	1062	4	.87
1092 (S)						1100 (S)	2	.74	1075	6	(1.0)			
						1196	1	(1.0)	1113	1	(1.0)			
						1243	1	(1.0)	1200	5	0.63	1200	14 (b)	0.79
1300	13	0.87	1302	16	0.83	1305	6	0.95	1331	21	.89	1300	1	
1356	6	(1.0)	1354	7	.79				1396	4	.66	1327	6	(1.0)
1444	13	0.87	1442	19	.97	1445	6	(1.0)				1462	10	0.97
1470	12	0.87	1470	13	.97	1475	5	(1.0)	1456	22	(1.0)			
1606	5	(1.0)	1600	10	.87				1612	31	0.78	1604	2	0.75
						2375 (S)	3							
						2437	20	0.16				2529 (very strong band)		
						2516	13	0.80						
2762	10	0.16	2775	8	0.23				2806	8	0.23	2890 (S)	3.3	0.3
2860	77	0.22	2885	89	0.34	2883	40	0.33	2954	114	0.44	2960	36	.44
2903	160	0.43	2917	200	0.53	2919	71	0.58	2974	112	0.28	2988	33	.30
												3070	3	.34
3304	73	0.15	3310	52	0.23	3337	2	0.34						
3366	67	0.77	3369	29	1.0									

^a See footnote of Table I for abbreviations.

TABLE III

RAMAN SPECTRA OF 1,4-BUTANEDIAMINE AND ITS DIHYDROCHLORIDE IN AQUEOUS SOLUTION (SPECTRA INCOMPLETE)

$\text{NH}_2(\text{CH}_2)_4\text{NH}_2$		$\text{NH}_3^+(\text{CH}_2)_4\text{NH}_3^+$	
$\Delta\nu$	<i>I</i> ^a	$\Delta\nu$	<i>I</i>
		361	1
		420	1
		995	W
1065	3	1066	3
1300	4	1330	5
1436	6	1453	6
1465			
2879	7	2950	7
2915	8	2982	7
3309	W		

^a Because of the presence of traces of fluorescent impurities the base line was not steady. The relative integral intensities are approximate. W stands for weak.

acid (Eastman) was clarified by Norit treatment. After its Raman spectrum had been recorded it was converted to the disodium salt with NaOH, and the spectrum again determined.

Results and Discussion

The spectra obtained are presented in Tables I–VI inclusive, and the detailed patterns of some of the Raman bands are shown in Fig. 1–4 inclusive.

The C–H Stretching Frequencies.—In the basic forms of the diamines and of ethanolamine, the values of these frequencies are similar to those found in the methylene groups of hydrocarbons, and lie in the region 2860–2875 (ρ 0.2–0.3) and 2910–2925 cm^{-1} (ρ 0.5–0.6). The higher of the two—presumably the asymmetrical stretching frequency—is generally the more intense. On dissolution of these bases in water, both these C–H stretching frequencies are displaced upward by 20–25 cm^{-1} , in the compounds containing only two or three CH_2 groups. In cadaverine, with five CH_2 groups, the displacement is in the same direction but of much smaller magnitude, about 10 cm^{-1} .

TABLE IV

RAMAN SPECTRA OF CADAVERINE AS PURE BASE, IN AQUEOUS SOLUTION, AND AS HYDROCHLORIDE

$\text{H}_2\text{N}(\text{CH}_2)_5\text{NH}_2$			$\text{NH}_2(\text{CH}_2)_5\text{NH}_2$			$\text{NH}_3^+(\text{CH}_2)_5\text{NH}_3^+$		
pure base			in H_2O			in H_2O		
$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ
294	2	0.19						
319	8	.19	313	2	0.08			
365	2	.21	355	1				
442	4	.39	440	3	0.23	425	4	0.69
497	1					490	2	0.45
521	1	0.44	515	1				
846	3	.14	829	4	0.22	823	3	0.09
877	3	.19	873	1	0.02	864	1	
			914	1		914 (S)	2	
983	3	0.16	975	3	0.16	944	6	0.39
						1013	7	.81
1083	19	0.65	1075	17	0.66	1073	11	.72
						1180	2	.60
1304	15	0.91	1304	14	0.93			
1360	5	.87	1358	4	(1.0)			
1446	23	.93	1442	19	(1.0)	1450	27	(1.0)
1475 (S)	6		1475 (S)	5				
1611	4	0.91	1608	5	0.74	1625	21	0.69
2761	2		2771	9		2788	4	.52
2861	90	0.19	2867	55	0.23	2877	22	.23
2902	185	0.53	2912	180	0.55	2930	130	.53
						3000	11	...
3320	26	0.14	3312	32	0.14			
3375	29	0.74	3372	15	0.87			

The increase in the methylene stretching frequencies in aqueous solution, when the adjoining amino groups acquire a positive charge, is considerably more striking. In ethylenediamine (Table I and Fig. 1) the two major bands near 2870 and 2925 cm^{-1} retain the same general pattern in the pure base and in aqueous solution, in spite of the upward displacement on dissolving the amine in water. The band pattern in the ethylenediammonium ion is very different. The strongest band, with its peak at 2990, is 40 cm^{-1} higher than the peak of highest frequency in the basic form. The two weaker bands at 2920 and 2839 cm^{-1} are almost like

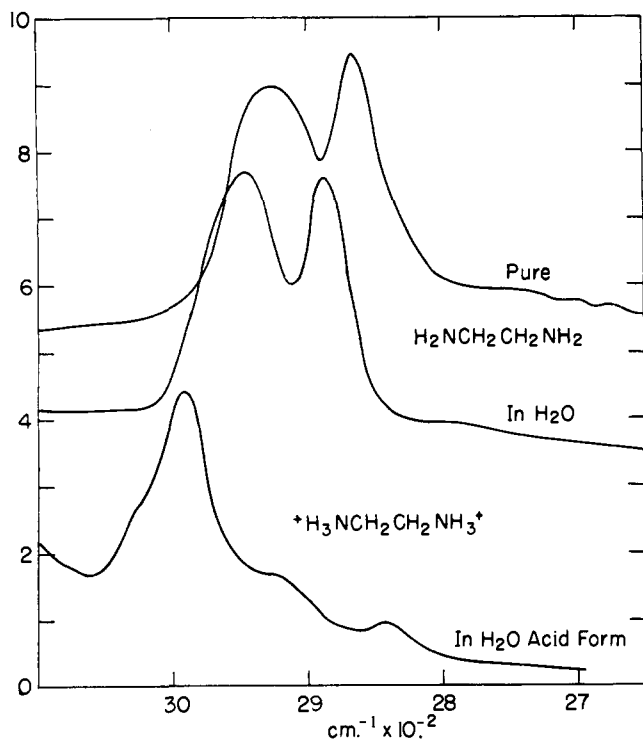


Fig. 1.—Raman spectra of ethylenediamine, as the pure liquid, in aqueous solution, and in acid, in the region of the C–H stretching frequencies. Note that the frequency shifts increase from right to left in this and subsequent figures. Values on the ordinate axis represent intensities on an arbitrary scale.

shoulders on the main peak. The 2990 band (ρ 0.28) in the ion is much more strongly polarized than the 2950 band (ρ 0.57) of the uncharged amine in water. The latter presumably is the asymmetrical stretching frequency; the very low ρ -value of the 2990 frequency in the ion raises the question whether it corresponds to a somewhat different mode of vibration.

TABLE V

RAMAN SPECTRA OF ETHANOLAMINE AND ITS HYDROCHLORIDE^a

HOCH ₂ CH ₂ NH ₂ pure liquid			HOCH ₂ CH ₂ NH ₂ in H ₂ O			HOCH ₂ CH ₂ NH ₃ ⁺ in H ₂ O		
$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ
338	2	0.32				337	2	(1.0)?
476	4	.39	474	6	0.41	466	3	0.62
514	2	.68				497	3	.53
844	9	.39	842	9	0.40	834	5	.40
868	12	.34	869	10	.33	865	14	.29
981	6	.39	977	4	.37	985 (b)77
1001	6	.55	1003	4	.37	1011	10	.98
1029	8	.71	1021	6	.68			
1076	16	.61	1075	12	(1.0)	1066	10	0.72
1091	12	.45	1098	7	0.40			
1169	2	.72	1170	1	.91	1134	5	0.87
1251	6	.76	1264	5	.55	1274	9	(1.0)
1305	9	.91	1315	9	(1.0)?	1345	10	(1.0)
1353	8	.90	1354	8	0.96	1393	2	(1.0)
1458	17	.95	1463	16	.88	1460	15	0.93
1597	4	.93	1599	3	.31			
2865	67	.25	2886	53	.20	2901	36	0.20
2924	100	.43	2946	100	.42	2973	100	.39
3184 (b)	Weak	...				3010	19	.78
3302	25	.17	3315	22	0.12			
3363	13	.69	3375	9	(1.0)			

^a A broad peak of medium intensity (ρ 0.88) was visible in the aqueous solutions—presumably the water band, but it is not listed here. The center of the band is near 1615 cm⁻¹.

In 1,3-propanediamine (Table II and Fig. 2) the general pattern is very similar. The presence of an extra methylene group introduces some added features. Notable among these is the weak band near 2770 in the basic form, which shifts to 2806 when both amino

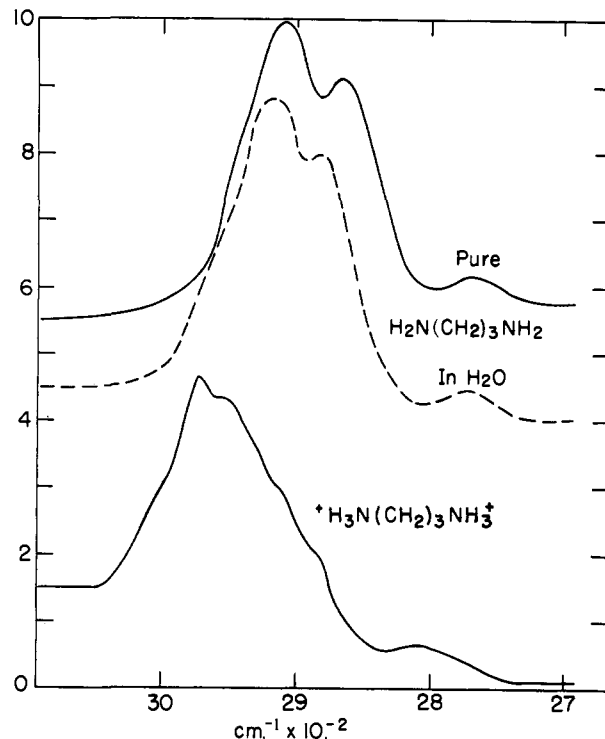


Fig. 2.—Raman spectra of 1,3-propanediamine, as the pure liquid, as solute in aqueous solution, and after acidification, in the region of the C–H stretching frequencies.

groups acquire positive charges. The peak of the band of highest frequency is at 2974 in the doubly charged cation, 57 cm⁻¹ higher than the highest frequency of the uncharged amine in aqueous solution. The depolarization factors for these two bands are virtually the same as in the ethylene diammonium ion and its conjugate base.

TABLE VI

RAMAN SPECTRA OF MALONIC ACID AND ITS SODIUM SALT IN WATER SOLUTION^a

—COOHCH ₂ COOH—			—COO ⁻ CH ₂ COO ⁻ —		
$\Delta\nu$	<i>I</i>	ρ	$\Delta\nu$	<i>I</i>	ρ
425	10.2	0.62	430	6.4	0.76
567	1.6		584	4.2	.52
652	2.6	0.87	689	1.6	.87
771	6.9	0.18			
			825	4.0	0.28
920	15.3	0.19	946	15.5	.16
1173	4.3	0.87	1177	3.5	.96
			1258	0.9	
			1366	9.3	0.87
1414	9.6	0.68	1437	27.5	.36
1650	6.6 (S)	.48	1590	8.8	.87
1732	30.8	.22			
2960	22.2	.14	2939	20.5	0.08
3003	10.6	.74	2975	11.4	0.6

^a Abbreviations as in Table I.

The spectra obtained for 1,4-butanediamine and its conjugate acid in water (Table III) were quite incomplete, because of the presence of fluorescent impurities. Nevertheless the two principal C–H stretching frequencies are clearly observed, and both are displaced upward by approximately 70 cm⁻¹ when the two amino groups acquire positive charges. In cadaverine (Table IV) the corresponding upward displacements are still present but are far smaller (12–18 cm⁻¹). Only two of the five methylene groups in cadaverine are immediately adjacent to amino groups, and the C–H vibrations of

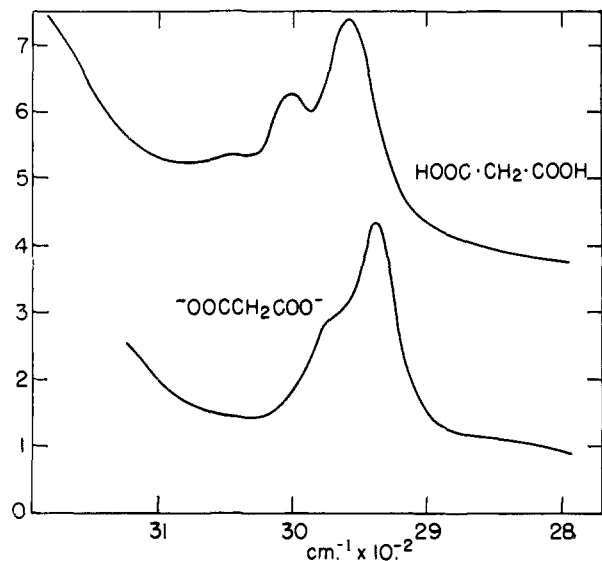


Fig. 3.—Raman spectra of malonic acid and the malonate ion in the region of the C—H stretching frequencies.

the other three groups are less likely to be influenced by a change in the state of ionization of the amino groups.

In ethanolamine (Table V) which contains only one amino group and two methylene groups the effects of adding a proton to the amino group on the C—H frequencies are relatively small. The highly polarized band at 2886 in the solution of the base in water increases only to 2901 on proton addition, and the more intense and somewhat less polarized band at 2946 shifts upward by 27 cm.^{-1} to 2973. These shifts are in the same direction as those found in the diamines, but smaller; indeed the effect on these two frequencies of dissolving anhydrous ethanolamine in water is of the same order of magnitude as the effect of proton addition in the aqueous solution.

The changes observed in these compounds on ionization, especially in the diamines, are similar to those previously reported⁴ for glycine and β -alanine. The C—H stretching frequencies for both these amino acids in aqueous solution are essentially unchanged by the ionization of the carboxyl group, but when the amino group loses a proton in alkaline solution there is a sharp downward shift of the C—H frequencies, and bands that were previously quite distinct become merged. Thus the two bands, near 2970 and 3015 cm.^{-1} , in the cation or dipolar ion of glycine, merge in the glycine anion in a single strong band at 2940. Likewise in β -alanine three strong bands (near 2940, 2980, and 3015 cm.^{-1}), which are clear and distinct in the cation and dipolar ion, merge on removal of the proton from the $-\text{NH}_3^+$ group to form an unresolved single broad band centered at 2925. Although there are differences in detail between the C—H stretching frequencies of the amino acids and those of the diamines, the marked decrease in these frequencies when the amino group loses a proton is characteristic of both classes of compounds.

The behavior of α -alanine,⁴ with one H atom and one $-\text{CH}_3$ group on the β -carbon, is entirely different. The three characteristic C—H stretching frequencies are almost unaffected by ionization of either the carboxyl or the amino group.

There is one obvious point of difference between the solutions of the diamines and those of their hydrochlorides, apart from the charged or uncharged state of the amino group itself. The hydrochloride solutions are necessarily studied at a very high total ionic strength. The amines in aqueous solution, on the other hand, are at a relatively very low ionic strength. We must

consider the possibility that the presence of ions at high concentration might influence the spectra. To test this we studied the spectrum of ethylenediamine in aqueous solution, before and after the addition of sodium chloride to a concentration of 3 M . The spectrum remained unchanged, within the limitation of experimental error, after the addition of the salt. Presumably, therefore, change of ionic strength alone, without change in the state of the charge of the amino group, does not influence the observed phenomena significantly.

In Table II we recorded the spectra of 1,3-propanediamine in which the NH_2 groups have been almost completely converted to ND_2 groups and the NH_3^+ groups to $-\text{ND}_3^+$ groups. It is plain from the recorded spectra that the methylene frequencies are not at all

TABLE VII
PRINCIPAL STRETCHING FREQUENCIES OF METHYLENE GROUPS
IN VARIOUS COMPOUNDS NOT CONTAINING METHYL GROUPS^a

Number	Substance	ν_1	ν_2
1	Satd. hydrocarbons	2853 (p)	2926 (dp)
2	$\text{HOCH}_2\text{CH}_2\text{OH}$	2866 (p)	2940 (p)
3	$\text{HOCH}_2\text{CH}_2\text{NH}_2$	2865 (0.25)	2924 (0.43)
4	$\text{HOCH}_2\text{CH}_2\text{NH}_2$ (aq)	2886 (.20)	2946 (.42)
5	$\text{HOCH}_2\text{CH}_2\text{NH}_3^+$ (aq)	2901 (.20)	2973 (.30) 3010 (.78)
6	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$	2863 (.18)	2925 (.41)
7	$\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ (aq)	2885 (.34)	2950 (.57)
8	$^+\text{H}_3\text{NCH}_2\text{CH}_2\text{NH}_3^+$ (aq)	2920 (.23)	2990 (.28)
9	HOCH_2COOH (aq)	2921 (—)	2956 (—)
10	ClCH_2COOH (aq)	2960 (—)	3002 (—)
11	$\text{ClCH}_2\text{COO}^-$ (aq)	2969 (—)	3021 (—)
12	$^+\text{H}_3\text{NCH}_2\text{COOH}$ (aq)	2974 (p)	3017 (dp)
13	$^+\text{H}_3\text{NCH}_2\text{COO}^-$ (aq)	2971 (p)	3013 (dp?)
14	$\text{H}_2\text{NCH}_2\text{COO}^-$ (aq)	2940 (p?)	Not observed
15	$^+\text{H}_3\text{NCH}_2\text{CH}_2\text{COOH}$ (aq)	2931 (—)	2987 (—) ^b
16	$^+\text{H}_3\text{NCH}_2\text{CH}_2\text{COO}^-$ (aq)	2952 (—)	2978 (—) ^b
17	$\text{H}_2\text{NCH}_2\text{CH}_2\text{COO}^-$ (aq)	2925 (—)	Not observed
18	HSCH_2COOH	2930 (0.14)	3000 (0.72)
19	HSCH_2COOH (aq)	2910 (.15)	2975 (.84)
20	$\text{HSCH}_2\text{COO}^-$ (aq)	2940 (.15)	2975 (.87)
21	$-\text{SCH}_2\text{COO}^-$ (aq)	2925 (.28)	2945 (.75)
22	Cysteine (pH 7) (aq)	2960 (.25)	3005 (.9)
23	Cysteine (pH 11.2) (aq)	2875 (weak)	2920 (.5)
24	$\text{HOOCCH}_2\text{COOH}$ (aq)	2960 (0.14)	3003 (.74)
25	$-\text{OOCCH}_2\text{COO}^-$ (aq)	2939 (0.08)	2975 (.6)
26	CH_2Cl_2	2985 (p)	3045 (dp)
27	CH_2Br_2	2988 (p)	3061 (dp)
28	$\text{BrCH}_2\text{CH}_2\text{Br}$	2970 (p)	3013 (dp)
29	Cyclopropane	3019 (p)	3078 (dp)
30	Ethylene oxide	3008 (p)	3060 (dp)
31	Ethylene imine	2998 (p)	3060 (dp)
32	Ethylene sulfide	2990 (p)	3085 (dp?)

^a The symbol (p) denotes a polarized, and (dp) a depolarized Raman band; numerical depolarization factors are given in parentheses for some compounds; (—) denotes absence of information concerning polarization; the symbol (aq) denotes a substance studied in aqueous solution. Values for CH_2 groups in saturated hydrocarbons from Jones and Sandorfy.⁷ Data for ethanolamine (3, 4, 5), ethylenediamine (6, 7, 8), malonic acid, and malonate ion (24, 25) from the present work. Tables V, I, and VI. Data for glycine (12, 13, 14) and β -alanine (15, 16, 17) from Takeda, *et al.*⁴; for cysteine (22, 23) from Garfinkel and Edsall⁸ and Elson and Edsall⁵; for thioglycolic acid (18–21) also from Elson and Edsall.⁵ Other data from Kohlrausch.⁹ ^b There is a third frequency close to 3010 cm.^{-1} in the cation and dipolar ion of β -alanine. This is considerably less intense than the two frequencies recorded in the table.

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affected by a change in mass of the hydrogen atoms attached to the adjoining amino groups. It is only the charged or uncharged state of the amino groups, not the mass of the attached atoms, that exerts a modifying influence on the methylene stretching frequencies. The same conclusion had already been reached by Takeda, *et al.*,⁴ in their studies of glycine and β -alanine.

In Table VII we have summarized the available data on the two principal methylene stretching frequencies for a large number of compounds containing one or two methylene but no methyl groups. Only cysteine (no. 22, 23) among all the compounds listed in this table contains a tertiary C-H bond. The frequency denoted by ν_1 is certainly in most cases, but perhaps not in all, the symmetrical stretching frequency. Similarly, ν_2 corresponds in most, but not necessarily all, cases to asymmetrical stretching. The presence of an uncharged hydroxyl or amino group immediately adjoining a methylene group appears to cause little shift in the methylene frequencies from those characteristic of hydrocarbons ($\nu_1 = 2853$, $\nu_2 = 2926$; see items 2, 3, and 6 in Table VII). The introduction of a carboxyl group adjoining the methylene group displaces both ν_1 and ν_2 upward. If we compare glycolic acid (no. 9) with ethylene glycol (no. 2), ν_1 increases by 55 cm.^{-1} and ν_2 by 16 cm.^{-1} . The comparison is not exact since glycolic acid contains only one methylene group and was studied in aqueous solution, whereas ethylene glycol, with two methylene groups, was studied as a pure liquid.

The effect of carboxyl ionization on the methylene frequencies is not entirely clear from the existing data. Our studies on malonic acid and its disodium salt (Table VI, and items 24 and 25 in Table VII) indicate a downward shift of $20\text{--}25 \text{ cm.}^{-1}$ in both ν_1 and ν_2 on ionization of both carboxyl groups. In this case the decrease of these frequencies on the loss of two protons is similar to, but much smaller than, the decrease in the methylene frequencies on removal of protons from the two amino groups of ethylenediamine or 1,3-propanediamine. It would be expected that carboxyl ionization would have less influence than that of the amino group; when a carboxyl group ionizes, the proton removed is one atom further away from the methylene group than when the ionizing group is an amino group directly attached to the methylene group.

On the other hand, the ionization of the carboxyl group in chloroacetic acid (Table VII, items 10 and 11) is accompanied by a slight upward shift in both the methylene frequencies ν_1 and ν_2 . It is difficult to correlate this observation with the effects observed in malonic acid.

The effect of a halogen atom in raising the stretching frequencies of an adjoining methylene group is well known. Items 23, 24, and 25 in Table VII illustrate this; the effects of the different halogens are very similar and the vibrational frequencies in the halogenated methane and ethane derivatives are more than 100 cm.^{-1} above those of the saturated hydrocarbons. The carbon-halogen bonds are, of course, highly polar, the halogen atom tending to withdraw electrons from the carbon. Similarly, the acquisition of a positive charge by an uncharged amino group, as in glycine or β -alanine, serves to attract electrons away from the adjoining methylene carbon. There are many correlations between the dipole moment of substituent groups and their influence upon vibrational frequencies; for example, the C=O vibrational frequency near 1700 cm.^{-1} in aldehydes, ketones, and carboxylic acids generally increases appreciably on substituting a chlorine or a charged amino group on the carbon atom immediately adjoining the C=O group.

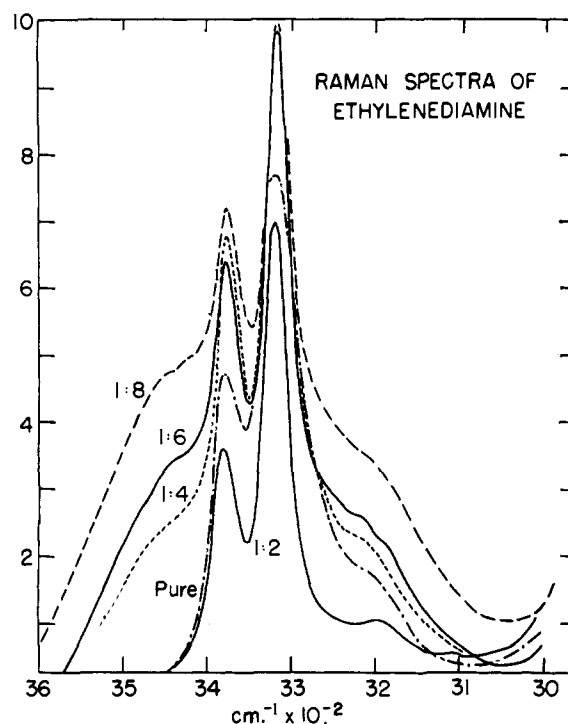


Fig. 4.—The N-H stretching frequencies of ethylenediamine in the pure liquid and after the addition of various amounts of water. The ratios indicated on the drawing represent the molar ratio of ethylenediamine to water.

An explanation in terms of polarity, however, is obviously inadequate to explain the high methylene stretching frequencies in cyclopropane and the other three-membered ring compounds listed in Table VII, items 26–29 inclusive. In these compounds it is evidently the structural modification imposed by the three-membered ring, with its effects on electron distribution and vibrational force constants, that is crucial. The data listed show that the substitution of a polar oxygen, nitrogen, or sulfur atom for one of the three nonpolar CH_2 groups of cyclopropane does not increase the vibrational frequencies, in spite of the polar character of these compounds. Indeed, all of these compounds actually show slightly lower methylene vibrational frequencies than cyclopropane itself except for ν_2 in the case of ethylene sulfide.

It is interesting to note that the N-H stretching frequencies near 3310 and 3370 cm.^{-1} are little affected by dissolving the anhydrous amines in water. These frequencies indeed undergo a slight upward displacement in water solution, but only by 10 cm.^{-1} in ethylenediamine, and by $3\text{--}6 \text{ cm.}^{-1}$ in propanediamine, the latter values being close to the experimental error of the measurements. Since the -NH_2 groups, on dissolution in water, presumably become largely hydrated by hydrogen bonding to form $\text{-NH}_3\text{OH}$ groups, the near constancy of the N-H frequencies is notable, particularly in contrast to the significant displacement of the C-H stretching frequencies. Figure 4 shows tracings of the band patterns for anhydrous ethylenediamine and for various molar ratios of water to the diamine. As the molar ratio of water to ethylenediamine increases, the position of the maxima is scarcely displaced at all. Indeed, at a molar ratio of 2:1 the pattern of intensity distribution is almost identical with that in the anhydrous amine. As more water is added the wings of the two principal bands spread outward and the pattern thus becomes more diffuse with no appreciable shift in the position of the central peaks.

The data reported here provide no new information concerning the NH frequencies in the charged amino group. On this point we have nothing to add to the studies reported earlier.¹⁰

Recent investigations, notably those of Frank and Wen¹¹ and of Némethy and Scheraga,¹² have emphasized the importance of interactions between hydrocarbon groups and surrounding water molecules in aqueous solutions. The presence of ionic groups in such solutions also leads to reorientation and compression of water molecules around the charged groups. The transformation of a basic amine to a positively charged alkylammonium ion in aqueous solution therefore involves highly significant changes in the surrounding water structure. In our studies we cannot clearly trace just what influence the surrounding water structure may exert on the vibrational frequencies of the solute molecules, but we believe that future, more adequate treatments of these systems must take account of such interactions.

Of the compounds whose spectra are reported here, only malonic acid and the ions derived from it have, to our knowledge, been previously studied in aqueous solution.¹³ The frequencies recorded here are in good agreement with those found in the earlier study except that we now find a somewhat greater downward displacement of the C-H stretching frequencies on ioniza-

tion of the two carboxyl groups. Ethylenediamine and ethanolamine have been previously studied as the anhydrous bases, but not apparently in water solution or in the cationic form. Data on anhydrous ethanolamine were reported by Kohlrausch, *et al.*¹⁴ Our data are in excellent agreement with theirs, although we find a few additional frequencies that they did not observe. Anhydrous ethylenediamine has previously been studied by several workers.¹⁵⁻¹⁷ Here again our data are for the most part in very good agreement with the earlier work, although we have not observed some of the previously reported weak bands below 600 cm.⁻¹. The polarization data of Chaudhuri¹⁷ are in general accord with ours in Table I, although the numerical agreement is far from precise. This is not surprising in view of the inherent difficulties and uncertainties of such measurements.

The bending frequency ("scissors" motion) of the methylene groups in all the compounds we have studied remains almost completely unchanged by dissolving the diamines in water or by adding acid to protonate the amino groups. In all cases it is close to 1460 cm.⁻¹ and the observed variations are scarcely outside the limits of experimental error. Thus the behavior of this bending frequency offers a marked contrast to the behavior of the C-H stretching frequencies.

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Thermal Unimolecular Geometric and Structural Isomerization of 1,2-Dideuterio-3-methylcyclopropane¹

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RECEIVED SEPTEMBER 21, 1963

The thermal geometric and structural unimolecular isomerization of methylcyclopropane and of *trans*-, *cis*-, and *cis,trans*-1,2-dideuterio-3-methylcyclopropane have been studied over a range of temperatures. Individual Arrhenius parameters have been determined for the various possible isomerization reactions. The total rate expressions are $k_{ds}(\text{struct}) = 10^{14.43} \exp(-62,300 \text{ cal./RT})$ and $k_{ds}(\text{geom. total}) = 10^{15.36} \exp(-60,500 \text{ cal./RT})$, and $k(\text{struct}) = 10^{14.61} \exp(-62,400 \text{ cal./RT})$. Isotope rate effects, including secondary effect, have been measured. The relation to other work and to the mechanisms of these reactions is discussed.

Introduction

The structural isomerization of cyclopropane to propene³ is one of the most studied examples of a unimolecular reaction. The experimental work encompasses thermal studies over a wide temperature⁴ and pressure^{5,6} range (although not a wide range of fall-off, unfortunately), the use of chemical activation techniques to produce highly vibrationally excited nearly monoenergetic cyclopropane molecules,⁷ and

the study of the magnitude of deuterium^{6,8} and tritium⁹ isotope effects. Attention has also been given to the structural isomerization reactions of substituted¹⁰⁻¹² cyclopropanes.

In addition to structural isomerization reactions, Rabinovitch, Schlag, and Wiberg¹³ discovered the reversible *cis-trans* geometric isomerization of cyclopropane-*d*₂, which they have interpreted in terms of a trimethylene *cum* expanded-ring^{6,7b,7c,14} intermediate. This discovery has initiated new discussions on the mechanism of the structural and geometric isomerization^{12,14} reactions and of the role of trimethylene.¹⁵

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(1) (a) Abstracted in part from the Ph.D. thesis of D. W. S., University of Washington, 1961; (b) this work was supported by the National Science Foundation.

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