

The Crystal Structure of some Polymethylenediammonium Adipates. I. Hexamethylenediammonium Adipate

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Crystallographic data of some polymethylenediammonium adipates (2-6, 4-6, 6-6 and 8-6) are given. They belong to a common space group C_{2h}^2 ($P2_1/n$ for 2-6, 6-6 and $P2_1/c$ for 4-6, 8-6). The unit cells contain two molecules of diamine and two molecules of diacid, having following dimensions: for 2-6, $a = 5.55$, $b = 10.82$, $c = 11.86$ Å, $\beta = 129^\circ$; for 4-6, $a = 7.68$, $b = 5.97$, $c = 17.21$ Å, $\beta = 125.5^\circ$; for 6-6, $a = 5.57$, $b = 15.48$, $c = 9.07$ Å, $\beta = 114^\circ$; and for 8-6, $a = 5.40$, $b = 6.72$, $c = 20.97$ Å, $\beta = 94^\circ$. Of these the crystal structure of hexamethylenediammonium adipate has first been determined. The structure shows that in the adipate ion the plane of each carboxylic group tilts from that of the carbon zigzag chain by 19° . The atoms except hydrogen in the hexamethylenediammonium component also form a coplanar zigzag chain. The structure may be described as consisting of layers, in which the axes of both the component chains orientate themselves parallel to each other. There are three types of N-H...O hydrogen bondings (2.72, 2.75 and 2.88 Å) which link component ions in the layer to each other as well as to those in neighbouring layers.

Introduction

X-ray analysis of the series of polymethylenediammonium polymethylenedicarboxylates, the so-called nylon salts, was first undertaken by one of the authors (Ohashi, 1942) in this laboratory. Unfortunately the work was interrupted because of the War, and we have taken up this problem anew, partly confirming the previous results and partly extending the preliminary investigation to other members of the series. An account of a part of our study done on hexamethylenediammonium adipate will be given here.

Crystallographic data

The salts studied were the di-, tetra-, hexa-, and octamethylenediammonium adipates, i.e. 2-6, 4-6, 6-6 and 8-6 salts, which all crystallize in the monoclinic system. Crystals of these salts, excluding 2-6, were grown from methyl alcohol-water solutions by slow evaporation. Main faces are (100) for 4-6, (010) for 6-6 and (100) for 8-6. As for 2-6, it seems that this salt is likely to crystallize as a hydrate, which is very unstable in the air; crystals of 2-6 were therefore grown from a hot methyl alcohol solution by slow cooling. They were thin needles, elongated in the direction of the c -axis, the main face being (100).

The cell dimensions and space groups were determined from oscillation and Weissenberg photographs. The densities of the crystals, ρ , were measured by flotation in toluene-carbon tetrachloride mixtures. The results are tabulated in Table 1.

The accuracy of the cell dimensions is about 0.2%, except for 8-6, for which the values are somewhat less

Table 1. Crystallographic data

	2-6	4-6	6-6	8-6
a (Å)	5.55	7.68	5.57	5.40
b (Å)	10.82	5.97	15.48	6.72
c (Å)	11.86	17.21	9.07	20.79
β ($^\circ$)	129	125.5	114	94
Molecules in the unit cell	2	2	2	2
ρ_o	1.23	1.21	1.20	1.26
ρ_c	1.24	1.22	1.21	1.28
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Molecular symmetry	Centre	Centre	Centre	Centre

accurate. It is interesting to note that they appear in two series in regard to the lattice parameters. As seen in Table 1, 2-6 and 6-6 have comparatively large values of the b axis, while 4-6 and 8-6 possess far smaller values.

Determination of the structure

In the present case, either efforts failed to distinguish peaks of two-dimensional Patterson projections and a Harker section, or the inequality relations proposed by Okaya & Nitta (1952) brought no success. Thus the three-dimensional Patterson series were synthesized using Beevers-Lipson strips at $1/60$ intervals along the b and c axes and $1/30$ along the a axis. This method supplied many useful results: for example O-O, C-O, C-C, N-O, etc. vectors could be distinguished in the synthesized maps. Making the centres of symmetry of the ordinary zigzag chain molecule models for the two components coincide with those of the space group, the most probable dispositions of the molecules were looked for in the two-dimensional projections. In

* Deceased in 1943.

Table 2. Comparison of observed and calculated structure factors

<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c	<i>hkl</i>	F_o	F_c
002	10.9	-14.9	068	< 2.8	- 2.3	0,14,0	6.5	- 7.5
004	4.0	- 5.9	069	< 2.5	1.8	0,14,1	4.6	7.9
006	5.7	4.4	0,6,10	< 2.2	1.0	0,14,2	10.1	-11.7
008	4.7	- 5.7				0,14,3	6.3	- 8.0
0,0,10	4.2	- 1.2	071	15.4	14.5	0,14,4	5.0	4.2
			072	13.2	-11.5	0,14,5	4.3	3.6
011	12.3	12.0	073	3.6	- 1.4	0,14,6	< 2.2	0.8
012	44.0	-44.2	074	5.5	- 6.9	0,14,7	3.0	2.9
013	10.4	5.7	075	7.2	- 6.5			
014	26.9	-21.4	076	3.7	0.9	0,15,1	4.1	- 2.4
015	14.9	-15.1	077	< 2.8	- 1.5	0,15,2	< 2.8	- 1.2
016	20.5	20.5	078	< 2.8	- 1.4	0,15,3	6.2	9.1
017	8.9	-11.0	079	4.2	- 2.4	0,15,4	4.6	2.6
018	14.1	-13.2				0,15,5	3.7	- 1.4
019	4.4	- 5.4	080	< 2.2	0	0,15,6	< 2.0	- 0.7
0,1,10	5.2	5.2	081	16.0	-14.9			
			082	14.6	12.1	0,16,0	8.7	-13.1
020	27.0	-33.1	083	12.1	-11.7	0,16,1	< 2.8	- 1.8
021	7.4	- 9.2	084	5.7	5.1	0,16,2	< 2.8	2.1
022	59.2	65.7	085	3.9	5.0	0,16,3	4.1	6.0
023	23.2	-18.8	086	< 2.8	0.1	0,16,4	< 2.5	1.0
024	4.5	4.5	087	4.6	6.2	0,16,5	4.1	- 4.0
025	12.8	- 8.6	088	< 2.8	- 4.3	0,16,6	3.0	- 6.7
026	4.5	4.2	089	< 2.2	- 2.0			
027	4.5	3.8				0,17,1	6.9	8.8
028	< 2.8	2.0	091	3.7	- 4.0	0,17,2	4.1	5.3
029	3.4	3.2	092	10.6	-13.6	0,17,3	4.1	- 4.8
0,2,10	6.0	- 6.0	093	9.0	12.5	0,17,4	3.9	- 5.1
			094	< 2.2	0.3	0,17,5	3.7	4.2
031	26.3	-27.1	095	12.3	10.4			
032	39.1	-40.8	096	16.0	-16.1	0,18,0	< 2.6	1.6
033	10.8	- 7.6	097	9.6	-11.0	0,18,1	3.2	- 3.1
034	11.9	11.1	098	3.2	- 2.6	0,18,2	4.6	- 3.9
035	16.8	15.8	099	2.4	- 2.7	0,18,3	4.1	- 4.9
036	15.5	-14.7				0,18,4	2.9	- 6.0
037	5.6	- 7.6	0,10,0	4.6	4.7			
038	< 2.8	- 0.5	0,10,1	13.4	14.0	0,19,1	2.2	- 1.6
039	4.0	- 5.1	0,10,2	4.1	- 4.4	0,19,2	2.9	- 3.0
0,3,10	3.2	- 2.8	0,10,3	3.9	- 4.9			
			0,10,4	4.6	4.2	10 $\bar{1}$	6.4	- 6.0
040	7.9	- 6.6	0,10,5	10.1	- 9.0	10 $\bar{3}$	14.5	14.5
041	27.8	32.5	0,10,6	4.3	- 4.6	10 $\bar{5}$	24.4	22.0
042	3.5	- 3.3	0,10,7	4.1	- 4.2	10 $\bar{7}$	4.0	- 9.6
043	3.0	4.0	0,10,8	< 1.8	0.7	10 $\bar{9}$	17.1	-16.5
044	31.7	33.1				1,0,1 $\bar{1}$	3.5	- 3.5
045	9.6	-10.1	0,11,1	3.7	2.0			
046	3.7	- 3.6	0,11,2	7.5	7.6	101	15.5	-16.4
047	5.9	- 4.5	0,11,3	4.3	3.6	103	9.5	7.8
048	< 2.8	0.4	0,11,4	18.3	-20.2	105	< 2.0	2.0
049	< 2.5	3.2	0,11,5	5.9	- 4.8	107	12.4	-13.3
0,4,10	3.2	5.1	0,11,6	3.7	- 3.7	109	7.9	- 6.6
			0,11,7	5.5	5.2			
051	12.8	11.5	0,11,8	4.6	- 5.4	200	29.6	34.5
052	33.2	39.8				20 $\bar{2}$	21.7	23.6
053	21.4	-16.9	0,12,0	< 2.8	- 1.5	204	2.5	- 2.1
054	14.8	-15.9	0,12,1	11.0	-13.2	20 $\bar{6}$	13.1	11.2
055	11.8	-13.9	0,12,2	< 2.8	- 1.9	20 $\bar{8}$	10.1	- 7.9
056	4.3	- 4.0	0,12,3	3.7	3.9	2,0,1 $\bar{0}$	19.2	15.4
057	5.0	6.6	0,12,4	15.8	-15.6			
058	< 2.8	- 2.6	0,12,5	4.1	- 7.4	202	14.4	-15.1
059	< 2.5	- 0.8	0,12,6	3.7	3.0	204	10.6	-10.7
0,5,10	< 2.2	- 3.1	0,12,7	4.6	- 3.7	206	19.6	-18.5
			0,12,8	3.2	3.9	208	4.3	3.4
060	42.0	41.6						
061	18.3	-15.9	0,13,1	< 2.8	2.0	30 $\bar{1}$	15.0	-13.8
062	16.8	13.7	0,13,2	16.0	-16.8	30 $\bar{3}$	10.3	10.8
063	2.8	4.0	0,13,3	5.0	- 6.1	30 $\bar{5}$	17.6	18.4
064	11.7	-11.3	0,13,4	4.6	2.7	30 $\bar{7}$	23.3	20.5
065	5.9	8.8	0,13,5	4.1	6.8	30 $\bar{9}$	7.9	- 9.2
066	3.2	3.3	0,13,6	< 2.2	- 0.3	3,0,1 $\bar{1}$	7.0	- 6.4
067	< 2.8	0.2	0,13,7	< 2.2	1.1			

Table 2 (cont.)

hkl	F_o	F_c	hkl	F_o	F_c	hkl	F_o	F_c
301	< 2.7	- 0.4	1,10,0	10.5	-10.6	3,13,0	< 2.4	3.2
303	4.0	- 3.6	1,11,0	5.0	- 3.7	3,14,0	< 2.3	- 3.2
305	5.0	- 5.6	1,12,0	8.2	- 7.0	3,15,0	6.0	8.4
307	8.6	8.0	1,13,0	13.5	-15.7	3,16,0	< 1.5	- 2.5
400	27.1	-28.3	1,14,0	6.1	- 6.9	3,17,0	< 1.4	- 0.8
40 $\bar{2}$	14.3	14.2	1,15,0	< 3.0	0.4	410	< 2.3	0.2
40 $\bar{4}$	10.4	- 8.7	1,16,0	< 2.7	- 1.8	420	< 2.3	- 4.0
40 $\bar{6}$	5.5	- 6.6	1,17,0	< 2.5	- 1.9	430	3.5	- 6.1
40 $\bar{8}$	5.6	5.3	1,18,0	< 2.1	3.6	440	3.5	- 2.8
4,0, $\bar{10}$	8.6	8.0	1,19,0	3.0	- 5.2	450	7.9	8.2
402	< 2.5	- 3.5	210	33.0	32.1	460	< 2.5	- 2.2
404	5.8	- 6.3	220	19.3	-20.5	470	3.5	- 5.5
406	7.8	- 9.0	230	37.2	-43.2	480	3.5	- 4.5
50 $\bar{1}$	17.9	-16.9	240	11.1	- 9.3	490	< 2.3	- 1.1
50 $\bar{3}$	11.4	12.2	250	18.0	-16.9	4,10,0	4.3	- 4.5
505	3.8	3.1	260	8.8	9.0	4,11,0	< 2.2	0.7
507	5.1	6.2	270	9.0	8.0	4,12,0	6.0	6.8
509	14.6	11.8	280	< 2.1	- 2.4	4,13,0	< 2.0	- 2.7
501	< 2.0	0.4	290	13.6	-12.4	4,14,0	< 1.8	0.8
503	2.2	1.9	2,10,0	5.5	- 4.5	4,15,0	4.2	4.5
600	2.0	- 1.9	2,11,0	16.1	-15.4	510	6.5	- 6.1
60 $\bar{2}$	< 2.0	- 1.8	2,12,0	< 2.4	1.1	520	9.2	9.4
604	14.3	-11.4	2,13,0	10.0	-14.3	530	< 2.3	- 5.2
60 $\bar{6}$	5.7	- 5.4	2,14,0	< 2.4	- 1.3	540	2.4	- 1.9
608	5.1	4.3	2,15,0	< 2.3	5.5	550	< 2.2	1.8
70 $\bar{3}$	2.4	- 0.7	2,16,0	< 2.0	- 0.3	560	< 3.3	3.7
705	< 1.4	- 0.9	2,17,0	4.5	- 3.3	570	4.9	- 6.3
110	14.0	16.1	2,18,0	< 1.5	2.8	580	3.7	5.6
120	62.3	-60.8	310	11.5	-10.4	590	< 2.0	1.6
130	68.0	72.6	320	28.2	-27.0	5,10,0	< 1.9	- 3.5
140	13.5	11.3	330	12.0	-10.6	5,11,0	< 1.7	- 3.2
150	45.3	-46.3	340	6.3	5.1	5,12,0	6.0	6.9
160	18.2	-14.5	350	3.7	2.5	610	3.3	- 3.4
170	15.0	11.5	360	9.8	- 9.8	620	3.3	0.3
180	4.2	- 3.7	370	2.3	- 1.5	630	3.3	4.9
190	17.9	16.4	380	< 2.3	1.6	640	5.0	- 2.1
			390	< 2.3	- 2.5	650	8.3	7.7
			3,10,0	13.9	-17.6	660	5.2	3.1
			3,11,0	< 2.5	- 3.6	670	< 1.3	- 1.8
			3,12,0	< 2.4	- 1.8			

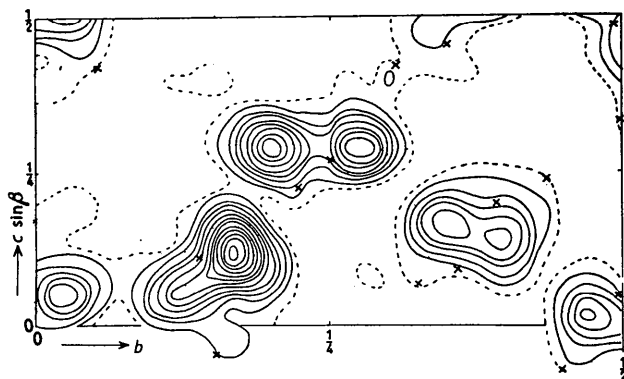


Fig. 1.

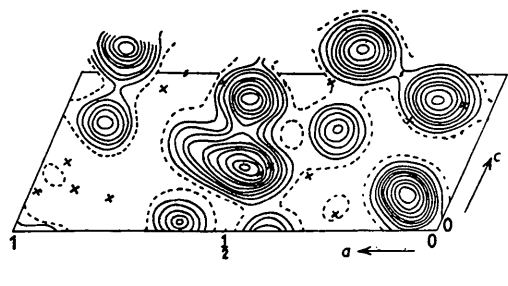


Fig. 2.

Fig. 1. Fourier projection of hexamethylenediammonium adipate on (100). Contours at intervals of approximately $1 \text{ e.}\text{\AA}^{-2}$. Broken line represents first contour. Crosses show the postulated positions of the hydrogen atoms. Scale: $1 \text{ cm.} = 1 \text{ \AA}$.
 Fig. 2. Fourier projection of hexamethylenediammonium adipate on (010). Contours, crosses and scale as in Fig. 1.

this way the double Fourier series of the electron density were synthesized along the three principal axes, of which the projection $\rho(x, y)$ showed very poor resolution of atoms. Such procedures were repeated

for better approximation. The final electron-density maps projected along the a and b axes are shown in Figs. 1 and 2.

The coordinate values of the resolved peaks were

determined graphically, the accuracy of the atomic parameter values being estimated to be ± 0.003 . Positions of the atoms C_1 , C_2 and C_5 remain unresolved in $\rho(x, z)$ and also C_3 and O_2 in $\rho(y, z)$. Their coordinate values were determined by the trial-and-error method. These values are thus expected to be less accurate. For the calculation of the structure factors, atomic scattering curves for H, C, N and O from *Internationale Tabellen* were corrected, using a temperature factor assumed to be $B = 2.50 \text{ \AA}^2$ from the slope of a plot of $\ln(F_c/F')$ against $\sin^2 \theta$.

It is to be noted that, as the hydrogen electrons in the 6-6 salt amount to 18% of the total, their contribution to structure factors cannot be neglected for lower-order reflexions. The hydrogen atom was thus assumed to be at 1.09 \AA or 1.02 \AA from the carbon or nitrogen atom in the required bond direction. In fact, the electron-density maps for this crystal showed the presence of some of these hydrogen atoms. The reliability indices were calculated to be $R = 0.127$ for ($h0l$), 0.158 for ($0kl$) and 0.123 for ($hk0$) reflexions, all up to $\sin \theta = 0.98$. Comparison of F_o and F_c is listed in Table 2. The atomic coordinates are collected in Table 3 and the interatomic distances (to $\pm 0.05 \text{ \AA}$)

Table 3. Atomic coordinates

	<i>x</i>	<i>y</i>	<i>z</i>
C_1	0.125	0.023	0.054
C_2	0.083	0.121	0.058
C_3	0.342	0.162	0.158
C_4	0.617	0.471	0.017
C_5	0.642	0.400	0.142
C_6	0.900	0.350	0.175
N	0.925	0.275	0.286
O_1	0.375	0.200	0.292
O_2	0.517	0.171	0.108

	<i>x</i>	<i>y</i>	<i>z</i>
For C_1	H_1 0.260	-0.010	0.017
	H_2 0.196	-0.002	0.177
For C_2	H_3 0.013	0.147	-0.063
	H_4 -0.057	0.134	0.111
For C_4	H_5 0.575	0.439	-0.103
	H_6 0.808	0.495	0.050
For C_5	H_7 0.473	0.357	0.092
	H_8 0.633	0.433	0.238
For C_6	H_9 0.900	0.325	0.067
	H_{10} 0.067	0.392	0.200
For N	H_{11} 0.792	0.228	0.225
	H_{12} 0.042	0.305	0.400
	H_{13} 0.092	0.258	0.267

Table 4. Intramolecular interatomic distances and bond angles

$C'_1-C_1 = 1.52 \text{ \AA}$	$C'_1-C_1-C_2 = 112^\circ$
$C_1-C_2 = 1.54$	$C_1-C_2-C_3 = 109$
$C_2-C_3 = 1.50$	$C_2-C_3-O_1 = 120$
$O_1-C_3 = 1.28$	$C_2-C_3-O_2 = 122$
$O_2-C_3 = 1.24$	$O_1-C_3-O_2 = 118$
$C'_2-C_4 = 1.54$	$C'_4-C_4-C_5 = 112$
$C_4-C_5 = 1.54$	$C_4-C_5-C_6 = 107$
$C_5-C_6 = 1.55$	$C_5-C_6-N = 110$
$C_6-N = 1.50$	

Table 5. Intermolecular interatomic distances and angles

Letters in brackets are related to those in Figs. 4 and 5

$N(B)-O_1(A')$ = 2.75 \AA	$C_6(B)-N(B)-O_2(A)$ = 104°
$N(B)-O_2(A)$ = 2.72	$C_6(B)-N(B)-O_1(A')$ = 100
$N(B)-O_2(C)$ = 2.88	$C_6(B)-N(B)-O_2(C)$ = 112
$N(B)-O_1(A)$ = 3.31	$O_2(A)-N(B)-O_1(A')$ = 108
$O_1(A')-O_2(A)$ = 4.42	$O_2(A)-N(B)-O_2(C)$ = 122
$O_1(A')-O_2(C)$ = 4.58	$O_1(A')-N(B)-O_2(C)$ = 109
$O_2(A)-O_2(C)$ = 4.90	
$C_6(B)-O_2(A)$ = 3.41	
$C_6(B)-O_1(A')$ = 3.36	
$C_6(B)-O_2(C)$ = 3.72	

and bond angles (to $\pm 5^\circ$) calculated from these data are given in Tables 4 and 5.

Discussion

The dimensions of the component ions are shown in Fig. 3.

In the component hexamethylenediammonium ion all atoms except hydrogen lie in a plane forming a

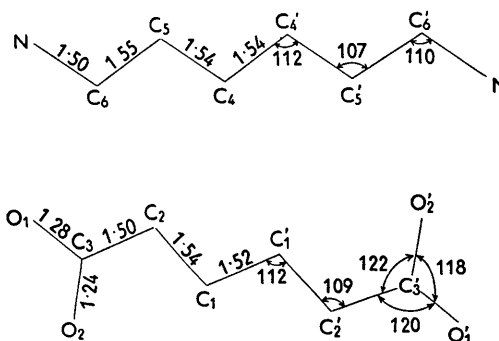


Fig. 3. Molecular dimensions of hexamethylenediammonium and adipate components in the nylon salt, 6-6.

zigzag chain, while in the other component of adipate ion a similar coplanar carbon zigzag chain is found with the carboxylic ends, of which planes of COO are tilted from the plane of the chain by an angle of 19° . Up to the present, several papers on the crystal structures of adipic acid (MacGillavry, 1941; Morrison & Robertson, 1949; Hirokawa, 1950) have been published. Comparison with the present data shows that there are no essential discrepancies except the tilt angles of the carboxylic group from the plane of the carbon zigzag chain; this angle was reported to be 6° by Morrison & Robertson in adipic acid. Besides, the O-C-O angle in the present case was calculated to be 118° , being somewhat less than the published data (123° by MacGillavry, 124° by Hirokawa and 126° by Morrison & Robertson). These differences may be attributed partly to the different modes of hydrogen bondings. The alternative bond shortening in the carbon chain described by Morrison & Robertson (1949) and by Binnie & Robertson (1950) could not be observed in this investigation.

The arrangements of component ions in this salt crystal viewed along [100] and [010] are shown in

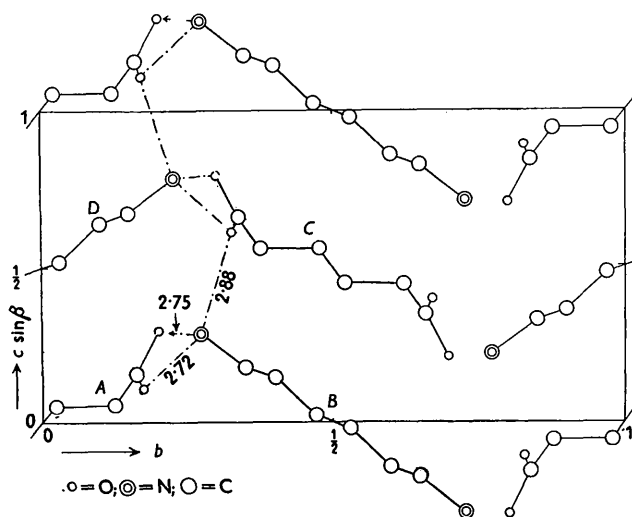


Fig. 4.

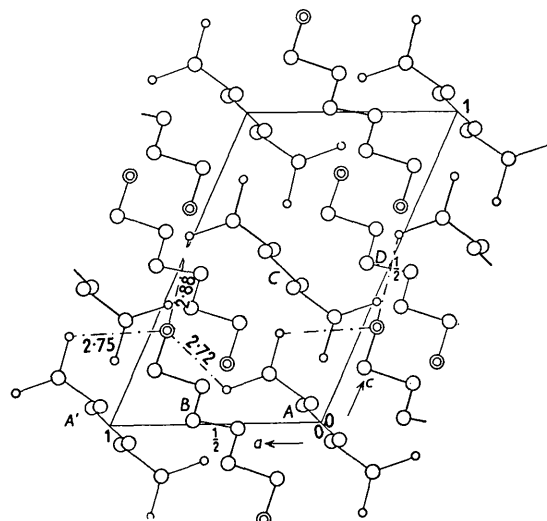


Fig. 5.

Fig. 4. Structure of hexamethylenediammonium adipate projected on (100). Chain lines represent hydrogen bonds. Scale: 1 cm. = 2 Å.

Fig. 5. Structure of hexamethylenediammonium adipate projected on (010). Chain lines represent hydrogen bonds. Scale: 1 cm. = 2 Å.

Figs. 4 and 5 respectively, where certain component ions are designated A , A' , B , C and D . Atoms of A (diacid) and B (diamine) occupy the positions given by the parameter values in Table 3. A and A' are equivalent components separated by the repeat distance a in the x direction. C and D are related respectively to A and B by the symmetry requirement.

The structure may be described as consisting of ionic layers, in each of which both component ions orientate their molecular axes nearly parallel to each other, but the planes of each zigzag chain are inclined at approximately 65° to each other. A component ion in each layer is surrounded by six ions, two of which are of the same kind as the central one. The manner of packing of the ions in the layer is thus a kind of deformed two-dimensional closest packing. The hydrogen bond linkage in such an ionic layer is effected between the nitrogen atom of the diammonium ion and

the oxygen atom of the adjacent diacid ion only at the one end of each ion. The dimension of this hydrogen bond is 2.88 Å. The above-mentioned nitrogen atom forms two further hydrogen bond links of lengths 2.75 and 2.72 Å with the oxygen atoms of the two diacids in the next layer. Thus the three-dimensional network is provided by these N-H...O bonds. The schematic drawing of these links is shown in Fig. 6.

This kind of hydrogen bonding between nitrogen and carboxylic oxygen atoms has been observed in several structures, e.g. in the work on DL-alanine (Donohue, 1950), in which the resonance character of the carboxylic group was discussed. In the present case the interatomic distances between C and O are 1.24 Å (C-O₂) and 1.28 Å (C-O₁), suggesting that resonance in the carboxylic group might be present to a certain extent.

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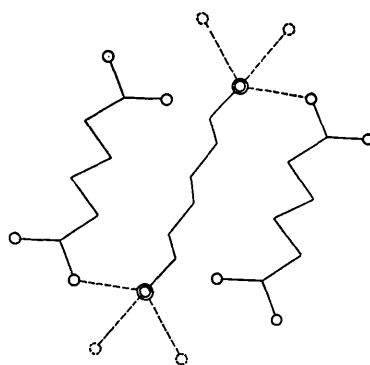


Fig. 6. Schematic drawing of the system of hydrogen-bond linkages. Oxygen atoms indicated by dotted circles are those of the next layers.