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The Crystal Structure of ε-Aminocaproic Acid*

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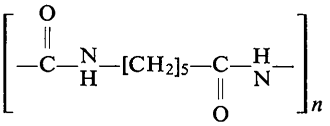
The crystal structure of ε-aminocaproic acid, $NH_2(CH_2)_5COOH$, which undergoes polycondensation in the solid state to form Nylon-6, has been determined. The unit cell is monoclinic with $a=8·555$, $b=5·872$, $c=15·274$ Å; $\beta=103·1°$. The space group is $P2_1/c$ and there are four molecules per unit cell. The signs of structure factors were determined by the symbolic addition procedure. Approximate atomic position coordinates were obtained from an *E*-factor map and the structure was refined by least-squares methods. The molecules are present in the crystal as zwitterions with three hydrogen atoms at 0·9 Å from each nitrogen atom. Each zwitterion forms three N–H–O bonds with adjacent molecules to form a double-layered structure. The hydrogen bond lengths (N–O) are 2·728, 2·753 and 2·814, all ±0·005 Å. Intramolecular bond lengths are: C–C 1·511 to 1·523 Å, C–O 1·235 and 1·261 Å, and C–N 1·485 Å, all ±0·004 Å. Bond angles are normal.

Introduction

Muller (1952) has reported that Nylon-6, polypentamethylene capramide:



$$\left[-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{H}{N}-[CH_2]_5-\underset{\underset{\displaystyle O}{\|}}{C}-\overset{H}{N}-\right]_n$$

can be prepared by the solid state polycondensation of ε-aminocaproic acid. Recently Morosoff, Lim & Morawetz (1964) showed that the polycondensation of single crystals of monomer yields highly oriented polycrystalline polymer specimens. Evidently the reactive functional groups in the monomer play important roles in determining the orientation as well as the nature of the reaction product. This investigation was undertaken to determine the crystal structure of the monomer and to study the relationships between the orientations of reactive groups in the monomer and in the polycondensation product, Nylon-6.

Experimental

Crystals of ε-aminocaproic acid were obtained by evaporation from benzene solutions. Full data in three dimensions were collected with a counter diffractometer using filtered Cu $K\alpha$ radiation. The crystal system is monoclinic; $a=8·855\pm0·002$, $b=5·782\pm0·002$, $c=15·274\pm0·004$ Å, $\beta=103·1\pm·1°$. The space group is $P2_1/c$ and there are four molecules per unit cell. Of the 1485 independent reflections accessible to Cu $K\alpha$ radiation, 1194 were measured and used in the structure determination. The others were either too weak to permit reasonably precise measurement or were not detected at all and were given zero weight in the least-squares analysis of the data. All 1194 reflection intensities were measured by the stationary-crystal stationary-counter method, with a target take-off angle of 5°. Background measurements were made on high and low angle sides of the reflections and the averaged values were used to correct the intensities for background effects. In addition, approximately 150 reflections, randomly distributed throughout the range of Bragg angles investigated, were measured by the moving-crystal moving-counter (θ–2θ) procedure. After being corrected for background effects, these 'integrated' intensities were plotted against the corresponding peak intensities as functions of the Bragg angle. The smoothed plot was used to convert all 'peak' intensities to 'integrated' intensities.

A trial scale factor and an isotropic molecular temperature factor were obtained by a statistical analysis of the intensity data in the manner described by Wilson (1942). The magnitudes of normalized structure factors ($|E_{\rm H}|$) were then computed using the equation:

$$E_{\rm H}^2=F_{\rm H}^2 \sum_{j=1}^{N} \varepsilon f_{j\rm H}^2 \qquad (1)$$

where N is the number of atoms in the unit cell and ε equals 2·0 for $h0l$ and $0k0$ reflections and 1·0 for other reflections. Only normalized structure factors with magnitudes greater than 1·2 (20% of the total) were used in the phase analysis.

Determination of the structure

The symbolic addition procedure (Karle & Karle, 1963) was used to determine phases from the magnitudes of the normalized structure factors. The phase determining procedure was facilitated by the use of a computer program previously described (Bednowitz & Post,

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1966; Okaya & Bednowitz, 1967). The principal phase relation used in this procedure is the Σ_2 formula of Hauptman & Karle (1953):

$$sE_{\mathbf{H}} \approx s\, \Sigma\, E_{\mathbf{K}} E_{\mathbf{H-K}} \qquad (2)$$

where s means 'sign of'. The right hand side or the 'double product sum' is modified in our procedure so that the residue of the dominant symbol determines the correct symbol assignment. The dominant symbol is the one whose double product sum is greater than the sum of all other double products associated with all other symbols. The difference between the double product sum of the dominant symbol and the sum of the double product of all other symbols is the residue (R_s). (R_s) must be less than or equal to the absolute magnitude of the double product sum when the actual signs (+ or −) are used. By modifying the usual probability formula (Karle & Karle, 1963; Woolfson, 1954) to

$$P_s(E_{\mathbf{H}}) \geq \tfrac{1}{2} + \tfrac{1}{2} \tanh \frac{\sigma_3}{\sigma_2^{3/2}}\, |E_{\mathbf{H}}| R_s \qquad (3)$$

automated decisions could be made on a reasonably quantitative basis.

In order to initiate the automatic phase determining procedure it is necessary to choose a set of starting phases. For space group $P2_1/c$ these three reflections are given arbitrary signs to fix the origin. Additional reflections with relatively large E factors, and with many interactions with other (strong) terms, are then assigned symbolic phases. The interaction list is usually computed before assigning the first set of phases. The starting set can be augmented by using additional phase relations. For example, for this structure the Σ_1 relation (4) (Hauptman & Karle, 1953),

$$s(E_{2\mathbf{H}}) \approx s(E_{\mathbf{H}}^2 - 1) \qquad (4)$$

was used to establish a positive sign for the reflection (46$\bar{8}$). The starting set used in the phase determination is listed in Table 1.

Table 1. *Starting set of phases*

HKL			*E*	Symbol	
1	5	$\bar{3}$	3·33	(+)	arbitrarily assigned to fix the origin
2	3	$\bar{4}$	3·11	(+)	
5	3	$\bar{6}$	2·99	(+)	
5	3	$\bar{2}$	3·09	*a*	initial assignments
3	3	$\bar{1}\bar{2}$	2·68	*b*	
4	6	$\bar{8}$	3·71	+	determined from Σ_1 relation
6	2	0	2·76	*c*	additional assignment

Using the starting set of six reflections and applying the symbolic addition procedure manually to the 68 reflections with $|E| > 2\cdot0$, 11 signs and 16 symbols were determined. In the next stage 108 reflections with $|E| > 1\cdot8$ were analyzed and yielded a cumulative total of 26 signs and 44 symbols. In order to facilitate the rapid development of more symbolic assignments, the symbol (c) was then assigned to (620).

In the second pass through the computer 199 reflections with $|E| > 1\cdot50$ were examined. A total of 42 signs and 123 symbols were known after this pass. For the third pass the minimum $|E|$ was reduced to 1·2 and 318 reflections were used and 49 signs and 193 symbols were established.

There were many indications that ($b = c$) ($a = -$) and ($b = +$) were the most probable sign assignments. Although additional phases could undoubtedly have been determined by substituting these signs for the symbols in the phase determining procedure and continuing that process, we decided to terminate the phase analysis and prepare E maps based on signs and symbols determined at the end of the third computer pass. The nine non-hydrogen atoms in the molecule were clearly revealed

Table 2. *Atomic coordinates and thermal parameters*

Estimated standard errors of the coordinates, the b_{ij} and their standard errors have been multiplied by 10^4. The thermal parameters are given by: $h^2b_{11} + k^2b_{22} + l^2b_{33} + 2hkb_{12} + 2hlb_{13} + 2klb_{23}$.

	x	σ_x	y	σ_y	z	σ_z	B	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
O(1)	0·6506	2	0·2975	2	0·0921	1		178 (3)	126 (4)	73 (1)	43 (3)	69 (1)	17 (2)
O(2)	0·5396	2	0·0183	2	0·1531	1		123 (2)	165 (4)	41 (1)	−2 (2)	31 (1)	−10 (1)
C(1)	0·6327	2	0·0932	3	0·1065	1		79 (3)	150 (6)	33 (1)	25 (3)	10 (1)	−2 (2)
C(2)	0·7333	2	0·9210	4	0·0688	1		93 (3)	174 (6)	40 (1)	29 (3)	17 (1)	−12 (2)
C(3)	0·9012	2	0·9039	4	0·1285	2		102 (3)	263 (8)	42 (1)	61 (4)	10 (1)	−21 (2)
C(4)	0·0047	2	0·7282	4	0·0951	1		95 (2)	195 (7)	46 (1)	37 (3)	17 (1)	−14 (2)
C(5)	0·1775	2	0·7302	4	0·1480	1		103 (3)	182 (6)	39 (1)	46 (3)	18 (1)	−17 (2)
C(6)	0·2791	2	0·5532	4	0·1152	1		92 (3)	157 (6)	43 (1)	24 (3)	18 (1)	−10 (2)
N	0·4502	2	0·5745	3	0·1627	1		99 (2)	143 (5)	42 (1)	28 (3)	24 (1)	7 (2)
H(1)	0·7438	26	0·9662	40	0·0093	16	3·3 (5) Å^2						
H(2)	0·6808	27	0·7729	45	0·0650	16	3·4 (4)						
H(3)	0·9639	29	0·0555	48	0·1367	16	4·1 (5)						
H(4)	0·8944	30	0·8790	50	0·1900	20	4·9 (6)						
H(5)	0·0081	30	0·7667	50	0·0275	18	4·6 (6)						
H(6)	0·9617	24	0·5975	42	0·1022	14	2·4 (4)						
H(7)	0·1836	30	0·7120	46	0·2157	19	4·7 (6)						
H(8)	0·2214	30	0·8884	49	0·1404	17	4·4 (6)						
H(9)	0·2414	26	0·4149	42	0·1207	14	2·8 (5)						
H(10)	0·2829	27	0·5877	44	0·0518	17	3·5 (5)						
H(11)	0·4551	25	0·5571	40	0·2241	16	3·2 (5)						
H(12)	0·4939	26	0·7142	48	0·1562	15	3·4 (5)						
H(13)	0·5181	27	0·4651	42	0·1361	15	3·3 (5)						

Table 3. $|F_{obs}|$ *and* $|F_{calc}|$

L	FØBS	FCAL
(H = 0)		
(K = 0)		
2	135	134
6	39	38
8	147	175
10	41	45
12	72	77
14	17	18
16	51	54
18	23	29
(K = 1)		
4	165	156
5	13	52
6	38	27
7	52	56
8	157	156
9	31	43
10	0*	2
11	46	53
12	74	79
13	32	38
14	0*	7
15	43	49
16	18	23
17	0*	10
18	0*	0
(K = 2)		
0	187	198
1	157	150
2	148	130
3	69	52
4	145	127
5	227	196
6	261	228
7	23	19
8	63	63
9	54	43
11	22	16
12	30	31
14	0*	2
15	0*	7
16	29	30
17	64	73
(K = 3)		
1	192	174
2	136	120
3	116	109
4	59	49
5	58	51
6	48	46
7	24	22
8	0*	3
9	49	50
10	44	45
11	21	23
12	24	26
14	26	34
15	30	21
16	0*	3
(K = 4)		
0	127	130
1	142	151
2	0*	12
3	92	95
4	67	69
5	99	101
6	46	49
7	47	46
8	0*	4
9	0*	5
10	41	45
11	25	24
12	42	44
13	62	65
14	30	31
15	0*	7
(K = 5)		
1	125	137
2	119	129
3	0*	7
4	27	26
5	173	182
6	31	34
7	74	79
8	0*	11
9	99	99
10	11	6
11	25	26
12	0*	2
13	26	26
(K = 6)		
0	160	160
1	68	66
2	28	27
3	0*	0
4	99	94
5	98	102
6	38	39
7	0*	11
8	0*	8
9	69	65
10	0*	12
(K = 7)		
1	64	64
2	60	54
3	95	88
4	0*	13
(H = 1)		
(K = 0)		
-18	64	61
-16	43	39
-14	0*	0
-12	140	136
-10	206	208
-8	281	275
-6	268	260
-4	229	225
-2	60	42
0	401	407
2	367	355
4	550	572
6	133	127
8	86	101
10	0*	14
12	67	72
14	0*	8
16	48	50
18	0*	22
(K = 1)		
-18	27	27
-17	30	29
-16	60	61
-15	40	43
-14	37	41
-13	0*	1
-12	25	21
-11	12	18
-10	0*	0
-9	29	33
-8	243	244
-7	74	79
-6	153	153
-5	170	169
-4	494	523
-3	439	480
-2	471	502
-1	431	451
0	398	427
1	432	464
2	389	391
3	319	319
5	60	51
6	165	168
7	0*	65
8	61	65
9	37	36
10	56	56
11	0*	3
12	58	61
13	38	37
14	0*	1
15	0*	8
16	31	30
17	0*	17
(K = 2)		
-18	0*	3
-17	0*	6
-16	34	32
-15	20	20
-14	19	19
-13	27	28
-12	18	16
-11	18	21
-10	98	96
-9	56	50
-8	151	154
-7	0*	1
-6	214	211
-5	319	308
-4	346	338
-3	55	52
-2	119	113
-1	462	505
0	372	433
1	45	41
2	125	112
3	94	88
4	108	97
5	112	112
6	143	142
7	65	76
8	75	83
9	100	108
10	62	65
11	0*	7
12	123	127
13	25	27
14	0*	2
15	44	43
16	84	80
17	22	21
(K = 3)		
-17	21	23
-16	16	12
-15	0*	2
-14	19	15
-13	58	59
-12	32	33
-11	0*	2
-10	35	38
-9	77	80
-8	64	61
-7	0*	1
-6	95	92
-5	0*	0
-4	16	10
-3	33	29
-2	52	49
-1	165	161
0	97	103
1	0*	2
2	148	147
3	202	205
4	0*	1
5	0*	9
6	0*	20
7	94	99
8	0*	51
9	0*	26
10	138	141
11	21	23
12	17	20
13	16	16
14	138	134
15	0*	9
16	0*	10
(K = 4)		
-15	45	44
-14	52	50
-13	26	26
-12	0*	4
-11	41	43
-10	101	98
-9	15	19
-8	20	18
-7	46	43
-6	131	132
-5	54	94
-4	14	26
-3	166	168
-2	109	120
-1	219	223
0	33	28
1	198	203
2	35	40
3	124	121
4	0*	25
5	132	134
6	0*	12
7	0*	36
8	0*	10
9	0*	36
10	0*	30
11	0*	12
12	0*	21
13	0*	37
14	0*	18
(K = 5)		
-13	18	17
-12	12	9
-11	60	57
-10	15	14
-9	0*	3
-8	85	80
-7	177	178
-6	74	73
-5	11	10
-4	121	125
-3	237	255
-2	81	84
-1	33	34
0	91	87
1	108	107
2	21	15
3	22	17
4	50	48
5	77	82
6	0*	4
7	17	18
8	0*	29
9	110	109
10	0*	2
11	0*	10
12	0*	5
(K = 6)		
-10	0*	2
-9	62	63
-8	63	62
-7	48	46
-6	28	26
-5	102	98
-4	87	83
-3	90	92
-2	13	13
-1	76	71
0	0*	21
1	93	96
2	12	2
3	0*	16
4	0*	33
5	0*	35
6	0*	20
7	0*	51
8	0*	18
9	0*	6
(H = 2)		
(K = 0)		
-18	57	53
-16	77	75
-14	60	61
-12	99	99
-10	160	159
-8	122	112
-6	259	251
-4	105	101
-2	45	36
0	115	113
2	560	552
4	312	308
6	307	301
8	101	97
10	0*	8
12	57	58
14	63	62
16	64	61
(K = 1)		
-18	0*	3
-17	66	64
-16	29	29
-15	0*	2
-14	0*	7
-13	0*	8
-12	107	105
-11	121	114
-10	103	98
-9	92	87
-8	60	59
-7	242	224
-6	231	219
-5	207	198
-4	176	173
-3	129	109
-2	201	191
-1	227	208
0	316	317
1	127	140
2	0*	10
3	250	248
4	236	228
5	0*	3
6	90	86
7	121	117
8	109	111
9	73	73
10	97	98
11	23	23
12	67	66
13	79	79
14	73	70
15	0*	3
16	22	22
17	30	33
(K = 2)		
-18	0*	5
-17	12	11
-16	57	59
-15	25	22
-14	38	37
-13	67	68
-12	43	43
-11	59	54
-10	162	160
-9	127	121
-8	66	65
-6	361	345
-5	18	13
-4	198	177
-3	197	181
-2	488	486
-1	171	158
0	109	105
1	151	155
2	12	3
3	25	28
4	53	54
5	44	45
6	183	182
7	125	125
8	0*	11
9	29	28
10	125	129
11	117	119
12	0*	19
13	21	20
14	47	45
15	42	38
16	25	22
(K = 3)		
-17	0*	12
-16	13	17
-15	15	15
-14	0*	4
-13	0*	13
-12	65	60
-11	45	44
-10	25	27
-9	0*	0
-8	248	239
-7	54	57
-6	121	125
-5	124	126
-4	423	435
-3	0*	10
-2	188	192
-1	234	237
0	263	275
1	103	93
2	27	20
3	204	208
4	0*	11
5	45	39
6	82	87
7	75	69
8	11	10
9	16	20
10	35	35
11	17	19
12	0*	5
13	0*	3
14	26	26
15	31	32
(K = 4)		
-15	49	51
-14	0*	23
-13	0*	6
-12	0*	22
-11	0*	156
-10	0*	7
-9	62	57
-8	53	52
-7	178	184
-6	71	72
-5	95	98
-4	92	101
-3	54	58
-2	137	146
-1	28	29
0	83	82
1	111	115
2	88	88
3	28	32
4	0*	13
5	0*	130
6	0*	1
7	84	82
8	76	82
9	84	84
10	0*	13
11	73	75
12	67	74
13	47	43
14	0*	7
(K = 5)		
-13	0*	6
-12	39	36
-11	0*	12
-10	18	16
-9	14	13
-8	0*	12
-7	79	83
-6	36	34
-5	0*	12
-4	0*	44
-2	0*	62
-1	0*	7
0	51	45
1	125	133
2	48	50
3	19	19
4	16	18
5	25	27
6	27	28
7	22	24
8	23	23
9	112	110
10	32	32
11	0*	2
12	23	21
(K = 6)		
-10	0*	34
-9	0*	22
-8	0*	28
-7	0*	22
-6	0*	11
-5	65	63
-4	52	48
-3	0*	16
-2	0*	28
-1	0*	83
0	0*	24
1	23	26
2	0*	0
3	29	30
4	29	27
5	50	55
6	0*	0
7	28	32
8	34	36
9	38	42
(K = 7)		
-5	0*	9
0	17	13
1	0*	22
2	36	32
3	35	32
(H = 3)		
(K = 0)		
-18	32	32
-16	33	31
-14	77	73
-12	54	54
-10	166	163
-8	21	25
-6	279	263
-4	17	24
-2	35	43
0	118	115
2	721	725
4	66	64
6	660	692
8	21	27
10	343	352
12	27	27
14	110	106
16	0*	0
(K = 1)		
-18	0*	6
-17	57	57
-16	0*	13
-15	44	45
-14	22	27
-13	31	30
-12	41	44
-11	79	78
-10	14	11
-9	143	139
-8	52	49
-7	158	150
-6	197	186
-5	420	409
-4	145	136
-3	148	138
-2	314	305
-1	280	272
0	107	103
1	0*	165
2	0*	146
3	15	15
4	96	94
5	219	214
6	33	34
7	0*	12
8	104	109
9	72	74
10	0*	1
11	0*	4
12	72	72
13	17	14
14	0*	11
15	0*	7
16	15	16
(K = 2)		
-18	13	13
-17	0*	7
-16	74	68
-15	51	49
-14	39	36
-13	12	16
-12	117	118
-11	141	141
-10	134	135
-9	49	49
-8	26	30
-7	240	231
-6	234	233
-5	101	101
-4	155	152
-3	182	173
-2	171	165
-1	30	14
0	208	207
1	93	92
2	52	52
3	74	71
4	40	43
5	88	87
6	72	74
7	0*	7
8	33	36
9	24	24
10	42	44
11	55	56
12	22	26
13	13	14
14	0*	9
15	30	30
(K = 3)		
-17	20	20
-16	79	71
-15	48	47
-14	41	37
-13	45	44
-12	160	151
-11	120	127
-10	64	70
-9	59	66
-8	134	128
-7	157	158
-6	73	77
-4	0*	2
-3	80	80
-2	48	46
-1	27	25
0	84	87
1	65	64
2	0*	3
3	0*	57
4	0*	1
5	0*	98
6	38	40
7	37	35
8	26	31
9	46	47
10	39	39
11	0*	6
12	0*	4
13	0*	5
14	0*	2
(K = 4)		
-15	0*	5
-14	59	58
-13	0*	0
-12	47	45
-11	80	82
-10	121	124
-9	17	15
-8	74	75
-7	173	177
-6	103	99
-5	92	91
-4	65	70
-3	137	146
-2	0*	0
-1	123	127
0	35	37
1	45	42
2	77	83
3	56	50
4	12	10
5	92	90
6	52	53
7	25	24
8	15	16
9	35	33
10	12	9
11	0*	34
12	23	24
13	12	9
14	0*	5
(K = 5)		
-13	0*	1
-12	0*	22
-11	21	24
-10	52	51
-9	0*	7
-8	0*	6
-7	0*	3
-6	39	40
-5	51	53
-4	55	55
-3	77	75
-2	30	29
-1	72	81
0	63	60
1	137	140
2	26	26
3	26	29
4	34	38
5	106	109
6	0*	2
7	58	57
8	81	78
9	27	24
10	0*	20
11	0*	76
12	0*	50
(K = 6)		
-10	36	33
-9	0*	4
-8	52	47
-7	24	28
-6	0*	4
-5	24	23
-4	42	38
-3	59	60
-2	42	40
-1	32	33
0	33	30
1	75	72
2	24	19
3	13	10
4	0*	2
5	52	43
6	95	90
7	30	27
8	29	29
(K = 7)		
0	0*	5
(H = 4)		
(K = 0)		
-18	0*	10
-16	17	18
-14	12	10
-12	72	75
-10	55	57
-8	14	36
-6	116	122
-4	12	11
-2	246	239
0	185	182
2	265	243
4	23	24
6	11	12
8	51	41
10	67	65
12	15	15
14	32	33
(K = 1)		
-18	28	27
-17	87	86
-16	32	30
-15	114	110
-14	127	125
-13	166	171
-12	90	89
-11	139	136
-10	218	217
-9	115	124
-8	197	187
-7	98	92
-6	154	147
-5	59	50
-4	193	183
-3	38	42
-2	160	156
-1	74	74
0	136	125
1	162	165
2	290	300
3	157	163
4	214	210
5	202	205
6	139	134
7	150	151
8	107	109
9	128	131
10	43	38
11	72	72
12	37	37
13	41	39
14	0*	4
15	14	13
(K = 2)		
-17	0*	7
-16	24	24
-15	38	34
-14	78	75
-13	35	35
-12	13	14
-11	35	30
-10	54	55

Table 3 (*cont.*)

L	FØBS	FCAL
-9	29	30
-8	27	29
-7	20	25
-6	70	66
-5	24	26
-4	121	118
-2	172	172
-1	0*	1
0	181	170
1	129	133
2	144	144
3	34	32
4	29	32
5	161	160
6	111	105
7	24	25
8	50	47
9	81	75
10	76	70
11	0*	6
12	29	31
13	24	22
14	20	18
(K = 3)		
-17	15	16
-16	42	44
-15	22	23
-14	13	14
-13	0*	10
-12	50	49
-11	77	81
-10	31	30
-9	13	7
-8	36	34
-7	128	133
-6	56	53
-5	23	19
-4	32	34
-3	76	81
-2	0*	5
-1	27	29
0	109	100
1	18	15
2	35	27
3	0*	6
4	39	43
5	63	65
6	0*	3
7	21	23
8	31	31
9	43	39
10	0*	5
11	22	25
12	27	24
13	13	10
(K = 4)		
-15	51	52
-14	15	12
-13	15	17
-12	26	22
-11	61	62
-10	0*	10
-9	79	82
-8	84	91
-7	23	25
-6	0*	17
-5	78	81
-4	101	106
-3	100	100
-2	63	62
-1	23	21
0	95	94
1	0*	5
2	60	63
3	86	84
4	59	65
5	108	111
6	0*	15
7	54	57
8	49	47
9	81	87
10	30	29
11	30	29
12	0*	16
(K = 5)		
-13	16	17
-12	51	53
-11	0*	3
-10	86	79
-9	0*	38
-8	66	62
-7	14	11
-6	67	58
-5	68	74
-4	20	17
-3	0*	2
-2	41	45
-1	131	142
0	83	80
1	0*	3
2	106	102
3	151	148
4	93	93
5	13	12
6	74	69
7	84	79
8	38	34
9	0*	11
(K = 6)		
-9	73	69
-8	126	123
-7	54	50
-6	0*	6
-5	44	41
-4	84	74
-3	74	73
-2	0*	56
-1	0*	17
0	0*	9
1	71	66
2	95	89
3	58	58
4	28	29
5	38	34
(H = 5)		
(K = 0)		
-18	19	17
-16	137	149
-14	0*	0
-12	210	226
-10	64	67
-8	208	209
-6	118	114
-4	130	130
-2	128	124
0	56	55
2	89	86
4	18	18
6	28	26
8	62	70
10	0*	12
12	40	43
14	18	19
(K = 1)		
-18	0*	51
-17	0*	30
-16	0*	0
-15	87	82
-14	65	62
-13	50	49
-12	20	24
-11	165	160
-10	46	52
-9	20	19
-8	0*	8
-7	115	108
-6	153	156
-5	106	100
-4	110	104
-3	82	80
-2	100	95
-1	237	233
0	122	118
1	169	169
2	39	44
3	102	96
4	46	46
5	102	101
6	66	66
7	46	49
8	0*	4
9	60	64
10	35	35
11	44	46
12	0*	3
13	33	36
14	23	23
(K = 2)		
-17	27	27
-16	15	17
-15	17	15
-14	54	53
-13	0*	4
-12	18	19
-11	0*	2
-10	72	73
-9	17	18
-8	14	14
-7	39	43
-6	0*	3
-5	0*	11
-4	50	47
-3	119	119
-2	91	88
-1	0*	2
0	205	202
1	123	129
2	34	35
3	41	40
4	162	168
5	31	29
6	26	28
7	0*	46
8	40	43
9	0*	5
10	17	22
11	21	22
12	18	19
13	0*	14
(K = 3)		
-16	52	54
-15	0*	6
-14	0*	0
-13	0*	11
-12	61	60
-11	16	42
-10	20	22
-9	57	58
-8	28	29
-7	67	64
-6	17	20
-5	76	80
-4	22	24
-3	0*	14
-2	120	121
-1	59	60
0	82	85
1	109	108
2	248	260
3	0*	4
4	94	96
5	105	112
6	182	186
7	19	16
8	48	45
9	64	65
10	72	74
11	20	18
12	0*	5
(K = 4)		
-14	0*	0
-13	37	32
-12	43	39
-11	56	57
10	0*	0
-10	19	16
-9	0*	11
-8	92	87
-7	48	48
-6	35	32
-5	109	120
-4	42	38
-3	64	65
-2	56	59
0	79	82
1	125	124
2	76	78
3	66	67
4	93	107
5	52	52
6	49	50
7	0*	0
8	50	50
9	0*	0
(K = 5)		
-12	0*	38
-11	81	69
-10	23	14
-9	0*	10
-8	19	14
-7	74	67
-6	37	39
-5	21	19
-4	0*	6
-3	35	32
-2	28	34
-1	0*	41
0	37	32
1	0*	4
2	22	23
3	59	58
4	56	52
5	0*	5
6	35	32
7	52	48
8	36	35
(K = 6)		
-8	33	34
-7	11	5
-6	33	30
-5	20	20
-4	71	68
-3	30	27
-2	47	43
-1	24	25
0	22	20
1	33	31
2	26	47
3	13	12
4	24	20
(H = 6)		
(K = 0)		
-16	0*	4
-14	33	32
-12	72	71
-10	53	52
-8	141	142
-6	16	19
-4	118	124
-2	42	38
0	55	53
2	45	40
4	0*	5
6	47	48
8	56	54
10	36	35
12	90	90
(K = 1)		
-17	0*	8
-16	15	12
-15	0*	0
-14	0*	8
-13	34	33
-12	28	27
-11	93	96
-10	39	34
-9	71	67
-8	44	45
-7	102	105
-6	99	95
-5	102	97
-4	13	10
-3	70	64
-2	58	58
-1	121	118
0	93	84
1	211	204
2	40	38
3	74	72
4	75	69
5	113	111
6	52	55
7	22	20
8	29	26
9	26	25
10	0*	9
11	58	56
12	12	7
(K = 2)		
-16	58	61
-15	18	16
-14	16	14
-13	61	63
-12	83	83
-11	0*	5
-10	63	68
-9	40	44
-8	0*	7
-7	17	18
-6	80	85
-5	82	87
-4	153	151
-3	49	53
-2	55	54
-1	170	171
0	234	219
1	83	80
2	15	16
3	129	127
4	105	101
5	54	55
6	0*	3
7	30	33
8	31	32
9	0*	13
10	0*	17
11	0*	7
12	13	13
(K = 3)		
-15	14	10
-14	0*	4
-13	12	10
-12	85	80
-11	0*	5
-10	45	47
-9	69	70
-8	28	20
-7	28	37
-6	134	135
-5	129	132
-4	69	72
-3	56	60
-2	206	207
-1	108	112
0	76	75
1	21	12
2	113	110
3	56	53
4	14	13
5	0*	10
6	11	7
7	0*	4
8	0*	1
9	0*	10
10	28	24
(K = 4)		
-13	35	28
-12	14	11
-11	34	31
-10	28	26
-9	0*	6
-8	52	56
-7	40	40
-6	39	40
-5	27	24
-4	111	111
-3	0*	9
-2	62	63
-1	98	102
0	81	80
1	94	94
2	48	43
3	86	83
4	0*	7
5	94	91
6	20	19
7	11	8
8	17	18
9	29	31
(K = 5)		
-11	22	23
-10	22	22
-9	31	34
-8	15	17
-7	29	30
-6	37	38
-5	24	27
-4	37	37
-3	47	48
-2	30	29
-1	16	19
0	34	32
1	35	34
2	21	20
3	0*	0
4	25	21
5	23	23
6	29	37
(K = 6)		
-4	44	40
-3	0*	0
-2	58	58
-1	26	27
(H = 7)		
(K = 0)		
-16	11	11
-14	0*	5
-12	0*	7
-10	61	61
-8	22	21
-6	28	37
-4	0*	8
-2	81	88
0	50	60
2	69	80
4	0*	16
6	13	23
8	40	32
10	0*	11
(K = 1)		
-16	0*	5
-15	18	21
-14	0*	10
-13	26	28
-12	32	32
-11	89	96
-10	15	12
-9	114	118
-8	119	123
-7	169	175
-6	92	92
-5	149	149
-4	192	191
-3	157	161
-2	163	166
-1	85	81
0	131	127
1	32	30
2	98	103
3	0*	3
4	0*	1
5	16	12
6	0*	0
7	21	24
8	38	37
9	24	24
10	46	41
(K = 2)		
-15	64	61
-14	18	14
-13	11	8
-12	68	68
-11	36	33
-10	31	41
-9	28	30
-8	86	93
-7	16	17
-6	63	67
-5	80	80
-4	39	40
-3	35	37
-2	55	55
-1	49	52
0	38	42
1	20	19
2	36	35
3	15	14
4	51	51
5	16	17
6	16	14
7	0*	10
8	27	24
9	0*	12
10	12	12
(K = 3)		
-14	42	48
-13	0*	5
-12	19	20
-11	13	11
-10	55	58
-9	31	31
-8	57	59
-7	0*	7
-6	41	43
-5	68	69
-4	0*	5
-3	11	10
-2	48	48
-1	54	54
0	42	43
1	17	18
2	38	38
3	18	13
4	0*	7
5	20	18
6	0*	4
7	0*	4
8	16	16
(K = 4)		
-12	0*	0
-11	21	17
-10	27	26
-9	66	71
-8	11	9
-7	34	34
-6	16	15
-5	100	103
-4	16	15
-3	52	53
-2	44	45
-1	42	43
0	34	32
1	35	34
2	45	42
3	32	30
4	46	43
5	18	15
6	35	29
(K = 5)		
-8	11	13
-7	22	20
-6	57	58
-5	0*	1
-4	54	52
-3	63	64
-2	69	68
-1	12	9
0	63	53
1	57	55
2	41	42
3	0*	7
(H = 8)		
(K = 0)		
-14	31	30
-12	13	11
-10	187	189
-8	18	15
-6	294	299
-4	19	18
-2	208	224
0	40	41
2	43	45
4	19	19
6	14	13
8	13	14
(K = 1)		
-15	19	19
-14	20	17
-13	0*	9
-12	66	68
-11	22	20
-10	21	21
-9	50	49
-8	81	81
-7	33	31
-6	16	19
-5	113	111
-4	40	43
-3	46	48
-2	0*	6
-1	87	90
0	23	12
1	0*	11
2	30	29
3	0*	2
4	31	23
5	43	36
6	28	28
7	23	22
8	0*	1
(K = 2)		
-14	0*	11
-13	27	26
-12	51	48
-11	72	70
-10	31	33
-9	21	18
-8	57	57
-7	35	35
-6	41	42
-5	35	35
-4	27	25
-3	13	14
-2	20	17
-1	30	33
0	14	15
1	0*	6
2	12	7
3	31	25
4	24	25
5	0*	7
6	35	29
7	58	56
(K = 3)		
-12	13	12
-11	24	20
-10	51	51
-9	0*	0
-8	25	23
-7	18	19
-6	54	55
-5	26	25
-4	16	15
-3	37	37
-2	31	30
-1	24	22
0	24	21
1	25	23
2	22	21
3	16	16
4	12	9
5	0*	13
6	0*	10
(K = 4)		
-10	0*	2
-9	26	23
-8	0*	0
-7	13	12
-6	41	40
-5	62	62
-4	19	18
-3	24	20
-2	62	59
-1	59	58
0	30	26
1	19	17
2	22	21
3	0*	6
(H = 9)		
(K = 0)		
-12	58	60
-10	18	18
-8	12	11
-6	66	66
-4	53	55
-2	93	99
0	24	24
2	35	35
4	0*	6
6	0*	11
(K = 1)		
-13	39	39
-12	11	9
-11	0*	9
-10	43	39
-9	38	37
-8	20	19
-7	40	41
-6	31	31
-5	0*	4
-4	30	30
-3	51	53
-2	0*	9
-1	43	38
0	31	33
1	31	32
2	0*	12
3	0*	5
4	16	18
5	19	16
6	20	23
(K = 2)		
-12	25	24
-11	77	76
-10	84	82
-9	25	22
-8	19	16
-7	87	88
-6	104	104
-5	0*	7
-4	0*	3
-3	43	45
-2	55	58
-1	12	8
0	18	15
1	28	25
2	36	31
3	0*	5
4	20	18
5	46	47
(K = 3)		
-10	33	31
-9	26	22
-8	16	14
-7	20	17
-6	77	71
-5	31	24
-4	25	25
-3	24	23
-2	40	35
-1	0*	1
0	43	34
1	36	33
2	11	14
(H = 10)		
(K = 0)		
-10	0*	6
-8	14	15
-6	0*	8
-4	42	45
-2	22	25
0	27	27
2	0*	5
(K = 1)		
-10	0*	0
-9	0*	1
-8	21	20
-7	15	18
-6	17	17
-5	0*	4
-4	0*	0
-3	50	49
-2	38	39
-1	51	46
0	21	29
1	53	55
2	0*	53
(K = 2)		
-8	58	54
-7	27	24
-6	16	35
-5	54	52
-4	0*	6
-3	0*	3
-2	42	37
-1	17	16
0	45	46

on one of the maps and the signs used to compute that map were used to refine the atomic coordinates. The indicated positions of these atoms were taken as the starting points of a least-squares analysis, using the set of 242 reflections for which phases had been established. Initially, the atoms were assumed to have isotropic thermal motion. The residual (*R*),

$$R=\frac{\Sigma\,||F_{\text{obs}}|-|KF_{\text{calc}}||}{\Sigma\,|F_{\text{obs}}|}$$

for this limited set of data was reduced to 0·128 before including additional reflection data in the least-squares analysis. Because of limitations in the least-squares program and in the programmed data storage area, the data were split arbitrarily into two groups, each containing about 750 reflections and refined separately to residuals of 0·22 and 0·20, with only slight differences (0·001–0·0012) among the atomic coordinates derived from the two sets separately.

Refinement was then continued with the use of all the data. The isotropic refinement converged to $R=0{\cdot}15$. After the introduction of anisotropic temperature factors, *R* decreased to 0·12. At this point an electron density difference map was computed. A composite drawing, based on this map, revealed the locations of all thirteen hydrogen atoms in the asymmetric unit of structure. It was also clear at this stage that one hydrogen atom had been shifted from the carboxyl to the amine group to form a zwitterion. After introduction of the hydrogen atoms into the least-squares analysis with fixed and finally with variable isotropic temperature factors, the residual was reduced to 0·05 (not including the unobserved reflections). The final atomic parameters and temperature factors are listed in Table 2. The observed and calculated structure factors are listed in Table 3; the unobserved reflections (given zero weight in the least-square analysis) are indicated by asterisks. The estimation of σ used in the standard weighting scheme was:

$$\begin{array}{ll} F_{\text{obs}}>10{\cdot}0 & \sigma=0{\cdot}1F_{\text{obs}} \\ F_{\text{obs}}\le 10{\cdot}0 & \sigma=1{\cdot}0 \\ F_{\text{obs}}=\ 0{\cdot}0 & \text{weight}=0\,. \end{array}$$

Discussion

Accuracy of the structure

The refinement of the structure was continued until changes of coordinates of non-hydrogen atoms between successive least-squares cycles were less than two per cent of their standard errors; the corresponding changes for hydrogen atoms were less than four per cent.

Standard errors of parameters were computed by inversion of the least-squares matrices. The indicated values were then multiplied by two and rounded off to the nearest significant digit before being included in this manuscript. Hamilton (1965) has emphasized the usefulness of a procedure of this sort to furnish a measure of the accuracy, rather than the precision, of a crystal structure determination. The final value of *R* for the 1194 observed reflections was 5·0%.

Temperature factors

Temperature factors are listed in Tables 2 and 6. The magnitudes of atomic thermal motions along the principal axes of the thermal ellipsoids are given in Table 6 together with the r.m.s. thermal displacements of the hydrogen atoms. As expected, the thermal motions of the carbon atoms are smallest along the molecular chain direction. The magnitudes of the thermal motions of the atoms in the molecular chain are largest near the center of the chain, *i.e.* at C(3) and C(4). The hydrogen bonds at both ends of the molecules restrict the freedom of movement of atoms nearest those bonds and have least effect on atoms near the chain centers. Only axis 3 of O(1) does not fit this description; its anomalously large value may reflect the fact that it is associated with only one hydrogen bond; O(2) is involved in two such bonds.

Molecular configuration

Fig. 1 is a schematic drawing of the molecule, listing bond lengths and approximate magnitudes and orientations of the principal axes of the atomic thermal ellipsoids relative to the long molecular direction. Intramolecular bond lengths and intermolecular N–H–O distances are listed in Tables 4 and 5. As might have been expected, the two carbon–oxygen bonds in the molecule are almost equal in length, 1·235 and 1·261 Å both ±0·005 Å; after correction for 'riding' of the oxygen atoms on the carbon atoms to which they are bonded (Busing & Levy, 1964) these become 1·263 and 1·271 Å. Similar results have been reported by Marsh and co-workers in their very precise analyses of the zwitterions L-lysine monochloride dihydrate (Wright & Marsh, 1962) with C–O distances of 1·246 and 1·250 Å and L-alanine (Simpson & Marsh, 1966) with 1·253 and 1·265 Å.

Table 4. *Bond lengths and angles*

Bond lengths*		Bond angles‡	
C(1)–O(1)	1·235 Å†	O(1)–C(1)–O(2)	124·0°
C(1)–O(2)	1·261†	O(1)–C(1)–C(2)	118·3
C(1)–C(2)	1·523	O(2)–C(1)–C(2)	117·7
C(2)–C(3)	1·520	C(1)–C(2)–C(3)	110·8
C(3)–C(4)	1·526	C(2)–C(3)–C(4)	112·7
C(4)–C(5)	1·516	C(3)–C(4)–C(5)	112·8
C(5)–C(6)	1·511	C(4)–C(5)–C(5)	112·5
(Average C–C	1·519)	C(5)–C(6)–N	110·9
		(Average C–C–C angle	112·2°)
C(6)–N	1·485		
N–H–O(1)	2·753		
N–H–O(2)	2·728		
N–H–O(2′)	2·814		

* The average standard deviation of the bond lengths is 0·005 Å; the largest is 0·006 Å, the smallest 0·004 Å.

† After correction for 'riding' of the oxygen on C(1) these become C(1)–O(1) = 1·263, C(1)–O(2) = 1·271 Å.

‡ The standard deviations of these bond angles range from 0·3 to 0·4°.

The average length of the five carbon–carbon bonds in ε-aminocaproic acid is 1·519 Å. For the two crystal structures mentioned above, Marsh and co-workers reported average carbon–carbon bond lengths of 1·523 and 1·525 Å. It appears that the 'normal' single carbon–carbon bond length, at least for molecules of this type, is in the range 1·519 to 1·525 Å.

Hahn (1957) reported an apparent lengthening of the carbon–nitrogen ($C–NH_3^+$) bond in a number of zwitterions; he listed an average value of 1·503 Å com-

Table 5. *Bond lengths and angles involving hydrogen atoms*

Lengths*		Angles†		Angles†	
C(2)–H(1)	0·97 Å	C(1)–C(2)–H(1)	109°	N——C(6)–H(9)	112°
C(2)–H(2)	0·97	C(3)–C(2)–H(1)	108	N——C——H(10)	102
C(3)–H(3)	1·03	C(1)–C(2)–H(2)	111		
C(3)–H(4)	0·97	C(3)–C(2)–H(2)	111	H(12)–N——H(11)	106
C(4)–H(5)	1·07	C(2)–C(3)–H(3)	110	H(13)–N——H(12)	104
C(4)–H(6)	0·92	C(4)–C(3)–H(3)	107	H(11)–N——H(13)	116
C(5)–H(7)	1·03	C(2)–C(3)–H(4)	114		
C(5)–H(8)	1·02	C(4)–C(5)–H(4)	113	H(1)—C(2)–H(2)	109
C(6)–H(9)	0·89	C(3)–C(4)–H(5)	109	H(3)—C(3)–H(4)	99
C(6)–H(10)	1·00	C(5)–C(4)–H(5)	106	H(5)—C(4)–H(6)	114
		C(3)–C(4)–H(6)	107	H(7)—C(5)–H(8)	106
(Average C–H = 0·99 Å)		C(5)–C(4)–H(6)	108	H(9)—C(6)–H(10)	112
N–H(11)	0·94	C(4)–C(5)–H(7)	111		
N–H(12)	0·92	C(6)–C(5)–H(7)	111	(Average H–C–H	108°)
N–H(13)	1·01	C(4)–C(5)–H(8)	107		
				(hydrogen bonds)	
(Average N–H	0·96 Å)	C(6)–C(5)–H(8)	110	N–H(13)–O(1)	174
		C(5)–C(6)–H(9)	110	N–H(12)–O(2)	166
		C(5)–C(6)–H(10)	109	N–H(11)–O(½)	179
		(Average C–C–H	109·5°)		

* The standard deviations of the bond lengths are 0·05 Å, except 0·06 Å for C(3)–H(3) and C(3)–H(4).

† The standard deviation of the bond angles involving one hydrogen atom is 3°; for those involving two hydrogen atoms it is 4°.

Table 6. *Thermal motions and orientations of thermal ellipsoids*

	R.M.S. components of thermal motion along principal axes (Å)				Angles between principal axes and vector defined by C(2)–C(6) (°)		
	Axis 1	Axis 2	Axis 3	$\sqrt{\overline{\mu^2}}$ (Å)	Axis 1	Axis 2	Axis 3
O(1)	0·138	0·194	0·312	0·39	132	56	61
O(2)	0·164	0·184	0·229	0·34	127	64	49
C(1)	0·143	0·181	0·196	0·30	24	114	94
C(2)	0·148	0·196	0·217	0·33	30	118	82
C(3)	0·151	0·204	0·256	0·36	21	110	95
C(4)	0·149	0·205	0·234	0·34	24	114	85
C(5)	0·149	0·210	0·213	0·33	26	92	64
C(6)	0·146	0·191	0·221	0·33	32	120	80
N	0·146	0·184	0·221	0·32	144	61	71

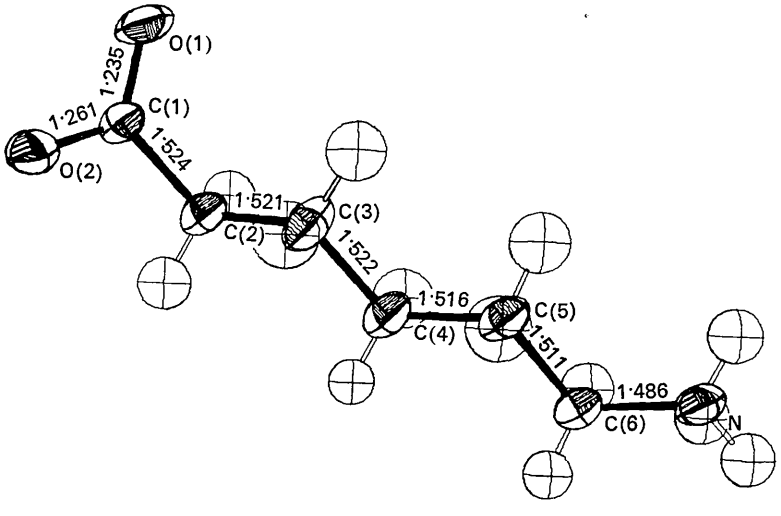

Fig. 1. Schematic drawing of the ε-aminocaproic acid molecule.

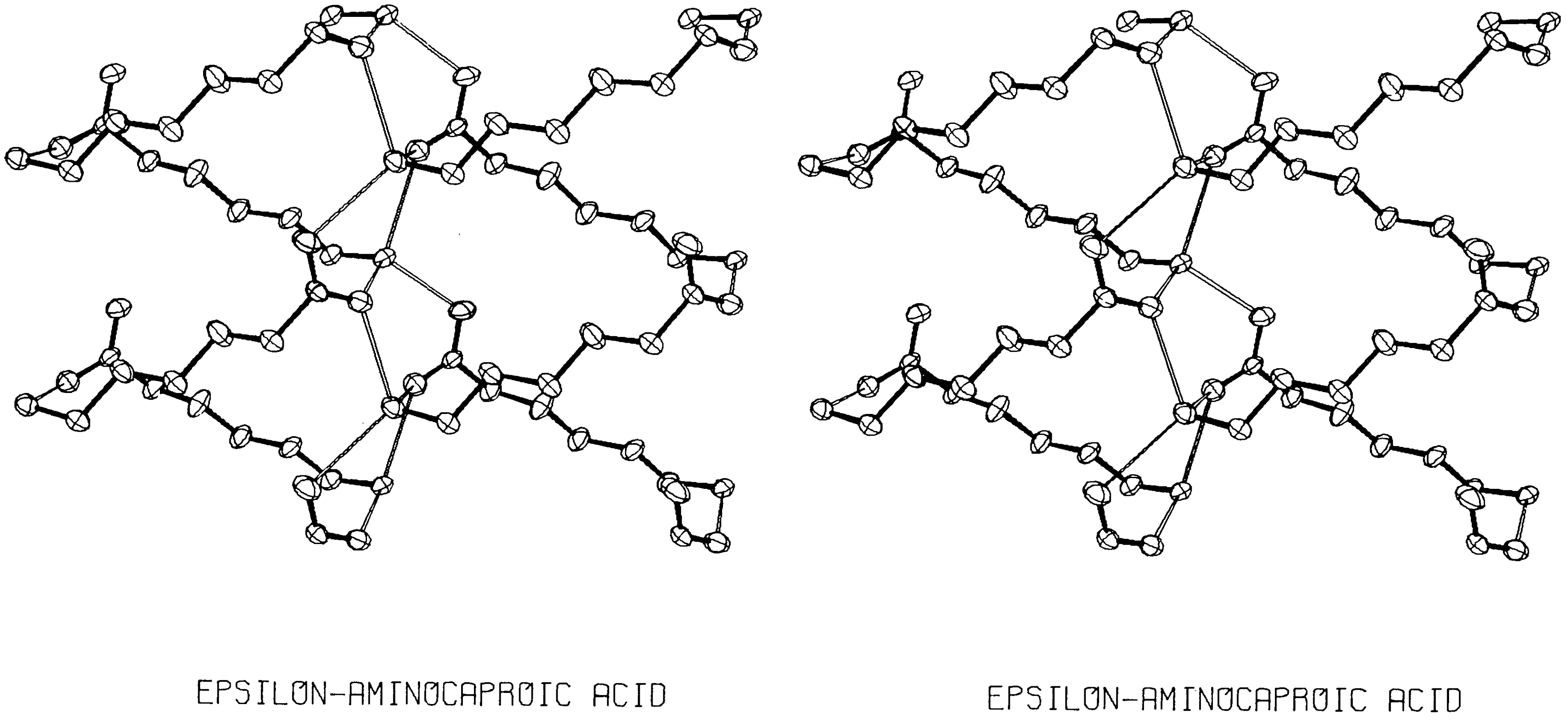

Fig. 2. Stereo pair view along the *c* axis.

pared with a normal carbon–nitrogen single bond length of 1·47 Å. In ε-aminocaproic acid this distance is 1·485 ± 0·005 Å; in the structures mentioned above, Marsh and co-workers reported corresponding values of 1·480, 1·484 and 1·491 Å. In view of the relatively high accuracy of these later values, it seems likely that the lengthening of this bond above the normal value is a real effect but one which is substantially smaller than indicated by the values quoted by Hahn.

The three hydrogen bonds formed by each nitrogen atom are: 2·753 [N–O(1)], 2·728 [N–O(2)] and 2·814 Å [N–O(2′)], all ± 0·005 Å. It is evident that the fact that O(2) participates in two hydrogen bonds, while O(1) is involved in only one, does not affect the lengths of the hydrogen bonds significantly.

The average distance between hydrogen atoms bonded to the same carbon atom is 1·59 ± 0·065 Å; the corresponding average distance among the hydrogen atoms in the NH_3^+ group is 1·55 ± 0·065 Å.

Bond angles in the molecule are 'normal', *i.e.* similar to those reported for molecules of this general type. The average C–C–C angle is 112·2°.

The spatial arrangement of the non-hydrogen atoms is conveniently described in terms of the dihedral angles between the planes of adjacent triatomic groups. Thus, the angle between O(1), O(2), C(1) and C(1), C(2), C(3) is 98·4°; it is 7·6° between C(1), C(2), C(3) and C(3), C(4), C(5) and 5·6° between the latter group and C(5), C(6), N ... all ± 0·2°.

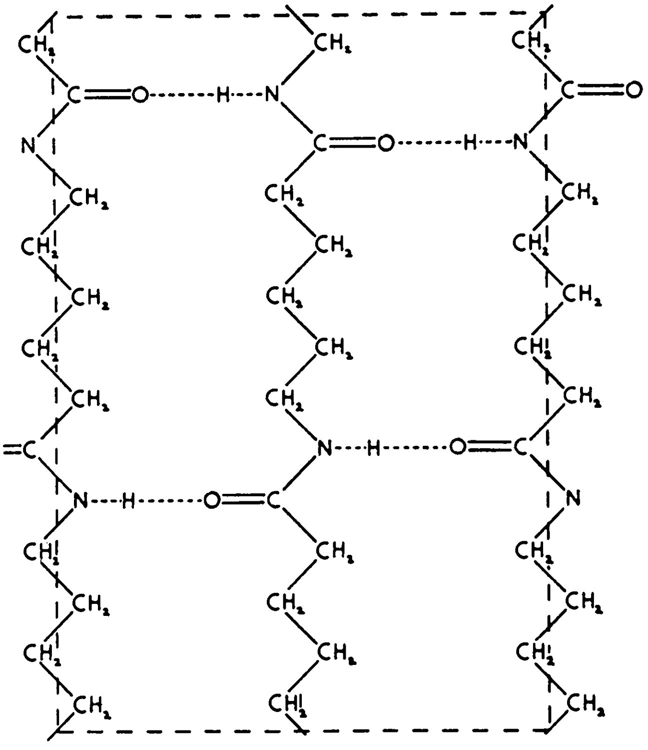

Fig. 3. Molecular layer in Nylon-6.

Molecular packing

A stereo pair drawing (Johnson, 1965) of a portion of the unit cell, viewed along **c**, is shown in Fig. 2. Two sets of molecular chains may be distinguished; one slopes down to the right along [110] and is inclined approximately 27½° to the horizontal axis **a**; the other is oriented along [1$\bar{1}$0]. Each set lies in one layer. There are four such layers in each unit cell, all roughly perpendicular to **c**.

Each nitrogen atom forms three hydrogen bonds; two link it with oxygen atoms [O(1) and O(2′)] in molecules in the layer containing the nitrogen atom. The third bond is directed to an oxygen atom O(2″) in an adjacent layer.

Hydrogen bonds of the latter type link the layer at $z=\frac{1}{8}$ to that at $\frac{3}{8}$ and the layer at $z=\frac{5}{8}$ to that at $\frac{7}{8}$, forming strongly bonded double layers. These in turn are held together by relatively weak intermolecular interactions.

The solid state conversion to Nylon-6

We have mentioned above that ε-aminocaproic acid undergoes polycondensation in the solid state. Under the combined influence of heat and high vacuum single crystals of the monomer transform to highly crystalline, oriented Nylon-6. It is possible to relate some structural features of the latter to the crystal structure of the monomer.

The crystal structure of Nylon-6 has been determined by Holmes, Bunn & Smith (1955). The unit cell is monoclinic with $a=9·56$, $b=17·2$, $c=8·01$ and $\beta=112·5°$; the space group is $P2_1$ and there are eight 'condensed' monomer units in the unit cell. The structure may be described in terms of polymeric chains linked to one another by N–H–O bonds to form layers parallel to *bc*. The chains are parallel to **b** (Fig. 3).

Examination of Fig. 3 reveals that the C=O, N, C sequence in one chain is reversed in successive chains within the layer. It will be recalled that in the monomer the reactive groups (*i.e.* carboxyl and NH_3^+) and the carbon atoms are arranged in the same sequence in all molecules in a given layer. The sequence is reversed in adjacent layers. It is evident that individual polymeric chains of Fig. 3 are derived from molecules lying within one layer in the crystal. At some stage the hydrogen bonds are broken and water is split out, leaving one hydrogen atom bonded to each nitrogen, and one oxygen atom in a carbonyl group. The carbon atom to which the oxygen is bonded [C(1)] forms a single bond link with the nitrogen atom.

Adjacent *chains* within one layer in Fig. 3 are derived from adjacent *layers* of the monomeric crystal. We have noted that the latter not only differ from one another in atomic sequence, but are inclined to each other by 55°. In the course of the polycondensation process these chains must change their relative orientations to become parallel to one another and to link up with one another by hydrogen bonding as shown in Fig. 3.

Recent electron microscope studies of crystalline Nylon-6 specimens prepared from single crystals of the monomer reveal that twinning is of frequent occurrence in the polymer crystals (Fischer, 1965). The twinning appears to involve rotation of successive layers, or groups of layers, of the type shown in Fig. 3, by 55° relative to one another. Such twinning is not observed in Nylon specimens prepared from the melts (Macchi, 1966). Although the detailed mechanism of the twinning is not known, it is not difficult to relate the 55° twin angle of the polymer to the 55° by which molecular chains in successive layers of the monomer are inclined to one another.

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The Crystal Structure of Thiodiglycollic Acid*

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Thiodiglycollic acid, $S(CH_2COOH)_2$, crystallizes in space group *Pnam* with 4 molecules in the unit cell of dimensions $a = 5{\cdot}050 \pm 0{\cdot}005$, $b = 6{\cdot}701 \pm 0{\cdot}003$, $c = 17{\cdot}742 \pm 0{\cdot}004$ Å. The structure has been solved from two-dimensional photographic data and has been refined by least squares with three-dimensional diffractometer data. The structure consists of parallel infinite chains of hydrogen bonded molecules. Hydrogen bonding takes place between carboxyl groups around the centre of symmetry; they are coplanar within experimental error.

Introduction

Thiodiglycollic acid, $S(CH_2COOH)_2$ (also known as methyl sulphide α,α-dicarboxylic acid or thiodiacetic acid), is of importance because of its use as a precipitating organic reagent for zirconium (Sant & Sant, 1959). It is used for the detection of copper, lead, mercury and silver, and also for the estimation of cadmium.

A preliminary report of the structure has already been published (Roy, 1965).

Experimental

Single crystals of thiodiglycollic acid were grown by slow evaporation of a concentrated aqueous solution at room temperature. The crystals appeared as thin plates elongated in the [100] direction. The unit-cell dimensions determined by means of a General Electric Single Crystal Orienter are: $a = 5{\cdot}050 \pm 0{\cdot}005$, $b = 6{\cdot}701 \pm 0{\cdot}003$, $c = 17{\cdot}742 \pm 0{\cdot}004$ Å.

Systematic absences as found on Weissenberg photographs about the *a* and *b* axes were consistent with the space groups *Pnam* and $Pna2_1$. The density as determined by flotation is 1·66 $g.cm^{-3}$, and the calculated density for four molecules per unit cell is 1·70 $g.cm^{-3}$.

The structure was solved from the two projections along [100] and [010]. The $0kl$ and $h0l$ intensities were estimated visually from the integrated Weissenberg photographs. The three-dimensional data used for the refinement of the structure were collected with a General Electric diffractometer equipped with a scintillation counter using β-filtered Cu $K\alpha$ radiation and discrimination.

Peak intensities were measured which were converted to integrated intensities in the following way. For a set of 30 reflexions of θ values, distributed over the accessible θ range, both peak intensities and inte-

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