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Precision Neutron Diffraction Structure Determination of Protein and Nucleic Acid Components. VII. The Crystal and Molecular Structure of the Amino Acid L-Lysine Monohydrochloride Dihydrate*

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A neutron diffraction study of L-lysine monohydrochloride dihydrate, $C_6H_{15}N_2O_2.Cl.2H_2O$, has been carried out. The structure is monoclinic, space group $P2_1$ with $Z=2$. Cell parameters are: $a=7{\cdot}492$ (1), $b=13{\cdot}320$ (4), $c=5{\cdot}879$ (1) Å, $\beta=97{\cdot}79$ (1)° [Wright & Marsh, *Acta Cryst.* (1962), **15**, 54]. Least-squares refinements based on 1240 reflections led to a conventional R value of 0·030. The neutron-diffraction results confirm the structure previously determined by X-ray diffraction [Raman *Z. Kristallogr.* (1959). **111**, 301; Wright & Marsh (1962)]; the main new feature is the precise determination of the hydrogen atom positions. The refined thermal parameters were fitted to rigid-body motions; these calculations indicate axial librations of 8·8 (5) and 12·7 (4)° for the α-NH_3^+ and ζ-NH_3^+ groups respectively. Assuming a threefold cosine potential, these librational amplitudes lead to estimated barriers to rotation of 7·0 kcal.mole^{-1} for the α-NH^3_+ group and 2·9 kcal.mole^{-1} for the ζ-NH^3_+ group.

The neutron diffraction study of L-lysine monohydrochloride dihydrate described here was performed to provide detailed information about the hydrogen atom stereochemistry in this crystalline amino acid. This paper describes one of a series of investigations of amino acid crystal structures, which should provide precise hydrogen bonding parameters for these systems, and which ultimately aims to arrive at a better understanding of the role of hydrogen bonding in larger, more complicated structures. Since completing this work, we have learned of a similar independent study by Bugayong, Sequeira & Chidambaram (1972).

Crystal data

L-Lysine monohydrochloride dihydrate, $NH_3^+[CH_2]_4CH(NH_3)^+COO^-.Cl^-.2H_2O$, monoclinic, $P2_1$, $Z=2$. An earlier X-ray study (Wright & Marsh, 1962) established the cell dimensions: $a=7{\cdot}492$ (1), $b=13{\cdot}320$ (4), $c=5{\cdot}879$ (1) Å and $\beta=97{\cdot}79$ (1)°. The density calculated from this unit cell is 1·25 g.cm^{-3} (Wright & Marsh, 1963).

Experimental

Large, well-formed, single crystals of L-lysine monohydrochloride dihydrate were grown by slow evaporation from aqueous 1 M NH_4Cl at pH 5·4. A crystal weighing 23·6 mg, elongated in the **c** direction and bounded by major faces {110} and {001}, was mounted on a four-circle diffractometer at the Brookhaven High Flux Beam Reactor. In order to minimize multiple diffraction effects, the **c*** axis of the crystal was aligned approximately five degrees off the diffractometer φ axis. The unit-cell parameters and orientation matrix were refined by least-squares calculations using as input the setting angles of 29 automatically centered reflections well distributed in reciprocal space. The cell parameters so obtained agree with the more precise X-ray values to better than two parts per thousand, and the latter have been used throughout this paper.

Data were collected automatically using the Brookhaven Multi-Spectrometer Control System (Beaucage, Kelley, Ophir, Rankowitz, Spinrad & van Norton, 1966) with a crystal-monochromatized {Ge(111)} neutron beam of wavelength 1·014 (1) Å. The length of the standard θ–2θ step scan was varied according to the formula $\Delta(2\theta)=1{\cdot}4°\ (1+8\tan\theta)$, and the step increment was chosen to give approximately 40 points in each scan. Intensities were measured for 3313 reflections with l positive and $d^*\le 1{\cdot}34$ Å^{-1}.

Background corrections were made by use of a method which divides peak and background in such a way that $\sigma_{\rm count}(I)/I$ is minimized (Lehmann, Hamilton & Larsen, 1972). Here I is the integrated intensity and $\sigma_{\rm count}(I)$ its estimated standard deviation (e.s.d.) based on counting statistics. An absorption correction was carried out by integration over a Gaussian grid. The neutron-absorption coefficient $\mu=2{\cdot}69$ cm^{-1} was calculated from tabulated mass-absorption coefficients (*International Tables for X-ray Crystallography*, 1961), assuming an incoherent neutron cross-section for hydrogen of 40 barns. Squared observed structure factors were obtained as $F_o^2=I_{\rm corrected}\sin 2\theta$, and were averaged over space-group symmetry to give mean values for 1484

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unique reflections. The agreement factor given by $\sum|F_o^2-\bar{F}_o^2|/\sum\bar{F}_o^2$, where $\bar{F}_o^2$ is the mean value for the symmetry equivalent reflections, is equal to 0·062. 1240 reflections having $F_o^2\geq 3\sigma_{\rm count}(F_o^2)$ were included in the subsequent refinements.

Structure refinement

The hydrogen atoms were located in a difference Fourier synthesis computed using phases calculated from the nonhydrogen atom positions determined by Wright & Marsh (1962). The structure was refined by full-matrix least-squares techniques varying position and isotropic temperature factors for all atoms. Refinements varying anisotropic temperature factors were then carried out by alternative variation of two blocks, each containing 235 out of the total of 289 parameters. Refinements were continued until the maximum shift in any parameter was less than one-fifth of its e.s.d. Neutron scattering lengths used were: $b_{\rm Cl}=0{\cdot}958$, $b_{\rm C}=0{\cdot}663$, $b_{\rm N}=0{\cdot}940$, $b_{\rm O}=0{\cdot}575$, and $b_{\rm H}=-0{\cdot}372$ (all $\times 10^{-12}$ cm). The quantity minimized in the refinements was $\sum w|F_o^2-|F_c|^2|^2$; weights were chosen as $w=1/\sigma^2(F_o^2)$ with $\sigma^2(F_o^2)=\sigma^2_{\rm count}(F_o^2)+(0{\cdot}04F_o^2)^2$.

The crystal used for data collection showed moderate extinction effects, and an extinction correction was introduced at the start of the refinement, following an approximation due to Zachariasen (1967). The extinction parameter g converged to a value of $0{\cdot}28\ (2)\times 10^4$, which gives a minimum extinction correction factor on F^2 of 0·76 for the 020 reflection.

The final weighted and unweighted R values on F^2 are

$$R_{F^2}=\sum|F_o^2-|F_c|^2|/(\sum F_o^2)=0{\cdot}045$$

$$R_{wF^2}=[\sum w|F_o^2-|F_c|^2|^2/(\sum wF_o^4)]^{1/2}=0{\cdot}067$$

and the conventional R value on F is 0·030. The final values of the squared structure factors are given in

Table 1. *Squared structure factors with e.s.d.'s used to derive weights for least-squares refinement*

The columns give h, l, F_o^2, $\sigma(F^o_2)$, $|F_c|^2$. Multiply by 0·01 to place on an absolute scale. Extinction corrections have been applied to F^o_2.

H	L	FO	SIG	FC
*** K= 0 ***				
0	1	227	9	229
0	2	32	3	33
0	3	1370	56	1335
0	4	1485	61	1530
0	5	4034	165	3795
0	6	71	21	70
0	7	806	42	701
1	-7	236	20	258
1	-6	117	13	131
1	-5	341	18	378
1	-4	5450	220	6400
1	-3	30	3	30
1	-1	53	3	44
1	1	64	3	60
1	3	212	10	200
1	4	7659	309	7516
1	5	788	37	789
1	7	92	16	82
2	-7	280	21	298
2	-6	1114	50	1222
2	-5	3215	132	3460
2	-4	68	7	57
2	-3	1847	75	1926
2	-2	658	27	646
2	-1	3748	151	3
2	0	8036	322	7
2	1	126	6	125
2	2	30	6	23
2	3	169	10	170
2	4	740	13	810
2	5	642	11	647
2	6	350	21	303
2	7	388	28	420
3	-7	105	17	116
3	-5	1499	64	1490
3	-4	4294	174	4671
3	-3	109	7	104
3	-2	621	26	618
3	-1	1553	63	1541
3	0	4066	162	4048
3	3	1606	59	1473
3	4	152	13	158
3	5	776	37	769
3	6	54	16	61
4	-5	852	19	796
4	-4	292	16	274
4	-3	20	5	12
4	-2	72	6	69
4	-1	4299	173	4334
4	0	1374	56	1366
4	2	42	5	47
4	3	356	18	373
4	4	52	17	28
4	6	109	20	53
5	-5	521	27	521
5	-4	4113	168	4048
5	-2	1295	56	1199
5	0	2553	103	2521
5	1	1674	69	1573
5	2	235	13	241
5	3	1206	52	1259
5	4	205	17	184
5	5	242	22	227
6	-5	42	10	47
6	-3	1095	47	1089
6	-2	429	21	436
6	-1	672	30	740
6	0	128	8	133
6	1	410	20	417
6	3	232	18	26
6	4	966	46	947
6	5	260	28	191
7	-5	392	26	372
7	-4	315	20	318
7	-3	247	16	286
7	-1	567	27	537
7	1	681	32	682
7	2	95	18	121
7	3	568	32	609
7	4	654	37	674
8	-4	36	10	7
8	-3	622	27	625
8	-2	232	18	232
8	-1	155	32	100
8	0	160	16	156
8	1	637	31	646
9	-1	235	26	199
9	1	311	26	287
9	2	356	28	376
10	-1	144	24	133
*** K= 1 ***				
0	1	1040	96	1062
0	2	4903	397	5150
0	4	720	111	773
0	5	2879	121	2822
0	6	170	22	186
1	-7	91	25	97
1	-6	77	7	73
1	-5	1359	62	1403
1	-4	2367	135	2482
1	-3	563	98	612
1	-2	286	26	299
1	-1	128	5	131
1	0	799	32	775
1	1	335	34	157
1	2	217	29	247
1	3	1624	219	1718
1	4	2428	319	2521
1	5	1769	200	1767
1	6	460	51	484
1	7	165	17	146
2	-6	124	10	115
2	-5	1683	61	1596
2	-4	2570	96	2211
2	-3	229	10	219
2	-2	1616	65	1572
2	-1	1194	48	1186
2	0	700	28	650
2	1	880	76	882
2	2	5530	466	5958
2	3	133	32	163
2	4	107	8	101
2	5	446	43	446
2	6	295	17	240
3	-7	122	28	136
3	-6	198	16	183
3	-5	406	24	372
3	-4	3102	142	3181
3	-3	1713	73	1665
3	-2	21	3	17
3	-1	1285	55	1229
3	0	1996	80	2027
3	1	6718	272	6810
3	2	385	22	385
3	3	802	73	828
3	4	891	56	916
3	6	70	17	73
4	-6	55	18	69
4	-5	254	14	247
4	-4	568	25	558
4	-3	1768	72	1750
4	-2	166	10	155
4	-1	2982	121	2906
4	0	2666	108	2619
4	1	291	13	272
4	2	561	25	580
4	3	788	59	868
4	4	424	24	405
4	5	305	30	270
5	-6	142	12	155
5	-5	87	11	116
5	-4	1351	57	1349
5	-3	1264	51	1236
5	-2	196	10	186
5	-1	2051	83	2036
5	0	580	24	584
5	1	1663	80	1653
5	2	204	10	208
5	3	125	10	116
5	4	280	10	288
5	5	104	14	104
5	6	220	28	251
6	-5	345	19	351
6	-4	307	26	323
6	-3	29	9	8
6	-2	129	8	131
6	-1	3615	146	3583
6	0	667	28	704
6	2	24	8	4
6	3	322	21	301
6	4	114	12	136
6	5	359	21	382
7	-6	329	26	269
7	-5	204	14	224
7	-4	465	24	405
7	-3	148	33	160
7	-2	319	16	312
7	-1	295	15	296
7	0	87	6	91
7	2	83	10	109
7	3	252	16	232
8	-5	258	20	249
8	-3	57	19	51
8	-2	102	12	83
8	-1	1661	71	1666
8	0	295	16	246
8	2	84	12	71
8	3	219	20	196
9	-4	127	15	113
9	-3	273	20	266
9	-2	56	13	59
9	-1	199	15	216
9	0	53	19	39
9	1	54	16	71
10	-1	163	21	373
*** K= 2 ***				
0	0	2996	120	2855
0	1	1072	86	1103
0	2	816	67	819
0	3	347	23	346
0	4	617	52	506
0	6	150	18	184
0	7	598	47	659
1	-7	176	18	157
1	-6	82	21	89
1	-5	70	7	72
1	-4	341	32	348
1	-3	1982	107	2070
1	-2	1012	61	965
1	-1	1350	55	[illegible]
1	0	58	3	57
1	1	2968	245	3229
1	2	266	46	288
1	3	929	125	985
1	4	1130	153	1181
1	5	38	7	28
1	6	121	12	126
1	7	313	52	319
2	-7	132	19	121
2	-6	635	27	645
2	-5	375	36	619
2	-4	217	24	223
2	-3	168	27	183
2	-2	746	34	672
2	-1	971	39	[illegible]
2	0	1787	72	1842
2	1	2800	278	2903
2	2	785	135	927
2	3	462	77	539
2	4	1340	177	1437
2	6	89	16	81
2	7	401	47	375
3	-6	115	12	105
3	-5	482	35	493
3	-4	551	24	548
3	-3	2611	105	2642
3	-2	3991	160	3823
3	-1	1812	73	1788
3	0	813	33	856
3	1	123	9	120
3	2	546	44	603
3	3	4535	511	4792
3	4	366	34	365
3	5	74	13	74
3	6	141	15	173
4	-7	64	14	42
4	-6	84	10	79
4	-5	369	18	387
4	-4	1328	61	1270
4	-3	286	13	275
4	-2	827	34	842
4	-1	1398	57	1420
4	0	65	3	48
4	1	856	38	856
4	2	330	21	305
4	3	1209	121	1162
4	5	168	11	171
4	6	115	13	116
5	-7	111	15	83
5	-6	360	25	393
5	-5	414	20	408
5	-4	1047	46	1040
5	-3	2005	84	2013
5	-2	2056	83	2099
5	-1	1042	43	1036
5	0	1066	44	1065
5	1	116	7	123
5	2	173	16	159
5	3	2897	169	2792
5	4	109	10	143
5	6	207	18	198
6	-6	520	47	550
6	-5	69	10	52
6	-4	450	21	443
6	-3	661	29	671
6	-2	2121	86	2084
6	-1	261	13	278
6	0	17	5	13
6	3	401	20	415
6	4	373	32	391
6	5	113	35	128
7	-6	458	74	496
7	-5	79	13	62
7	-4	357	33	341
7	-3	137	31	99
7	0	262	16	283
7	1	362	18	392
7	2	207	14	174
7	3	556	27	553
7	4	158	22	136
8	-5	95	16	42
8	-3	201	17	218
8	-2	665	37	686
8	-1	89	10	84
8	0	102	32	56
8	1	186	17	176
8	3	173	17	153
9	-4	127	32	151
9	1	176	14	170
9	2	125	18	128
*** K= 3 ***				
0	1	659	42	662
0	2	121	6	116
0	3	776	70	782
0	4	110	16	121
0	5	519	48	529
0	6	505	56	518
0	7	952	107	982
1	-7	445	45	432
1	-6	49	14	48
1	-5	699	36	714
1	-4	104	7	91
1	-3	73	4	72
1	-2	2866	136	2740
1	-1	1105	48	1055
1	0	942	38	911
1	1	171	19	168
1	2	2269	197	2406
1	3	19	4	15
1	4	261	26	281
1	5	392	69	450
1	6	243	17	244
1	7	130	14	95
2	-7	1033	80	1060
2	-6	263	13	255
2	-5	673	33	716
2	-4	78	7	82
2	-3	217	20	238
2	-2	570	29	598
2	-1	102	4	106
2	0	640	26	654
2	1	196	30	408
2	2	1544	164	1796
2	3	1555	215	1638
2	4	356	58	196
2	5	171	37	173
2	6	139	17	97
2	7	243	60	246
3	-7	486	28	504
3	-5	488	23	491
3	-4	627	30	616
3	-3	2076	84	2087
3	-2	205	9	204
3	-1	929	39	894
3	0	46	4	40
3	1	1873	126	1916
3	2	790	84	849
3	3	821	109	844
3	4	267	46	289
3	5	216	26	227
3	6	25	8	24
4	-7	408	22	462
4	-6	149	12	128
4	-5	167	13	176
4	-4	261	13	261
4	-3	436	19	443
4	-2	397	18	432
4	-1	240	11	237
4	0	756	14	746
4	1	64	12	66
4	2	3277	228	3378
4	3	456	53	476
4	4	596	67	666
5	-7	110	13	136
5	-5	59	9	69
5	-4	668	29	673
5	-3	511	29	504
5	-2	1542	63	1496
5	-1	1265	52	1228
5	0	602	25	610
5	1	543	30	512
5	2	1637	76	1070
5	3	88	10	65
5	4	157	12	185
5	5	217	18	186
6	-6	362	62	349
6	-5	26	7	29
6	-4	282	15	258
6	-2	468	21	458
6	-1	341	16	314
6	0	390	17	372
6	1	412	27	458
6	2	208	12	212
6	3	159	12	158
6	4	155	14	170
6	5	200	36	190
7	-6	176	25	142
7	-5	49	10	19
7	-4	285	14	300
7	-3	162	13	167
7	-2	729	12	733
7	-1	94	16	86
7	2	253	14	212
7	3	120	11	117
7	4	50	13	45
8	-3	160	14	135
8	-2	115	12	96
8	-1	527	26	547
8	0	161	19	412
8	1	201	14	213
8	2	54	12	64
8	3	58	14	49
9	-3	130	28	157
9	-2	223	17	241
9	1	104	18	103
9	2	84	19	92
*** K= 4 ***				
0	0	1623	46	1535
0	1	1126	56	1118
0	2	59	16	67
0	3	1642	110	1712
0	4	635	61	646
0	5	250	29	249
0	6	164	12	117
1	-7	54	12	67
1	-5	1028	44	1014
1	-4	243	12	242
1	-3	1016	42	967
1	-2	2571	132	2478
1	-1	59	4	58
1	0	69	4	77
1	1	183	16	152
1	2	1974	212	2030
1	3	572	70	678
1	4	727	130	897
1	5	475	77	464
1	6	117	9	97
1	7	465	85	407
2	-6	199	26	192
2	-5	862	48	865
2	-4	475	21	464
2	-3	1552	61	1462
2	-2	623	28	626
2	-1	648	28	680
2	0	877	36	823
2	1	1147	122	1168
2	2	644	89	721
2	3	305	22	328
2	4	436	66	390
2	5	52	13	29
2	6	87	15	90
3	-7	100	19	83
3	-6	115	16	129
3	-5	932	40	902
3	-4	515	10	517
3	-3	255	12	267
3	-2	300	14	278
3	-1	203	9	198
3	0	81	4	78
3	1	186	14	175
3	2	576	59	597
3	3	3604	413	3690
3	4	168	30	171
3	5	62	10	64
3	6	548	55	547
4	-6	97	14	103
4	-5	910	39	893
4	-4	47	6	67
4	-3	382	17	373
4	-2	2198	97	2166
4	-1	426	26	428
4	0	210	9	207
4	1	103	15	106
4	2	1756	129	1821
4	3	149	10	143
4	4	27	8	42
4	5	153	15	176
4	6	352	70	321
5	-6	224	16	236
5	-5	320	18	307
5	-4	705	31	756
5	-2	293	16	287
5	-1	33	5	36
5	0	149	7	151
5	1	476	26	469
5	2	711	48	760
5	3	1275	87	1337
5	4	99	22	99
5	5	143	33	153
6	-6	89	13	99
6	-5	156	18	167
6	-4	92	11	75
6	-3	61	8	79
6	-2	1297	54	1304
6	-1	608	26	583
6	0	405	19	397
6	1	417	26	420
6	2	433	22	409
6	4	130	28	136
6	5	103	31	71
7	-5	208	29	213
7	-4	148	18	142
7	-3	355	41	340
7	-2	176	12	181
7	-1	380	40	362
7	0	152	9	135
7	1	436	21	459
7	2	50	15	55
7	3	126	21	147
7	4	224	47	167
8	-5	32	11	31
8	-3	63	12	51
8	-2	296	17	302
8	-1	27	7	31
8	0	92	11	82
8	1	121	15	101
8	2	277	20	268
8	3	129	15	116
9	-3	45	14	30
9	-2	356	44	351
9	-1	126	27	144
9	1	271	18	256
*** K= 5 ***				
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0	2	2258	187	2285
0	4	840	90	827
0	5	334	63	361
0	6	192	14	185
0	7	278	41	266
1	-7	165	32	170
1	-6	102	9	74
1	-5	68	9	59
1	-4	25	6	26
1	-3	1026	45	1001
1	-2	420	17	403
1	-1	465	29	481
1	0	3591	144	3417
1	1	436	35	408
1	2	156	13	220
1	3	991	126	1053
1	4	69	7	67
1	5	159	20	165
1	6	120	14	122
1	7	174	47	161
2	-7	716	66	709
2	-5	1065	52	990
2	-4	667	28	620
2	-3	376	16	373
2	-2	1374	62	1302
2	-1	261	11	247
2	0	1084	45	1054
2	1	395	30	403
2	2	1791	166	1839
2	3	582	87	584
2	4	151	11	160
2	6	252	26	239
3	-7	217	99	247
3	-6	179	18	158
3	-4	581	25	583
3	-3	1566	75	1545
3	-2	25	3	22
3	-1	2572	106	2567
3	0	1069	43	990
3	1	1536	89	1571
3	2	18	4	17
3	3	586	85	631
3	5	352	56	389
3	6	128	18	97
4	-7	348	23	326
4	-6	155	11	142
4	-5	466	39	438
4	-4	1299	57	1232
4	-3	586	25	579
4	-2	76	5	76
4	-1	799	33	787
4	0	302	13	316
4	1	1852	123	1982
4	2	238	12	255
4	3	1050	127	1197
4	4	464	65	412
4	6	58	14	60
5	-6	78	13	92
5	-4	586	33	560
5	-3	360	22	377
5	-2	652	30	632
5	-1	967	40	967
5	0	186	17	172
5	1	1015	61	1055
5	2	78	22	85
5	3	98	12	98
5	4	35	10	26
5	5	170	15	188
6	-5	33	11	11
6	-4	318	16	341
6	-3	72	11	46
6	-2	263	14	259
6	-1	731	31	710
6	0	686	29	740
6	1	1321	91	1336
6	3	191	15	188
6	4	282	14	249
6	5	62	16	60
7	-4	868	86	898
7	-3	299	16	289
7	-2	110	9	111
7	-1	99	9	87
7	0	78	9	75
7	2	76	12	72
7	3	120	22	138
7	4	72	14	51
8	-1	249	15	240
8	0	267	15	278
8	1	232	16	206
8	2	95	13	61
8	3	182	21	194
9	-3	68	15	59
9	-2	126	16	113
9	-1	288	18	294
9	0	110	14	82
*** K= 6 ***				
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0	1	211	9	211
0	2	414	31	471
0	3	144	20	164
0	4	966	114	941
0	5	2280	286	2328
0	6	27	9	33
0	7	143	18	149
1	-6	201	14	200
1	-5	173	12	180
1	-4	1499	94	1479
1	-3	2102	116	2204
1	-2	684	33	669
1	-1	656	27	664
1	0	230	11	241
1	1	345	26	352
1	2	1876	162	1972
1	3	1415	174	1416
1	4	1191	188	1148
1	5	321	37	326
1	6	529	38	524
1	7	80	19	60
2	-7	154	13	168
2	-6	60	11	51
2	-5	1266	66	1207
2	-4	294	16	292
2	-3	863	39	828
2	-2	409	17	393
2	-1	79	8	81
2	0	1475	67	1795
2	1	1024	57	1019
2	2	144	12	146
2	3	295	46	312
2	4	1321	197	1265
2	5	280	32	285
3	-6	74	9	66
3	-5	369	18	360
3	-4	868	46	871
3	-3	510	25	500
3	-2	91	6	89
3	-1	1107	45	1115
3	0	2353	95	2306
3	1	410	18	444
3	2	756	68	812
3	3	1538	193	1589
3	4	321	53	374
3	5	331	58	318
3	6	326	40	351
4	-6	167	14	155
4	-5	778	50	787
4	-4	414	19	424
4	-3	356	18	362
4	-2	1031	44	1033
4	-1	303	16	305
4	0	1538	62	1520
4	1	257	20	288
4	2	746	62	695
4	3	114	9	110
4	4	87	21	71
4	5	459	74	437
4	6	364	44	297
5	-6	189	18	173
5	-5	165	24	129
5	-4	337	27	331
5	-3	38	6	28
5	-2	709	46	710
5	-1	381	17	372
5	0	464	19	455
5	1	140	9	147
5	3	515	40	450
6	-6	122	16	105
6	-5	354	21	365
6	-4	217	13	210
6	-3	73	9	58
6	-2	1408	85	1347
6	-1	241	13	228
6	0	613	28	602
6	1	104	9	94
6	2	482	28	507
6	3	83	13	73
6	4	392	11	370
7	-2	258	16	250
7	-1	178	19	426
7	0	68	7	50
7	1	150	13	128
7	4	303	19	297
8	-4	108	14	102
8	-2	239	16	246
8	0	77	9	102
8	2	267	19	281
9	-2	307	50	308
9	-1	428	28	428
9	0	127	18	121
9	1	222	33	189
*** K= 7 ***				
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0	2	51	6	51
0	3	1191	116	1151
0	4	560	70	554
0	5	785	89	817
0	6	39	10	48
0	7	289	21	237
1	-6	33	8	34
1	-5	1306	124	1231
1	-3	243	15	271
1	-2	553	26	536
1	-1	212	11	215
1	0	841	35	885
1	1	1913	96	1950
1	2	256	28	290
1	4	1147	190	1452
1	5	2060	254	2047
1	6	32	10	29
2	-7	411	31	382
2	-5	441	21	439
2	-4	418	19	401
2	-3	1320	59	1341
2	-2	153	11	156
2	-1	265	12	263
2	0	837	34	825
2	1	1986	122	2006
2	2	438	15	475
2	3	132	17	137
2	4	130	31	165
2	5	629	93	619
2	6	123	12	133
3	-6	1177	49	1137
3	-3	204	11	196
3	-2	161	8	161
3	-1	1956	81	1895
3	0	959	19	981
3	1	4349	192	4136
3	2	195	29	207
3	3	121	15	117
3	4	468	59	385
3	5	273	24	273
4	5	554	38	578
4	-4	1562	97	1569
4	-3	1749	86	1762
4	-2	402	18	407
4	-1	668	12	606
4	0	5469	219	5449
4	1	898	62	990
4	2	125	14	109
4	3	681	70	696
4	4	170	14	155
4	5	342	22	291
5	-5	104	18	131
5	-4	2038	208	2049
5	-3	361	17	387
5	-2	202	13	202
5	-1	967	42	958
5	0	76	6	71
5	1	835	35	824
5	2	27	8	17
6	-5	239	25	244
6	-4	716	72	768
6	-3	375	24	380
6	-2	208	13	222
6	-1	71	9	76
6	0	2263	92	2257
6	1	230	29	259
6	3	183	26	161
6	4	146	15	122
7	-5	64	11	71
7	-4	1071	146	1104
7	-2	121	14	96
7	1	263	17	213
7	2	60	9	35
7	3	141	16	101
8	-4	201	18	210
8	-2	67	11	58
8	0	377	27	415
8	1	43	13	31
8	2	48	10	35
9	-1	136	17	133
9	0	52	15	33
*** K= 8 ***				
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0	1	960	40	907
0	2	1371	140	1327
0	3	560	43	536
0	4	537	65	576
0	5	207	44	194
0	6	228	18	263
1	-6	366	21	357
1	-4	767	64	754
1	-3	789	64	799
1	-2	1353	61	1314
1	-1	1508	61	1486
1	0	111	6	116
1	1	418	18	386
1	2	903	70	860
1	3	1656	167	1688
1	4	622	54	690
1	5	456	74	445
1	6	524	48	547
2	-6	169	12	110
2	-5	402	36	397
2	-4	305	46	314
2	-3	627	37	622
2	-2	1597	71	1609
2	-1	1592	65	1565
2	0	97	5	98
2	1	1745	86	1674
2	2	1031	95	999
2	3	1317	168	1319
2	4	577	47	609
2	5	276	29	248
2	6	351	32	349
3	-6	170	11	192
3	-5	112	18	66
3	-4	106	13	91
3	-3	1808	103	1828
3	-2	132	11	124
3	-1	2830	116	2882
3	0	283	12	276
3	1	964	54	979
3	2	487	33	464
3	3	2887	306	2901
3	4	240	47	274
3	5	411	38	413
3	6	362	34	408
4	-5	403	37	444
4	-4	1075	75	1047
4	-3	175	12	173
4	-2	2573	135	2606
4	-1	1093	65	1107
4	0	279	11	288
4	1	1000	63	1014
4	2	319	34	306
4	3	283	35	283
4	4	146	15	151
4	5	217	21	218
5	-6	591	34	573
5	-4	47	15	36
5	-3	319	22	307
5	-2	1089	52	1039
5	-1	1618	91	1636
5	0	81	6	82
5	1	1088	47	1072
5	2	138	28	97
5	3	426	24	411
5	4	133	21	141
5	5	139	34	136
6	-5	331	19	348
6	-4	399	27	427
6	-3	307	17	301
6	-2	1192	50	1284
6	-1	112	11	102
6	0	145	9	145
6	1	104	12	122
6	2	349	20	313
6	4	178	18	145
7	-4	49	13	59
7	-3	38	12	57
7	-1	299	18	277
7	0	87	15	73
7	1	882	69	886
8	-3	136	15	172
8	-2	227	36	231
8	0	129	15	101
8	1	308	20	269
8	2	180	15	158
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0	2	4366	272	4225
0	3	516	63	555
0	4	67	9	61
0	5	292	33	281
0	6	113	18	107
1	-6	265	23	263
1	-5	61	9	30
1	-4	412	20	418
1	-3	1115	72	1104
1	-2	2450	141	2371
1	-1	74	5	78
1	0	1533	63	1456
1	2	2628	177	2567
1	3	1410	157	1447
1	4	260	25	221
1	6	152	21	167
2	-6	222	19	224
2	-5	112	11	101
2	-4	155	22	130
2	-2	4444	287	4305
2	-1	24	6	23
2	0	959	43	1005
2	1	1181	76	1229
2	2	277	20	280
2	3	440	68	427
2	4	181	20	184
2	5	154	47	368
2	6	87	10	71
3	-6	313	34	296
3	-5	30	9	38
3	-4	36	9	25
3	-3	1793	136	1864
3	-2	1952	117	1987
3	-1	275	13	279
3	0	1357	57	1346
3	1	85	7	89
3	2	2130	173	2210
3	3	666	61	728
3	5	282	51	244
4	-6	271	20	256
4	-5	216	35	218
4	-4	157	12	133
4	-3	1021	52	1004
4	-2	2563	154	2572
4	-1	36	6	35
4	0	739	32	725
4	1	335	16	312
4	2	530	31	540
4	3	119	11	122
4	5	327	45	303
5	-5	51	13	64
5	-4	366	72	396
5	-3	1345	83	1456
5	-2	60	8	64
5	0	92	6	92
5	1	343	22	338
5	2	365	36	375
5	3	420	52	420
5	4	86	21	46
6	-5	149	31	124
6	-3	371	46	364
6	-2	372	19	377
6	-1	257	11	260
6	0	299	14	307
6	1	402	20	406
6	2	237	26	253
7	-4	220	23	209
7	-3	293	24	298
7	-2	179	15	186
7	-1	134	38	127
7	1	71	11	72
7	3	525	41	538
8	-3	112	19	126
8	-2	51	14	66
8	-1	177	16	169
8	0	156	22	131
8	1	405	27	342
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0	2	1575	116	1513
0	3	2038	204	2137
0	4	615	84	626
0	5	74	13	73
0	6	341	26	313
1	-6	133	14	147
1	-4	483	50	462
1	-3	627	32	460
1	-2	857	59	885
1	-1	564	27	542
1	0	361	15	347
1	1	22	5	26
1	2	240	17	261
1	3	992	107	1028
1	4	99	13	96
1	5	72	11	57
1	6	69	20	70
2	-6	197	17	201
2	-4	364	28	386
2	-3	865	67	841
2	-2	287	14	295
2	-1	36	10	19
2	0	981	41	911
2	1	264	14	280
2	2	4695	359	4547
2	3	1541	160	1617
2	4	326	30	292
2	5	88	12	89
3	-6	670	50	677
3	-4	300	29	283
3	-3	167	10	165
3	-2	1352	62	1384
3	-1	464	24	434
3	0	329	14	321
3	1	851	41	860
3	2	388	28	420
3	3	375	58	431
3	4	46	8	56
4	-5	99	27	72
4	-4	212	18	207
4	-3	489	36	482
4	-2	847	50	900
4	-1	54	6	50
4	0	448	20	425
4	1	333	31	325
4	2	974	84	955
4	3	457	56	455
4	5	295	34	260
5	-5	54	13	10
5	-3	220	14	238
5	-2	238	15	240
5	-1	607	35	614
5	0	409	19	424
5	1	1347	57	1349
5	2	461	22	440
5	3	121	18	124
6	-4	69	15	86
6	-3	444	24	469
6	-2	100	11	97
6	-1	68	10	57
6	0	155	11	151
6	1	59	10	85
6	2	50	11	56
6	3	121	13	128
7	-4	80	17	75
7	-3	375	24	375
7	-2	150	15	121
7	-1	282	39	366
7	0	70	14	69
7	1	550	27	536
7	2	330	29	344
*** K= 11 ***				
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0	2	269	13	278
0	3	430	62	437
0	5	183	60	149
0	6	481	42	473
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1	-4	127	12	140
1	-3	26	8	21
1	-2	289	20	296
1	-1	1922	124	1956
1	0	1433	59	1313
1	1	1734	109	1706
1	2	91	15	110
1	3	235	29	248
2	-6	292	23	239
2	-3	47	8	47
2	-1	244	17	250
2	0	65	11	63
2	1	1256	76	1297
2	2	645	80	635
2	3	291	45	280
2	4	102	17	101
2	5	1036	119	983
3	-4	236	16	236
3	-3	69	8	81
3	-2	449	56	457
3	-1	1250	70	1296
3	0	73	9	78
3	1	998	59	947
3	2	28	8	22
3	3	127	11	126
3	5	404	23	391
4	-5	188	28	189
4	-4	100	30	117
4	-3	115	11	112
4	-2	120	19	114
4	-1	121	10	132
4	0	239	16	228
4	1	1886	124	1924
4	2	565	44	559
4	4	147	28	150
5	-5	149	17	154
5	-4	554	92	596
5	-2	334	25	330
5	-1	72	17	79
5	0	126	9	138
5	1	752	56	744
5	2	142	12	160
5	3	233	23	267
6	-4	168	16	131
6	-3	239	16	233
6	-1	126	12	128
6	0	267	13	276
6	1	325	19	355
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7	-3	191	20	171
7	-2	67	13	69
7	-1	73	14	82
7	1	269	18	249
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1	-4	219	24	197
1	-3	74	18	77
1	-2	314	18	316
1	-1	1309	66	1262
1	0	141	12	142
1	1	908	51	867
1	2	168	11	171
1	3	37	9	39
1	5	247	26	241
2	-5	130	30	124
2	-2	92	16	104
2	0	587	26	591
2	1	528	43	534
2	2	346	20	356
2	3	118	13	127
2	4	151	19	166
3	-5	120	20	109
3	-4	257	21	246
3	-3	128	12	115
3	-2	58	9	58
3	-1	130	9	134
3	0	383	17	381
3	1	484	23	493
3	3	205	15	199
3	4	189	32	144
4	-5	277	43	249
4	-4	527	47	512
4	-3	97	14	76
4	-2	119	12	125
4	-1	220	14	225
4	0	767	32	779
4	1	265	16	267
4	2	128	23	116
4	4	135	18	110
5	-3	85	25	91
5	-1	132	12	118
5	0	577	12	568
5	1	246	20	224
6	-1	109	15	98
6	0	204	13	190
6	1	55	15	75
7	-2	203	18	174
7	-1	73	13	68
7	0	181	14	164
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0	2	263	17	278
0	3	143	13	139
0	5	119	10	95
1	-5	203	21	172
1	-3	95	12	74
1	-2	60	10	49
1	-1	77	12	87
1	0	507	29	479
1	3	173	13	169
1	4	90	28	80
1	5	239	54	227
2	-4	136	13	148
2	-3	206	34	222
2	-2	336	18	321
2	-1	64	8	70
2	0	259	14	282
2	2	167	13	161
2	3	224	22	221
2	4	463	27	467
3	-2	400	21	412
3	-1	204	18	204
3	0	97	8	93
3	1	165	11	150
3	4	276	70	278
4	-3	226	18	235
4	-2	45	10	51
4	-1	54	14	49
4	0	182	15	184
4	1	121	11	109
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5	0	130	23	77
5	1	106	26	93
5	2	138	16	131
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0	2	72	23	90
0	3	183	16	177
0	4	46	14	45
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1	-1	152	23	156
1	1	238	50	296
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1	4	46	13	18
2	-3	96	24	97
2	-2	156	13	160
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2	0	207	16	219
2	1	136	25	124
2	2	42	12	73
2	3	252	23	236
2	4	66	11	23
3	-3	83	13	70
3	-2	98	15	100
3	0	100	15	89
3	1	511	52	520
3	3	109	16	112
4	-2	68	13	41
4	0	130	11	119
4	1	190	26	151
4	2	68	14	24
5	0	163	12	166
5	1	234	15	253
5	2	61	14	67
6	-1	208	24	185
*** K= 15 ***				
0	1	148	33	177
0	2	202	37	230
0	4	50	15	25
1	-2	560	30	560
1	-1	221	17	217
1	1	394	49	376
1	2	963	119	963
1	3	396	62	417
2	-3	150	40	127
2	-2	245	16	245
2	-1	85	12	80
2	1	27	9	47
2	3	23	7	32
3	-3	257	18	251
3	-2	350	56	357
3	-1	66	18	68
3	1	37	12	52
3	2	632	35	583
4	-3	390	62	376
4	-2	242	40	249
4	-1	77	21	80
4	0	158	24	159
5	-2	50	15	33
5	-1	77	22	98
*** K= 16 ***				
0	0	46	12	18
0	2	196	17	187
0	3	343	59	357
1	-3	176	62	145
1	-2	133	20	169
1	2	98	28	91
1	3	649	33	618
2	-3	188	22	203
2	-2	278	40	315
2	-1	276	29	302
2	0	36	10	44
2	2	795	78	785
3	-2	293	31	276
3	-1	52	15	49
3	0	116	17	130
3	1	157	37	199
4	-1	201	56	205
4	0	121	15	121
*** K= 17 ***				
0	1	88	19	145
1	-1	406	38	497
1	1	814	189	895
2	-1	299	19	287
2	0	213	16	211
2	1	264	61	296

Table 1 for those reflections included in the refinement, and the refined atomic coordinates and thermal parameters are listed in Table 2.

Both water molecules in the crystal structure have high thermal parameters. The value of u_{11} is 0·152 (4) Å^2 for O^{w1} and 0·113 (3) Å^2 for O^{w2}. It seems possible that these high thermal parameters partially reflect a tendency of the crystals to lose water, but this conjecture could not be proved on the basis of the neutron-diffraction data. Attempts were made to refine occupancy factors along with position and thermal parameters for the atoms of the water molecules, leaving the parameters for the other atoms in the structure fixed. The resulting occupancies did not differ significantly from unity.

The molecular structure

The lysine molecule, which is drawn in Fig. 1, is a singly charged zwitterion with the extra positive charge carried by the terminal ammonium group, as was found to be the case in two prior X-ray studies (Raman, 1959; Wright & Marsh, 1962). Molecular bond distances and angles are not tabulated here, as Bugayong, Sequeira & Chidambaram (1972) have presented a detailed comparison of our bonding parameters with the results of their parallel neutron diffraction study and with the X-ray results of Wright & Marsh. Torsion angles defined according to the latest IUPAC conventions (IUPAC-IUB Commission on Biochemical Nomenclature, 1970) are given in Table 3.

Table 3. *Torsion angles*

IUPAC-IUB designation	Atoms involved	Angle
φ^1	H^1-N-C^α-C	– 49·2 (3)°
φ^2	H^2-N-C^α-C	71·6 (3)
φ^3	H^3-N-C^α-C	–166·4 (3)
ψ^1	O^1-C-C^α-N	– 19·2 (3)
ψ^2	O^2-C-C^α-N	162·7 (2)
χ^1	N -C^α–C^β–C^γ	– 56·4 (2)
χ^2	C^α–C^β–C^γ–C^δ	–176·0 (1)
χ^3	C^β–C^γ–C^δ–C^ε	–171·1 (2)
χ^4	C^γ–C^δ–C^ε–N^ζ	179·2 (2)
$\chi^{5,1}$	C^δ–C^ε–N^ζ–$H^{\zeta1}$	– 51·4 (4)
$\chi^{5,2}$	C^δ–C^ε–N^ζ–$H^{\zeta2}$	72·0 (4)
$\chi^{5,3}$	C^δ–C^ε–N^ζ–$H^{\zeta3}$	–169·5 (3)

Molecular packing and hydrogen bonding

There are ten hydrogen bonds per asymmetric unit of the crystal structure, one involving each hydrogen atom covalently bonded to nitrogen or oxygen. The packing scheme, which is shown in Fig. 2, consists of chains of lysine cations inclined approximately 30° to the **b** axis

Table 2. *Final atomic coordinates* ($\times 10^5$) *and thermal parameters* ($\times 10^4$)

The temperature factor is of the form $\exp[-2\pi^2(u_{11}h^2a^{*2}+u_{22}k^2b^{*2}+u_{33}l^2c^{*2}+2u_{12}hka^*b^*+2u_{13}hla^*c^*+2u_{23}kb^*c^*)]$.

The atom designations are: $CA \equiv C^\alpha$, $CB \equiv C^\beta$, $CG \equiv C^\gamma$, $CD \equiv C^o$, $CE \equiv C^\varepsilon$, and $NZ = N^\zeta$. Because of the widespread and standard atomic nomenclature in amino acids and peptides, we choose to use this notation rather than the prescribed C(1), C(2) ... suggested in the *Acta Cryst. Notes for Authors*. The numbering used by Wright & Marsh is given alongside the standard IUPAC designation.

		X	Y	Z	U11	U22	U33	U12	U13	U23
Cℓ	Cℓ	20686(17)	50030	-11335(24)	344(6)	420(7)	365(7)	27(5)	84(5)	56(6)
C	C_1	25000(20)	7646(16)	-24918(28)	255(6)	295(8)	220(7)	-6(6)	22(5)	30(7)
C^α	C_2	30402(20)	3407(17)	-677(27)	219(6)	287(8)	209(7)	0(6)	32(5)	29(7)
C^β	C_3	27275(26)	-7906(17)	-1032(33)	391(9)	272(9)	298(9)	26(7)	59(8)	20(8)
C^γ	C_4	31367(28)	-12933(17)	22497(36)	462(10)	294(10)	334(10)	-11(7)	35(8)	49(8)
C^δ	C_5	29230(27)	-24274(18)	20678(36)	499(10)	300(10)	329(10)	12(8)	98(9)	44(8)
C^ε	C_6	30368(26)	-29240(17)	43995(36)	386(9)	318(10)	320(10)	-9(7)	42(8)	36(8)
N	N_1	19806(16)	8541(14)	15524(22)	327(6)	325(7)	232(6)	17(5)	59(4)	-2(6)
N^ζ	N_2	27970(18)	-40272(13)	41498(24)	359(6)	330(8)	327(7)	-30(5)	40(5)	82(6)
O^1	O_2	10390(28)	12151(21)	-28916(39)	303(9)	496(14)	329(10)	95(8)	21(8)	125(10)
O^2	O_1	35738(26)	5943(19)	-39049(35)	332(9)	495(13)	234(9)	2(9)	75(7)	18(10)
O^{W1}	W_1	12580(78)	31597(37)	53331(82)	1515(40)	517(22)	655(25)	-163(26)	296(27)	6(22)
O^{W2}	W_2	29787(63)	28991(29)	15924(85)	1127(29)	406(19)	647(23)	-23(18)	193(22)	65(19)
H^1	H_1	20534(61)	16220(33)	13171(75)	672(25)	363(23)	420(21)	38(18)	156(19)	22(19)
H^2	H_3	6545(47)	6320(36)	12965(70)	344(17)	622(27)	454(20)	37(16)	107(15)	-78(20)
H^3	H_2	25067(52)	7215(33)	32909(62)	504(17)	467(20)	282(18)	38(17)	98(14)	28(17)
H^α	H_{19}	44600(40)	5000(32)	4781(65)	281(14)	574(23)	392(17)	-18(14)	-4(12)	58(18)
$H^{\beta1}$	H_{17}	13281(62)	-9487(35)	-7935(90)	615(25)	487(24)	597(27)	-159(20)	-130(20)	57(23)
$H^{\beta2}$	H_{18}	36147(82)	-11086(37)	-12557(87)	919(34)	483(25)	484(24)	179(24)	313(23)	75(23)
$H^{\gamma1}$	H_{16}	45150(75)	-11077(45)	30426(105)	729(30)	639(30)	735(35)	-178(23)	-225(25)	211(30)
$H^{\gamma2}$	H_{15}	22421(92)	-10157(40)	34200(95)	1100(42)	521(29)	442(25)	80(26)	310(27)	5(24)
$H^{\delta1}$	H_{14}	16204(81)	-26083(44)	10996(104)	889(32)	522(27)	588(29)	-201(25)	-247(25)	103(25)
$H^{\delta2}$	H_{13}	39685(91)	-27369(40)	11413(103)	1110(42)	486(24)	705(34)	251(28)	506(34)	152(28)
$H^{\varepsilon1}$	H_{11}	43249(67)	-27858(42)	54261(98)	691(28)	617(27)	644(29)	-170(23)	-203(22)	110(29)
$H^{\varepsilon2}$	H_{12}	19526(77)	-26559(41)	53045(98)	873(33)	568(29)	612(30)	235(27)	331(27)	87(28)
$H^{\zeta1}$	H_4	16646(73)	-41814(46)	30492(105)	830(31)	563(29)	721(33)	-283(27)	-345(27)	158(29)
$H^{\zeta2}$	H_5	39199(74)	-43356(36)	36130(95)	797(30)	447(24)	629(29)	25(22)	358(25)	15(23)
$H^{\zeta3}$	H_6	26378(58)	-43609(33)	56821(75)	586(20)	467(24)	451(21)	-29(17)	174(17)	139(20)
H^{W11}	H_8	12653(87)	25262(49)	61130(132)	835(33)	617(36)	872(42)	17(28)	241(32)	140(36)
H^{W12}	H_7	14675(113)	36665(52)	64829(136)	1204(49)	600(36)	730(39)	-30(35)	259(37)	-23(37)
H^{W21}	H_{10}	24346(102)	30833(46)	29135(130)	1132(44)	472(30)	623(36)	-68(31)	80(33)	-12(28)
H^{W22}	H_9	27647(103)	34630(54)	6455(122)	1215(50)	565(36)	708(39)	-32(33)	86(36)	191(35)

and interconnected through the water molecules and chloride ions. Hydrogen bond distances and angles are summarized in Table 4.

The three hydrogen atoms of the α-ammonium group are donated respectively to the second water molecule, to the chloride ion, and to the carboxyl oxygen O^2 belonging to a neighboring lysine molecule. The $N–H^1\cdots O^{w2}$ hydrogen bond, which is somewhat bent, forms part of the sequence $N–H^1\cdots O^{w2}–H^{w22}\cdots Cl\cdots H^{\zeta3}$ which binds the infinite chains of lysine molecules in the structure together. The hydrogen bond $N–H^3\cdots O^2$, with an $H^3\cdots O^2$ distance of 1·740 (5) Å, is the strongest $N–H\cdots O$ bond in the structure. Significantly, the $N–H^3$ bond distance is 1·059 (4) Å, making this bond more than 0·02 Å longer than each of the five other N–H bonds in the lysine molecule. In general, N–H distances are quite sensitive to the strengths of the hydrogen bonds which may be formed; we have observed a very good inverse correlation between N–H and $H\cdots B$ bond lengths in amino acids. For example, in L-alanine the short $N–H^2\cdots O^2$ bond has N–H and $H\cdots O$ distances of 1·047 (2) and 1·780 (2) Å respectively (Lehmann, Koetzle & Hamilton, 1972).

There is no evidence for the formation of an intramolecular hydrogen bond. The α-NH_3^+ group is rotated in such a way as to produce an approximately staggered configuration with respect to the carboxyl group; the distances from O^1 to H^1 and H^2 are 2·546 (5) and 2·635 (5) Å respectively.

Besides forming a hydrogen bond to O^1, atom $H^{\zeta1}$ of the ζ-ammonium group possesses a short van der Waals contact $N–H^{\zeta1}\cdots Cl$. Here the $H^{\zeta1}\cdots Cl$ distance is 2·741 (7) Å, while the angle $N^{\zeta}–H^{\zeta1}\cdots Cl$ is 117·9 (5)°. We believe this contact should not be classified as a hydrogen bond, although the weak interaction present may explain why the $N^{\zeta}–H^{\zeta1}\cdots O^1$ bond is found to be severely bent as well as being by far the longest $N–H\cdots O$ hydrogen bond in the structure. In fact, the chloride ion is slightly closer to H^{α} from a nearby lysine molecule than it is to $H^{\zeta1}$ [the $Cl\cdots H^{\alpha}$ distance involved is 2·660 (3) Å]. A large number of short intermolecular and intramolecular contacts found in this and other amino acids implies that a van der Waals radius for hydrogen of 1·0 Å, as proposed by Baur (1972), may be more appropriate than the 1·2 Å previously assumed (Pauling, 1960). If this is the case, then the two short $Cl\cdots H$ distances found here are only slightly less than the value of 2·8 Å expected for a normal van der Waals contact.

The two water molecules each accept a single hydrogen bond. One of these bonds $O^{w2}–H^{w21}\cdots O^{w1}$ connects the water molecules to one another and lies nearly along a lone pair of O^{w1}. By contrast, the $N–H^1\cdots O^{w2}$ hydrogen bond does not fall along an oxygen lone pair, and O^{w2} with its three neighboring hydrogens forms a distorted trigonal pyramid. Water molecules of this type possessing irregular hydrogen-bonding patterns do not seem to be particularly unusual in crystalline hydrates (Donohue, 1968).

The chloride ion is surrounded by a distorted octahedron of hydrogen atoms. In addition to accepting four hydrogen bonds, Cl^- possesses the two short van der Waals contacts with H^{α} and $H^{\zeta1}$ discussed above. There are no additional abnormally short non-bonded contacts in the structure.

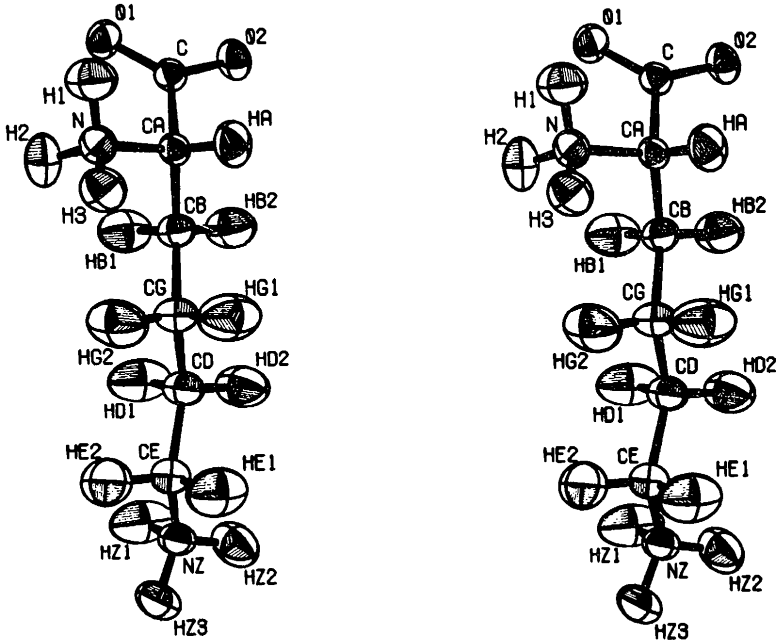

Fig. 1. Stereoscopic view of the lysine molecule with thermal ellipsoids drawn to enclose 50% probability.

Thermal motion

The non-hydrogen atoms of the lysine molecule undergo thermal motion which is of quite low amplitude and is also fairly isotropic, as can be seen from Fig. 1. Only for the carboxyl oxygen atoms is the mean square amplitude in the direction of the long principal axis of thermal motion more than twice that along the short principal axis. For both O^1 and O^2, the long axis is nearly perpendicular to the C–O bond, as might be expected. The hydrogen atoms undergo larger and more anisotropic thermal motions than do the nonhydrogen atoms, and with the exception of the α-ammonium group hydrogens, the entire lysine chain appears to be librating principally about its long axis.

It seemed that the quality of the data here and the relatively small thermal motion amplitudes justified a closer analysis of the thermal motion than would usually be the case, in order that the results might be used to decide upon the best method of treatment in our other amino acid studies. Attempts were made to fit the atomic thermal parameters u_{ij} to the motions of a rigid body described in terms of **T**, **L**, and **S** tensors (Schomaker & Trueblood, 1968). In calculation I, only the nonhydrogen backbone has been included in the rigid body, and the r.m.s. value of Δu_{ij}, the difference between observed and calculated thermal parameters, is $\overline{\Delta u_{ij}^2}^{1/2} = 0{\cdot}004$ Å². This value may be compared with 0·001 Å², the precision with which the u_{ij} for nonhydrogen atoms are determined from the least-squares refinement. The effective screw translations are found to be small, and the largest principal axis of **L** has an amplitude of 0·0037 (27) rad², corresponding to a libration of 3·5 (12)° about an axis inclined approximately

Table 4. *Hydrogen bond distances* (Å) *and angles* (°)

A–H···B–C	A–H	A···B	H···B	∠A–H···B	∠H···B–C
H^{w2} $N{-}H^1\cdots O^{w2}$ H^{w22}	1·034 (4)	2·824 (4)	1·836 (6)	158·5 (4)	96·4 (4) 131·2 (6)
$N{-}H^2\cdots Cl^-$	1·028 (4)	3·217 (2)	2·196 (4)	172·0 (4)	
$N{-}H^3\cdots O^2{-}C$	1·059 (4)	2·795 (3)	1·740 (5)	173·4 (4)	110·9 (2)
$N^\zeta{-}H^{\zeta1}\cdots O{-}C$	1·016 (5)	2·887 (3)	2·083 (6)	134·4 (6)	135·4 (2)
$N^\zeta{-}H^{\zeta2}\cdots O^2{-}C$	1·024 (5)	2·788 (2)	1·865 (6)	148·3 (5)	131·2 (2)
$N^\zeta{-}H^{\zeta1}\cdots Cl^-$	1·026 (4)	3·173 (2)	2·150 (5)	174·8 (4)	
$O^{w1}{-}H^{w11}\cdots O^1{-}C$	0·960 (9)	2·805 (5)	1·857 (7)	169·2 (7)	113·5 (2)
$O^{w1}{-}H^{w12}\cdots Cl^-$	0·953 (11)	3·220 (5)	2·273 (8)	172·7 (6)	
H^{w11} $O^{w2}{-}H^{w21}\cdots O^{w1}$ H^{w12}	0·957 (11)	2·718 (6)	1·775 (9)	167·9 (6)	111·2 (6) 123·9 (6)
$O^{w2}{-}H^{w22}\cdots Cl^-$	0·936 (9)	3·254 (4)	2·329 (7)	169·7 (6)	

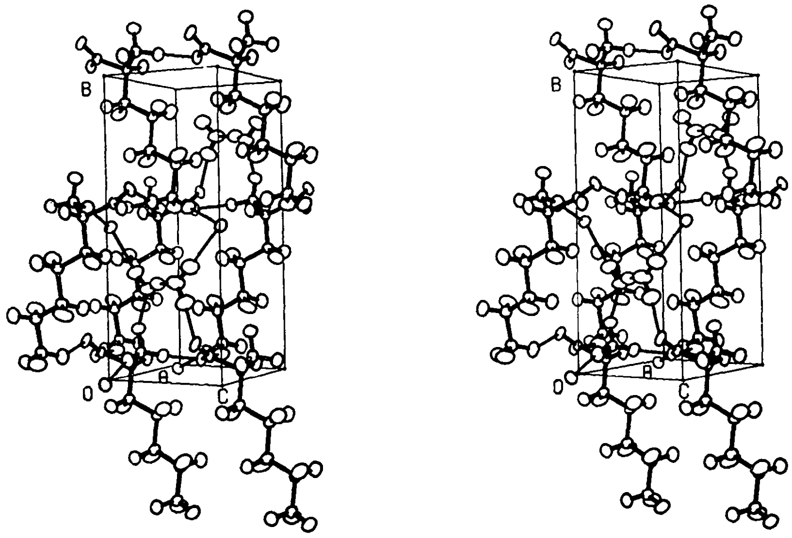

Fig. 2. Stereoscopic view of the packing around one unit cell with thermal ellipsoids drawn to enclose 30% probability. Molecular bonds are drawn thick and hydrogen bonds thin.

30° to the long axis of the lysine molecule. The remaining two principal axes of **L** have amplitudes which are within 0·0008 rad^2 of zero.

Calculation II was carried out including in the rigid body the entire lysine molecule except H^1, H^2 and H^3 of the α-NH_3^+ group. In this case $\overline{\Delta u_{ij}^2}^{1/2} = 0{\cdot}011$ Å^2, implying a considerably worse fit than for the backbone alone. Part of the increase in $\overline{\Delta u_{ij}^2}^{1/2}$ compared with the value found in calculation I is explained by the precision of the hydrogen atom u_{ij}'s which range from 0·002 to 0·004 Å^2, but there is undoubtedly a significant amount of non-rigid-body motion involving the hydrogen atoms. Because of this the magnitude of the rigid-body motions has probably been overestimated whenever hydrogen atoms have been included in the rigid body. This calculation II led to a libration of 0·0271 (23) rad^2 or 9·4 (4)° about the long molecular axis, and essentially zero librations normal to this axis. The screw components were quite small as was the case for those found in calculation **I.**

In order to obtain the best possible fit to the thermal parameters of the NH_3^+ groups (and thus possibly the best corrections to bond lengths), separate rigid-body calculations III were carried out for each of these groups. In the case of the α-NH_3^+ group, the rigid body consisted of C^α, N, H^1, H^2, and H^3, while for the ζ-NH_3^+ group, the rigid body was made up of C^ε, N^ζ, $H^{\zeta1}$, $H^{\zeta2}$, and $H^{\zeta3}$. No constraints based upon symmetry were imposed on the motion of either group. In both cases, the fit proved to be extremely good. The value of $\overline{\Delta u_{ij}^2}^{1/2}$ for each group is 0·002 Å^2, which compares well with the precision of the individual u_{ij}. The largest principal axis of **L** has an amplitude of 0·0238 (30) rad^2 for the α-NH_3^+ group and 0·0493 (28) rad^2 for the ζ-NH_3^+ group, corresponding to librations of 8·8 (5)° and 12·7 (4)° about the C^α–N and C^ε–N^ζ bonds, respectively. The ζ-NH_3^+ group, which contains the weakly hydrogen-bonded atom $H^{\zeta1}$, is expected to undergo a larger axial libration than the α-NH_3^+ group in which all three hydrogens form strong hydrogen bonds. Estimates of the librational frequencies ν and the heights of the barrier to rotation V_0 have been obtained for the ammonium groups, assuming a harmonic oscillator approximation to a threefold cosine hindered rotor (Schlemper, Hamilton & La Placa, 1971). For the α-NH_3^+ group, $\nu = 361$ cm^{-1} and $V_0 = 7{\cdot}0$ kcal.mole^{-1}, while for the ζ-NH_3^+ group, the corresponding values are 233 cm^{-1} and 2·9 kcal.mole^{-1}. The precision of these frequencies and barrier heights is of the order of 10 to 20%.

Additional rigid-body calculations IV were carried out of the ammonium groups, constraining the motion to have threefold (3) symmetry. In these treatments, the contribution of the rigid-body motion of the lysine backbone was subtracted from the u_{ij} for the hydrogen atoms of each ammonium group. The resulting values of Δu_{ij} were then used to determine appropriately constrained **T**, **L**, and **S** tensors. As might be expected, the fit was not nearly so good as was the case in the unconstrained calculations III; here values of $\overline{\Delta u_{ij}^2}^{1/2}$ are 0·007 Å^2 for the α-NH_3^+ group and 0·020 Å^2 for the ζ-NH_3^+ group. The calculated librational amplitudes about the C–N axis are 0·0301 (66) rad^2 or 9·9 (11)° for the α-NH_3^+ group and 0·0595 (206) rad^2 or 14·0 (24)° for the ζ-NH_3^+ group. These values agree within one e.s.d. with the more precise results of calculation III.

The thermal motion of the four CH_2 groups and of the two water molecules was treated in a final set of rigid-body calculations V. In a modification of procedures used to analyse the rigid-body motions in ice IX (Hamilton, La Placa, Kamb & Prakash, 1972) the u_{ij} for the three atoms in each group were fitted to a general translation given by T, and to a rocking libration about an axis normal to the plane of the group. The origin was fixed at the carbon or oxygen atom. The agreement was quite good for these highly constrained calculations, except in the case of the first water molecule where $\overline{\Delta u_{ij}^2}^{1/2} = 0{\cdot}012$ Å^2. Values of $\overline{\Delta u_{ij}^2}^{1/2}$ for the CH_2 groups and for the second water molecule fall between 0·005 and 0·008 Å^2. The calculated amplitudes of rocking libration are roughly the same for all four CH_2 groups and are in the range 12·7 (10) to 15·3 (10)°, thus supporting the observation that the entire lysine chain librates about its long axis in an approximately rigid fashion.

Corrections to molecular bond lengths and angles have been derived in the usual way from the rigid-body librations found in calculations I–V. The very small corrections for the lysine nonhydrogen atom framework were obtained from the results of calculation I and are less than 0·003 Å for distances and 0·2° for angles. It did not seem worthwhile tabulating the corrected parameters here.

Because of the non-rigid-body character possessed by the thermal motion of the hydrogen atoms, it is difficult to appropriately correct the bond lengths and angles involving hydrogen atoms for the effects of thermal motion. In any event, the corrections which need to be applied to the C–H bond lengths are certainly quite small, for the mean of the uncorrected C–H distances is 1·092 (2) Å, very close to the standard value of 1·096 Å (*Tables of Interatomic Distances and Configuration in Molecules and Ions*, 1965). Table 5 presents a comparison of X–H bond lengths corrected for rigid-body motion with values to which the commonly used riding correction and the minimum correction (Busing & Levy, 1964) have been applied. The riding approximation, which leads to a mean C–H distance of 1·131 (3) Å, clearly overcorrects the bond lengths and does not appear to be very useful here. The results using the minimum correction set a lower bound of 1·100 (2) Å for the mean C–H distance determined in this study. Rigid-body calculation I, which does not include the effects of hydrogen atom thermal motion, leads to a mean corrected C–H distance of 1·094 (2) Å, or only 0·002 Å larger than the uncorrected value. Calculations IV and V, in which constraints of symmetry have been applied, give generally larger corrections to

Table 5. X–H *Bond distances* (Å) *corrected for thermal motion*

	Uncorrected	I	II	III	IV	V	Minimum Correction*	Riding Correction†
$C^{\alpha}-H^{\alpha}$	1·090 (3)	1·091	1·104				1·094	1·113
$C^{\beta}-H^{\beta 1}$	1·093 (5)	1·093	1·107			1·110	1·100	1·127
$C^{\beta}-H^{\beta 2}$	1·097 (5)	1·098	1·111			1·114	1·104	1·133
$C^{\gamma}-H^{\gamma 1}$	1·102 (5)	1·103	1·117			1·124	1·113	1·148
$C^{\gamma}-H^{\gamma 2}$	1·088 (5)	1·090	1·102			1·109	1·096	1·128
$C^{\delta}-H^{\delta 1}$	1·088 (6)	1·089	1·103			1·114	1·098	1·132
$C^{\delta}-H^{\delta 2}$	1·094 (5)	1·095	1·107			1·119	1·104	1·141
$C^{\varepsilon}-H^{\varepsilon 1}$	1·082 (5)	1·084	1·097			1·104	1·092	1·126
$C^{\varepsilon}-H^{\varepsilon 2}$	1·090 (5)	1·091	1·104			1·111	1·099	1·132
Mean C–H	1·092 (2)	1·093 (2)	1·106 (2)			1·113 (2)	1·100 (2)	1·131 (3)
$N-H^{1}$	1·034 (4)	1·034		1·049	1·057		1·038	1·059
$N-H^{2}$	1·028 (4)	1·029		1·041	1·050		1·032	1·051
$N-H^{3}$	1·059 (4)	1·061		1·074	1·082		1·060	1·073
$N^{\zeta}-H^{\zeta 1}$	1·016 (5)	1·017	1·029	1·047	1·048		1·031	1·075
$N^{\zeta}-H^{\zeta 2}$	1·024 (5)	1·025	1·037	1·049	1·056		1·030	1·057
$N^{\zeta}-H^{\zeta 3}$	1·026 (4)	1·027	1·029	1·058	1·057		1·028	1·047
Mean N–H	1·031	1·032	1·032	1·053	1·058		1·037	1·060
$O^{w1}-H^{w11}$	0·960 (9)					0·967	0·961	
$O^{w1}-H^{w12}$	0·953 (11)					0·960	0·953	
$O^{w2}-H^{w21}$	0·957 (11)					0·963	0·957	0·957
$O^{w2}-H^{w22}$	0·936 (9)					0·942	0·937	0·954
Mean O–H	0·952					0·958	0·952	0·956

* Defined as $\frac{(|u_2^{1/2}-u_1^{1/2}|)^2}{2R}$ where u_2 and u_1 are total mean-square displacements normal to the bond for the two atoms, and *R* is the uncorrected bond distance.

† Defined as $\frac{(u_2-u_1)}{2R}$ where atom 2 rides on atom 1.

the N–H and C–H bond lengths, respectively, than do the unconstrained calculations III and II.

In the absence of a detailed knowledge of the nature of the thermal vibrations taking place in the crystal, an accurate assessment of the relative merits of the X–H bond length corrections based on rigid-body calculations II–V and on the minimum correction is impossible. Generally speaking, one would expect the corrections to the N–H bond lengths to be even smaller than those to the C–H bond lengths, because the ammonium group hydrogen atoms are tied down by hydrogen bonds. If this is the case, then the corrected N–H bond distances derived from calculations III and IV are clearly too large. The minimum correction, which rests on the somewhat unphysical assumption that the motions of two atoms normal to the bond connecting them are completely in phase, appears to give very reasonable corrected bond distances in this structure. In cases where non-rigid-body motions are important the minimum correction has the advantage over rigid-body treatments of considering each bond individually and gives a theoretical lower bound to the corrected distance.

Corrections to X–X–H and H–X–H bond angles based on the rigid-body calculations were less than one e.s.d. for almost all angles, and the corrected values have not been presented in detail.

All computations described in this paper were performed on CDC 6600 computers, using programs from the Brookhaven Crystallographic Computing Library. A brief summary of these programs has been given by Schlemper *et al.*, (1971).

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A Neutron Diffraction Study of the Structure of L-Lysine Monohydrochloride Dihydrate

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The intensities of 1431 (875 independent) neutron Bragg reflexions from a single crystal of L-lysine monohydrochloride dihydrate have been measured at a wavelength of 1·170 Å, using the diffractometer in the symmetrical setting. The structure has been refined by the method of least squares and the final conventional R value is 0·070. An inter-experimental comparison is made with an independent neutron-diffraction study (preceding paper) and with the X-ray results [Wright & Marsh *Acta Cryst.* (1962), **15**, 54].

Introduction

Preliminary studies of the space group and cell constants of L-lysine monohydrochloride dihydrate were carried out by Srinivasan (1956). The structure was first solved using X-ray data by Raman (1959), who suggested that the molecule is in the zwitterion form and also proposed a network of ten hydrogen bonds in the structure. A more accurate X-ray study was reported by Wright & Marsh (1962) whose hydrogen bonding scheme agrees with Raman's except in the bonding of the terminal amino group. The present neutron study was carried out to obtain detailed knowledge of the hydrogen atom positions in this amino acid crystal. A parallel neutron-diffraction study, of which we were unaware until recently, has been carried out independently by Koetzle, Lehmann, Verbist & Hamilton (1972).

Crystal data

L-Lysine monohydrochloride dihydrate, $NH_3^+[CH_2]_4CH(NH_3)^+COO^-.Cl^-.2H_2O$, is monoclinic, $P2_1$, with two molecules per unit cell. The following cell parameters were established from the X-ray study of Wright & Marsh (1962): $a=7{\cdot}492$ (1), $b=13{\cdot}320$ (4), $c=5{\cdot}879$ (1) Å and $\beta=97°47{\cdot}4$ (7)′. The calculated density is 1·249 g.cm^{-3}.

Experimental

Large, clear and well-formed single crystals of L-lysine $HCl.2H_2O$ were easily obtained by slow evaporation from a saturated aqueous solution at room temperature. The crystals were of pyramidal shape with (010) as the basal face and {110} and {011} as the principal side faces, and they were elongated along the **c** direction. The density measured by flotation was 1·246 g.cm^{-3}.

Neutron intensity data were recorded using the four-circle neutron diffractomer 3D-FAD (Momin, Sequeira & Chidambaram, 1969) at the CIRUS reactor in Trombay. The specimen crystal was cut in the shape of a rectangular parallelepiped with a height of 4·94 mm along the b axis and with lateral dimensions of 3·68 and 2·93 mm respectively along and perpendicular to the c axis. The crystal was given a thin coating of an adhesive (brand name Stickfast) to prevent exposure to air, and dipped in liquid nitrogen several times to reduce extinction effects. It was then mounted on the diffractometer with its b axis parallel to the φ-axis of the Eulerian Cradle. The cell parameters and the crystal orientation were refined from the optimised 2θ, χ and φ values for some 30 strong reflexions chosen at random, using the program *REFINE* (Srikanta & Sequeira, 1968). The refined values of the cell parameters were in agreement with the more precise X-ray values listed above to better than two parts per thousand. The systematic absences were checked and found to be consistent with the space group $P2_1$.

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