Acta Cryst. (1962). 15, 54

The Crystal Structure of *l*-Lysine Monohydrochloride Dihydrate*

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(Received 27 February 1961)

The crystal structure of *l*-lysine monohydrochloride dihydrate has been determined by analysis of complete three-dimensional data from copper X-radiation. The approximate structure was obtained from a Patterson superposition map derived from the Cl–Cl vector. Refinement of the positional parameters for all 32 atoms and of the individual anisotropic temperature factors for the 13 heavier atoms was by the method of least squares. The final R factor for 1261 observed reflections of non-zero weight is 0.057, and the estimated limits of error are 0.015–0.018 Å in the bond distances involving the C, N, and O atoms and 33–40' in the bond angles.

The lysine molecule is a zwitterion, each nitrogen atom having an extra proton. The two $C-NH_3^+$ distances are equal within experimental error, the average value being 1.482 Å. The side chain is in an extended, nearly planar configuration, and the average C–C distance is 1.524 Å. The apparent C–H, N–H, and O–H bond lengths are only slightly shorter than the standard internuclear separations.

Introduction

Lysine— $NH_2(CH_2)_4CH(NH_2)COOH$ —is one of four essential amino acids having basic side chains. The detailed crystal structure analysis of lysine monohydrochloride dihydrate is one of a series of X-ray diffraction studies of protein derivatives that has been in progress in these Laboratories for many years. The results reported here reflect extensive three-dimensional refinement of the positions of all 32 atoms and of the anisotropic vibrational parameters of the 13 heavier atoms. The accuracy achieved allows structural features to be discussed with confidence.

An approximate solution of the structure was published during the course of this investigation by Raman (1959), and is in substantial agreement with the results found here. Raman did not, however, attempt complete refinement.

Experimental

l-Lysine monohydrochloride crystallizes readily as a dihydrate from saturated aqueous solutions allowed to evaporate at room temperature (20 °C). The colorless monoclinic crystals are stable for some months in dry air, particularly if the crystal faces are not damaged, before surface decomposition to a sticky white powder occurs, presumably due to loss of water. Though most crystals were twinned, a few single crystals were found in each crystallization, and were

used for the collection of the X-ray data. Serious radiation damage was noticed, particularly under hot humid conditions, but was greatly reduced by dessication with silica gel during photography.

Complete intensity data for $Cu K \alpha$ radiation were collected by the multiple-film equi-inclination angle Weissenberg technique. As the linear absorption coefficient of the salt is 31.8 cm.⁻¹, considerable care was taken to choose crystals having regular shapes. They tended to be elongated along c, but if necessary they could be cut with a scalpel blade. No pronounced cleavage plane was observed. The five crystals used in this work were thick needles elongated about either a or c, and 0.2-0.4 mm. on the edge. All layer lines about the a and c axes with equi-inclination angles less than 45° (that is, layer lines 0 to 6 about a and 0 to 5 about c), as well as the zero layer about the b axis, were recorded with $\operatorname{Cu} K\alpha$ radiation. The intensities were estimated visually and corrected as usual for Lorentz and polarization factors, no absorption corrections being applied. Of 1348 independent reflections within the effective copper sphere $(\sin \theta < 0.98)$, 1284 were observed. Of these, 1024 reflections were measured about both the a and caxes and used to put all reflections on a single scale, as well as to give an estimate of the expected standard deviation, $\sigma(F)$, in an observed structure factor (Ibers, 1956). These standard deviations were averaged over regions of similar F values and fitted to the equation

$$\sigma(F) = a + b|F| + c|F|^2;$$

the resulting values for a, b, and c were $4.00, 2.34 \times 10^{-3}$, and 2.58×10^{-4} . The weighting schemes used in the least-squares refinement of the atomic parameters were based on this pattern of estimated uncertainties.

^{*} Contribution No. 2681 from the Gates and Crellin Laboratories of Chemistry. This investigation was supported in part by a research grant No. H-2143 from the National Heart Institute, National Institutes of Health, Public Health Service.

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Three-dimensional intensity data for molybdenum $K\alpha$ radiation were also collected (layer lines 0-8 about c, and 0-2 about α for correlation). Time did not allow further work with these data.

Table 1. Unit-cell dimensions of l-lysine monohydrochloride dihydrate

	(Cu $K\alpha_1, \lambda = 1.5405$)	1)
	This investigation*	Shrinivasan (1956)†
a	7.492 ± 0.001 Å	7.48
ь	13.320 ± 0.004	13.31
с	$5 \cdot 879 \pm 0 \cdot 001$	5.85
β	97° $47 \cdot 4' \pm 0 \cdot 7'$	97° 48′

 \ast Estimated errors set at about 3 times the standard deviations given by the least-squares analysis.

† Errors estimated at about 1%.

The unit-cell dimensions, given in Table 1, were determined from Straumanis-type single-crystal rotation photographs about b and c. Eighteen high-angle h0l reflections (sin $\theta > 0.76$) and six hk0 reflections (sin $\theta > 0.84$) were indexed by comparison with the corresponding Weissenberg photographs, and their measured values of sin² θ were used as input for a least-squares determination of the four cell parameters. The results are in good agreement with those of Srinivasan (1956), which are also listed in Table 1. The systematic absence of 0k0 reflections with k odd confirms Srinivasan's choice of space group $P2_1$.

The density of newly precipitated crystals, measured by flotation in mixed solvents, is $1\cdot250 \pm 0\cdot003$ g. cm.⁻³, which corresponds to $1\cdot91$ molecules of water of hydration per lysine molecule. The calculated density for two molecules of the perfect dihydrate per unit cell, $1\cdot259$ g. cm.⁻³, is just significantly higher. The apparent deficiency of $0\cdot35$ electrons for each water oxygen was not detected during the refinement, either in the least-squares calculations or in the difference Fourier syntheses. Any effect on the structure factors of such a slight deficiency would probably be masked by the temperature-factor parameters.

Determination of the structure

The first attempts to derive an approximate structure made use of the three sets of two-dimensional data. The position of the chlorine atom was readily deduced from the Patterson projections and used to calculate approximate phases for the zonal structure factors. However, the subsequent electron density projections could not be interpreted. The use of a single phasedetermining atom introduced a false mirror plane of symmetry in the short a and c axis projections, making them too confused to be solved, and the (010) projection had severe overlap (indicating that the carbon chain might lie approximately parallel to the b axis). After testing and rejecting several structures, twodimensional work was abandoned.

Two three-dimensional syntheses—an electron density map based on the phase angles of the chlorine atom (and which also contained a false mirror plane), and a sharpened Patterson map- were now calculated. The near-origin peaks of the Patterson map confirmed that the carbon-atom side chain of the lysine molecule extended along the b axis. However, this was not enough of a clue to allow the Fourier map to be readily interpreted. Accordingly the Patterson superposition map was plotted, using the Cl-Cl vector in the Harker section at $v = \frac{1}{2}$ as the second origin; only superpositions of Patterson peaks greater than 10% of the Cl-Cl peak height were noted. The correct structure was now obvious. All atoms except one water oxygen were immediately identified, and there were only four spurious peaks. The missing oxygen was found as a well-defined peak in the electron density map by considering the possible hydrogen-bonding network. It was now apparent that the electron density map had defined the atoms of the polar groupings, but not those of the carbon chain.

Finally, all coordinates were adjusted to give the best agreement with the Patterson vectors. Estimated isotropic temperature factors were assigned to all atoms and structure factors were calculated for the reflections out to $\sin \theta = 0.6$. The initial R factor was 0.22.

Refinement of the parameters

The structure, now essentially determined, was refined by a series of least-squares analyses of the complete Cu $K\alpha$ data. Atomic form factors of Berghuis et al. (1955) were used for C, N, O, and Cl⁻, and McWeeny (1951) values were used for hydrogen. First calculations were carried out on a Datatron 205 computer with a program written by Pasternak (1956) which accepted individual isotropic or anisotropic temperature factors in its structure-factor routine but only adjusted positional parameters in the least-squares calculations. Hence, preliminary adjustments of the temperature factors were estimated from three-dimensional difference Fourier syntheses. A constant weighting factor applied to all reflections in the first leastsquares calculations was quickly rejected as inadequate, probably because of large observational errors in the large structure factors. The function being minimized was $\sum w(\varDelta F^2)^2$, and for each reflection the weighting factor 1/w should be taken proportional to the reciprocal of the expected uncertainty in ΔF^2 . As large errors due to incorrect parameters were still present, a compromise factor, $\sqrt{w} = 1/\sigma(F)$, was chosen (see Experimental). An auxiliary weight, allowing for the number of independent observations of a given reflection and also giving low or zero weight to observations considered of low reliability, was also used. As this weighting scheme led to a rapid convergence it was retained until the last stages of refinement.

Four structure-factor least-squares cycles, during which the scale factor and an average isotropic temperature parameter were adjusted graphically, reduced the R factor for all observed reflections of non-zero weight to 0.16. It was now noticed that, with two minor exceptions, every large structure factor calculated appreciably larger than its observed value. This effect was presumably due to extinction, and an empirical correction was found from the relation discussed by Hamilton (1957),

$$\ln (F_o^2/F_T^2) = kT_o ,$$

where k is a secondary extinction factor and F_T , the true value of the structure factor, was assumed equal to F_c . A reliable value of k was found only for the crystal mounted about the a axis, allowing 56 reflections to be corrected. The minimum correction was 6% in F.

Actually, the apparent extinction effect could, in substantial measure, arise from another source—a low film factor in the multiple-film visual technique of estimating intensities. However, the form of the correction would still be valid and its use is justified empirically. When refinement was almost complete the corrections were recalculated, but no adjustment seemed feasible. The corrected structure factors were given half weight in all succeeding least-squares calculations, and all uncorrected strong reflections were given zero weight.

A series of five least-squares cycles and three difference-Fourier syntheses completed refinement on the Datatron 205. The difference maps were interpreted by the method of Leung *et al.* (1957). Individual anisotropic temperature factors were assigned to the chlorine and water oxygen atoms, and corrections calculated for the isotropic temperature factors of all other atoms. After these calculations the *R* factor had fallen to 0.102.

At this time the Datatron 205 computer was replaced by a faster computer, the Burrough's 220. Also during this period a solution of the structure was reported by Raman (1959), who solved the phase problem by considering the anomalous dispersion effects of the chlorine atom and carried through partial refinement of the two acentric projections (a and c). The structure he derived is in substantial agreement with that published here, though it should be noted that Raman's coordinates refer to a monoclinic unit cell with an acute, rather than obtuse, angle β . The sign of the y coordinate of his atom C_1 is reversed, and his analysis did not allow the hydrogen bonding network to be fully elucidated. The observed structure factors he reports are in general agreement with those used in this analysis with the exception of 6k0 data with k=2n, where serious discrepancies occur.

The monoclinic structure-factor least-squares program written for the Burrough's 220 computer accepts and optimises ten parameters for each atom: a scale (population) parameter, three positional parameters and six vibrational parameters. The matrix of the normal equations is semi-diagonalized by neglecting

,	x	σ_x	у	σ_y	N	σ_z	$10^4 \alpha$	σ_{α}	$10^4\beta$	σ_{eta}	$10^4 \gamma$	σ_{γ}	$10^4 \delta$	σs	$10^4 \varepsilon$	σ_{ϵ}	$10^4\eta$	σ_η
0	0.3568	(4)	0.0596	(3)	-0.3904	(5)	174	(2)	64	(2)	180	(8)	5	(2)	73	(6)	13	(9)
°°,	0.1038	(4)	0.1213	(3)	-0.2893	(2)	153	(9)	64	(2)	255	(10)	36	(2)	22	(11)	09	(7)
່ ບົ	0.2503	(2)	0.0761	(3)	-0.2483	(9)	130	(2)	47	(2)	167	(11)	-20	(9)	44	(11)	2	(2)
່ ບໍ	0.3026	(2)	0.0339	(3)	-0.0066	(9)	113	(2)	38	(2)	182	(11)	9	(2)	35	(11)	I	(9)
N	0.1982	(4)	0.0855	(2)	0.1560	(5)	148	(2)	43	(2)	193	(10)	14	(2)	66	(11)	-1	(9)
ົບ້	0.2721	(9)	-0.0793	(3)	-0.0082	(1)	183	(6)	33	(2)	251	(14)	9	(9)	58	(14)	61	(2)
ີ ບໍ	0.3126	(9)	-0.1293	(3)	0.2250	(1)	186	(6)	42	(2)	235	(13)	6	(9)	39	(14)	20	(8)
్రో	0.2920	(9)	-0.2430	(3)	0.2044	(8)	218	(11)	42	(2)	261	(14)	9 -	(2)	78	(16)	20	(8)
ి రో	0.3034	(9)	-0.2927	(3)	0.4389	(2)	183	(6)	47	(2)	202	(12)		(9)	33	(13)	10	(2)
'n,	0.2800	(5)	-0.4027	(3)	0.4158	(9)	174	(8)	43	(2)	229	(11)	- 14	(2)	46	(12)	34	(2
V,, (H ₂ O),*	0.1283	(8)	0.3156	(3)	0.5342	(8)	584	(19)	68	(3)	402	(11)	- 59	(12)	278	(27)	22	(11)
V ₃ , (H ₂ O) ₂ *	0.2945	(2)	0.2897	(3)	0.1563	(2)	465	(16)	52	(2)	368	(15)	1	(8)	153	(21)	46	(6)
G	0.2077	(1)	0.5003	(1)	-0.1137	(2)	163	(2)	56	(1)	242	(3)	x	(2)	87	(3)	30	(?)

The standard deviations, obtained from the least-squares analysis, are multiplied by 10^4

Table 2. The final parameters and their standard deviations

Table 3. The hydrogen atom parameters

(a) Positional parameters, and standard deviations, from the final least-squares analysis.

The thermal parameters, B_i , where $T_i = \exp(-B_i \sin^2 \theta / \lambda^2)$, were not refined

(b) Positional parameters from the final difference synthesis

					(a)					(b)	
Atom	Bonded to	x	$10^3\sigma_x$	y	$10^3 \sigma_y$	z	$10^3 \sigma_z$	B	x	y	z
$\substack{\mathbf{H_1}\\\mathbf{H_2}\\\mathbf{H_3}}$	(N ₁)	0·197 0·263 0·086	(8) (8) (8)	0·153 0·076 0·066	(5) (5) (5)	0·140 0·317 0·111	(10) (11) (10)	4·0 4·0 4·0	$0.198 \\ 0.266 \\ 0.083$	0·155 0·077 0·070	0·140 0·318 0·106
$\substack{\mathbf{H_4}\\\mathbf{H_5}\\\mathbf{H_6}}$	(N ₂)	0·172 0·380 0·263	(9) (9) (8)	-0.421 -0.427 -0.430	(6) (6) (6)	0·291 0·411 0·565	(12) (11) (11)	4·5 4·5 4·5	$0.168 \\ 0.394 \\ 0.267$	-0.420 -0.431 -0.429	0·276 0·397 0·566
$_{ m H_7}^{ m H_7}$	(W_1)	$0.122 \\ 0.129$	(13) (13)	$0.358 \\ 0.248$	(9) (9)	$0.650 \\ 0.612$	(15) (14)	8·0 8·0	0·110 0·108	$0.356 \\ 0.254$	$0.664 \\ 0.602$
H9 H10	(<i>W</i> ₂)	$0.291 \\ 0.247$	(10) (11)	$0.354 \\ 0.314$	(10) (7)	$0.063 \\ 0.302$	(13) (15)	7·0 7·0	$0.301 \\ 0.252$	$0.353 \\ 0.315$	$0.068 \\ 0.312$
${}^{ m H_{11}}_{ m H_{12}}$	(C ₆)	$0.425 \\ 0.221$	(9) (9)	-0.282 - 0.258	(6) (7)	$0.543 \\ 0.543$	(13) (11)	$5 \cdot 0 \\ 5 \cdot 0$	$0.436 \\ 0.213$	$-0.282 \\ -0.252$	$0.537 \\ 0.532$
H ₁₃ H ₁₄	(C_5)	$0.414 \\ 0.169$	(9) (9)	-0.277 - 0.270	(6) (7)	$0.121 \\ 0.110$	(11) (11)	$5 \cdot 0 \\ 5 \cdot 0$	0·418 0·170	-0.274 - 0.264	$0.123 \\ 0.125$
${_{\rm H_{15}}^{\rm H_{15}}}$	(C ₄)	$0.227 \\ 0.438$	(8) (9)	-0.107 - 0.114	(6) (6)	$0.357 \\ 0.307$	(11) (11)	$4.5 \\ 4.5$	0·228 0·438	-0.104 - 0.112	$0.352 \\ 0.292$
$\substack{\mathrm{H_{17}}\\\mathrm{H_{18}}}$	(C ₃)	$0.140 \\ 0.367$	(8) (9)	-0.091 -0.115	(6) (5)	-0.096 -0.109	(10) (11)	4∙0 4•0	0·140 0·366	-0.090 - 0.116	-0.088 - 0.106
H ₁₉	(C_2)	0.420	(8)	0.041	(5)	0.058	(10)	3.0	0.424	0.039	0.061

all interatomic cross terms, though for an individual atom all cross terms between the temperature and scale parameters, as well as those between the x and zpositional parameters, are collected.

The initial refinement was completed with four least-squares cycles during which the R factor fell to 0.078 and the maximum corrections in the parameters became approximately equal to their standard deviations. Positional parameters for all (19) hydrogen atoms were now calculated. Tetrahedral configurations were assumed for the carbon and nitrogen atoms, with C-H and N-H distances of 0.95 and 0.90 Å respectively. The orientations of the $-NH_3^+$ groups were indicated by the hydrogen-bond network. The hydrogen atoms of the water molecules were also positioned by considering the hydrogen bonding, and by assuming O-H distances of 0.90 Å and H-O-H angles of 104.5° . Once calculated, each hydrogen was identified as a peak in the latest difference map. Each hydrogen atom was assigned an isotropic temperature factor with a value of B approximately one unit higher than the average value for the atom to which it was bonded.

Eight more cycles of least-squares calculations completed the refinement. The ten parameters for each of the heavier atoms and three positional parameters of each hydrogen atom were optimized. A shift factor of 0.5 was applied to all parameter changes. After two cycles the R factor had fallen to 0.062, showing the discrepancies to be little larger than the observational errors, and accordingly the weighting scheme was changed to reflect the expected uncertainties in F_o^2 —that is, 1/w was changed from $1/\sigma(F)$ to $1/\sigma(F^2)$. The calculated standard deviations in the atomic parameters decreased after this change, particularly for the chlorine atom, and small but significant corrections to the parameters followed. The final *R* factor was 0.057, again including only those reflections of non-zero weight.

The final positional and temperature-factor parameters for the heavier atoms are given in Table 2 and for the hydrogen atoms in Table 3. The observed and final calculated structure factors are given in Table 4.

Finally, two three-dimensional Fourier summations were calculated: a difference map, to confirm the hydrogen positions, and an electron density map. For the difference map, the amplitudes, ΔF , were taken as the differences between the absolute values of the observed structure factors and those calculated from the heavier atoms alone; the phase angles, however, included the calculated contributions of the hydrogen atoms. A composite drawing of this synthesis is given in Fig. 1, while for comparison the final threedimensional electron density map is shown in Fig. 2. Every hydrogen atom peak in the difference map is greater than 0.35 e.Å⁻³, and with the exception of one peak of $0.3 \text{ e.} \text{Å}^{-3}$ no other positive region exceeds 0.2 e.Å⁻³. There are some negative regions (as large as -0.5 e.Å⁻³), but they are usually associated with the chlorine atom. The two oxygen atoms of the water molecules are in regions of 0.0 and -0.25 e.Å⁻³ respectively, giving no conclusive evidence of a defect structure.

Parameters for the hydrogen atoms were obtained from the difference map using a 27-point Gaussian

Table 4. Observed and calculated structure factors

The five columns within each group contain the values of k, $10F_o$, $10|F_c|$, $10A_o$ and $10B_o$. Reflections indicated by an asterisk (*) were given zero weight in the least-squares calculations. The values listed for $10F_o$, $10A_o$, and $10B_o$ for the $\overline{1}17$ reflection are in error; the correct values are 36, 27, and -24

OEO	0k7	1166	6 46 43 42 -17	216	Žx7	500	6 29 28 -28 5
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12 56 56 -56 13 13 44 42 5 44 14 42 41 -31 -29 15 33 31 -4 33	16 20 22 20 5 1k3 0 60 48 60 0 1 *265 313 3 285 2 173 158 49 -166	1 216 215 202 -75 5 149 154 -18 -18 6 175 154 -18 -18 7 18 15 11 15 8 92 89 -44 -81 9 118 121 117 -17 10 <10 3 10 -2 11 17 16 5 -16	11 95 97 51 -87 12 46 47 26 -58 13 59 56 -5 -59 14 54 55 54 56 -59 15 23 20 15 -18 285	9 59 52 -53 10 80 84 -15 -78 11 84 84 -29 -81 12 22 20 -20 -9 13 50 47 -15 -47 14 12 11 11 4 15 58 40 8 -58	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	1 00 11 25 -76 8 70 68 70 -4 9 26 21 5 25 10 55 53 55 -3 11 53 52 15 51 12 58 57 49 30 13 22 26 0 22	4 kk 0 45 43 - 11 20 2 22 19 -11 20 2 46 45 -46 -83 3 90 28 -30 3 4 30 28 -30 3 5 67 68 -79 56 6 86 84 -79 56
0 74 72 -73 0 1 54 57 -53 8 2 114 125 -99 -56 3 70 59 25 66 4 131 128 -124 -42 5 79 77 -28 74 6 62 59 -61 14 7 30 30 -14 -26	5 65 65 -57 31 4 116 125 113 -26 5 135 145 -32 131 6 114 112 111 22 7 16 11 14 8 8 131 136 113 66 9 110 116 -93 59 10 -10 10 -10 0 11 23 25 -14 19	13 <9 4 2 2 14 17 18 -17 -2 15 42 40 -41 -9 Lut 14 0 163 169 -163 0	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	244 0 78 77 78 0 1 139 142 117 -75 2 51 48 -54 -59 3 86 79 19 -84 4 114 105 112 19 5 70 68 -5 -69	8 115 122 -107 -41 9 63 66 11 -67 10 24 22 12 -20 11 32 31 8 -31 12 30 52 26 -16 13 32 30 1 -32 14 12 14 -2 12	5 k5 0 158 158 158 0 1 131 123 33 127 2 97 90 86 43 3 80 77 -26 76 4 86 86 33 82 5 31 59 26 17	8 42 14 4-53 9 10 10 -9 4 10 32 50 -31 -6 11 27 28 -19 -19
8 55 55 45 92 9 27 25 -6 27 10 80 86 -67 44 11 18 16 6 17 12 46 47 -46 7 15 12 11 -11 4 14 35 34 -52 -5	12 15 11 15 4 17 22 18 22 0 14 14 14 11 -7 15 41 48 29 29	1 199 225 -6 -199 2 44 -1,1 -33 7 7 6 99 14 -9 -1 5 6 6 -2 -49 6 18 20 -14 -11 7 50 91 42 -9 8 98 91 42 -98 8 98 91 28 -98 9 100 96 21	$\begin{array}{cccccccccccccccccccccccccccccccccccc$		5 x 4 0 <10 4 -10 0 1 122 120 -77 -95 2 73 72 70 -20 3 106 106 -8 -105 4 43 34 15 -41 5 59 53 21 -55 6 53 52 52 7	6 51 40 -30 34 7 68 69 -22 64 8 28 24 -12 22 9 56 57 -1 56 10 16 17 3 -16 11 16 18 2 16 12 19 19 19 4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$
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0166 0 51 52 -51 0 1 74 67 5 -73 2 38 42 -21 -52 3 90 86 15 -89 4 16 67 - 9	1145 0 86 82 -86 0 1 108 102 55 95 2 55 87 -51 97 3 98 89 15 97 4 52 48 -39 38 5 88 84 5	8 48 47 44 -19 9 28 25 8 -27 10 8 5 8 -27 11 10 11 -5 4 12 14 11 -12 7 Деб	2k5 0 6 0 0 0 1 69 66 47 50 2 33 24 30 13 3 66 52 11 59 4 62 20 22 4	Žucé 0 87 90 87 0 1 55 51 -27 45 2 71 74 49 51 5 58 52 6 57	8 54 58 55 7 9 35 36 51 -17 10 86 89 17 19 -346 0 10 7 10 0	1 22 25 -1 21 2 19 25 -19 -5 5 50 55 -5 50 4 21 23 -14 -15 5 18 17 -16 8 4 20	0 249 285 249 0 1 63 60 -12 -47 1 9 160 182 -19 3 104 185 -42 -53 4 181 185 176 33 5 96 96 40 -57 6 116 111 115 10 7 25 26 25 -2 8 92 92 66 61
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 50 -56 -58 7 68 65 -51 26 8 65 65 -62 12 9 22 19 -21 4 10 20 22 -16 -12 11 26 25 -19 17 12 18 16 15 -8	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	5 44 43 -8 43 6 62 59 62 5 7 42 40 41 3 8 30 30 22 -20 9 46 50 33 32 10 24 25 23 -6 11 66 73 2 65	4 34 33 22 26 5 29 26 6 28 6 45 38 44 9 7 35 33 16 31 8 40 37 20 -35 9 27 27 -25 10 10 33 38 33 1	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 94 102 94 0 1 169 191 56 160 2 84 82 82 -16 3 171 181 17 170 4 86 90 84 -18 5 85 86 -13 84	9 54 29 -8 -33 10 47 44 47 -1 11 52 52 31 -42 12 38 36 38 2 13 22 19 16 -16 14 41 41 40 -6 15 12 12 12 12 -1

		Table 4. (cont.)	
⊊k2	5k0 5k5	5kas 37 42 25 27 5kas	744 8162
116 123 116 0 19 19 19 1 142 145 152 -51 73 75 41 -60 107 112 89 -60 60 54 55 24	0 74 71 -74 0 0 47 48 47 0 1 57 59 34 45 1 25 24 -11 -22 2 155 154 155 5 2 37 36 -31 19 3 45 47 20 -29 4 114 111 113 -6 4 54 55 -54 7 5 35 35 32 -45 5 2 77 26 25 11	0 105 110 -105 0 4 20 20 19 -54 0 29 28 28 29 0 1 26 110 -105 0 6 6 5 8 99 112 54 0 29 28 28 0 54 54 55 54 55 55 55 55 55 55 55 55 55	0 25 25 25 0 0 21 21 -21 0 1 70 62 48 -51 1 -9 4 -7 -5 2 37 31 -34 14 2 38 30 -37 -6 2 28 27 13 -25 3 7 7 -3 -6 2 82 27 33 51 -25 5 7 7 -3 -6 5 36 35 35 1 4 58 55 -58 3 5 3 7 2 2 -17 -6 3 <
$\begin{array}{cccccccccccccccccccccccccccccccccccc$	0 95 91 95 0 0 96 94 -12 7 166 16 8 -15 7 9 9 -3 -3 8 19 40 39 -59 -9 -8 -3 9 19 19 -4 -19 -10 -10 -10 -10 -11 -50 -50 -57 -50 -50 -57 -50 -50 -51 -11 -54 -12 -12 -13 -51 -50 -50 -50 -51 -50	0 53 54 54 54 54 56 57 56 57 56 57 56 57 56 57 56 57 56 57 56 57 </td <td>6 cc 79 -04 19 6 46 49 45 45 7 17 15 -11 -1 6 8 55 47 -46 25 9 28 26 -3 -28 845 10 60 54 -60 -3 11 18 18 4 -18 0 <6 4 -6 0 1 10 9 -4 -9 0 0 1 - 10 9 -4 -9</td>	6 cc 79 -04 19 6 46 49 45 45 7 17 15 -11 -1 6 8 55 47 -46 25 9 28 26 -3 -28 845 10 60 54 -60 -3 11 18 18 4 -18 0 <6 4 -6 0 1 10 9 -4 -9 0 0 1 - 10 9 -4 -9
38 38 27 -27 23 27 -22 6	12 14 40 41 38 13 1 116 116 -57 101 2 93 77 31 87	720 0 14 11 -14 0 2-1	7µ2 5 26 32 6 425
5k3 31 31 31 0 43 41 32 29 48 46 42 -23 153 160 52 144 74 72 49 -36 102 90 -39 94 102 80 -39 94 103 68 -31 38 104 99 -13 83	Sk1 5 66 56 46 12 22 22 14 0 96 91 96 91 6 99 97 23 97 1 171 16 -00 16 6 95 16 17 16	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
49 49 46 17 88 88 71 51	11 45 46 -8 44 12 47 47 47 -2 50	6k1 12 21 21 -21 2 6k1 13 18 18 -2 17 7k1	Ť≥3 ⁸ ≥2
56 56 46 31 29 26 28 7 52 53 18 49 18 18 18 -1 504 505 57 -85 0 62 55 -36 55	$\begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$	$ \begin{array}{c ccccccccccccccccccccccccccccccccccc$
69 64 19 66 31 32 -13 26	6 24 23 11 -22 11 72 71 43 55 7 61 60 -5 60 12 16 17 -16 2	11 94 94 90 -17 7 36 38 -30 -20 11 38 46 -7 -38 12 18 17 12 13 8 98 105 -91 -38	5425 7721 0 76 77 77 0
92 94 12 91 79 76 -57 55 98 99 50 85 73 73 -71 11 58 56 -10 57 45 46 -42 -17 49 52 0 49	0 00 00 -2 13 50 53 -11 46 9 49 -40 25 13 50 53 -11 46 10 26 26 -5 -25 11 44 45 17 41 12 8 9 3 -7 13 31 54 -5 31 54 0 32 29 -32 50	10 7.1 7.4 7.4 7.4 7.1 7.1 7.1 7.2 7.1 7.2	1 2 51 50 49 16 0 67 77 67 0 4 51 28 50 49 16 1 45 45 45 51 28 50 29 28 71 3 45 34 29 2 43 46 35 71 3 45 45 36 45 14 15 7 3 4 56 46 51 15 7 8 8 1 8 5 62 66 55 16 22 29 14 15 7 8 8 1 8 5 62 66 6 66 16 8 29 14 1.6 7 7 8 8 1 8 5 62 66 6 66 6 6 6 6 6 6 6 6 6 6 15 7

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-110 20 11 -142 0 20 11 31 934 3 -6 13 18 -26 -5 -7 57 -17 49 -19 15 -7 31 16 8 22 5497894-54299 2 34 56789 ********* *42807575 078977-979 5 2827878797962839 ********* 08 25 8 78 7 7 2 4 28 5 ők: 375-488889997 ፟^አッዸ፟፟፟፟፟ዸ፝ጜጜጜጜዹ፟ጜ፟፟፟፟ጜ 148 396 67 53 32 21 67 20 35 19 26 47 16 21 22 24 5 19 28 22 330 25 161 826 35 8 20 27692955547°Y \$1169558972 6k3 45 68 19 18 11 24 24 52 54 73 756 55 24 73 19 25 0 39 94 14 19 378 ****** 1178 55 - 576 512 ኯ፟፟፟፟፟፟፟፟፟፟፟፟ጞኯ፟ኯ፟ኯኯ፟ኯኯ፟ኯ 18 19 35 25 **x**6 201221 095845-09 26 59 21 47 16 22 0 34 56 78 0-14-0 -1-6-1 -7-14 18 71ek 6¥ 65 5 5 2 2 2 2 2 2 2 2 2 64 33 9 31 ahibo 5 30 9 32 -4 29 -67 -2 10 ğ۳ < 10





Fig. 1. A composite drawing of the final difference map, viewed along a. The contributions of the hydrogen atoms were omitted from the amplitudes of F_c but were included in the phase angles. Contours are at intervals of $0.1 \text{ e.} \text{Å}^{-3}$, beginning with the $0.2 \text{ e.} \text{Å}^{-3}$ contour.

Fig. 2. A composite drawing of the final electron density map, viewed along a. Contours are at intervals of 2 e.Å⁻³, be-ginning with the 2 e.Å⁻³ contour.

analysis of the peaks (Shoemaker et al., 1950), and are included in Table 3. They are not significantly different

26 -1 16 -17

18-1751

from the parameters given by the final least-squares calculations. Of 57 parameters, 7 differ by more than one standard deviation (as obtained from the least-squares residuals) from the least-squares values, the maximum difference being 1.6σ . The bond lengths and angles listed in Table 6 are derived from the least-squares coordinates.

During the final eight refinement cycles in which the hydrogen atom contributions were included, the average shift in the parameters of the carbon, nitrogen, and oxygen atoms was 0.019 Å, the maximum shift being 0.042 Å for the water oxygen W_1 . The chlorine atom moved by 0.004 Å. Since the heavy atom parameters seemed to have converged before the hydrogen atoms were introduced, the effect of the hydrogen atoms was to alter the apparent positions of the heavier atoms by several standard deviations. The hydrogen atoms moved an average of 0.18 Å from their original calculated positions, the maximum shift being 0.34 Å for H₆.

The Patterson analysis had placed all the carbon, nitrogen, and oxygen atoms quite accurately. During the entire refinement their average shift was 0.15 Å, with the maximum shift, again for W_1 , being 0.39 Å.

Accuracy of the results

It seems that the structure has been refined to the limit of accuracy feasible with the present experimental observations. The final R factor for 1261 observed reflections with non-zero weight stands at 0.057, close to the value predicted by comparing the values of intensities measured about both a and c axial settings. Moreover, the standard deviation of an observation of unit weight (Peterson & Levy, 1957) is calculated to be 1.16, close to the ideal value of 1.00. This agreement also implies that the weighting scheme adopted during the final stages of refinement reflects the true observational errors.

The standard deviations of the parameters given in Tables 2 and 3 were calculated from the sum of the weighted residuals and the diagonal terms of the inverse matrices of the least-squares normal equations. The limits of error (chosen as three times the standard deviations) are 0.015-0.018 Å in the bond lengths and 33-40' in the bond angles between the heavier atoms. The internal consistency of bond lengths and angles expected to be equivalent shows these uncertainties to be realistic. The estimated limits of error for the hydrogen parameters are 0.2-0.3 Å.

The values for the uncertainties in the temperature parameters are more difficult to assess. The standard deviations in their numerical values, calculated as above from the least-squares coefficients (see Table 2), give no clue as to the importance of such effects as extinction, absorption, scaling, and spot shape. However, all these effects have much the same dependence upon the scattering angle as an isotropic vibration, and a single isotropic temperature parameter should be sufficient to allow for these systematic experimental errors, particularly as the crystals were regular in shape and without pronounced cleavage. The uncertainties reported for the temperature parameters, then, can be extended to apply to the relative values of the vibrational amplitudes, and there seems no reason to doubt the pattern of anisotropic thermal motions discussed below.

Discussion of the results

(i) Geometry of the molecule

The lysine molecule is dominated by two planar configurations, the carboxylate grouping $O_1O_2C_1C_2$ and the aliphatic side chain terminating in the ε nitrogen atom N₂. As expected, the molecule is a zwitterion, with both nitrogen atoms accepting a proton (from the two acid groupings) and assuming the tetrahedral configuration C-NH₃+. The bond lengths and angles found for the heavier atoms are given in Table 5 and shown in Fig. 3, while those involving the hydrogen atoms are given in Table 6.

Table 5.	Bond	lengths	and	anales
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Bond		Angle	
$\substack{\mathrm{C_1-O_1}\\\mathrm{C_1-O_2}}$	1·250 Å 1·246	$\begin{array}{c} {\rm O_1-C_1-O_2}\\ {\rm C_2-C_1-O_1}\\ {\rm C_2-C_1-O_2} \end{array}$	125·5° 116·8 117·7
$\substack{\mathbf{C_2-N_1}\\\mathbf{C_6-N_2}}$	1·484 1·480	$\substack{ C_1 - C_2 - N_1 \\ C_3 - C_2 - N_1 \\ C_5 - C_6 - N_2 }$	109·7 111·8 110·9
$C_1 - C_2$ $C_2 - C_3$ $C_3 - C_4$ $C_4 - C_5$ $C_5 - C_6$	1·529 1·524 1·518 1·526 1·521	$\begin{array}{c} {\rm C_1-\!C_2-\!C_3} \\ {\rm C_2-\!C_3-\!C_6} \\ {\rm C_3-\!C_4-\!C_5} \\ {\rm C_4-\!C_5-\!C_6} \end{array}$	109·8 114·6 111·0 111·5

The dimensions of the amino acid group are quite similar to those reported for glycine (Marsh, 1958), and are in general agreement with the values reported for other amino acids (summarized recently in a paper by Hahn, 1957). The two C–O bond lengths are equal within experimental error, with their average value of 1.248 ± 0.004 Å (the uncertainty is the e.s.d. assuming the individual values to be equivalent) in good agreement with the average value of 1.254 ± 0.003 Å for glycine.* The two C–NH₃+ bond lengths are also equal within experimental error, and again the average value of 1.482 ± 0.004 Å is close to the (single) value found in glycine, 1.474 ± 0.003 Å. Somewhat higher values for this bond length have been reported else-

^{*} The magnitudes of the principal thermal vibrations of atoms O_1 and O_2 (Table 8) indicate that a correction of approximately 0.012 Å should be applied to each of the C-O bonds (Cruickshank, 1956). The resulting value is 1.260 Å. close to the similarly corrected value 1.263 Å in glycine and in agreement with the value deduced by Hahn for 50°_{6} double-bond character.

	d(X-H)		$< \begin{pmatrix} \mathbf{C} \\ \mathbf{N} - \mathbf{X} - \mathbf{H} \end{pmatrix}$		< (H–X–H)
$\substack{\substack{N_1-H_1\\N_1-H_2\\N_1-H_3}}$	0·91 Å 1·01 0·88	${}^{\mathrm{C_2-N_1-H_1}}_{\mathrm{C_2-N_1-H_2}}_{\mathrm{C_2-N_1-H_3}}$	113° 108 103	${ { H_1 - N_1 - H_2 } \atop { H_2 - N_1 - H_3 } \atop { H_3 - N_1 - H_1 } }$	103° 124 106
$\substack{ {\rm N_2-H_4} \\ {\rm N_2-H_5} \\ {\rm N_2-H_6} }$	1·04 0·82 0·97	${}^{C_6-N_2-H_4}_{C_6-N_2-H_5}_{C_6-N_2-H_6}$	112 107 108	$\substack{ \mathbf{H_4-N_2-H_5} \\ \mathbf{H_5-N_2-H_6} \\ \mathbf{H_6-N_2-H_4} }$	120 97 111
$W_1 - H_7 W_1 - H_8$	0·89 1·00			$H_{7}-W_{1}-H_{8}$	10 3
$W_{2} - H_{9}$ $W_{2} - H_{10}$	$1.01 \\ 1.02$			$H_{9}-W_{2}-H_{10}$	102
$C_6-H_{11} C_6-H_{12}$	1.04 1.03	$\substack{ \mathbf{C}_5 - \mathbf{C}_6 - \mathbf{H}_{11} \\ \mathbf{C}_5 - \mathbf{C}_6 - \mathbf{H}_{12} \\ \mathbf{N}_2 - \mathbf{C}_6 - \mathbf{H}_{11} \\ \mathbf{N}_2 - \mathbf{C}_6 - \mathbf{H}_{12} } $	114 112 106 115	H_{11} - C_6 - H_{12}	98
C_5-H_{13} C_5-H_{14}	1·18 1·07	$\substack{ C_4 - C_5 - H_{13} \\ C_4 - C_5 - H_{14} \\ C_6 - C_5 - H_{13} \\ C_6 - C_5 - H_{14} }$	110 116 105 105	H_{13} - C_5 - H_{14}	108
$C_4-H_{15} C_4-H_{16}$	1·11 1·02	$\substack{ \mathbf{C_3-C_4-H_{15}}\\ \mathbf{C_3-C_4-H_{16}}\\ \mathbf{C_5-C_4-H_{15}}\\ \mathbf{C_5-C_4-H_{15}}\\ \mathbf{C_5-C_4-H_{16}} }$	117 113 105 108	$H_{15}-C_4-H_{16}$	101
C_3-H_{17} C_3-H_{18}	1.07 1.09	$\substack{ \mathrm{C_2-C_3-H_{17}} \\ \mathrm{C_2-C_3-H_{18}} \\ \mathrm{C_4-C_3-H_{17}} \\ \mathrm{C_4-C_3-H_{17}} \\ \mathrm{C_4-C_3-H_{18}} }$	106 109 116 104	H_{17} - C_2 - H_{18}	108
$\rm C_2\!{-}H_{19}$	0.91	$C_1 - C_2 - H_{19}$ $C_3 - C_2 - H_{19}$ $N_1 - C_0 - H_{10}$	118 104 104		

 Table 6. Bond distances and angles involving the hydrogen atoms, calculated from the least-squares parameters of Table 3

where, leading Hahn to deduce an average value 1.503 Å. This is possibly a little high.

The equation for the least-squares plane through atoms $O_1O_2C_1C_2$ is

$$0.4702X' + 0.8673Y + 0.2094Z' = 1.3732$$
,

where the direction cosines refer to the orthogonal axes a*bc. The deviations of the individual atoms from the plane are:

$$O_1 = 0.004, O_2 = 0.004, C_1 = 0.010, C_2 = 0.003 \text{ Å}$$

The nitrogen atom N₁ lies 0.446 Å out of the plane; the value found in glycine is 0.436 Å.

An interesting result of this investigation is the determination of accurate bond lengths and angles in a medium length (5 atom) aliphatic carbon chain. As Bonham & Bartell (1959) point out, there is no reliable value for the normal carbon-carbon singlebond length, for the very good reason that there is a dearth of accurate structural information. Bartell (1959) further argues that the standard most commonly accepted, the bond length in diamond, is unsuitable for this purpose because of interactions peculiar to the diamond structure. He proposes, instead, the average value 1.533 + 0.003 Å found in electron diffraction studies of the normal hydrocarbons butane through heptane. The average value of the C-C single bonds in lysine is 1.524 + 0.003 Å, significantly shorter than the diamond value and slightly shorter than the value proposed by Bartell. The average value of the four C-C-C angles is 111.7°, significantly greater than the tetrahedral value but close to the value of 112.4° found by Bonham & Bartell in *n*-butane. However, the angle $C_2-C_3-C_4$, 114.6°, is appreciably larger than the other three. Similar results are found in other amino acids and peptides, and in the case of leucylprolylglycine (Leung & Marsh, 1958) it was suggested that the widening of this angle might be due to the steric effect of an atom hydrogen bonded to the NH₃⁺ group. In lysine an oxygen atom O_1 , which is hydrogen bonded to N₁, is only 3.37 Å from C₄ and 2.77 Å from H₁₅.

The aliphatic side chain has a fully extended configuration, the five carbon atoms and the terminal nitrogen being approximately coplanar. The leastsquares plane of these atoms is

$$-0.9729X' + 0.119Y + 0.2024Z' = 2.1535$$
,



Fig. 3. Bond distances and angles.

and the small, though significant, deviations from it are,

$$C_2 = -0.003, C_3 = -0.058, C_4 = 0.040 \text{ A}, C_5 = 0.081, C_6 = -0.039, N_2 = -0.022 \text{ Å}.$$

The dihedral angle between this plane and that of the carboxyl group is 71.4° .

The average C-H bond length is 1.06 ± 0.04 Å, quite close to the value of 1.09 Å usually taken as the standard internuclear separation. Thus this investigation, unlike some other recent investigations carried out in these and other Laboratories, has given little support to the theories of an apparent shortening in the C-H bond length when it is measured by X-ray methods. In addition, the average O-H bond length, 0.98 Å, is close to the internuclear separation, 1.01 Å, found by Peterson & Levy (1957) in a neutron diffraction study of heavy ice. However, the average N-H bond length of 0.94 Å is considerably shorter than the expected internuclear separation, though it is longer than the value of 0.87 Å found in glycine. Thus it is still not clear just where the effective X-ray scattering center of a bonded hydrogen atom lies.

(ii) Packing of the molecules

Drawings of the structure viewed along [001] and [100] are shown in Figs. 4 and 5, respectively. The molecules of lysine are in an extended configuration parallel to the *b* axis, and the packing is dominated by a three-dimensional network of hydrogen bonds. All ten protons of the nitrogen atoms and the water molecules participate in this network, though one of the protons of nitrogen atom N_2 forms a bifurcated bond.

The hydrogen bond lengths and angles are given in Table 7. The nitrogen N_1 of the amino acid grouping forms three such bonds—to a chloride ion, a water oxygen, and an oxygen of the carboxylate group. The terminal (ε) nitrogen N_2 is at hydrogen bonding distances from four atoms—two chloride ions and two oxygens of different carboxylate groups. It forms two normal hydrogen bonds, one to a chloride ion and



Fig. 4. A drawing of the structure viewed along [001].

	•	118.9°	101.9	107.8	92.5	125-4	104.9	16.91	89.3	171.8	129-0	85.2
	$(A \cdots D \cdots A)$	$\mathbf{O_2}\cdots W_1\cdots \mathbf{Cl}$	$CI \cdots W_2 \cdots W_1$	$c_1 \cdots N_1 \cdots O_1$	$0_1 \cdots N_1 \cdots W_2$	$W_2 \cdots N_1 \cdots Cl$	$0_1 \cdots N_2 \cdots Cl$	$0_2 \cdots N_2 \cdots Cl^*$	$0_2 \cdots N_2 \cdots Cl$	$0_2 \cdots N_2 \cdots 0_1$	$Cl^* \cdots N_2 \cdots Cl$	$CI^* \cdots N_s \cdots O_t$
acceptor atoms (A)	$(\mathrm{C-N}\cdots A)$			$C_2^{-}N_1\cdots Cl 111\cdot l^\circ$	$C_2-N_1\cdots O_1$ 111.4	$C_2-N_1 \cdots W_2$ 106.9		$C_6-N_2 \cdots Cl 110.9$	$C_6-N_2\cdots O_1$ 94.5	$C_6-N_2 \cdots Cl^*$ 118.0	$C_6-N_2\cdots O_2$ 90.9	
those of Table 2; those of a lues by the relations given	$(P- ext{H}- ext{d})$	W_1 -H ₈ ··· O ₂ 170° W_1 -H ₇ ··· Cl 156	W_2 -H ₉ ··· Cl 164 W_2 -H ₁₀ ··· W_1 160	$N_1-H_3 \cdots Cl 162$	$N_1-H_2 \cdots O_1$ 175	$N_1-H_1 \cdots W_2$ 157		$N_2-H_3 \cdots Cl 175$	$N_2-H_5 \cdots O_1$ 162	$N_2-H_4 \cdots Cl^* 124$	$N_2-H_1 \cdots O_2$ 126	
s (D) are table val				13°	en	16		e	13	41	37	
leters of donor atom re derived from the	$(\mathrm{H} extsf{-}D\cdots A)$			$H_{3}-N_{1}\cdots Cl$	$H_2^{-N_1} \cdots O_1$	$\mathrm{H_{1}^{-}N_{1}}\cdots W_{2}$		$H_{6}-N_{2}\cdots Cl$	$H_{5}-N_{2}\cdots O_{1}$	$H_4-N_2\cdots Cl^*$	${ m H_4-N_2}\cdots { m O_2}$	
ie positional param a	$d(D \cdots A)$	2·804 Å 3·218	3·245 2·712	3.224	2.789	2.813		3.166	2.791	3.346	2.889	
í.	Acceptor, at	O ₂ , $(x, y, z+1)$ CI, $(x, y, z+1)$	Cl. (x, y, z) W_1 , (x, y, z)	Cl. $(\bar{x}, y - \frac{1}{2}, \bar{z})$	$O_1, (x, y, z+1)$	$W_2, (x, y, z)$		Cl, $(x, y-1, z+1)$	$0_1, (\overline{x}+1, y-\frac{1}{2}, \overline{z})$	$Cl^*, (x, y-1, z)$	$0_2, (\bar{x}, y - \frac{1}{2}, \bar{z})$	
	Donor	W_1 W_1	$W_2^W_2$	N1	N1	N_1		N_2	$\mathbf{N_2}$	$\mathbf{N_2}$	$\mathbf{N_2}$	

Table 7. Hydrogen-bond lengths and angles

one to a carboxylate oxygen, which orient the third proton in a direction approximately half way between the other two atoms, though at distances appreciably further than normal from both. The $H_4 \cdots Cl^*$ and $H_4 \cdots O_2$ distances are 2.64 and 2.14 Å, respectively, while the four other $H \cdots Cl$ distances in the structure range from 2.19 to 2.38 Å and the five other $H \cdots O$ distances from 1.73 to 2.00 Å. This configuration is usually called a 'bifurcated hydrogen bond', and though objection may be made to the use of the word 'bond' some added stabilization should result from the interaction between the hydrogen atom and its negatively charged neighbors. No attempt was made to judge if this stabilization is appreciably greater than that due to normal van der Waals interactions.

The water molecules are an integral part of the hydrogen bond system, each being the donor of two

Table 8. Magnitudes and direction cosines of the principal axes of the vibration ellipsoids, referred to orthogonal axes a*bc

At	tom	Axis i	B_i	g_i ¹	g_i^2	g_i^3
(D 1	1	4.601	0.139	0.986	0.094
	-	2	3.842	0.985	-0.147	0.086
		3	2.340	-0.099	-0.080	0.992
(\mathcal{D}_2	1	5.180	0.287	0.870	0.402
	-	2	3.710	0.715	0.085	-0.694
		3	2.567	-0.637	0.486	-0.598
(C1	1	3.571	-0.488	0.866	0.110
	-	2	2.664	0.867	0.466	0.174
		3	2.221	-0.100	-0.180	0.979
(C ₂	1	2.762	0.388	0.919	-0.068
		2	2.486	-0.422	0.243	0.873
		3	2.421	0.819	-0.310	0.482
1	N ₁	1	3.462	0.829	0.551	0.091
		2	2.920	-0.504	0.809	-0.301
		3	2.530	-0.540	0.204	0.949
(33 C	1	4.054	0.995	0.069	-0.068
		2	3.398	0.066	0.024	0.998
		3	2.321	0.070	0.997	-0.019
0	24	1	4.153	0.974	0.098	-0.204
		2	3.406	0.110	0.583	0.805
		3	2.744	-0.198	0.807	-0.557
0	3. 25	1	4.819	0.998	-0.062	0.003
		2	3.651	0.023	0.412	0.911
		3	2.792	0.058	0.909	-0.413
(2 ₆	1	4.086	0.976	-0.068	-0.209
		2	3.356	0.114	0.970	0.215
		3	2.705	0.188	-0.234	0.954
1	N ₂	1	4.057	0.806	-0.452	-0.382
		2	3.468	0.585	0.508	0.632
		3	2.522	0.092	0.733	-0.674
٢	N_1	1	13.089	-0.988	0.135	-0.074
		2	5.510	0.018	0.577	0.817
		3	4.248	0.153	0.806	-0.572
١	N_2	1	10.252	-1.000	-0.018	0.010
		2	5.234	0.001	0.416	-0.909
		3	3.379	-0.021	0.909	-0.416
C	21	1	4.260	0.362	0.820	0.443
		2	3.541	-0.886	0.451	-0.111
		3	2.941	0.291	0.352	-0.889



Fig. 5. A drawing of the structure viewed along [100].

bonds and the acceptor for one. Any substantial loss of water would presumably lead to the destruction of the crystal, though the density measurements seem to indicate that a slight deficiency (5%) can be tolerated. By way of contrast some recent investigations (Leung & Marsh, 1958; Sutor, 1958; Gerdil, 1961; Hughes, Yakel & Freeman, 1961) have shown structures stable with only 80% or less of the water sites occupied. In these cases the role of the water molecules appears to be principally one of space filling.

(iii) The temperature factors

The magnitudes and direction cosines of the principal axes of the ellipsoids of thermal motion, derived from the anisotropic temperature factor coefficients of Table 2, are given in Table 8.

By far the greatest thermal motion is associated with the two water molecules, as would be expected, for they are held in place solely by hydrogen bonds. In each case the direction of maximum vibration is within 12° of normal to the plane defined by the three neighboring hydrogen bonded atom, and, as it happens, nearly parallel to the *a* axis. The smallest vibration is associated with the central carbon atom C_2 , and is nearly isotropic. The major axes of the carboxylate oxygen atoms O_1 and O_2 are approximately perpendicular to the plane of that group, and the major axes of the carbon atoms of the side chain (C_3 to C_6) are approximately perpendicular to its plane.

The temperature factors cannot be interpreted in terms of rigid body vibrations. The greatest vibration of a side chain atom is associated not with the terminal atom N₂ but with the penultimate carbon atom C₅. Also, the direction of maximum vibration of N₂ differs by more than 30° from that of the other side chain atoms. Apparently the hydrogen bonds formed by N₂ inhibit the thermal vibrations associated both with it and its immediate neighbors.

We should like to thank Mr David Barker who measured the density and assisted in the final calculations. D. A. Wright acknowledges gratefully a Fulbright grant for travel between Auckland, New Zealand, and Pasadena.

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