

but no attempts were made to estimate the extent of disorder in the crystal.

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References

- BAILEY, N. A., HARRISON, P. M. & MASON, R. (1968). *Chem. Commun.* **10**, 559.
BERGIN, R. (1971). *Acta Cryst.* **B27**, 381.
BERGIN, R. & CARLSTRÖM, D. (1968). *Acta Cryst.* **B24**, 1506.

- BERGIN, R. & RINGERTZ, H. (1969). In *Stereochemical Aspects of Purine Degradation*. Thesis of H. RINGERTZ. Stockholm: Balder.
CARLSTRÖM, D. & BERGIN, R. (1967). *Acta Cryst.* **23**, 313. *International Tables for X-ray Crystallography* (1962). Vol. III. Birmingham: Kynoch Press.
JOHNSON, C. K. (1965). *ORTEP, a Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations*. Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee.
PHILLIPS, D. C. (1954). *Acta Cryst.* **7**, 159.
STEWART, J. M. & HIGH, D. (1965). *X RAY 63, Program System for X-ray Crystallography for the IBM 709-7090-7094*. Depts. of Chemistry, Univ. of Washington, Seattle, and Univ. of Maryland, College Park, U.S.A.

Acta Cryst. (1971). **B27**, 2152

The Crystal Structure of L- α,γ -Diaminobutyric Acid Monohydrochloride

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The crystal structure of L- α,γ -diaminobutyric acid monohydrochloride, $\text{NH}_3^+(\text{CH}_2)_2\text{CHNH}_3^+\text{COO}^- \cdot \text{Cl}^-$, has been determined using three-dimensional intensity data obtained with Mo $K\alpha$ radiation. The crystal is monoclinic with the space group $P2_1$. There are two formula units in a cell of dimensions $a = 8.355$, $b = 8.267$, $c = 5.316$ Å, $\beta = 109.37^\circ$. The structure was solved by the heavy atom method and refined by the method of block-diagonal least squares. The final R value was 0.057 for 1858 observed reflexions of non-zero intensity. The L- α,γ -diaminobutyric acid molecule exists as a zwitterion, each nitrogen atom having an extra proton and forming a three-dimensional network of the hydrogen bonds. All the bond lengths and angles in the molecule are as a whole similar to those found in lysine and ornithine. The two C-NH $_3^+$ distances are equal within experimental errors, the average value being 1.495 Å. The side chain with γ nitrogen atom is of an extended, nearly planar configuration, and the average C-C distance is 1.530 Å.

Introduction

L- α,γ -Diaminobutyric acid, $\text{NH}_2(\text{CH}_2)_2\text{CHNH}_2\text{COOH}$, is a synthetic amino acid. In connexion with the molecular structure of lysine (Wright & Marsh, 1962) and that of ornithine (Chiba, Ueki, Ashida, Sasada & Kakudo, 1967), it seems worth while to determine the molecular structure of this compound.

In the present study, the crystal structure of L- α,γ -diaminobutyric acid monohydrochloride is determined by X-ray diffraction, and the bond lengths obtained are compared with those of lysine and ornithine.

Experimental

L- α,γ -Diaminobutyric acid monohydrochloride, synthesized at the Department of Polymer Science of Hokkaido University, was supplied to us. The single crystals,

grown from aqueous solutions at about 5°C, were colourless plates elongated along the b axis. The space group was determined from Weissenberg and precession photographs. Systematic absence of reflexions for $0k0$ with k odd suggested that the space group is either $P2_1$ or $P2_1/m$, and the former was adopted since the compound is optically active. The unit-cell parameters were obtained from a least-squares procedure by minimizing the quantity $\sum w(\sin^2 \theta_{\text{obs}} - \sin^2 \theta_{\text{calc}})^2$. Values of 2θ for 25 reflexions, measured on a diffractometer, were used and the weight assigned was proportional to $1/\sin^2 2\theta$. The confidence limits are subjectively set to be three times the estimated standard deviations obtained from the least-squares calculation.

Crystal data

L- α,γ -Diaminobutyric acid monohydrochloride

Formula: $\text{C}_4\text{H}_{10}\text{N}_2\text{O}_2 \cdot \text{HCl}$

M.W. 154.6

Monoclinic

$a = 8.355 \pm 0.004$, $b = 8.267 \pm 0.004$, $c = 5.316 \pm 0.003$ Å
 $\beta = 109.37 \pm 0.06^\circ$; $U = 346.4$ Å 3

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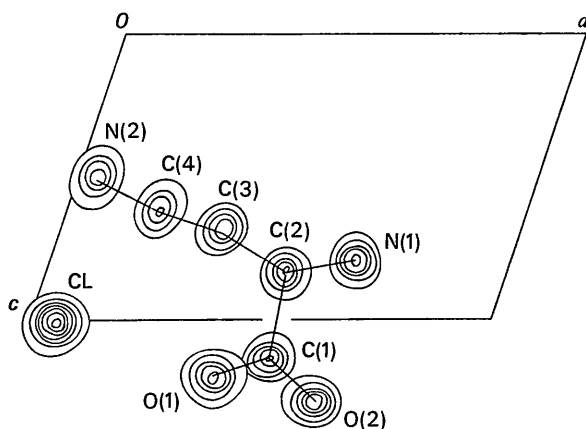


Fig. 1. Composite drawing of the final electron-density map viewed along the b axis. Contours are drawn at intervals of $2 \text{ e.}\text{\AA}^{-3}$ beginning at $2 \text{ e.}\text{\AA}^{-3}$ for the light atoms, and at intervals of $4 \text{ e.}\text{\AA}^{-3}$ beginning at $2 \text{ e.}\text{\AA}^{-3}$ for the chlorine atom.

$$D_m = 1.45 \text{ g.cm}^{-3} \quad (\text{by flotation})$$

$$D_x = 1.48 \text{ g.cm}^{-3}$$

$$F(000) = 164, Z = 2$$

$$\lambda(\text{Mo } K\alpha) = 0.71069 \text{ \AA}$$

Intensity data were measured on a Rigaku automatic four-circle diffractometer, controlled by a FACOM 270-20 computer with Mo $K\alpha$ radiation monochromated by a LiF crystal, using the ω - 2θ scan technique. The dimensions of the crystal were $0.20 \times 0.20 \times 0.25$ mm. The scanning speed was 2° per minute and the scan range $\Delta 2\theta$ was varied according to the relation $\Delta 2\theta = 2^\circ + 0.8^\circ \tan \theta$. The background was measured for twenty seconds at the beginning and the end of each scan. As a check of the stability of the crystal and the instruments, the three standard reflexions were monitored every 50 reflexions: no significant variation in their intensities was noticed. 2727 independent reflexions corresponding to $\sin \theta / \lambda < 1.0 \text{ \AA}^{-1}$ were measured. Reflexions with $|F_o| < 3\sigma(|F_o|)$ were assigned zero intensity, where $\sigma(|F_o|)$ was estimated from counting statistics. In view of the small linear absorption coefficient ($\mu = 4.8 \text{ cm}^{-1}$ for Mo $K\alpha$ radiation), the absorption correction was not made. In the structure determination, 2012 independent reflexions with $\sin \theta / \lambda < 0.9 \text{ \AA}^{-1}$ were used.

Structure determination and refinement

The coordinates of the chloride ion were deduced from a three-dimensional Patterson function. A three-dimensional Fourier synthesis based on the coordinates of the chloride ion revealed the approximate structure, and an R value of 0.37 was obtained. All calculations were performed on HITAC 5020E and FACOM 230-60 computers using the *Universal Crystallographic Com-*

puting System (1967). The structure refinement was then carried out by a series of the least-squares calculations, including four cycles of the block-diagonal least-squares calculations with individual isotropic temperature factors, and three cycles of the full-matrix least-squares calculations with anisotropic temperature factors. As a result, the R value reduced to 0.11. A three-dimensional difference Fourier synthesis was calculated at this stage in order to locate the hydrogen atoms. Peaks with heights ranging from 0.5 to $0.8 \text{ e.}\text{\AA}^{-3}$ were observed at the expected positions for all the hydrogen atoms except for H(3) and H(6). These hydrogen atoms were included in the subsequent structure factor calculations and the least-squares refinement, where the isotropic temperature factor for each hydrogen atom was assumed to be the same as that determined for the atom to which it was bonded. Throughout the following least-squares calculations, however, the temperature factors of the hydrogen atoms were not further refined. Four other cycles of the block-diagonal least-squares refinement including these hydrogen atoms led to the R value of 0.065. The three-dimensional difference Fourier synthesis was then calculated, and the positions of the two hydrogen atoms, H(3) and H(6), clearly showed up.

In the final least-squares calculations, several reflexions affected by extinction were omitted. At the last cycle, the maximum parameter shift for the non-hydrogen atoms was less than one-third of their standard deviations, and that for the hydrogen atoms less than their standard deviations. The final R value was 0.057 (or 0.068 if reflexions of zero intensity are included). In these calculations unit weight was applied to all reflexions, except for those of zero intensity to which a weight 0.1 was given. Atomic scattering factors used for Cl⁻, O, N, C, and H are those listed in *International Tables for X-ray Crystallography* (1962).

The final atomic parameters for the non-hydrogen atoms together with their standard deviations are listed in Tables 1 and 2, those for the hydrogen atoms in Table 3, and the observed and the calculated structure factors in Table 4. Fig. 1 shows the composite electron-density map, and Fig. 2 shows the composite difference Fourier synthesis using the calculated structure factors which contain only the contributions from the non-hydrogen atoms.

Table 1. Final atomic coordinates and their standard deviations, $\sigma (\times 10^4)$

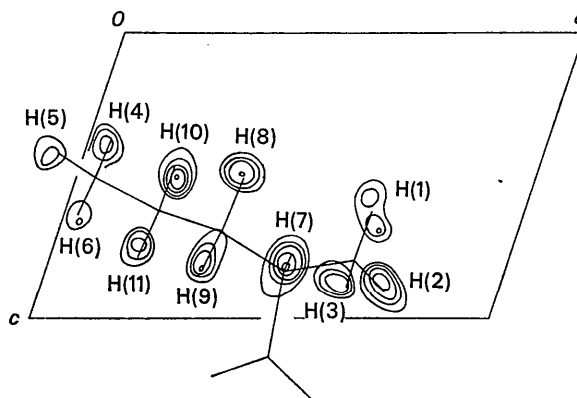
	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cl	0.0587	1	0.2500	—	0.0067	1
O(1)	0.4368	3	0.6313	3	1.2007	5
O(2)	0.6743	3	0.4851	4	1.2862	4
N(1)	0.6611	3	0.4579	4	0.7901	4
N(2)	0.0416	3	0.4684	4	0.4980	5
C(1)	0.5445	3	0.5563	4	1.1321	3
C(2)	0.5162	3	0.5458	4	0.8315	5
C(3)	0.3502	3	0.4574	4	0.6842	5
C(4)	0.1980	3	0.5685	4	0.6128	6

Table 2. *Thermal parameters and their standard deviations* ($\times 10^4$)The thermal parameters are of the form: $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

	β_{11}	σ	β_{22}	σ	β_{33}	σ	β_{12}	σ	β_{13}	σ	β_{23}	σ
Cl	105	1	104	1	219	2	4	2	91	2	-3	3
O(1)	94	3	114	4	178	7	26	6	112	7	-27	9
O(2)	89	3	166	5	116	5	73	7	51	7	57	9
N(1)	54	2	118	4	116	6	7	6	65	6	14	8
N(2)	58	3	118	4	201	8	6	6	33	8	1	10
C(1)	66	3	80	3	121	6	-11	6	75	7	-4	8
C(2)	53	3	86	4	105	6	3	5	47	6	12	8
C(3)	49	3	80	3	171	7	-9	6	28	7	-31	9
C(4)	55	3	95	4	228	10	19	7	10	9	9	11

Table 3. *Final parameters of the hydrogen atoms*The thermal parameters, B , are of the form: $\exp[-B(\sin \theta/\lambda)^2]$.

	x	y	z	B	Bonded to
H(1)	0.663	0.471	0.620	1.7	N(1)
H(2)	0.753	0.511	0.895	1.7	N(1)
H(3)	0.662	0.358	0.842	1.7	N(1)
H(4)	0.046	0.399	0.358	2.0	N(2)
H(5)	-0.055	0.533	0.426	2.0	N(2)
H(6)	0.027	0.395	0.627	2.0	N(2)
H(7)	0.522	0.662	0.771	1.5	C(2)
H(8)	0.360	0.412	0.499	1.7	C(3)
H(9)	0.336	0.365	0.811	1.7	C(3)
H(10)	0.201	0.649	0.449	2.3	C(4)
H(11)	0.189	0.628	0.780	2.3	C(4)
$\langle \sigma(x) \rangle$	0.006,	$\langle \sigma(y) \rangle$	0.007,	$\langle \sigma(z) \rangle$	0.010.

Fig. 2. Composite drawing of the final difference Fourier synthesis viewed along the b axis. Contours are at intervals of $0.1 \text{ e.}\text{\AA}^{-3}$ beginning at $0.3 \text{ e.}\text{\AA}^{-3}$.

Description of the structure

The bond lengths and angles in the molecule are given in Table 5 and shown in Fig. 3, while those involving the hydrogen atoms are given in Table 6. The e.s.d.'s of the bond lengths and angles among C, N, and O atoms are about 0.005 \AA and 0.3° , respectively.

In Table 7 the average bond lengths are compared with those of lysine and ornithine. The average of two C-NH $_3^+$ bond lengths, 1.495 \AA , is longer than the normal single-bond length between the carbon and nitrogen atoms, and practically equal to the average value of the C-NH $_3^+$ distance, 1.493 \AA , of the amino acid hitherto investigated (Kakudo, 1966). The length of two C-C bonds, C(1)-C(2) and C(2)-C(3), are practically the same, while the bond C(3)-C(4) is a little shorter than these two C-C distances. The first two are close to the standard value commonly accepted. As shown in Table 7, however, the average of the two C-C bond lengths in the side chain, 1.526 \AA , is close to the average of the C-C bond lengths in the side chain of lysine and that of ornithine. The average value of six N-H bond lengths, 0.93 \AA , and that of five C-H's, 1.06 \AA , are also very close to those found in lysine and ornithine. It is concluded, therefore, that the bond lengths and angles in the L- α,γ -diaminobutyric acid molecule are as a whole quite similar to those found in lysine and ornithine.

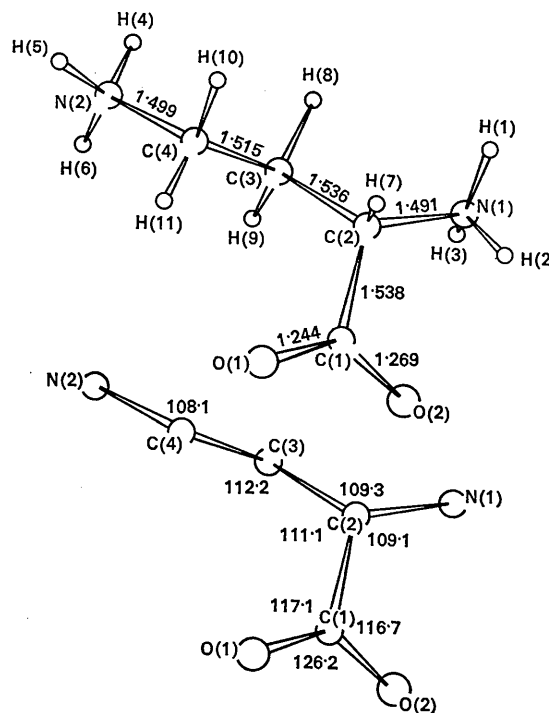


Fig. 3. Bond lengths and angles in the molecule.

Table 4. Final observed and calculated structure factors (×10)

Reflexions indicated by an asterisk (*) were omitted from the final least-squares calculations.

Table with multiple columns representing different reflections (h k l) and their corresponding observed and calculated structure factors. Reflexions with asterisks in the original image are omitted from the final calculations.

Table 6. Bond lengths and angles involving the hydrogen atoms

Bond	$d(X-H)$	Angle	ζ_{N-X-H}	Angle	H-X-H
N(1)-H(1)	0.92 Å	C(2)-N(1)-H(1)	112°	H(1)-N(1)-H(2)	105°
N(1)-H(2)	0.91	C(2)-N(1)-H(2)	104	H(2)-N(1)-H(3)	111
N(1)-H(3)	0.88	C(2)-N(1)-H(3)	110	H(3)-N(1)-H(1)	115
N(2)-H(4)	0.95	C(4)-N(2)-H(4)	113	H(4)-N(2)-N(5)	106
N(2)-H(5)	0.94	C(4)-N(2)-H(5)	111	H(5)-N(2)-H(6)	111
N(2)-H(6)	0.95	C(4)-N(2)-H(6)	111	H(6)-N(2)-H(4)	103
$\langle N-H \rangle$	0.93				
C(2)-H(7)	1.03	N(1)-C(2)-H(7)	107	H(8)-C(3)-H(9)	113
C(3)-H(8)	1.08	C(1)-C(2)-H(7)	105	H(10)C(4)-H(11)	114
C(3)-H(9)	1.06	C(3)-C(2)-H(7)	115	$\langle \sigma(H-X-H) \rangle =$	5
C(4)-H(10)	1.10	C(2)-C(3)-H(8)	108		
C(4)-H(11)	1.04	C(2)-C(3)-H(9)	107		
$\langle C-H \rangle$	1.06	C(4)-C(3)-H(8)	107		
$\langle \sigma(X-H) \rangle =$	0.06	C(4)-C(3)-H(9)	110		
		N(2)-C(4)-H(10)	105		
		N(2)-C(4)-H(11)	108		
		C(3)-C(4)-H(10)	109		
		C(3)-C(4)-H(11)	112		
		$\langle \sigma_{N-X-H} \rangle =$	3.3		

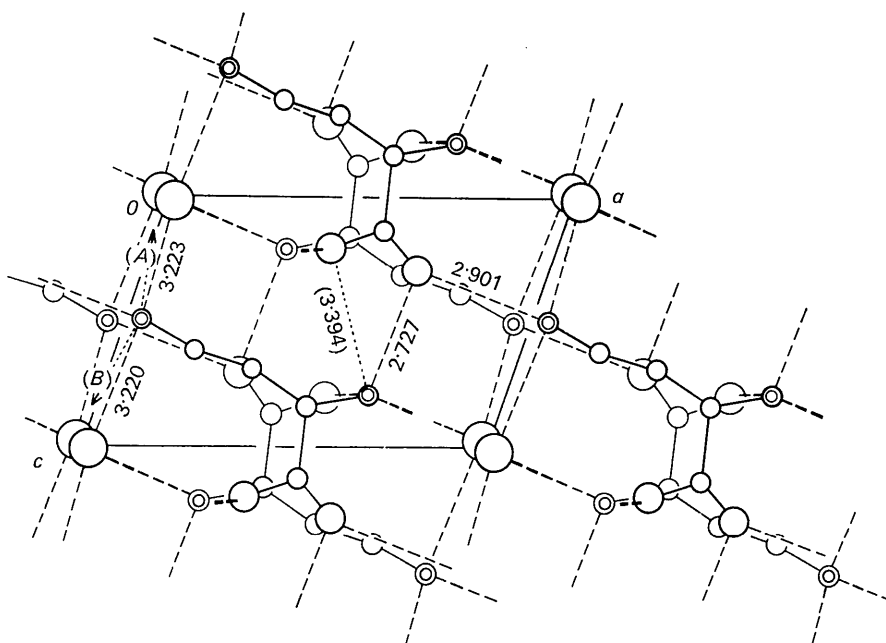


Fig. 4. Structure viewed along the b axis. The proposed hydrogen bonds (broken lines) and other close contacts (dotted lines) are shown. Close contacts are (A) $N(2) \cdots Cl^{viii}$, 3.449 Å; (B) $N(2) \cdots Cl^{ix}$, 3.814 Å. Positions of these chlorine atoms are given in Table 8.

Table 7. Comparison of the average bond lengths with those of lysine and ornithine

	Present molecule	Lysine*	Ornithine†
$\langle C-NH_3^+ \rangle$	1.495 Å	1.482 Å	1.491 Å
$\langle C-C \rangle^\ddagger$	1.526	1.522	1.526
$\langle C-C \rangle^\S$	1.530	1.524	1.530
$\langle N-H \rangle$	0.93	0.94	0.95
$\langle C-H \rangle$	1.06	1.06	1.05

* Wright & Marsh (1962).

† Chiba *et al.* (1967).

‡ The average of the C-C bond lengths in the side chain.

§ The average of all the C-C bond lengths in the molecule.

The L- α,γ -diaminobutyric acid molecule is described by two planar groups, one being the carboxyl group and the other the side chain terminating at the γ nitrogen atom N(2). The equation of the least-squares plane of the carboxyl group and the C(2) atom is:

$$0.5412X + 0.8386Y + 0.0615Z = 5.6056,$$

where the direction cosines are referred to the orthogonal axes a, b , and c^* , and X, Y , and Z are expressed in Å. The deviations of the atoms from the plane are:

$$O(1), -0.002; O(2), -0.002;$$

$$C(1), 0.006; C(2), -0.002 \text{ Å.}$$

Table 8. *Dimensions of the proposed hydrogen bonds and other close contacts*

Donor	Acceptor	N...A	\angle C-N...A	\angle N-H...A	\angle H-N...A
C(2)-N(1)-H(1)	\cdots O(2 ⁱ)	2.727 Å	113.8°	176°	2°
C(2)-N(1)-H(2)	\cdots Cl ⁱⁱ	3.297	96.5	151	21
C(2)-N(1)-H(3)	\cdots O(1 ⁱⁱⁱ)	2.839	102.4	152	8
C(2)-N(1)	$\cdots\cdots\cdots$ Cl ^{iv}	3.580			
C(2)-N(1)	$\cdots\cdots\cdots$ O(1 ^v)	3.394			
C(4)-N(2)-H(4)	\cdots Cl ^{vi}	3.223	112.1	176	1
C(4)-N(2)-H(5)	\cdots O(2 ^{vii})	2.901	143.1	134	33
C(4)-N(2)-H(6)	\cdots Cl ^{viii}	3.220	100.4	164	5
C(4)-N(2)	$\cdots\cdots\cdots$ Cl ^{ix}	3.449			
C(4)-N(2)	$\cdots\cdots\cdots$ Cl ^{ix}	3.814			
(i)	$x, y, -1+z$	(ii)	$1-x, \frac{1}{2}+y, 1-z$	(iii)	$1-x, -\frac{1}{2}+y, 2-z$
(iv)	$1+x, y, 1+z$	(v)	x, y, z	(vi)	$-1+x, y, -1+z$
(vii)	$x, y, 1+z$	(viii)	$-x, \frac{1}{2}+y, -z$	(ix)	$-x, \frac{1}{2}+y, 1-z$

The α nitrogen atom N(1) lies 0.067 Å out of the plane. The side chain with γ nitrogen atom N(2) has a fully extended configuration, in which the three carbon atoms and the terminal nitrogen atom are approximately coplanar. The least-squares plane of these atoms is:

$$-0.4135X - 0.5191Y + 0.8965Z = 1.8012,$$

and the deviations of the atoms from the plane are:

$$C(2), 0.038; C(3), -0.041;$$

$$C(4), -0.035; N(2), 0.038 \text{ \AA}.$$

The dihedral angle between the two plane is 72.4°.

Figs. 4 and 5 illustrate the crystal structure viewed along the b and c axes, respectively. They show the packing of the molecule, the proposed hydrogen bonds (broken lines) and other close contacts (dotted lines). The dimensions of the proposed hydrogen bonds and other close contacts are listed in Table 8. These hydrogen bonds make a three-dimensional network in the crystal. The arrangement of the hydrogen atoms proves that the L- α,γ -diaminobutyric acid molecule exists as a zwitterion, and thus the formula is to be written as $\text{NH}_3^+(\text{CH}_2)_2\text{CHNH}_3^+\text{COO}^- \cdot \text{Cl}^-$.

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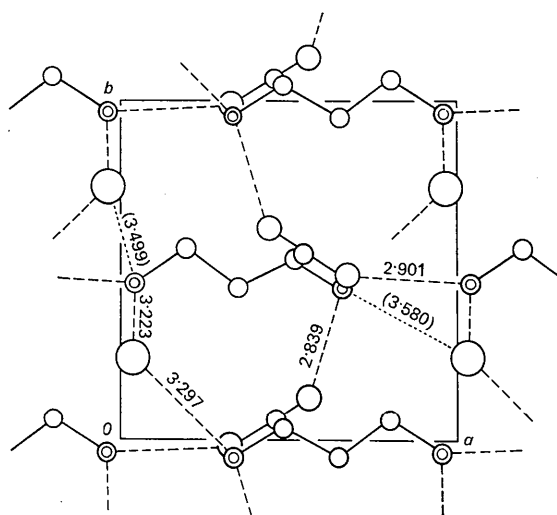


Fig. 5. Structure viewed along the c axis. The molecules shown are those existing in the region $-0.5 \leq z \leq 0.5$.

References

- CHIBA, A., UEKI, T., ASHIDA, T., SASADA, Y. & KAKUDO, M. (1967). *Acta Cryst.* **22**, 863.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 KAKUDO, M. ED. (1966). *Yūki Kesshō Kagaku*. p. 150 (in Japanese). Kyoto: Kagakudōjin.
Universal Crystallographic Computing System (1967). Edited by T. SAKURAI. Japanese Crystallographic Association.
 WRIGHT, D. A. & MARSH, R. E. (1962). *Acta Cryst.* **15**, 54.