octahedral arrangement of oxygen atoms), the O–Na–O angles vary from 55 to 140° with the smallest angle involving oxygen atoms which share an edge with the sulfate tetrahedron. The next smallest angle (66°) involves the oxygen atoms forming the smallest intersulfate separation mentioned above; hence, this edge is shared by three identical, but rotated, polyhedra. However, such an octahedral environment appears to be too restrictive for the coordination about the sodium ion. By considering the next two closest oxygen atoms [O(6′) and O(4′)] in the coordination sphere, a distorted Archimedean antiprism (Fig. 2) is obtained. In this idealized polyhedron, the O(4) type oxygen atoms are displaced toward the sodium ion from the top plane of that required for a regular antiprism. The calcium ion in $CaNa_2(SO_4)_2$ (Cocco, Corazza & Sabelli, 1965) is also situated in a distorted antiprism consisting of six closer (2·36–2·47 Å) and two more distant (2·74 Å) oxygen atoms.

Lithium sodium sulfate belongs to a class of compounds of the form $M'M''XO_4$ which are all trigonal or higher in symmetry, but belong to different space groups, and which have lattice constants related by simple multiples. Among these compounds are: (1) $LiNaSO_4$ in space group $P31c$; (2) $KLiSO_4$ and $KAlSiO_4$ in space group $P6_32$ (Claringbull & Bannister (1948) showed these to be related to hexagonal tridymite, nepheline and kaliophilite); (3) $NaK_3(SO_4)_2$ and $NaKSO_4$ in space group $P\bar{3}m1$ (Bellanca, 1943); (4) anhydrous alums such as $KAl(SO_4)_2$ in space group $P321$ (Vegard & Maurstad, 1929); and (5) silicates such as $NaAlSiO_4$ and $KLaSiO_4$ in space group $P6_3$ (subcell to $KLiSO_4$; Eitel, Herlinger & Trömel, 1930). With the exception of the last set of silicates, for which the detailed crystal structure has not been proposed, all these compounds have sulfate or silicate groups situated on the threefold axes. The relative locations of the XO_4 groups appear to be governed by the manner in which the metal ions form their coordination polyhedra.

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The Crystal Structure of L-Leucine Hydrobromide*

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The crystal structure of L-leucine hydrobromide has been determined. The orthorhombic unit cell has the dimensions $a = 7·29$, $b = 24·51$, $c = 5·54$ Å and the space group is $P2_12_12_1$. There are four molecules of $C_6H_{14}NO_2^+ . Br^-$ in the cell. The trial structure, obtained by a combination of the 'heavy atom' method and the method of structure invariants applied to the c-axis projection, has been refined by three-dimensional least-squares method to an R value of 0·11. All available hydrogen atoms are involved in hydrogen bonding.

Introduction

The investigation of the crystal structure of leucine was taken up as part of a program of research work in this department on the structure analysis of amino acids and proteins. Leucine is among the most important amino acids essential for the growth and maintenance of living organisms, and, while the crystal structures of most of the amino acids have been determined, the structure analysis of leucine has not so far been reported except as an N-terminal residue in the tripeptide leucylprolylglycine (Leung & Marsh, 1958). Knowledge of the stereochemistry of leucine as a structural unit in proteins would be of great value and consequently the structure analysis was taken up.

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Experimental

Crystals of leucine hydrobromide were obtained by dissolving L-leucine in 30% hydrobromic acid and allowing the solution to evaporate. The crystals grow as thin plates with principal faces (010) and elongated parallel to the *c* axis. They are very soft, highly hygroscopic, and decompose quickly on exposure to air; hence the freshly prepared crystals were immediately sealed in Lindemann-glass capillary tubes. X-ray photographs taken with equi-inclination Weissenberg as well as precession methods established the crystallographic data summarized in Table 1. The space group absences were of the type *h*00, *h* odd; 0*k*0, *k* odd; and 00*l*, *l* odd. Three-dimensional intensity data for Cu $K\alpha$ radiation were obtained from multiple-film equi-inclination Weissenberg photographs, with the crystal rotated about the *c* axis ($l=0$ to 4). Of the 1098 reflexions which could have been recorded in the various layers, only 593 were observed. The intensities were estimated visually by using calibrated filmstrips and were corrected for Lorentz and polarization factors by means of the chart due to Cochran (1948). Except for a few very low-angle reflexions, no spot-size correction was applied. The linear absorption coefficient of the crystal for Cu $K\alpha$ radiation is 59·8 cm^{-1}. The crystal used had a cross-section of $0\cdot01\times0\cdot02\ \text{cm}^2$. Thus the maximum error in the relative values of the structure factors because of absorption is about 30%, although the average error will be considerably smaller than this. However no corrections for absorption were made.

Table 1. *Crystal data for* L-*leucine hydrobromide*

$C_6H_{13}NO_2.HBr$	M.W. 212·1
Orthorhombic	Space group $P2_12_12_1$
$a=$ 7·29 Å	$Z\ =4$
$b=$24·51	$\varrho_o\ =1\cdot423\ \text{g.cm}^{-3}$
$c=$ 5·54	$\varrho_c\ =1\cdot435\ \text{g.cm}^{-3}$
$\lambda=$Cu $K\alpha$ (1·5418 Å)	$F_{000}=436$

Photographs about the *a* axis could not be taken since the crystals disintegrated on cutting. Consequently, a crystal was mounted along the *c* axis on a precession camera and the 0*kl* zone was recorded with Cu $K\alpha$ radiation; this photograph had reflexions up to $l=3$. The intensities were estimated visually, corrected for Lorentz and polarization factors by the tables given by Nordman (1959), and used to correlate intensities from the Weissenberg photographs for $l=0$ to 3. Approximate scale and temperature factors ($B=5\cdot0$ Å^2) were derived by the method of Wilson (1942); final scaling, however, was achieved by comparing $\Sigma|F_o|$ with $\Sigma|F_c|$ for each layer. Atomic scattering factors of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for carbon, nitrogen, and oxygen and of Thomas & Umeda (1957) for bromine, were used in projection calculations.

Derivation of the trial structure

A *c*-axis Patterson projection gave the approximate coordinates $x=0\cdot250$, $y=0\cdot073$ for the bromine atom, and a bromine-phased electron-density projection was calculated. However, with $x=0\cdot25$, the bromine atom does not contribute to *hk*0 reflexions having $h+k$ odd, and the omission of these terms from the Fourier synthesis resulted in spurious mirror planes at $x=\frac{1}{4}$ and $\frac{3}{4}$. Since most of the light-atom peaks lay near these planes, it was difficult to choose between a peak and its spurious mirror-related mate, and continued attempts to derive a satisfactory structure were unsuccessful. The structure was eventually solved by the application of the method of structure invariants (Woolfson, 1957).

Application of the method of structure invariants

It has been shown by various workers (*e.g.*, Sayre, 1952; Cochran, 1952; Zachariasen, 1952; Hughes, 1953) that the signs of the largest unitary structure factors [$U(\mathbf{h})$, $U(\mathbf{h}')$ and $U(\mathbf{h}+\mathbf{h}')$] are most probably related by the equation

$$s(\mathbf{h}')s(\mathbf{h}+\mathbf{h}')\sim s(\mathbf{h})\,. \qquad (1)$$

The method of structure invariants consists in finding a series of relations of the type (1) in which the $s(\mathbf{h})$'s now represent the signs of the structure-invariant reflexions, *i.e.* reflexions whose signs are independent of the choice of origin. The structure-variant reflexions are related in pairs with a structure invariant, so that if the signs of the latter are known, these relationships lead to a series of sign linkages between the former.

The centrosymmetric (001) projection for leucine hydrobromide has the plane-group symmetry *pgg* and the signs of the structure-invariant reflexions are known (since the bromine atom contributes to all reflexions with $h+k=2n$). The unitary structure factors for the *hk*0 reflexions were calculated by using the expression

$$|U(\mathbf{h})|=\frac{|F_o(\mathbf{h})|}{\sum\limits_i f_i}\left[\frac{\Sigma f_i^2}{\langle I\rangle}\right]^{\frac{1}{2}},$$

where $|F_o(\mathbf{h})|$ is the relative structure amplitude of the *hk*0 reflexion. In applying the above expression, the procedure adopted was to subtract the bromine contribution from the scaled F_o values for reflexions of the type with $h+k=2n$, thus assuming that the signs of these reflexions were the same as those given by bromine. However, only those reflexions for which $|F_{\text{Br}}(\mathbf{h})|/|F_o(\mathbf{h})|$ was greater than 0·5 were included. In this way the problem is reduced to that of solving a light atom structure with the difference that the signs of half of the reflexions are already known.

Those terms for which $|U(\mathbf{h})|>0\cdot20$ were then selected and the method of Woolfson was applied to obtain the signs of 14 *hk*0 reflexions with $(h+k)$ odd.*

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* In the final analysis, the signs of three of these reflections were found to be wrongly determined.

These terms were then included in a Fourier summation for the *c*-axis projection, which is shown in Fig. 1. The spurious mirror symmetry had completely broken down and the map could be very easily interpreted in terms of the known chemistry of the molecule. The resulting trial structure has been plotted in Fig. 1; it gave an R index of 0·25 for the $hk0$ reflexions. A difference-Fourier synthesis drawn at this stage indicated large shifts for a number of atoms and pronounced anisotropy of thermal motion for the bromine atom. The anisotropy was, however, neglected but the shifts in the positional parameters were estimated and a fresh set of $hk0$ structure factors was calculated. A few cycles of Fourier refinement brought the R index for these reflexions down to 0·22.

The z coordinate of the bromine atom was obtained from a Patterson projection on (100), calculated from the relatively few $0kl$ reflexions available on the upper-level Weissenberg photographs about **c**. The z coordinates of the lighter atoms were then deduced by fitting a model of the molecule to the *c*-axis and *a*-axis electron-density projections (Figs. 1 and 2).

Three-dimensional least-squares refinement

Preliminary structure-factor least-squares calculations were carried out on an Elliott 803 computer and, later, on a CDC-3600, in each case using a diagonal least-squares program written by the author specifically for the space group $P2_12_12_1$. The function minimized was $\Sigma\, w(|F_o|-|F_c|)^2$, with unit weights assigned at the start. The scattering factors were calculated by an analytical approximation due to Vand, Eiland & Pepinsky (1957) and with the constants given by Forsyth & Wells (1959).

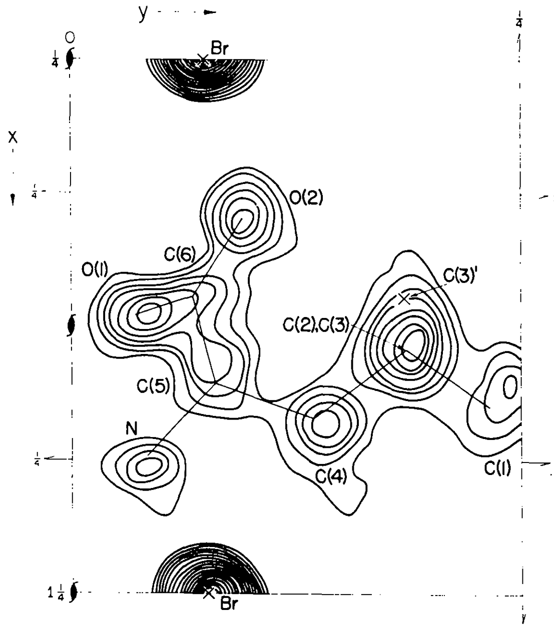

Fig. 1. *c*-Axis bromine-phased electron-density projection, with signs of some of the reflexions with $h+k$ odd determined by the method of structure invariants. Contours are at arbitrary equal intervals.

The first three-dimensional calculation led to an R index of 0·26 (throughout, $R=\Sigma\,||F_o|-|F_c||/\Sigma\,|F_o|$); after several cycles of refinement, in which the individual isotropic temperature factors as well as the atomic coordinates were adjusted, convergence was reached at $R=0{\cdot}18$. During this refinement the temperature factor for C(3) [C(3) is the carbon atom of the methyl group attached to C(2); C(1) is that of the other methyl group (Fig. 4)] reached the unrealistically large value of 10·2 Å^2, raising suspicion that this atom might have been misplaced. A three-dimensional difference map was therefore calculated, the contributions of C(3)

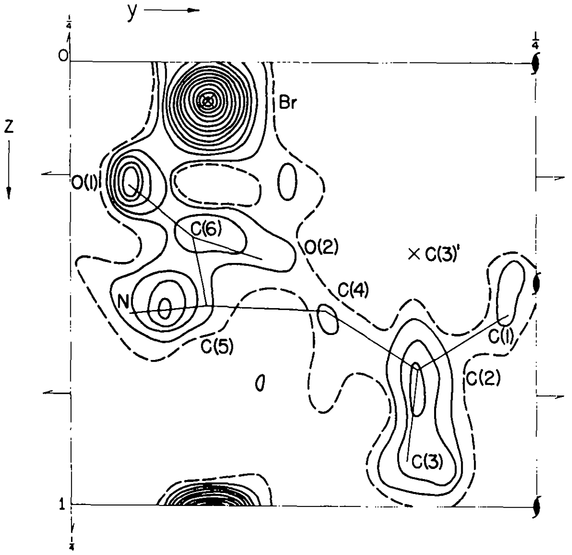

Fig. 2. *a*-Axis electron-density projection, phased on the contribution from the bromine atom.

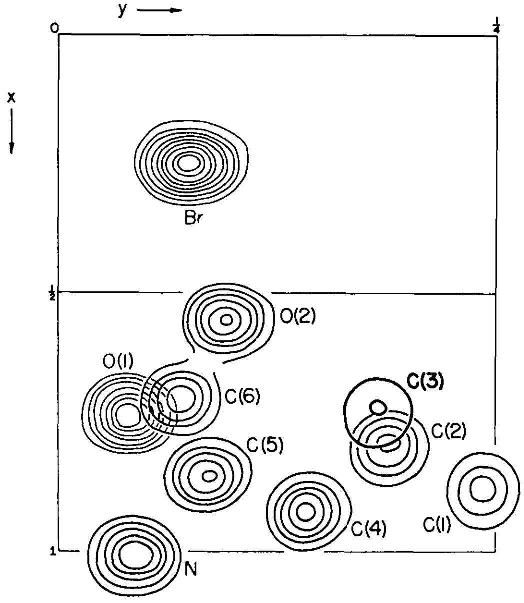

Fig. 3. Final electron density projected down the *a* axis.

having been omitted from the values of F_c. This map showed a peak of approximately one-half the expected height at the position assumed for C(3), and a second peak of about the same height approximately 1·4 Å from C(2) and roughly along the remaining tetrahedral direction (presumably occupied by the hydrogen atom). Although this second peak was very broad, it suggested that C(3) might be disordered between two positions corresponding to a random interchange between the hydrogen and C(3) in different molecules. This peak is indicated by C(3)′ in Figs. 1 and 2 (the crosses).

Two atoms with half the carbon scattering power were therefore assumed at C(3) and C(3)′ and the least-squares refinement was continued. It was found that while the thermal parameter for C(3) was quite normal, that for C(3)′ increased to 22·0 Å^2, although the R value itself converged to 0·16.

It was therefore felt that the abnormal value of B for C(3)′ probably indicated the absence of any atom there, and that the peak for C(3)′ mentioned earlier might be spurious. In addition, the short interatomic distance (~2·7 Å) between C(3)′ of one molecule and C(1) of a molecule related by the twofold screw axis parallel to the a axis makes it improbable that there would be any disorder at all. It appears that the large temperature factor of C(3) merely reflects a large thermal motion due to loose packing in this region of the structure.

It was therefore decided to omit C(3)′ and to continue the refinement with full strength at C(3). The atomic coordinates were the same as those used at the beginning of the cycles of refinement which included C(3)′. With a modified Hughes (1941) weighting scheme convergence was soon reached at $R = 0{\cdot}16$.

Refinement was concluded at the California Institute of Technology, using the CRYRM system (Duchamp, 1964) on an IBM 7094 computer. The quantity minimized was $\Sigma\, w(F_c^2 - F_o^2)^2$ with weights taken according to the expressions

$$w = 1/F_o^2 \qquad F_o > 40$$
$$w = 1/40F_o \qquad F_o < 40\,.$$

Unobserved reflexions were included only when the calculated structure factors exceeded the visual threshold.

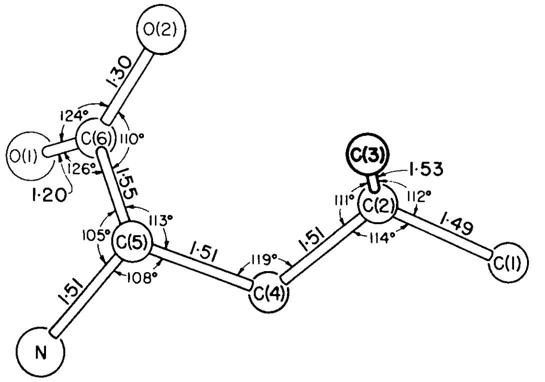

Fig. 4. Bond distances and bond angles observed in the molecule of leucine. E.s.d.'s are 0·03 – 0·04 Å and 4° respectively.

Three cycles of full-matrix refinement with individual isotropic temperature factors for all the atoms resulted only in a slight decrease in R from 0·211 to 0·198 (the higher index being due to the inclusion of many unobserved reflexions). Six cycles of further refinement in which the bromine atom was allowed to become anisotropic brought the R index down to 0·139.

A three-dimensional Fourier synthesis calculated at this stage failed to show any strength near the C(3)′ position, thus confirming the earlier observation regarding its spurious nature. Difference Fourier syntheses were then calculated for sections likely to contain the hydrogen atoms. Except for the hydrogen atoms attached to C(1) and N, the positions of the hydrogen atoms were not apparent, and they were therefore fixed purely from spatial considerations; no attempt was made to determine the positions of the hydrogen atoms attached to C(3) in view of the latter's large thermal motion. These hydrogen atoms were included in the subsequent structure factor calculations with their thermal parameters assumed to be the same as those of the atoms to which they are covalently bonded. A few cycles of full-matrix anisotropic refinement were then carried out for all the light atoms ($R = 0{\cdot}122$); however, the thermal ellipsoids for most of the atoms did not make physical sense. Consequently the anisotropic refinement for the light atoms was ignored and all of them were refined isotropically again until no shift was greater than 10% of its e.s.d. The final R index for all the reflexions was 0·113. Fig. 3 shows the final electron density projected down the a-axis.

Table 2 lists the F_o's and F_c's, while Tables 3 and 4 give the final parameters for all the atoms.

Discussion

In spite of the large standard deviations (0·04 Å in C–C bonds and 0·03 Å in C–N and C–O bonds; ~4° in bond angles), due mainly to lack of sufficient data and the predominant scattering power of bromine, all the bond distances and angles are quite resaonable (Fig. 4). The carboxyl group and the α-carbon atom [C(5)] are coplanar within limits of accuracy of the data. The equation of the mean plane passing through them, in terms of the direction cosines and the origin-to-plane distance, is given by

$$-0{\cdot}320X - 0{\cdot}780Y + 0{\cdot}538Z = 1{\cdot}705\ \text{Å}\,.$$

The deviations of the individual atoms from this plane are C(5) = −0·01 Å, C(6) = 0·04, O(1) = −0·02, and O(2) = −0·01. The nitrogen atom is 0·24 Å away from this plane. The conformation about the various bonds is shown in Fig. 5. It is seen that all the bonds assume a staggered conformation.

Intermolecular arrangement

The intermolecular packing arrangement, viewed down the c and a axes, is shown in Figs. 6 and 7. The hydrogen bonds are indicated by dashed lines. Table 5 lists the hydrogen bond distances and angles. Fig. 8 shows a stereoscopic view of the molecule, together with the hydrogen bonding.

There are four hydrogen atoms available for hydrogen-bond formation – three associated with the amino nitrogen atom and one with the carboxyl oxygen atom O(2). All of them are utilized in hydrogen bonding. The nitrogen atom is at hydrogen-bonding distance from four atoms – three bromide ions and an oxygen atom [Br(II), Br(III), Br(IV), and O(1)(IV) in Table 5].

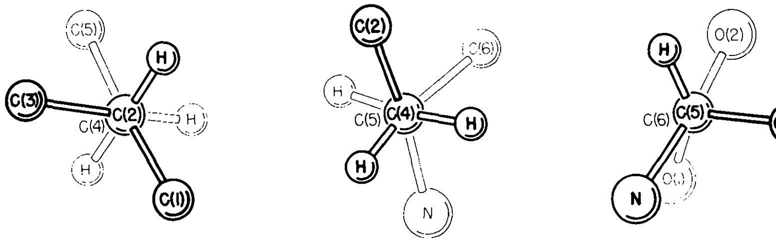

Fig. 5. Conformation about the various bonds in the molecule of leucine.

Table 2. *Observed and calculated structure factors*

Values given are 10 $|F_o|$, 10 $|F_c|$ and α.

0 K 0			
0	---*	4247	0
2	703*	1115	0
4	357	398	180
6	960*	1486	180
8	951*	1215	180
10	304	281	180
12	524	524	0
14	357	317	0
16	185	135	0
18	354	304	180
20	216	155	180
22	-96	16	0
24	-94	48	0
26	-88	94	0
28	-77	68	0
30	-60	0	0
1 K 0			
1	218	269	90
2	254	253	90
3	523	479	90
4	55	21	270
5	779	856	270
6	240	208	90
7	555	622	270
8	330	357	90
9	161	169	270
10	182	151	90
11	173	170	90
12	229	209	270
13	527	580	90
14	73	107	270
15	365	339	90
16	-81	1	270
17	-85	7	90
18	-88	9	90
19	91	94	270
20	-93	74	270
21	286	211	270
22	-96	4	270
23	-95	47	270
24	-94	0	270
25	-91	34	90
26	-87	18	90
27	-82	25	90
28	-75	29	90
29	-67	10	90
30	-58	27	90
31	-44	8	270
2 K 0			
0	1082*	1287	180
1	272	270	0
2	583	572	180
3	301	299	180
4	143	133	0
5	81	85	180
6	695	740	0
7	151	150	180
8	980	1032	0
9	118	119	0
10	-65	11	0
11	107	78	180
12	427	428	180
13	-75	33	0
14	350	385	180
15	-82	34	0
16	268	235	180
17	124	103	0
18	220	147	0
19	-93	46	180
20	320	268	0
21	-96	38	180
22	166	132	0
23	-94	1	180
24	-92	3	180
25	-89	7	0
26	84	88	180
27	-78	17	0
28	-71	54	180
29	-62	17	0
30	-51	12	180
3 K 0			
1	641	673	270
2	57	47	270
3	83	21	90
4	61	72	90
5	781	854	90
6	164	132	90
7	533	591	90
8	295	267	90
9	-71	40	90
10	183	136	90
11	275	283	270
12	77	84	270
13	510	601	270
14	83	110	270
15	261	255	270
16	-90	69	270
17	-92	85	90
18	-94	43	270
19	209	171	90
20	-96	31	90
21	135	102	90
22	-94	0	270
23	-91	26	90
24	-88	2	90
25	-83	20	270
26	-77	10	270
27	-70	13	270
28	-62	4	270
29	-51	12	270
4 K 0			
0	899	923	0
1	-71	21	180
2	575	630	0
3	-72	3	180
4	138	126	180
5	-74	7	180
6	470	470	180
7	92	64	0
8	570	634	180
9	195	127	0
10	115	103	180
11	119	89	180
12	179	149	0
13	153	132	180
14	261	217	0
15	-93	6	0
16	94	88	0
17	-96	49	0
18	96	57	180
19	-95	52	0
20	165	119	180
21	-92	26	0
22	-89	46	180
23	-85	13	180
24	-80	16	0
25	-74	25	180
26	-67	60	0
27	-58	32	180
28	-46	44	0
5 K 0			
1	383	398	90
2	-83	2	90
3	118	111	90
4	-85	8	90
5	340	346	270
6	-87	50	90
7	464	480	270
8	-89	1	90
9	222	182	270
10	-92	21	270
11	176	162	90
12	92	56	90
13	325	318	90
14	-96	24	270
15	183	184	90
16	-95	31	270
17	-95	1	90
18	-93	21	270
19	130	123	270
20	-87	9	270
21	104	106	270
22	-79	1	90
23	-73	14	270
24	-66	10	90
25	-58	49	90
26	-47	11	90
6 K 0			
0	458	454	180
1	-93	69	180
2	283	241	180
3	186	131	180
4	174	137	0
5	180	148	180
6	341	315	0
7	-95	19	0
8	249	235	0
9	-96	32	0
10	-96	35	0
11	96	69	0
12	183	159	180
13	-94	4	0
14	220	181	180
15	-91	11	180
16	-89	48	180
17	-86	5	180
18	-83	66	0
19	-79	3	180
20	-74	76	0
21	-68	3	0
22	-61	39	0
23	-53	13	0
24	-40	5	0
7 K 0			
1	278	238	270
2	-95	33	90
3	-95	18	270
4	96	83	90
5	229	204	90
6	-94	38	90
7	284	247	90
8	-92	25	270
9	91	86	90
10	-90	13	270
11	142	122	270
12	-86	11	90
13	209	169	270
14	-81	24	90
15	114	111	270
16	-73	15	270
17	-69	4	90
18	-63	19	270
19	57	64	90
20	-49	12	270
8 K 0			
0	221	211	0
1	-83	11	0
2	164	142	0
3	-83	50	0
4	-82	19	180
5	-81	48	0
6	192	176	180
7	-78	1	180
8	151	137	180
9	-74	37	180
10	-71	30	180
11	-68	34	180
12	65	76	0
13	-61	8	180
14	56	71	0
15	-50	15	0
16	-41	17	0
9 K 0			
1	150	121	90
2	-56	5	90
3	-55	10	90
4	-54	9	90
5	99	76	270
6	-49	8	90
7	106	102	270
8	-41	5	270
0 K 1			
1	81*	223	270
2	158	212	180
3	308	402	90
4	729	920	180
5	199	211	90
6	201	227	180
7	121	82	90
8	157	152	0
9	642	610	270
10	213	215	0
11	417	372	270
12	181	182	0
13	151	124	270
14	53	48	180
15	226	203	90
16	116	95	180
17	277	253	90
18	-61	40	180
19	261	218	90
20	92	62	180
21	-66	23	270
22	94	78	0
23	115	124	270
24	94	65	0
25	-63	67	270
26	-60	26	0
27	-56	2	270
28	-52	9	0
29	-46	12	90
30	-39	13	180
31	-28	9	90
1 K 1			
0	533	566	270
1	568	581	251
2	960	1151	183
3	236	253	269
4	1075	1153	180
5	218	250	199
6	312	316	157
7	254	244	119
8	600	560	0
9	539	569	74
10	704	708	7
11	446	426	52
12	401	396	359
13	50	53	311
14	163	136	172
15	160	162	258
16	422	351	178
17	294	265	268
18	269	240	168
19	64	75	294
20	-65	25	285
21	66	54	142
22	67	89	333
23	-66	38	137
24	67	96	351
25	-62	37	136
26	-59	37	350
27	-55	18	213
28	-51	13	195
29	-45	15	279
30	-38	26	165
2 K 1			
0	155	154	90
1	756	639	249
2	550	507	331
3	1010	1022	274
4	835	775	4
5	611	587	278
6	365	323	9
7	149	132	34
8	115	108	62
9	422	420	87
10	174	143	220
11	460	402	96
12	299	275	171
13	91	78	143
14	-55	30	103
15	210	192	263
16	104	94	30
17	192	160	279
18	-64	71	291
19	92	59	348
20	-66	19	229
21	67	73	104
22	66	71	170
23	65	60	93
24	-63	51	170
25	-60	18	118
26	-57	13	137
27	-52	13	239
28	-47	11	13
29	-41	31	270
30	-32	36	336
3 K 1			
0	101	86	90
1	187	161	116
2	458	424	350
3	341	304	121
4	796	719	1
5	137	103	119
6	434	377	354
7	111	77	250
8	243	222	189
9	498	427	287
10	541	498	176
11	316	256	312
12	294	296	170
13	-58	38	6
14	-60	20	204
15	88	102	115
16	253	203	5
17	158	140	106
18	217	200	349
19	67	94	118
20	67	74	346
21	-66	15	354
22	67	83	179
23	-63	24	292
24	63	93	180
25	-56	24	281
26	-52	33	164
27	-47	12	163
28	-41	19	354
29	-32	17	173
4 K 1			
0	99	96	270
1	371	343	70
2	396	328	186
3	532	480	85
4	469	420	178
5	364	334	87
6	187	152	154
7	235	197	233
8	157	144	27
9	424	395	258
10	239	215	332
11	420	356	275
12	154	143	347
13	-63	17	241
14	111	100	129
15	198	187	84
16	115	118	161
17	227	222	87
18	-66	59	177
19	67	71	109
20	-65	27	325
21	-63	46	255
22	-61	61	334
23	58	72	268
24	60	46	339
25	-50	35	294
26	-44	6	309
27	-38	14	8
28	-27	18	120
5 K 1			
0	-56	22	270
1	58	72	276
2	509	398	184
3	143	154	268
4	506	423	186
5	60	70	218
6	95	86	212
7	62	56	106
8	256	214	13
9	177	167	93
10	346	292	0
11	142	138	101
12	194	171	16
13	94	90	29
14	94	71	136
15	66	92	309
16	184	163	180
17	94	100	278
18	114	98	185
19	-62	61	255
20	-60	22	203
21	-57	30	197
22	-53	32	338
23	-49	31	158
24	-44	37	357
25	-38	24	121
26	-29	32	342
6 K 1			
0	103	71	270
1	157	160	248
2	224	187	347
3	414	330	269
4	260	239	1
5	304	271	271
6	191	150	36
7	-66	37	344
8	64	64	173
9	257	234	80
10	136	124	179
11	204	194	91
12	67	57	213
13	-65	36	82
14	-64	19	358
15	60	77	250
16	-61	45	22
17	86	100	264
18	-56	23	20
19	-53	45	277
20	-49	17	183
21	-45	32	79
22	-40	37	180
23	-34	53	77
7 K 1			
0	-66	18	270
1	94	91	141
2	173	185	352
3	94	123	112
4	246	226	0
5	94	88	58
6	93	95	31
7	92	86	331
8	91	89	167
9	90	89	286
10	156	146	181
11	98	88	264
12	106	106	195
13	-57	26	216
14	-55	25	324
15	55	43	90
16	52	74	2
17	47	48	96
18	46	54	2
19	-37	23	92
20	-30	9	71
8 K 1			
0	-57	6	270
1	102	94	65
2	59	74	175
3	191	170	87
4	57	67	185
5	56	89	91
6	-54	36	214
7	-53	30	230
8	-51	21	347
9	117	122	257
10	-48	52	16
11	84	98	260
12	-43	33	38
13	-40	22	265
14	-36	11	98
15	-31	54	78
9 K 1			
0	-37	8	90
1	-37	23	288
2	85	78	177
3	-36	59	271
4	81	102	188
5	-33	42	259
6	-31	31	208
7	-27	27	108
0 K 2			
1	911	882	90
2	218	269	0
3	71	79	90
4	321	324	180
5	380	390	270
6	495	580	180
7	591	580	270
8	328	300	180
9	286	284	270
10	57	60	0
11	83	63	90
12	343	334	0
13	363	342	90
14	314	265	0
15	214	207	90
16	89	85	0
17	57	55	270
18	59	56	180
19	185	196	270
20	63	73	180
21	-60	33	270
22	-60	50	180
23	-59	20	90
24	-57	16	180
25	-54	67	90
26	-51	1	180
27	-47	47	90
28	-42	15	0
29	-36	3	270
30	-27	9	0
1 K 2			
0	619	679	180
1	563	597	125
2	583	600	189
3	357	349	134
4	211	217	349
5	216	250	224
6	607	603	9
7	370	348	277
8	541	579	18
9	233	237	263
10	95	113	66
11	46	73	358
12	268	276	196
13	99	89	92
14	348	326	192
15	87	72	91
16	107	101	194
17	-56	40	245
18	-58	26	356
19	87	107	311
20	146	143	357
21	63	59	305
22	63	101	356
23	-58	20	130
24	-56	5	288
25	-54	51	104
26	-50	32	170
27	-46	40	103
28	-41	37	164
29	-34	17	163
30	-24	26	153
2 K 2			
0	161	150	180
1	443	458	265
2	244	234	105
3	64	84	200
4	160	163	358
5	501	457	92
6	301	312	356
7	546	552	88
8	272	274	343
9	140	167	46
10	87	57	235
11	317	314	267
12	282	276	182
13	307	328	263
14	315	304	170
15	180	172	271
16	141	157	163
17	60	37	73
18	-59	34	41
19	117	143	91
20	139	141	334
21	107	102	93
22	107	101	3
23	-57	26	114
24	-55	26	7
25	-51	31	272
26	-48	10	160
27	-43	26	275
28	-37	15	163
29	-29	8	38
3 K 2			
0	789	721	0
1	566	521	284
2	380	323	9
3	99	97	282
4	175	180	173
5	309	280	82
6	536	511	172
7	348	310	98
8	357	343	175
9	203	192	142
10	95	110	207
11	120	112	210
12	285	279	354
13	145	131	281
14	306	313	353
15	60	53	310
16	107	104	6
17	88	117	31
18	125	112	167
19	88	78	66
20	125	128	179
21	-58	17	119
22	56	62	182
23	-54	21	216
24	-51	10	324
25	-47	32	231
26	-43	31	350
27	-37	23	266
28	-29	34	11
4 K 2			
0	296	278	0
1	392	385	90
2	179	159	3
3	162	162	124
4	132	118	167
5	248	237	255
6	348	273	198
7	385	339	278
8	226	218	181
9	202	186	277
10	57	45	73
11	58	74	110
12	157	164	344
13	143	154	108
14	170	168	7
15	107	123	98
16	63	73	17
17	-60	44	0
18	-59	26	216
19	58	60	301
20	57	64	176
21	55	62	283
22	-52	41	168
23	-49	7	301
24	-45	11	121
25	-40	27	126
26	-34	12	340
27	-24	31	109
5 K 2			
0	461	466	180
1	236	230	99
2	271	251	188
3	168	141	129
4	128	99	11
5	132	129	225
6	419	381	2
7	231	216	245
8	281	285	8
9	175	148	299
10	63	56	99
11	-60	30	344
12	201	207	174
13	63	80	69
14	156	150	182
15	63	65	60
16	-58	54	226
17	-57	12	180
18	-55	80	329
19	-53	51	242
20	50	83	354
21	-47	39	269
22	44	31	353
23	-39	6	13
24	-34	28	163
25	-25	32	63
6 K 2			
0	173	165	180
1	224	200	264
2	60	66	195
3	-60	15	258
4	115	113	323
5	175	169	92
6	173	156	354
7	173	171	89
8	88	102	12
9	88	81	75
10	-59	30	157
11	63	46	275
12	121	118	165
13	166	151	268
14	102	109	192
15	81	105	277
16	-52	39	191
17	-50	6	121
18	-47	29	4
19	44	55	96
20	-40	41	11
21	-35	49	101
22	-29	30	33
7 K 2			
0	180	186	0
1	158	143	282
2	105	115	20
3	57	49	310
4	57	70	151
5	59	89	95
6	137	149	175
7	125	114	85
8	99	142	194
9	-54	57	112
10	-53	39	291
11	51	37	223
12	74	93	359
13	47	67	245
14	68	91	5
15	-43	33	273
16	-39	31	15
17	-36	31	16
18	-31	33	164
8 K 2			
0	-47	73	0
1	130	140	93
2	-47	41	19
3	47	48	113
4	-46	38	117
5	82	102	263
6	44	65	179
7	99	136	270
8	42	66	206
9	-40	52	265
10	-38	27	264
11	-35	36	93
12	32*	41	351
13	28*	76	92
0 K 3			
1	111	107	90
2	197*	374	180
3	-29	33	270
4	440	581	180
5	-37	24	90
6	-41	14	180
7	50	76	90
8	383	470	0
9	-51	11	270
10	454	549	0
11	-58	46	270
12	214	224	0
13	-64	18	270
14	76	100	180
15	-69	14	270
16	249	261	180
17	-72	62	90
18	191	206	180
19	-74	6	270
20	118	123	180
21	-73	25	270
22	-71	41	0
23	-68	6	270
24	-64	72	0
25	-60	9	270
26	-54	48	0
27	-48	13	90
28	-38	19	0
1 K 3			
0	239	277	270
1	393	411	284
2	81	77	275
3	542	602	265
4	137	109	166
5	411	448	262
6	86	95	75
7	47	51	225
8	-50	22	344
9	309	301	84
10	-56	52	84
11	284	311	81
12	-62	48	358
13	-65	37	70
14	-67	11	120
15	111	133	261
16	-71	22	96
17	180	173	262
18	-74	36	85
19	-74	15	210
20	-73	49	214
21	72	89	73
22	-70	38	268
23	-67	76	84
24	-63	15	281
25	-59	26	94
26	-53	8	349
27	-46	20	259
28	-36	15	344
2 K 3			
0	202	206	270
1	173	149	209
2	465	446	358
3	112	80	308
4	622	567	6
5	125	109	344
6	203	187	35
7	54	64	355
8	262	237	167
9	58	85	96
10	397	389	187
11	-63	14	198
12	311	313	194
13	68	95	202
14	-70	28	329
15	-71	31	172
16	192	210	0
17	-74	18	328
18	177	168	16
19	-73	39	20
20	-72	43	13
21	-70	14	125
22	-68	47	196
23	-64	9	312
24	-60	57	185
25	-55	4	29
26	-49	27	193
27	-40	5	285
3 K 3			
0	-55	47	270
1	227	212	87
2	-55	66	263
3	578	511	86
4	-57	48	321
5	462	386	98
6	-60	46	283
7	-61	45	87
8	-63	22	66
9	309	316	271
10	-67	41	107
11	181	199	265
12	79	104	132
13	-71	22	336
14	-73	49	93
15	73	85	91
16	-74	34	38
17	74	84	93
18	-73	34	327
19	-72	37	61
20	-70	31	295
21	-67	51	257
22	-63	28	248
23	-59	63	268
24	-54	15	215
25	-48	25	259
26	-39	3	244
4 K 3			
0	65	64	90
1	-65	19	341
2	397	327	179
3	-66	53	0
4	404	342	179
5	-67	13	195
6	-68	32	211
7	79	91	158
8	321	294	344
9	-71	50	181
10	346	333	0
11	-73	13	24
12	191	191	6
13	-74	32	329
14	84	98	164
15	-73	37	334
16	189	205	169
17	-71	31	0
18	139	150	186
19	-67	12	112
20	-64	37	224
21	-60	33	166
22	-56	37	347
23	-50	14	165
24	-43	49	359
25	-33	11	318
5 K 3			
0	-72	18	90
1	201	149	251
2	82	72	208
3	345	295	265
4	82	68	199
5	258	198	289
6	-73	5	165
7	-74	44	328
8	-74	64	32
9	186	148	89
10	-74	47	3
11	195	161	90
12	-73	18	76
13	82	76	125
14	-71	28	159
15	-69	70	266
16	-67	20	194
17	65	96	278
18	-62	21	256
19	-58	36	280
20	-54	8	346
21	-48	24	69
22	-42	8	24
23	-31	35	97
6 K 3			
0	73	69	270
1	-73	20	169
2	242	201	353
3	-73	6	338
4	305	257	5
5	-73	31	346
6	82	90	19
7	-72	25	332
8	182	148	161
9	-70	22	316
10	182	195	183
11	-68	15	131
12	66	85	192
13	-64	34	143
14	-62	40	339
15	-59	39	172
16	-56	82	349
17	-52	16	193
18	-47	60	5
19	-41	9	263
20	-32	11	34
7 K 3			
0	-66	27	270
1	102	105	70
2	-66	30	233
3	224	194	84
4	-65	25	286
5	164	152	104
6	-63	23	58
7	-62	40	182
8	-60	26	95
9	118	99	262
10	-57	19	149
11	108	104	276
12	-52	6	153
13	-48	40	324
14	-44	17	111
15	-39	40	75
16	-31	9	50
8 K 3			
0	-48	32	90
1	-48	23	17
2	-48	86	172
3	-47	25	80
4	-46	83	184
5	-45	22	111
6	-43	21	238
7	-41	17	215
8	-37	60	338
9	-33	23	209
0 K 4			
1	266	318	90
2	-70	31	180
3	96	118	90
4	75	76	0
5	242	206	270
6	150	160	0
7	307	242	270
8	120	119	0
9	163	136	270
10	-46	12	0
11	-48	14	270
12	126	134	180
13	192	168	90
14	107	124	180
15	107	93	90
16	-54	64	180
17	-54	25	270
18	-54	64	0
19	68	63	270
20	-51	47	0
21	-49	41	270
22	-46	8	0
23	-43	12	90
24	-39	5	180
25	-33	36	90
26	-24	14	180
1 K 4			
0	406	449	180
1	165	175	253
2	260	260	208
3	143	139	235
4	182	134	329
5	132	104	117
6	422	320	357
7	148	117	89
8	443	320	4
9	81	76	108
10	60	16	125
11	-49	15	61
12	188	182	175
13	-52	26	285
14	168	171	187
15	-54	9	299
16	98	87	189
17	-54	23	40
18	-54	47	14
19	-52	26	6
20	105	95	24
21	-48	26	78
22	45	48	3
23	-42	10	209
24	-38	11	324
25	-32	16	243
2 K 4			
0	176	116	0
1	372	255	254
2	113	62	65
3	111	57	257
4	146	107	157
5	315	252	89
6	194	158	188
7	237	258	81
8	128	113	193
9	63	59	93
10	90	88	355
11	114	113	271
12	149	149	349
13	183	189	260
14	97	95	12
15	98	80	258
16	-54	43	24
17	-54	30	112
18	-53	28	175
19	51	72	59
20	-49	47	183
21	45	63	71
22	-43	28	172
23	-39	10	122
24	-34	11	174
25	-25	22	243
3 K 4			
0	465	342	0
1	208	165	97
2	216	164	20
3	60	49	113
4	136	94	156
5	88	82	264
6	283	228	174
7	112	98	253
8	262	222	193
9	67	63	265
10	68	72	235
11	-54	37	215
12	157	134	355
13	69	71	101
14	162	168	8
15	67	37	65
16	68	90	22
17	67	34	310
18	50	55	152
19	-48	52	306
20	45	75	191
21	-42	21	320
22	-38	43	200
23	-32	12	134
4 K 4			
0	52	58	180
1	290	240	97
2	67	48	161
3	132	99	127
4	68	55	312
5	186	153	266
6	96	66	335
7	227	210	280
8	98	76	1
9	110	104	279
10	-54	21	125
11	69	55	46
12	69	48	148
13	107	104	80
14	68	53	176
15	66	67	113
16	-49	31	181
17	-47	21	211
18	-45	14	246
19	-42	40	256
20	-38	26	317
21	-34	35	256
22	-27	20	30
5 K 4			
0	252	232	180
1	140	136	275
2	156	139	196
3	-54	51	236
4	98	75	316
5	98	92	119
6	252	198	346
7	136	119	102
8	160	151	1
9	-53	37	99
10	-52	34	87
11	-51	40	292
12	91	98	178
13	63	50	297
14	61	86	173
15	-45	13	355
16	-42	30	182
17	-39	25	67
18	-35	25	347
19	-30	32	115
6 K 4			
0	-51	34	0
1	132	132	280
2	-51	22	72
3	50	53	349
4	-50	42	139
5	91	109	62
6	-49	39	196
7	99	117	99
8	-47	28	229
9	61	65	125
10	-45	19	271
11	56	60	220
12	-41	37	340
13	89	89	266
14	47	48	13
15	61	65	288
16	-27	26	39
7 K 4			
0	84	99	0
1	53	52	87
2	40	71	26
3	-40	16	51
4	39*	38	150
5	-38	27	260
6	61	92	176
7	-36	44	258
8	34	70	181
9	-32	22	264
10	-29	14	266
11	-24	18	139

Table 3. *The final parameters and their estimated standard deviations*

For the bromine atom the temperature factor is of the form $T=\exp[-(b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl)]$.

	x	y	z	B
Br	0·2478 (4)	0·0741 (1)	0·0796 (5)	*
O(1)	0·7385 (26)	0·0396 (5)	0·2546 (28)	5·0 (3) Å^2
O(2)	0·5592 (26)	0·0943 (7)	0·4657 (35)	6·3 (4)
N	1·0130 (25)	0·0439 (7)	0·5837 (38)	4·5 (4)
C(1)	0·8790 (51)	0·2421 (12)	0·6065 (55)	7·5 (7)
C(2)	0·7999 (35)	0·1871 (10)	0·6592 (52)	5·7 (6)
C(3)	0·7312 (57)	0·1826 (16)	0·9188 (73)	10·7 (11)
C(4)	0·9246 (32)	0·1403 (9)	0·5965 (50)	5·0 (5)
C(5)	0·8546 (28)	0·0828 (8)	0·6242 (40)	3·8 (4)
C(6)	0·7103 (25)	0·0674 (8)	0·4297 (43)	4·1 (4)

For Br $b_{11}=0·0190$ (4)
$b_{22}=0·0034$ (1)
$b_{33}=0·0452$ (13)
$b_{12}=0·0007$ (4)
$b_{13}=0·0117$ (17)
$b_{23}=0·0006$ (4)

Table 4. *Coordinates (fractional) of the hydrogen atoms*

H(*ij*) indicates the *j*th hydrogen attached to the *i*th atom.

	x	y	z
H(11)	0·84	0·27	0·72
H(12)	1·01	0·24	0·61
H(13)	0·88	0·25	0·44
H(21)	0·71	0·19	0·54
H(41)	1·04	0·14	0·70
H(42)	0·97	0·14	0·42
H(51)	0·77	0·08	0·80
H(71)	1·11	0·05	0·69
H(72)	1·07	0·05	0·43
H(73)	0·98	0·01	0·59
H(81)	0·44	0·11	0·51

Table 5. *Hydrogen bond distances and angles*

I x, y, z
II $x+1, y, z$
III $x+1, y, z+1$
IV $-x+\frac{3}{2}, -y, z+\frac{1}{2}$

N(1)···Br(II)	3·36 Å
N(I)···Br(III)	3·32
N(1)···O(1)(IV)	2·91 Å
O(2)(I)···Br(I)	3·16
N(I)···Br(IV)	3·38
C(5)(I)–N(I)–Br(II)	112°
C(5)(I)–N(I)–Br(III)	98
C(5)(I)–N(I)–Br(IV)	159
C(5)(I)–N(I)–O(1)(IV)	85
Br(II)–N(I)–Br(III)	112
Br(II)–N(I)–Br(IV)	85
Br(III)–N(I)–Br(IV)	86
O(1)(IV)–N(I)–Br(II)	138
O(1)(IV)–N(I)–Br(III)	102
O(1)(IV)–N(I)–Br(IV)	74
C(6)(I)–O(2)(I)–Br(I)	115
C(6)(IV)–O(1)(IV)–N(I)	124

Two of the hydrogen bonds [to Br(II) and Br(III)] are nearly in the tetrahedral direction. Regarding the third bond, the angles C(5)–N–Br(IV) and C(5)–N–O(1)(IV) (159 and 85° respectively) together with the comparatively large deviations from the tetrahedral angle

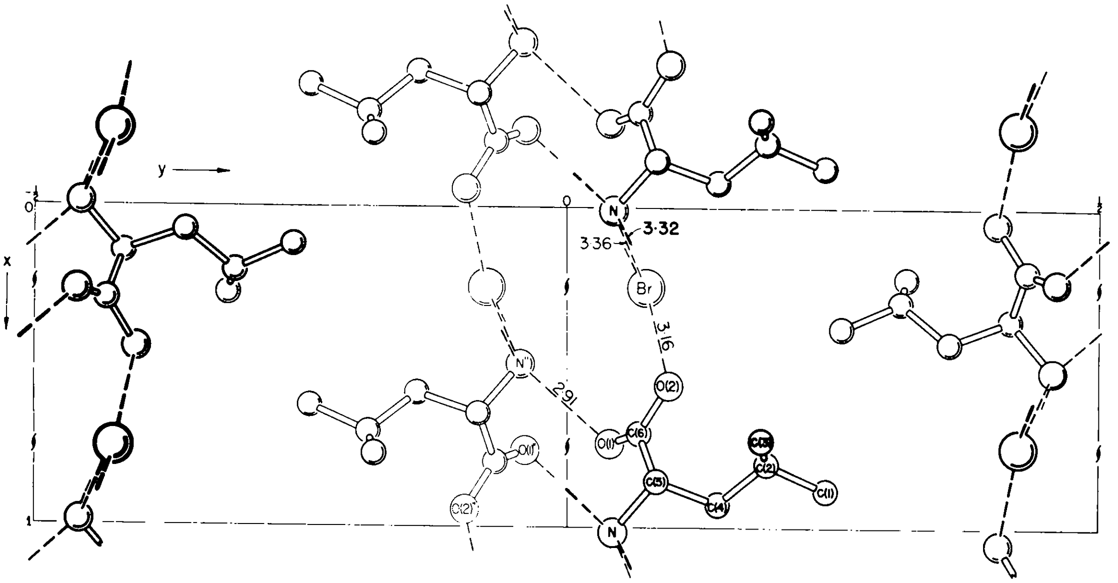

Fig. 6. Intermolecular packing viewed down the *c* axis.

of Br(II)–N–Br(IV) and Br(III)–N–Br(IV) as compared with Br(II)–N–O(1)(IV) and Br(III)–N–O(1)(IV) (Table 5) seem to indicate a hydrogen bonding to the oxygen atom only, and not to the bromine atom. These considerations also rule out the possibility of bifurcation of the hydrogen bond between the oxygen and the bromine. The N$\cdots$Br(IV) distance of 3·38 Å would then have to be treated as a short contact rather than a hydrogen bond. Short contacts occurring under similar circumstances have been reported (Donohue, 1952). In these cases, after all the hydrogen atoms on the $-\mathrm{NH}_3^+$ group have been used up in hydrogen-bond formation, a short contact occurs with a chloride ion which is generally situated (at hydrogen bond distance) approximately on the extension of the X–N covalent bond, so that the angle X–N$\cdots$Cl$^-$ is near 180°.

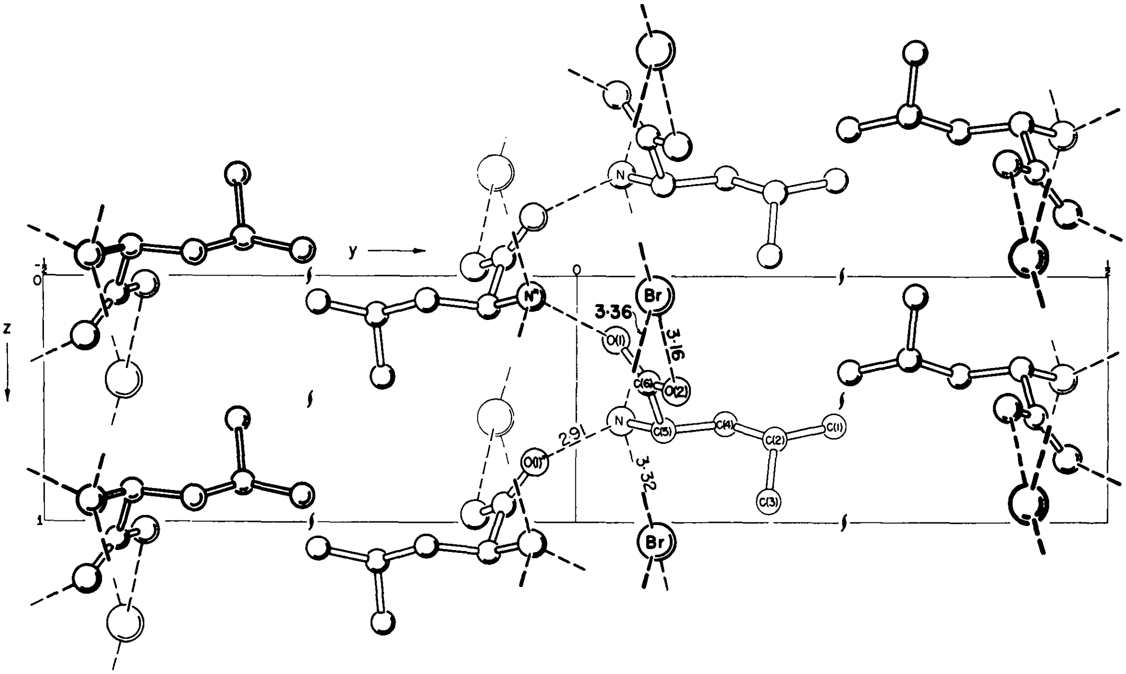

Fig. 7. Intermolecular packing viewed down the *a* axis.

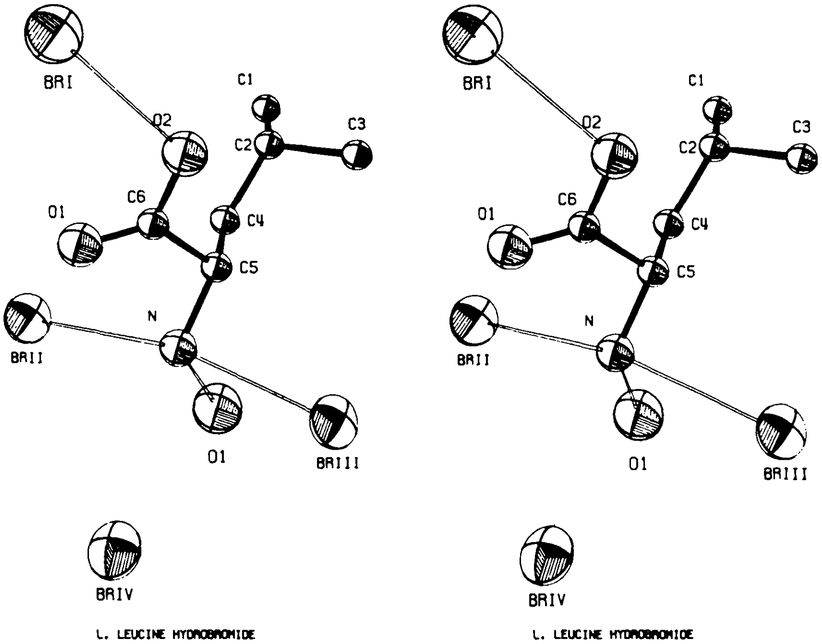

Fig. 8. Stereoscopic view of the molecule.

It is interesting to note that the hydrogen bond network forms sheets of molecules perpendicular to the *b* axis. The sheets are held together only by van der Waals forces. Intermolecular contacts less than 4 Å are listed in Table 6.

Table 6. *Intermolecular contacts less than* 4 Å

Roman numerals indicate the relation of the second atom to the first at (x, y, z)

I $\frac{1}{2}+x, \frac{1}{2}-y, 1-z$
II $\frac{3}{2}-x, -y, \frac{1}{2}+z$
III $x, y, z+1$
IV $x+1, y, z+1$
V $x-1, y, z$

Atom 1	Atom 2	Distance
C(1)	C(1)(I)	3·85 Å
C(1)	C(2)(I)	3·82
N	C(6)(II)	3·71
C(5)	O(1)(II)	3·16
C(6)	O(1)(II)	3·20
N	O(1)(II)	2·91
O(2)	O(1)(II)	3·94
O(1)	O(1)(II)	3·39
N	Br(II)	3·38
C(3)	O(2)(III)	3·93
C(3)	O(1)(III)	3·97
C(5)	O(1)(III)	3·75
C(4)	Br(IV)	3·92
C(5)	Br(IV)	3·82
N	Br(IV)	3·32
Br	N(V)	3·36
Br	O(1)(V)	3·93

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