respectively. The observed and calculated amplitudes are listed in Table 1. Omitting the values for 220, 040 and 004, which were assumed to be affected by extinction, the reliability factors as normally defined are 0·18 for *hk*0 and 0·16 for *h*0*l*.

The bond lengths within the coordination square are Pt–Br_1 2·45 Å, Pt–N approximately 1·9 Å. Within the chain the Pt–Br_2 bonds are of length 2·50 and 3·03 Å, i.e. the bromine atom is attached to the closer platinum by a normal bond, but is also involved in a weak interaction with the more distant platinum atom. It should be noted that on neither projection did the peak corresponding to Br_2 show any elongation in the direction of the Pt–Br bond as would be expected if the bonds in the square and octahedral complexes were markedly different in length. No diffuse streaking was detected on the even layer lines and, although this would have been more difficult to see than on the odd lines because of the heavier background, it may be concluded that the disorder is effectively restricted to the atom Br_1. The non-equivalent coordinates listed in Brosset's paper, which lead to differing bond lengths in the groups, appear to have been chosen arbitrarily.

Numerous attempts were made to obtain more ordered crystals by modifying the crystallization procedure, but these were not successful. Similar disorder effects have been observed in other compounds of the same chemical and structural type, namely $Pd(NH_3)_2Cl_3$ (E. W. Hughes, private communication) and Wolffram's red salt, $Pt(C_2H_5NH_2)_4Cl_32H_2O$ (B. M. Craven & D. Hall, to be published).

The authors wish to thank Dr F. J. Llewellyn for valuable discussions, and to acknowledge financial assistance from the Research Grants Committee of the University of New Zealand.

References

BOOTH, A. D. (1946). *Proc. Roy. Soc.* A, **188**, 77.
BROSSET, C. (1948). *Ark. Kemi, Min. Geol.* **25 A**, 19.
COHEN, A. J. & DAVIDSON, N. (1951). *J. Amer. Chem. Soc.* **73**, 1955.
Internationale Tabellen zur Bestimmung von Kristallstructuren (1935). Berlin: Borntraeger.
SUTOR, D. J., CALVERT, L. D. & LLEWELLYN, F. J. (1954). *Acta Cryst.* **7**, 767.

Acta Cryst. (1958). **11**, 626

Crystal Structure of the Low-Temperature Form of Monoethylamine Hydrobromide

BY F. JELLINEK

*Laboratorium voor Kristalchemie der Rijksuniversiteit, Utrecht, the Netherlands**

(*Received* 28 *January* 1958)

The structure of *l.t.*-$C_2H_5NH_3Br$ has been determined by the heavy-atom method. The unit-cell dimensions are: $a = 8{\cdot}361$, $b = 6{\cdot}261$, $c = 4{\cdot}630$ Å, $\beta = 93{\cdot}0°$. The space group is $P2_1/m$ and the two molecules in the unit cell lie in the mirror planes. The x and z parameters and the temperature factors of Br, N and C are refined by a modification of the difference-synthesis method. After application of a semi-empirical correction for secondary extinction, maxima in the electron density are found about the expected H positions. The final reliability index for ($h0l$) reflexions is 2·39%. An empirical scattering curve for Br is determined and found to be in good agreement with recent theoretical values by Thomas & Umeda.

1. Introduction

The complete crystal structures of the lower mono-*n*-alkylammonium halides are known, except for the monoethylammonium halides. $C_2H_5NH_3Br$ and $C_2H_5NH_3I$ exist in a low-temperature and a high-temperature modification; the transition temperatures are 92° C. and 55° C. respectively. For $C_2H_5NH_3Cl$ no transition was found below the melting point (96 °C.).

Groth (1906) gives crystallographic data for *l.t.*-$C_2H_5NH_3Br$ (monoclinic; probably sphenoidic; $a:b:c = 1{\cdot}3329:1:0{\cdot}7413$; $\beta = 93°\ 1'$; $D_m = 1{\cdot}741$ g.cm.$^{-3}$) and the isomorphous *l.t.*-$C_2H_5NH_3I$ ($a:b:c = 1{\cdot}3096:1:0{\cdot}7255$; $\beta = 92°\ 6'$; $D_m = 2{\cdot}100$ g.cm.$^{-3}$). Hendricks (1928), who investigated these compounds by X-ray diffraction, found the following unit-cell dimensions (after a rearrangement of axes to conform to the usual conventions):

$C_2H_5NH_3Br$: $a=8{\cdot}32$, $b=6{\cdot}24$, $c=4{\cdot}63$ kX.; $\beta=93°\ 1'$.
$C_2H_5NH_3I$: $a=8{\cdot}68$, $b=6{\cdot}63$, $c=4{\cdot}81$ kX.; $\beta=92°\ 6'$.

---

* Present address: Anorganisch- en Fysisch-Chemisch Laboratorium der Rijksuniversiteit, Bloemsingel 10, Groningen, the Netherlands.

From absences, the space group was derived to be $P2_1$ (cf. § 3). There are two molecules in the unit cell with all atoms in position $2(a)$: $x, y, z;\ -x, \frac{1}{2}+y, -z$. The halogen parameters were determined as $x_{\mathrm{Br}} = 0{\cdot}15$, $z_{\mathrm{Br}} = 0{\cdot}39$; $x_{\mathrm{I}} = 0{\cdot}16$, $z_{\mathrm{I}} = 0{\cdot}38$. The positions of the other atoms were not determined.

A detailed investigation of the structure of *l.t.*–$C_2H_5NH_3Br$ was undertaken by us, originally intended as a test of Peerdeman & Bijvoet's (1956*a*, *b*) method of direct structure determination of non-centrosymmetric heavy-atom compounds. In the course of our investigation it was found, however, that $C_2H_5NH_3Br$ actually is centrosymmetric. $C_2H_5NH_3Cl$ was found to be isomorphous with the bromide.

2. Experimental

Single crystals of $C_2H_5NH_3Br$ were ground to cylinders about the b and c axes (diameters 33×10^{-3} and 20×10^{-3} cm. respectively). About both axes rotation photographs, non-integrated Weissenberg diagrams of the zero and first layer lines, and integrated equatorial Weissenberg diagrams (Wiebenga & Smits, 1950) were made, using both the multiple-film and fixed-exposure-times techniques. The exposures were taken with CuK radiation on 'Ilfex' films, which were developed for 6 min. with developer Ilford ID 42 at 18° C.; in most exposures the β radiation was filtered off by a Ni foil. The optical densities of the $(h0l)$ reflexions were photometered (Smits & Wiebenga, 1953); the intensities of the other reflexions were estimated only visually.

Structure factors for the $(h0l)$ reflexions were calculated by the equation:

$$n.p(\theta).(10D)^{q(D)} = I' \equiv \frac{1+\cos^2 2\theta}{\sin 2\theta}\cdot F^2.A(\mu R, \theta)\,. \quad (1)$$

Here D stands for the optical density of the reflexion, n includes film and scale factors (the scale factor was recalculated after every cycle of refinement); $p(\theta)$ is an empirical correction factor for the splitting of the reflexions into an α_1 and an α_2 component. For $1 > D > 0{\cdot}1$ a linear relationship was found to exist between optical densities and intensities of the reflexions ($q(D) = 1$); for the very weak reflexions ($D < 0{\cdot}1$), however, the measured optical densities consistently led to too high intensity values. It was empirically found that this error could be adequately corrected for by substituting $q(D) = 1{\cdot}28$, when $D < 0{\cdot}1$. The transmission factor $A(\mu R, \theta)$ was interpolated from tables given by Bradley (1935) with $\mu_0 R = 1{\cdot}7$ (cf. § 5).

A detailed analysis showed that the accuracy of the experimental intensity values is limited, not by the measurement, but by the quality of the crystal itself. The standard deviation in the intensities of strong and moderate reflexions (77 out of 97) was determined to be 2·6%, increasing to several times that value for the weakest reflexions. The 'experimental reliability factor' $\Sigma|F_{\mathrm{true}}-F_o| \div \Sigma|F_{\mathrm{true}}|$ is calculated to be 1·1%, as far as random errors are concerned.

3. Unit cell and space group

The unit-cell dimensions of *l.t.*–$C_2H_5NH_3Br$ and of the isomorphous $C_2H_5NH_3Cl$ were determined to be:

$C_2H_5NH_3Br$:

$$a=8{\cdot}361\pm0{\cdot}010,\quad b=6{\cdot}261\pm0{\cdot}005,\quad c=4{\cdot}630\pm0{\cdot}005\ \text{Å};$$
$$\beta = 93{\cdot}0°\pm0{\cdot}2°;$$
$$U = 242{\cdot}1\ \text{Å}^3;\quad D_X = 1{\cdot}729\ \text{g.cm.}^{-3};$$
$$a:b:c = 1{\cdot}335:1:0{\cdot}7395\,.$$

$C_2H_5NH_3Cl$:

$$a = 8{\cdot}18,\quad b = 5{\cdot}95,\quad c = 4{\cdot}51\ \text{Å};\quad \beta = 93{\cdot}2°;$$
$$U = 219\ \text{Å}^3;\quad D_X = 1{\cdot}24\ \text{g.cm.}^{-3};$$
$$a:b:c = 1{\cdot}375:1:0{\cdot}758\,.$$

The only systematic absences are $(0k0)$ for k odd. Therefore, the space group is either $P2_1$ (non-centrosymmetric) or $P2_1/m$ (centrosymmetric). In $P2_1$ the general position is twofold, in $P2_1/m$ it is fourfold. As there are only two molecules in the unit cell, the molecules (except some hydrogens) must lie in the mirror planes, if $P2_1/m$ is the correct space group. In that case the intensities of reflexions (h_1, k, l_1) for $k = 0, 2, 4, \ldots$ and also for $k = 1, 3, 5, \ldots$ should show only the normal decline; this was indeed found to be so. Furthermore, no significant differences were observed between the intensities of $(h_1, k_1, 0)$ and $(-h_1, k_1, 0)$; in the non-centrosymmetric space group $P2_1$ such differences are to be expected because of anomalous scattering by Br. These observations, together with the negative result of a piezo-electric test,* led to the adoption of $P2_1/m$–C_{2h}^2 as the space group. Br, N, C_1, C_2 and two of the hydrogens (H_1 and H_2) are to be placed in the twofold position (e): $\pm(x, \frac{1}{4}, z)$; the other hydrogens in the general fourfold position (f): $\pm(x, y, z;\ x, \frac{1}{2}-y, z)$.

4. Structure determination

Rough x and z parameters of Br were derived from one-dimensional Patterson syntheses and found to be in agreement with Hendricks' values. A first Fourier projection along the b axis was calculated. Improved Br parameters and the positions of the C and N atoms were determined from this map. Structure factors were calculated, using for Br Thomas–Fermi scattering factors (*Internationale Tabellen*, 1935) corrected for dispersion and anomalous scattering (Dauben & Templeton, 1955), while for both C and N we adopted

---

* I am very grateful to Dr W. G. Perdok of the Kristallografisch Instituut der Rijkskuniversiteit, Groningen, the Netherlands, for performing the piezo-electric test.

the C scattering factors given by Hoerni & Ibers (1954). An overall temperature factor with $B = 3{\cdot}2$ Å^2 was applied. The value of the 'reliability index' R was 18·9%. The signs of almost all ($h0l$) structure amplitudes were now known and refinement of the structure proceeded mainly by difference syntheses.

The ($h0l$) reflexions were divided into two groups: (i) reflexions with $\sin\theta/\lambda > 0{\cdot}355$ ($\sin^2\theta > 0{\cdot}3$); (ii) reflexions with $\sin\theta/\lambda < 0{\cdot}355$. Group (i) reflexions will be the most sensitive to changes in atomic positions and temperature factors; group (ii) reflexions are susceptible to such effects as extinction, absorption errors (due to deviations from the assumed cross-section of the crystal), hydrogen atoms, possibly ionization and bonding electrons. It was thought to be of advantage to refine groups (i) and (ii) separately; group (i) was tackled first.

A difference synthesis of group (i) reflexions indicated changes of the atomic positions and a reduction of the overall temperature factor to a value with $B = 2{\cdot}85$ Å^2. The reliability index R—including all reflexions—dropped to 13·4%. A new difference synthesis was computed. By some slight parameter shifts, the distinction of N and C—Hoerni & Ibers' (1954) scattering factors were used for both—and the assignment of individual temperature factors, that of Br being anisotropic, R was reduced to 6·37%. The agreement was further improved to $R = 4{\cdot}77\%$ by replacing the Thomas–Fermi scattering factors for Br by values interpolated by MacGillavry (1957) (see Table 3)—which caused an alteration of temperature and scale factors—and by introducing an anisotropic temperature factor for atom C_2.

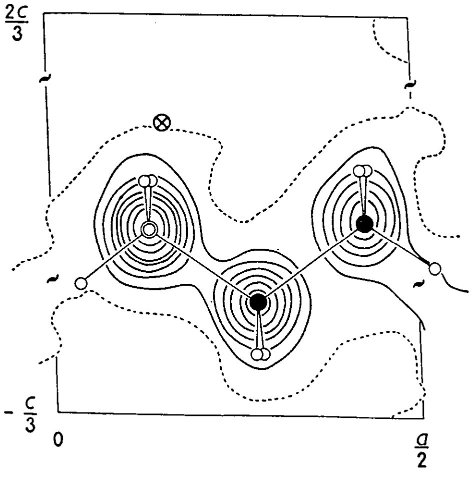

Fig. 1. Projection of the electron density of the monoethylammonium ion in $C_2H_5NH_3Br$ along the b axis; the Br contributions have been subtracted from the observed structure amplitudes. Contours are at intervals of 1 e.Å^{-2}; the 1 e.Å^{-2} line is broken.

5. Hydrogen atoms; extinction

At this stage the structure-factor agreement of group (i) reflexions had become fairly satisfactory, but that of group (ii) reflexions was considerably less so. Inclusion of the hydrogen atoms at calculated positions—assuming N–H and C–H distances of 1·0 Å and tetrahedral bond angles—with scattering factors as given by McWeeny (1951) and an estimated isotropic temperature factor, improved the overall reliability factor to 3·86%. A difference synthesis of group (ii) reflexions showed vague maxima at approximately the expected hydrogen positions, but revealed also a distinct minimum around the Br position. This effect was ascribed to extinction; probably it would have been masked to a considerable degree, if all reflexions had been refined simultaneously, because of erroneous temperature and scaling factors.

We tried to treat the discrepancies—which amounted up to 13% in F for the strongest reflexion (101)—as due to secondary extinction. In that case $A(\mu R, \theta)$ in equation (1) should be replaced by $A\{(\mu_0+\Delta\mu)R, \theta\}$, where $\Delta\mu = k.I'/A$. Now in the range of $\mu R \approx 1{\cdot}7$, $A(\mu R, \theta)$ appears to be adequately approximated by $A(\mu R, \theta) \approx A(\mu R)+A(\theta)$. Therefore

$$(\Delta A)_\theta = \frac{d\{A(\mu R)\}}{d\mu}\cdot\Delta\mu$$

is independent of θ, and

$$\frac{\Delta F}{F} = -\tfrac{1}{2}\frac{\Delta A}{A} = -\tfrac{1}{2}k\cdot\frac{d\{A(\mu R)\}}{d\mu}\cdot\frac{I'}{A^2} \equiv \varkappa\cdot\frac{I'}{A^2}\,.$$

By substituting F_c-F_o' for ΔF and plotting $\Delta F/F$ versus I'/A^2 a linear relationship with $\varkappa = 7{\cdot}1\times10^{-7}$ was indeed found to hold with a good approximation.

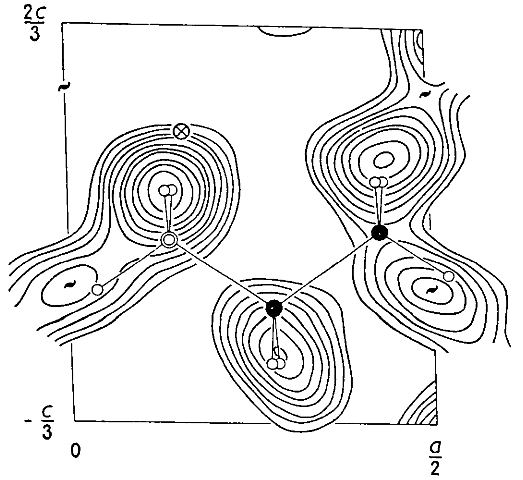

Fig. 2. Difference synthesis of group (ii) ($h0l$) reflexions ($\sin\theta/\lambda < 0{\cdot}355$) of $C_2H_5NH_3Br$. The calculated Br, N and C contributions have been subtracted from the observed structure amplitudes, which are corrected for extinction. Maxima are found around the expected hydrogen positions. Contours are at intervals of 0·1 e.Å^{-2}; the lowest contour is at 0·4 e.Å^{-2}.

Table 1. *Atomic positions and temperature factors*

	x/a	y/b	z/c	$B_{\text{max.}}$ (Å²)	$B_{\text{min.}}$ (Å²)	Direction of major ellipse axis
Br	0·1619	$\frac{3}{4}$	0·3968	3·38	2·53	[$\bar{1}$04]
N	0·135	$\frac{1}{4}$	0·125	3·35		
C_1	0·281	$\frac{1}{4}$	−0·050	3·35		
C_2	0·430	$\frac{1}{4}$	0·153	4·75	3·44	[2,0,69], i.e. ⊥ [100]
H_1	0·04	$\frac{1}{4}$	−0·01	3·88 (assumed)		
H_2	0·53	$\frac{1}{4}$	0·04			
H_3	0·14	0·12	0·25			
H_4	0·28	0·12	−0·17			
H_5	0·43	0·12	0·28			

When the observed structure factors were corrected for the extinction effect, R decreased to 2·65%. In a new difference synthesis of group (ii) reflexions (see Fig. 2) hydrogen atoms are clearly indicated, showing that the model adopted is not far from reality. The originally calculated hydrogen positions were therefore maintained.

6. The final structure

A new difference synthesis of group (i) reflexions was calculated, using the corrected values of F_o and including the hydrogen contributions in F_c. The slight changes in parameters and temperature factors thus derived reduced R to 2·39%. The atomic positions and temperature factors so found are given in Table 1. The y parameter of Br ($\frac{1}{4}$ or $\frac{3}{4}$) was decided on by a comparison of the intensities of ($h1l$) reflexions; the y parameters of the hydrogen atoms were computed from the model. Table 2 lists observed (without and with extinction correction) and calculated structure factors. Fig. 1 shows the projection of the electron density of the $C_2H_5NH_3^+$ ion on the ac plane; the contribution of Br is subtracted from the structure amplitudes for clarity and to suppress series-termination effects.

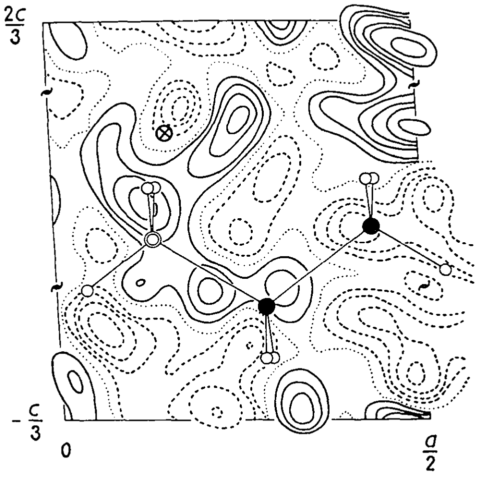

Fig. 3. Final (F_o-F_c) synthesis of $C_2H_5NH_3Br$, projected along the b axis. Contours are at intervals of 0·1 e.Å^{-2}. The zero line is dotted; positive regions are indicated by full lines, negative regions by broken lines.

Finally a difference synthesis including all ($h0l$) reflexions was computed (see Fig. 3); it indicates that a few more small changes in atomic positions and temperature factors might lead to still better agreement. However, a further refinement of temperature factors was not thought worth while, as the thermal movement in the y direction is not known. As to atomic parameters, the limit of physically significant refinement is evidently reached, as the indicated shifts are smaller than the calculated standard deviations in the atomic positions (for C: $\sigma(x) \approx \sigma(z) \approx 0{\cdot}01$ Å).

During the whole process of refinement one curious discrepancy remained: for ($\bar{3}03$) F_o is much greater than F_c; the difference is eight times as large as the r.m.s. difference for the other reflexions. The apparent high intensity of ($\bar{3}03$) can be explained by double reflexion against the strongly reflecting planes ($\bar{2}01$) and ($\bar{1}02$). The conditions for double reflexion are fulfilled in the (010) plane:

$$\theta_{(\bar{2}01)} = 14{\cdot}01°;\ \theta_{(\bar{1}02)} = 19{\cdot}94°;\ \theta_{(\bar{3}03)} = 33{\cdot}95°;$$
$$(I'/A)_{(\bar{2}01)} = 7353;\quad (I'/A)_{(\bar{1}02)} = 1628;$$
$$(I'/A)_{(\bar{3}03)_o} = 34{\cdot}9;\quad (I'/A)_{(\bar{3}03)_c} = 1{\cdot}8\,.$$

The hypothesis of double reflexion is confirmed by the observation that in non-integrated Weissenberg diagrams the shape of the ($\bar{3}03$) reflexion is distinctly different from that of the other reflexions, while for ($\bar{3}03$) no Cu $K\beta$ reflexion is observed ($\theta_{(\bar{2}01)\beta} = 12{\cdot}63°$; $\theta_{(\bar{1}02)\beta} = 17{\cdot}95°$; $\theta_{(\bar{3}03)\beta} = 30{\cdot}31°$). The reflexion ($\bar{3}03$) was not included in the difference syntheses, nor in R.

7. Bromine scattering factors

From our data an experimental scattering curve for Br can be computed, using $\Delta f' = -0{\cdot}9$ and $\Delta f'' = 1{\cdot}5$, as given by Dauben & Templeton (1955). In Table 3 our experimental values are compared with theoretical values. It must be borne in mind that our values are strongly biased towards the MacGillavry values, which were employed in the later stages of refinement. However, it is encouraging that our values are in still better agreement with recently published values by Thomas & Umeda (1957). The trend towards higher f_0 values for low values of $\sin\theta/\lambda$ might be due to ionization of bromine in $C_2H_5NH_3Br$.

Table 2. *Observed and calculated structure factors of (h0l) reflexions*

The signs given for F_c refer to the real parts of the structure factors

F_o': without extinction correction; F_o with extinction correction.
F_c: with H contributions; F_c' without H contributions.

h0l	F_o'	F_o	F_c	F_c'
000			+122·24	106·24
100	27·03	29·10	+29·10	30·76
200	27·91	28·98	−29·04	30·22
300	52·37	56·54	−56·50	55·30
400	28·64	29·08	−29·04	29·32
500	9·12	9·13	+9·56	10·02
600	26·75	26·90	+26·52	26·72
700	23·02	23·10	+22·96	22·32
800	4·89	4·89	−5·10	5·06
900	13·92	13·94	−14·32	14·28
10,0,0	8·70	8·71	−8·80	8·76
001	21·52	22·07	−20·80	24·56
$\bar{1}01$	13·33	13·45	+11·68	10·62
101	53·86	61·06	−61·18	60·62
$\bar{2}01$	44·05	47·04	+47·00	45·08
201	19·82	20·07	−17·68	17·16
$\bar{3}01$	47·76	50·36	+49·90	46·24
301	20·03	20·21	+20·30	22·92
$\bar{4}01$	9·07	9·08	−8·14	7·28
401	43·60	44·86	+44·96	42·34
$\bar{5}01$	32·60	32·98	−33·62	32·76
501	7·69	7·69	+7·48	7·38
$\bar{6}01$	27·53	27·70	−28·38	28·30
601	16·84	16·88	−17·60	17·80
$\bar{7}01$	2·08	2·08	+2·38	2·38
701	16·89	16·92	−17·46	17·46
$\bar{8}01$	14·51	14·53	+15·14	15·10
801	6·50	6·50	−6·66	6·62
$\bar{9}01$	13·06	13·07	+12·66	12·70
901	7·94	7·94	+7·82	7·88
$\overline{10},0,1$	3·31	3·31	+3·16	3·08
10,0,1	9·58	9·59	+9·02	9·12
002	13·25	13·30	+12·64	14·80
$\bar{1}02$	25·64	26·00	−25·24	24·28
102	38·47	39·61	+40·02	38·26
$\bar{2}02$	38·06	39·07	−38·94	40·76
202	21·34	21·50	+22·22	21·92
$\bar{3}02$	1·43	1·43	−1·42	2·28
302	13·24	13·27	−12·32	12·80
$\bar{4}02$	17·81	17·87	+17·04	16·34
402	22·34	22·45	−22·74	23·46
$\bar{5}02$	21·86	21·95	+22·58	22·94
502	22·24	22·32	−22·18	22·56
$\bar{6}02$	7·79	7·79	+8·18	7·72
602	4·17	4·17	+3·96	4·04
$\bar{7}02$	9·55	9·56	−9·94	9·52
702	17·28	17·31	+18·04	18·36
$\bar{8}02$	13·82	13·83	−14·18	14·10
802	13·39	13·40	+13·26	13·20
$\bar{9}02$	6·47	6·47	−6·52	6·50
902	1·80	1·80	−1·60	1·58
$\overline{10},0,2$	6·54	6·54	+6·26	6·22
003	9·09	9·10	+7·92	7·70
$\bar{1}03$	29·16	29·41	+29·58	30·28
103	18·30	18·35	−17·84	18·32
$\bar{2}03$	20·02	20·10	+20·48	19·66
203	32·78	33·08	−33·84	34·82
$\bar{3}03$	(5·32)*	(5·32)*	−1·22	0·58
303	12·14	12·15	−12·04	12·36
$\bar{4}03$	20·52	20·58	−21·38	21·70
403	17·33	17·36	+17·38	17·80
$\bar{5}03$	17·75	17·78	−17·90	18·10
503	21·57	21·63	+22·00	21·82
$\bar{6}03$	3·46	3·46	+3·60	3·38
603	9·62	9·62	+9·72	9·86
$\bar{7}03$	11·21	11·22	+11·64	11·72
703	7·84	7·84	−7·76	7·74
$\bar{8}03$	8·69	8·69	+8·64	8·72
803	12·13	12·14	−11·60	11·60
$\bar{9}03$	1·23	1·23	−1·40	1·40
004	19·54	19·58	−19·94	20·36
$\bar{1}04$	20·12	20·17	−20·46	20·72
104	1·69	1·69	+1·30	1·46
$\bar{2}04$	1·05	1·05	−1·02	1·14
204	13·92	13·94	+14·58	14·24
$\bar{3}04$	16·86	16·89	+16·62	16·86
304	17·82	17·85	+17·66	17·76
$\bar{4}04$	15·92	15·94	+16·52	16·62
404	3·79	3·79	+3·78	3·88
$\bar{5}04$	1·24	1·24	+1·08	0·98
504	10·47	10·48	−10·58	10·56
$\bar{6}04$	7·40	7·40	−7·52	7·48
604	13·51	13·53	−12·80	12·86
$\bar{7}04$	10·26	10·27	−10·38	10·40
704	3·07	3·07	−3·08	3·14
$\bar{8}04$	3·04	3·04	−3·26	3·30
005	12·34	12·35	+11·62	11·60
$\bar{1}05$	2·63	2·63	+2·60	2·42
105	9·04	9·04	+9·06	9·10
$\bar{2}05$	6·26	6·26	−6·04	6·02
205	3·65	3·65	−4·30	4·26
$\bar{3}05$	10·14	10·15	−10·38	10·42
305	10·65	10·66	−10·14	10·18
$\bar{4}05$	4·14	4·14	−4·12	4·16
405	6·18	6·18	−6·38	6·42
$\bar{5}05$	3·71	3·71	+3·82	3·88
505	2·84	2·84	+3·08	3·08
$\bar{6}05$	8·24	8·25	+8·46	8·48

* Enhanced by double reflexion against ($\bar{2}01$) and ($\bar{1}02$).

8. Discussion

The bond distances found from the final parameters are N–C_1=1·499±0·012 Å and C_1–C_2=1·521±0·014 Å; the angle N–C_1–C_2 is 109° 16′. N–H and C–H distances were adopted as 1·0 Å with tetrahedral bond angles. The anisotropic temperature movement of C_2 is compatible with an oscillation of the molecule about N–C_1 as axis; this picture leads to a large temperature movement of C_2 in the *y* direction (which was not determined). Therefore, the deviation of the C_1–C_2 distance—which is uncorrected for thermal movement—from the normal value of 1·54 Å is certainly not significant. The elongation of the N–C_1 bond distance, as compared with a normal value of 1·47 Å, is to be regarded as significant and is probably due to ionization of the –NH_3 group.

The H_1 atom and the two H_3 atoms bound to N

Table 3. *Atomic scattering factors of bromine*

$\sin\theta/\lambda$	P&Sh	Th–F	McG	Th&U	Exp.
0·00	35·00	35·0	35·00	35·00	
0·05				34·22	
0·10	31·20	31·6	32·06	32·21	$32{\cdot}5^5$
0·15				29·70	29·7
0·20	26·40	26·6	27·26	27·27	$27{\cdot}4^5$
0·25				25·14	25·4
0·30	23·72	22·3	23·62	23·24	$23{\cdot}4^5$
0·35				21·51	$21{\cdot}6^5$
0·40	21·24	18·9	20·36	19·95	$20{\cdot}0^5$
0·45				18·57	$18{\cdot}6^5$
0·50	18·24	16·7	17·76	17·35	17·4
0·55				16·24	16·4
0·60	15·23	14·8	15·50	15·22	15·6
0·65				14·32	
0·70	12·81	13·1	13·40	13·50	

P&Sh: Pauling & Sherman (1932).
Th–F: Thomas–Fermi (*Internationale Tabellen*, 1935).
McG: MacGillavry (1957).
Th&U: Thomas & Umeda (1957).
Exp.: experimental values for *l.t.*-$C_2H_5NH_3Br$.

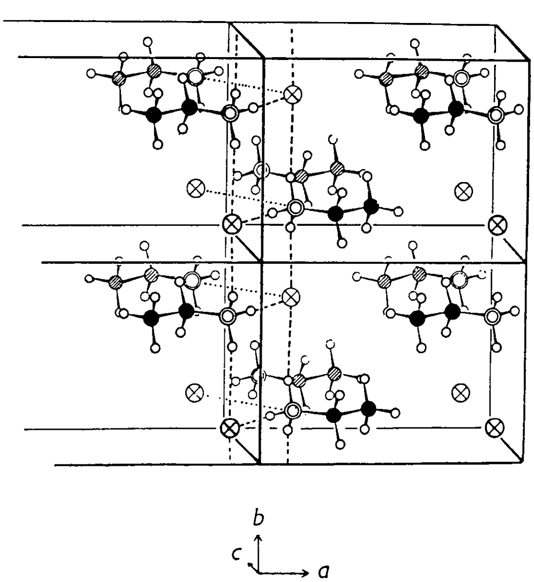

Fig. 4. The packing in *l.t.*-$C_2H_5NH_3Br$. N–H · · · Br bridges are indicated by broken lines; these bridges link the molecules to form chains running in the *b* direction. These chains are mutually joined by N · · · Br contacts (indicated by dotted lines) which probably correspond to ionic attraction. In this way double sheets parallel (100) are formed. These sheets are bound to each other by van der Waals forces only.

point in the directions of one Br each (the angles N–H–Br are 169° and 160° respectively). These H–Br contacts of 2·4 Å may be regarded as N–H · · · Br bridges; the corresponding N–Br distances are 3·37 and 3·38 Å respectively. A fourth N–Br contact of 3·41 Å, almost collinear with the C_1–N bond, apparently has a different character. While the three nearly coplanar N–H · · · Br bridges around each Br link the molecules to form helical chains running in the *b* direction (see Fig. 4), the N–Br contacts of 3·41 Å, perpendicular to the planes of the N–H · · · Br bridges, probably correspond to ionic bonds which link the chains to form double sheets parallel to (100). (The major axis of the Br thermal movement in the *ac* plane is also approximately perpendicular to the plane of the N–H · · · Br bridges.) These sheets are bound to each other only by weak van der Waals forces, which fact explains the very perfect cleavage of the crystals along (100).

Intermolecular contacts are all through hydrogen. Each H_1 and H_3 atom has two hydrogen neighbours in other molecules, each H_2, H_4 and H_5 atom four; all these van der Waals contacts lie in the range 2·8–2·9 Å. Furthermore, each hydrogen has one Br neighbour at a distance of 3·2–3·4 Å. The shortest Br–Br distances are 4·28 Å.

The author wishes to express his gratitude to Prof. J. M. Bijvoet for encouragement and advice in the course of this investigation and to Drs A. de Vries for his help in the structure refinement.

References

Bradley, A. J. (1935). *Proc. Phys. Soc.* **47**, 879.
Dauben, C. H. & Templeton, D. H. (1955). *Acta Cryst.* **8**, 841.
Groth, P. (1906). *Chemische Krystallographie*, vol. 1, p. 186. Leipzig: Engelmann.
Hendricks, S. B. (1928). *Z. Kristallogr.* **67**, 119.
Hoerni, J. A. & Ibers, J. A. (1954). *Acta Cryst.* **7**, 744.
Internationale Tabellen zur Bestimmung von Kristallstrukturen (1935), vol. 2, p. 572. Berlin: Borntraeger.
MacGillavry, C. H. (1957). Private communication.
McWeeny, R. (1951). *Acta Cryst.* **4**, 513.
Pauling, L. & Sherman, J. (1932). *Z. Kristallogr.* **81**, 1.
Peerdeman, A. F. & Bijvoet, J. M. (1956*a*). *Proc. K. Ned. Akad. Wet.* **B**, **59**, 312.
Peerdeman, A. F. & Bijvoet, J. M. (1956*b*). *Acta Cryst.* **9**, 1012.
Smits, D. W. & Wiebenga, E. H. (1953). *J. Sci. Instrum.* **30**, 280.
Thomas, L. H. & Umeda, K. (1957). *J. Chem. Phys.* **26**, 293.
Wiebenga, E. H. & Smits, D. W. (1950). *Acta Cryst.* **3**, 265.