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The Crystal Structure of β-D-Galactosamine Hydrochloride

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The crystal structure of β-D-galactosamine hydrochloride has been determined from three-dimensional intensities obtained with Cu $K\alpha$ radiation. The needle-shaped crystals are orthorhombic, space group $P2_12_12_1$, with eight molecules in a unit cell of dimensions $a=9{\cdot}794$, $b=19{\cdot}686$ $c=9{\cdot}385$ Å. The final R index is 0·045 and the e.s.d.'s of the coordinates of C, N and O atoms are about 0·005 Å. Bond lengths and angles in galactosamine are very close to those of similar compounds already reported. The galactosamine ring has the normal Sachse *trans* configuration with 1*e*2*e*3*e*4*a*5*e*.

Introduction

D-Galactosamine (2-amino-2-desoxy-D-galactose or chondrosamine) is one of the important amino-sugars. It is a constituent of complex polysaccharides, glucoprotein of mucoid, mucin and chondroitin sulphate. In most of these compounds, D-galactosamine occurs together with glucosamine. The crystal structures of α-D-glucosamine hydrochloride and hydrobromide have been determined by Chu & Jeffrey (1965). In this structure, the glucopyranose ring has the normal Sachse *trans* configuration with lower energy conformation 1a2e3e4e5e. The preliminary studies on β-D-galactosamine hydrochloride have been reported by Werner (1952). The crystal structure, however, was still undetermined. In view of its relation to other pyranose sugars and biochemical interest, it was of interest to determine the conformation of the galactopyranose ring in this compound.

Experimental

The crystals of β-D-galactosamine hydrochloride were recrystallized from aqueous acetone solution. They are

colourless needles, elongated along the crystallographic *b* axis, and can be cut with a scalpel blade. A crystal with dimensions of $0{\cdot}07\times0{\cdot}23\times0{\cdot}11$ mm was used throughout the experiment. Oscillation and Weissenberg photographs were taken for a preliminary X-ray investigation of the crystal. The cell dimensions were obtained with the use of a diffractometer and Cu $K\alpha$ radiation. The Weissenberg photographs showed absences $h00$, $0k0$ and $00l$ for h, k and l odd respectively. The density was measured by floating the crystals in a chloroform–carbon tetrachloride mixture.

The three-dimensional intensity data were collected on a Rigaku Denki automatic four-circle diffractometer, using Ni-filtered Cu $K\alpha$ radiation operated in the ω-2θ scanning mode. The 1359 independent reflexions within a sphere of radius $2\sin\theta/\lambda=1{\cdot}123$ ($2\theta<120°$) were measured, of which 1248 reflexions had intensities significantly above background. The usual Lorentz and polarization corrections were applied, but no corrections were made for absorption or extinction.

Crystal data

$C_6H_{11}O_5NH_3^+Cl^-$, F.W. 215·5.
Orthorhombic,
$a=9{\cdot}794\pm0{\cdot}002, b=19{\cdot}686\pm0{\cdot}002, c=9{\cdot}385\pm0{\cdot}001$ Å,
$U=1808{\cdot}9$ Å^3,
$D_m=1{\cdot}591$ g.cm^{-3}, $D_x=1{\cdot}583$ g.cm^{-3},
$Z=8$.
Systematic absences,
$h00$ with $h=2n+1$, $0k0$ with $k=2n+1$, $00l$ with $l=2n+1$.
Space group $P2_12_12_1$.

Determination of the structure

There are two kinds of galactosamine molecule in the crystal which are not symmetrically equivalent.

The heavy atom vectors, Cl–Cl, were identified on the three-dimensional Patterson function. The heavy

Table 1. *Final fractional atomic coordinates and their standard deviations*(Å)

Values are $\times10^4$.

	x	$\sigma(x)$	y	$\sigma(y)$	z	$\sigma(z)$
Cl(1)	13733	19	1191	17	1186	17
Cl(2)	5466	19	3750	16	2272	15
C(1)	10229	71	460	56	4069	60
C(2)	11212	69	118	54	3037	57
C(3)	10525	67	−460	55	2248	58
C(4)	9223	70	−197	58	1540	60
C(5)	8335	68	120	56	2685	61
C(6)	7001	69	375	66	2041	65
N(2)	12395	62	−142	51	3900	54
O(1)	10909	48	1036	41	4548	42
O(3)	11445	47	−723	38	1208	41
O(4)	9561	51	318	42	498	40
O(5)	9027	46	689	38	3338	41
O(6)	6067	47	573	43	3131	45
C(7)	12020	68	2992	60	2151	64
C(8)	10967	66	2662	55	1162	63
C(9)	10204	71	2090	57	1900	59
C(10)	9613	70	2345	55	3301	61
C(11)	10777	66	2638	58	4182	59
C(12)	10308	77	2867	64	5621	64
N(8)	11744	58	2374	54	−80	56
O(7)	12463	50	3580	40	1455	47
O(9)	9164	45	1851	39	958	41
O(10)	8595	45	2867	37	3035	44
O(11)	11370	48	3206	37	3438	40
O(12)	11456	51	3002	41	6549	45

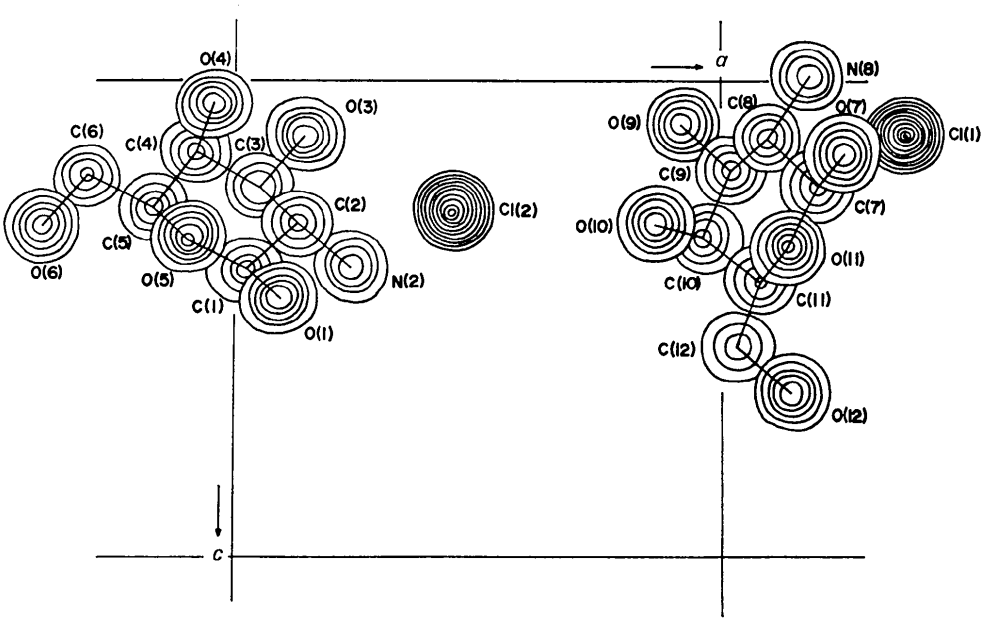

Fig. 1. A composite drawing of the final electron density map, viewed along the *b* axis. Contours are drawn at 2,4,6, ... e.Å^{-3} for light atoms and at 2,6,10 ... e.Å^{-3} for the chlorine atom.

atom Fourier map obtained by using Cl phases could reveal only a part of the structure. With the aid of the minimum function, which was synthesized on the basis of the coordinates of the Cl ions, several sites were picked as possible locations of atoms. After several cyclic procedures of least-squares refinement followed by the synthesis of an electron density map, the approximate locations of all the C, N and O atoms were established, the R index being 0·079 at this stage. Further refinement by the block-diagonal least-squares method gave $R=0·069$ after three cycles with anisotropic thermal factors for Cl, C, N and O atoms. The final R index was 0·045, with all hydrogen atoms included. The final parameters are given in Tables 1, 2 and 3. The observed and calculated structure factors are listed in Table 4. The atomic scattering factors for the chloride ion and neutral C, N, O and H atoms were taken from *International Tables for X-ray Crystallography* (1962). The anomalous dispersion terms were ignored.

Description of the structure and discussion

A composite drawing of the final electron density map viewed along the b axis is shown in Fig. 1. The interatomic distances and angles are illustrated in Fig. 2. The estimated standard deviations of the bond lengths and angles are 0·009 Å and 0·6 respectively.

Geometry of galactosamine

The two galactosamine molecules have almost the same size and conformation. Each galactopyranose ring has the normal Sachse *trans* configuration as expected by analogy with α-D-glucose (M^Donald & Beevers, 1952) and β-D-glucose (Ferrier, 1963; Chu &

Table 3. *Hydrogen atom parameters*

	x	y	z
H(C1)	1·004	0·015	0·507
H(C2)	1·168	0·049	0·233
H(C3)	1·023	−0·080	0·303
H(C4)	0·868	−0·066	0·103
H(C5)	0·806	−0·022	0·348
H(C61)	0·650	−0·003	0·142
H(C62)	0·731	0·074	0·130
H(N21)	1·287	0·014	0·450
H(N22)	1·209	−0·042	0·467
H(N23)	1·305	−0·038	0·342
H(O1)	1·057	0·103	0·553
H(O3)	1·156	−0·116	0·131
H(O4)	0·939	0·006	−0·025
H(O6)	0·528	0·071	0·275
H(C7)	1·298	0·269	0·226
H(C8)	1·027	0·303	0·073
H(C9)	1·091	0·172	0·217
H(C10)	0·915	0·192	0·389
H(C11)	1·157	0·223	0·417
H(C121)	0·964	0·328	0·549
H(C122)	0·983	0·246	0·606
H(N81)	1·240	0·205	0·021
H(N82)	1·122	0·220	−0·078
H(N83)	1·224	0·272	−0·042
H(O7)	1·331	0·363	0·174
H(O9)	0·916	0·146	0·096
H(O10)	0·784	0·256	0·312
H(O12)	1·156	0·345	0·651

$\langle\sigma(x)\rangle=0·073$ Å $\langle\sigma(y)\rangle=0·066$ Å $\langle\sigma(z)\rangle=0·071$ Å

Table 2. *Thermal parameters and their standard deviations* ($\times 10^4$)

Temperature factor $=\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	B_{11}	σ	B_{22}	σ	B_{33}	σ	B_{12}	σ	B_{13}	σ	B_{23}	σ
Cl(1)	80	3	22	0	90	2	0	2	−20	4	−1	2
Cl(2)	81	3	23	0	62	2	17	2	−2	4	−5	2
C(1)	70	10	13	2	62	7	5	6	−10	14	−13	6
C(2)	54	9	13	1	51	7	−4	6	13	13	8	6
C(3)	48	9	14	2	58	7	0	6	−8	14	−3	6
C(4)	76	10	15	2	55	7	6	6	20	14	5	6
C(5)	66	10	13	2	66	7	−10	6	−11	14	3	6
C(6)	51	10	23	2	74	8	8	7	−6	15	−16	7
N(2)	55	7	21	2	82	7	9	6	−13	13	−3	6
O(1)	91	7	18	1	71	5	−1	5	−11	10	−5	4
O(3)	83	7	14	1	67	5	8	5	34	11	−7	4
O(4)	102	7	20	1	54	5	−2	5	7	11	15	4
O(5)	74	6	14	1	68	5	8	4	−28	10	−12	4
O(6)	62	7	23	1	85	6	16	5	14	10	3	5
C(7)	64	10	17	2	71	8	10	6	−18	15	−15	6
C(8)	60	9	13	1	67	8	−4	6	20	14	−10	6
C(9)	70	10	14	2	61	7	−7	6	43	14	−10	6
C(10)	67	9	12	1	73	8	6	7	11	15	11	6
C(11)	59	9	16	2	58	8	3	6	−5	13	6	6
C(12)	78	10	20	2	73	8	−10	7	10	16	−3	7
N(8)	71	8	22	2	65	6	17	6	−11	12	−17	6
O(7)	77	7	17	1	110	6	13	5	−22	12	0	5
O(9)	69	6	15	1	72	5	9	4	29	10	−4	4
O(10)	53	6	13	1	96	6	−9	4	−4	10	0	4
O(11)	89	7	12	1	66	5	8	5	−25	10	−15	4
O(12)	88	7	19	1	85	6	−16	5	38	11	−6	5

Jeffrey, 1968). There are two stable anomeric isomers for galactosamine, α-D and β-D. In this crystal the rings have the *C*1 chair form with lower energy conformation 1*e*2*e*3*e*4*a*5*e*; therefore, the molecule is the β isomer. Least-squares planes of a pyranose ring are formed by the four carbon atoms: C(1), C(2), C(4), C(5) and C(7), C(8), C(10), C(11). The deviations of these atoms from their respective planes are within 0·04 Å (Table 5).

Table 4. *Calculated and observed structure factors* (×2)

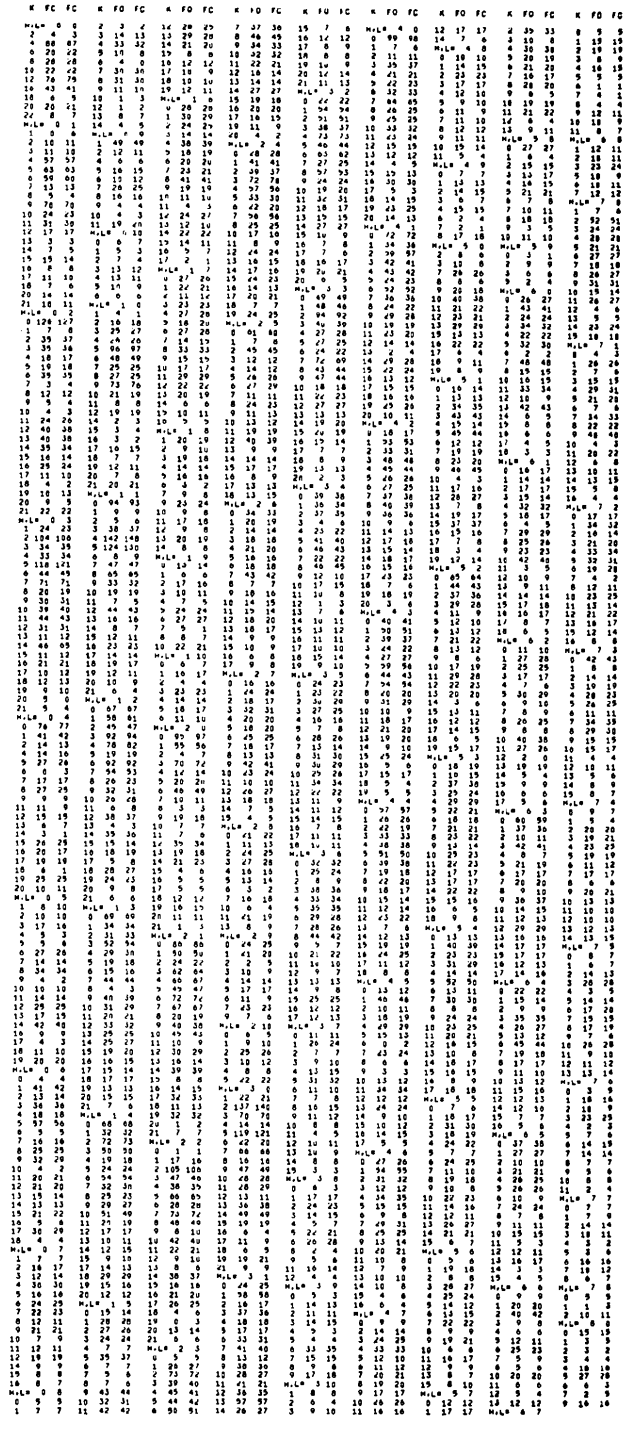

Table 5. *Least-squares planes in the galactosamine molecule*

Equation of plane: $AX+BY+CZ+D=0$, where X, Y, Z are in Å.

Atoms in plane		Distance from best plane		Given constant
1	C(1)	C(1)	0·022 Å	$A=$ 0·052
	C(2)	C(2)	−0·032	$B=$ 0·867
	C(4)	C(4)	0·025	$C=-0·495$
	C(5)	C(5)	−0·011	$D=$ 0·605
		C(3)	−0·687	
		O(5)	0·691	
		O(1)	0·801	
		N(2)	−0·815	
		O(3)	−0·604	
		O(4)	1·404	
		C(6)	0·654	
		O(6)	0·438	
2	C(7)	C(7)	0·015	$A=-0·492$
	C(8)	C(8)	−0·018	$B=$ 0·870
	C(10)	C(10)	0·042	$C=-0·023$
	C(11)	C(11)	−0·036	$D=$ 0·732
		C(9)	−0·649	
		O(11)	0·666	
		O(7)	0·825	
		N(8)	−0·859	
		O(9)	−0·535	
		O(10)	1·433	
		C(12)	0·549	
		O(12)	0·206	

Dihedral angle between the planes 1 and 2 is 42·2°.

The mean C–C bond length is 1·520 Å ($\sigma=0·010$ Å), and that of the C–O bond 1·431 Å ($\sigma=0·008$ Å). The C(2)–N(2) and C(8)–N(8) bond lengths are 1·503 Å ($\sigma=0·009$ Å). The bond lengths for equatorial bonds, C(1)–O(1) and C(7)–O(7) are shortened by about 0·03 Å, relative to the other C–O bonds. Similar observations for the anomeric C–O bond have been recorded in many previous investigations of sugars (Chu & Jeffrey, 1967; Kim & Jeffrey, 1967; Berman, Chu & Jeffrey, 1967; Fries, Rao & Sundaralingam, 1971; Beevers & Hansen, 1971). These authors suggest that it is a property of free sugars.

Fig. 3 shows a composite drawing of the final difference map viewed along the *b* axis. The mean values of the C–H, N–H and O–H bond lengths are 1·08, 0·92 and 0·91 Å respectively.

Hydrogen bonds

The hydrogen-bonds are seen in Figs. 4 and 5, and listed in Table 6. There are thirteen hydrogen bonds in an asymmetric unit: NH···Cl,4; OH···Cl,3; OH···O,4; and NH···O,2. Among the hydrogen atoms which belong to the functional groups, only one, H(O9) bonded to O(9), does not participate in hydrogen bonding. The hydrogen bonds directly linking the sugar ions are: O(12)–H(O12)···O(6), O(3)–H(O3)···O(10) and O(10)–H(O10)···O(12). These

Table 6. *Hydrogen bonding distances, angles and their standard deviations*

The asymmetric units are denoted as follows:

Coordinates			Notation	Coordinates			Notation
x	y	z	i	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$	vi
$1+x$	y	z	ii	$-\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$	vii
$-1+x$	y	z	iii	$2-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	viii
$\frac{1}{2}+x$	$\frac{1}{2}-y$	$-z$	iv	$2\frac{1}{2}-x$	$-y$	$\frac{1}{2}+z$	ix
$1\frac{1}{2}+x$	$-y$	$\frac{1}{2}+z$	v				

Donor	H	Acceptor	$d(D\ldots A)$	$d(\mathrm{H}\ldots A)$	$(D\text{–H}\ldots A)$	$(\mathrm{C}\text{–}D\ldots A)$
N(2)	H(N21)	O(2, ix)	2·980 Å	2·07 Å	166°	119·4°
N(2)	H(N22)	Cl(1, ix)	3·177	2·23	170	108·4
N(2)	H(N23)	Cl(2, viii)	3·218	2·33	162	123·2
N(8)	H(N81)	Cl(1, i)	3·260	2·32	170	106·8
N(8)	H(N82)	Cl(2, iv)	3·271	2·46	150	123·3
N(8)	H(N83)	O(9, iv)	2·936	2·11	150	115·4
O(1)	H(O1)	Cl(2, vi)	3·012	2·10	159	112·5
O(3)	H(O3)	O(10, viii)	2·867	2·00	162	99·9
O(4)	H(O4)	O(6, v)	2·896	2·02	175	92·6
O(6)	H(O6)	Cl(1, iii)	3·168	2·31	161	98·8
O(7)	H(O7)	Cl(2, ii)	3·058	2·17	175	105·7
O(10)	H(O10)	O(12, vii)	2·733	1·78	175	93·3
O(12)	H(O12)	O(6, vii)	2·847	2·00	156	98·0
			$\langle\sigma\rangle$=0·006 Å	$\langle\sigma\rangle$=0·07 Å	$\langle\sigma\rangle$=6°	$\langle\sigma\rangle$=0·3°

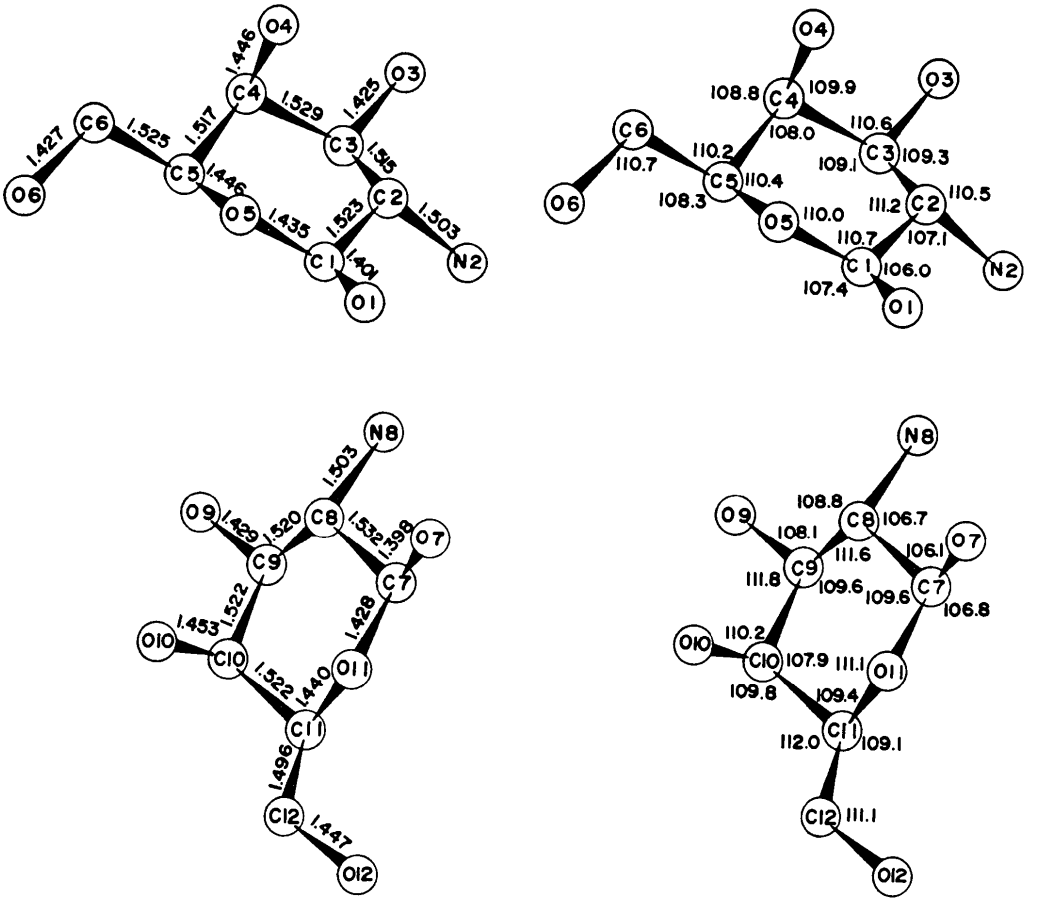

Fig. 2. Interatomic distances and angles in the galactosamine molecule.

hydrogen bonds dominate the intermolecular packing in this crystal.

The computations were carried out on the NEAC 2200–500 of Osaka University, the FACOM 230–60 of Kyoto University and the HITAC 5020E of the Computing Centre of the University of Tokyo. The computer programs were written by one of the authors (T.A.) The authors are obliged to Dr T. Ueki for his kind cooperation.

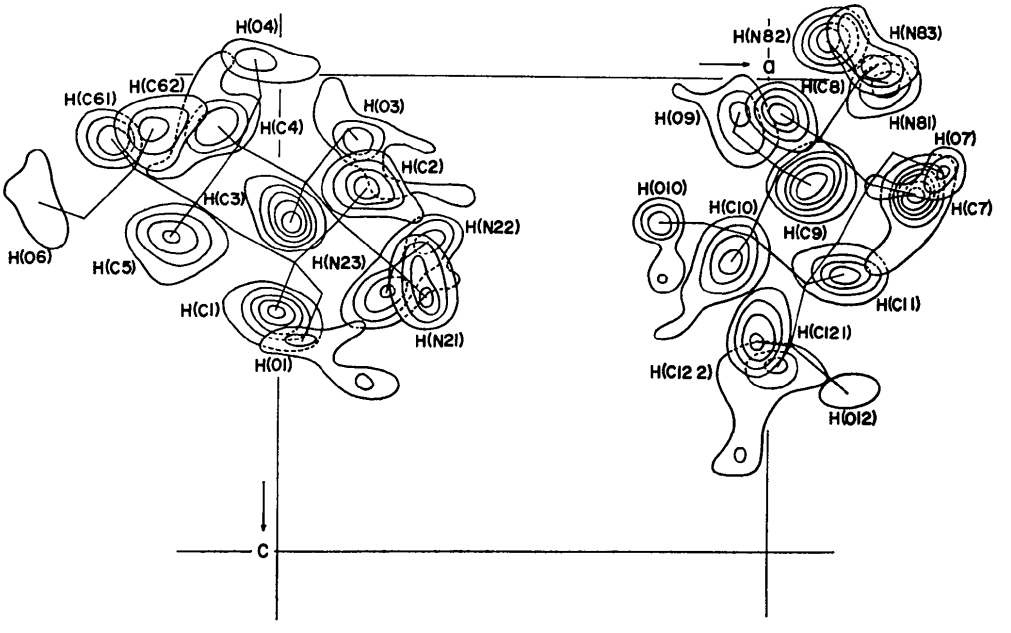

Fig. 3. A composite drawing of the final difference map, viewed along the *b* axis. Contours are at intervals of 0·1 e.Å^{-3}, starting at 0·3 e.Å^{-3}.

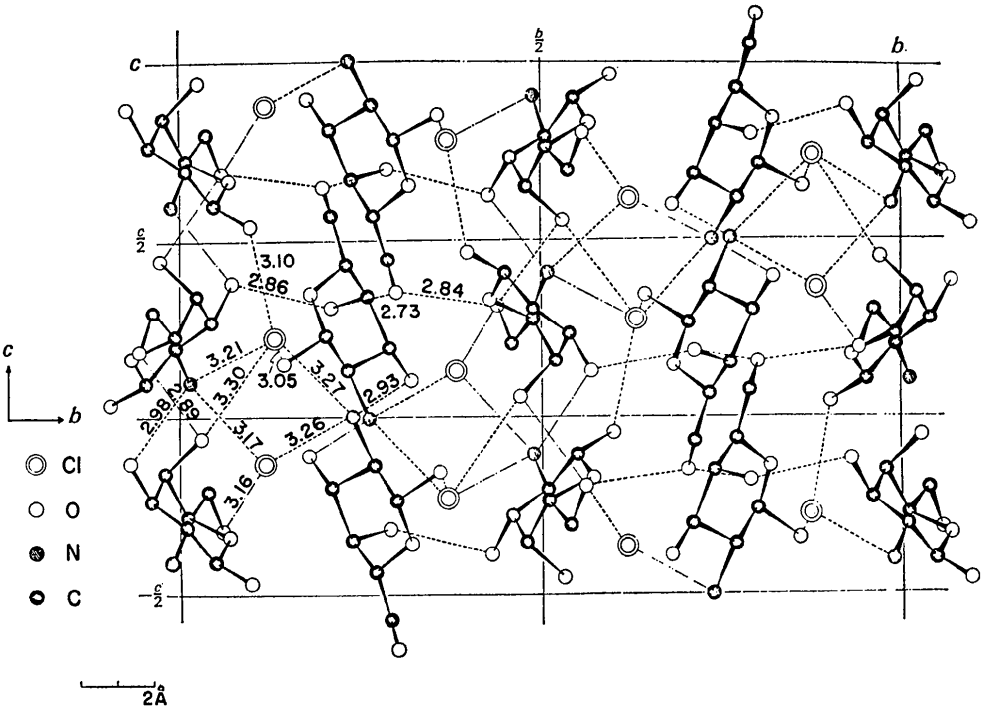

Fig. 4. The structure viewed along the *a* axis. Hydrogen bonds are indicated by broken lines.

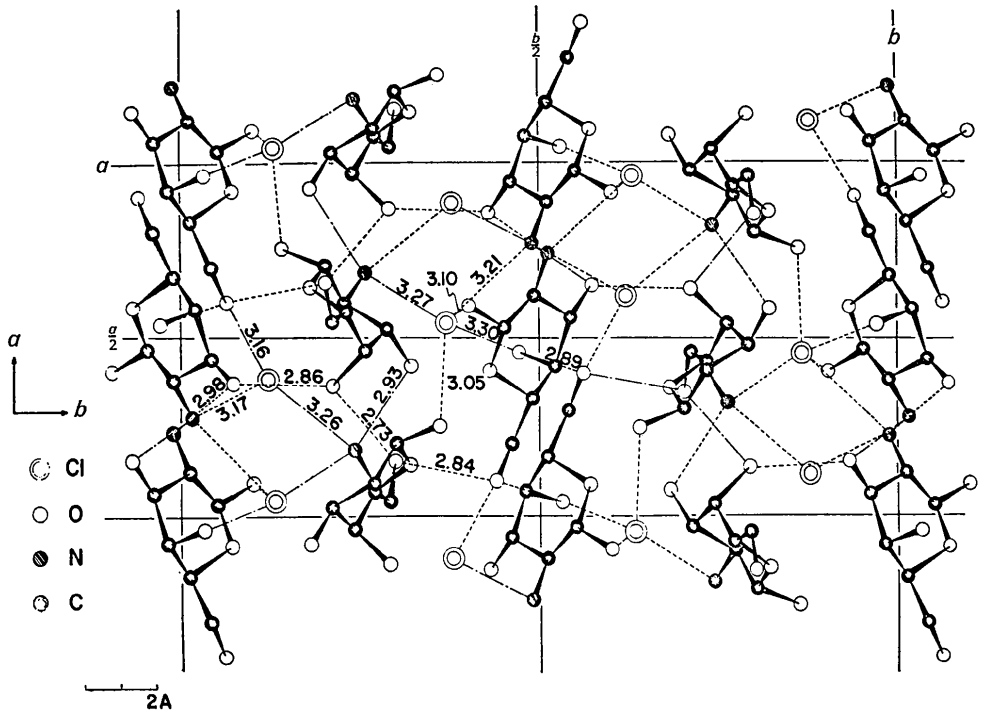

Fig. 5. The structure viewed along the *c* axis.

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