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The Crystal Structure of 3-*N*-Methylaminomethylpinane Hydrobromide

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Dedicated to Prof. K. Dornberger-Schiff on her 60th birthday

The compound 3-*N*-methylaminomethylpinane hydrobromide is monoclinic, space group $P2_1/c$, with four molecules in a unit cell of dimensions $a=12{\cdot}086$, $b=7{\cdot}590$, $c=15{\cdot}349$ Å, $\beta=93{\cdot}18°$. The carbon atom C(3) inclines to the side of the molecule carrying the *gem*-dimethyl group. The *N*-methylaminomethyl group on C(3) and the methyl group on C(2) are both equatorial. The molecules are connected in the **a** and **c** directions by van der Waals bonds and in the **b** direction by hydrogen bonds which form chains around the screw axis.

Introduction

The investigation of the crystal structure of 3-*N*-methylaminomethylpinane hydrobromide, $C_{12}H_{24}BrN$, was undertaken to determine the configuration of the molecule, including bond lengths and angles. Especially interesting was the arrangement of the carbon atom C(3) relative to the *gem*-dimethyl group and the position of the *N*-methylaminomethyl group on C(3). We also wanted to study the intermolecular bonds.

The crystal specimens were kindly supplied by Professor Mühlstedt from the Institut für Organische Chemie der Karl-Marx-Universität, Leipzig. The preparation of the substance will be described by Mühlstedt in a separate paper.

Experimental

By the use of a rather irregular crystal, X-ray photographs obtained with Cu $K\alpha$ radiation gave the following crystal data:

Space group: $P2_1/c$ (systematic absences $0k0$ with $k=2n+1$ and $h0l$ with $l=2n+1$).

Unit cell: $a=12{\cdot}086\pm0{\cdot}012$ Å
$b=7{\cdot}590\pm0{\cdot}008$
$c=15{\cdot}349\pm0{\cdot}009$
$\beta=93{\cdot}18\pm0{\cdot}09°$

4 molecules of $C_{12}H_{24}BrN$ per unit cell.

The calculated density of 1·24 g.cm^{-3} compares well with the density of 1·22 g.cm^{-3} measured by flotation. The lattice constants were determined with the help of Weissenberg and rotation photographs calibrated with gold powder. In order to increase the accuracy a special least-squares program was used.

For the structure determination 1341 independent reflexions hKl with $K=0, 1\cdots5$ and 126 reflexions $0kl$ obtained by multiple Weissenberg photographs were used. The intensities were measured photometrically without integration and corrected for background, Lorentz and polarization factors and a factor allowing for the resolution of α_1 and α_2 at different θ values. No corrections were made for absorption, primary or secondary extinction. (The approximate dimensions of the crystal were $150\times200\times160$ μm^3 while the linear absorption coefficient μ is 39·4 cm^{-1}.)

Structure determination

From the Patterson projections $P_0(uw)$, $P_0(vw)$ and from the generalized Patterson projection $P_1^{\cos}(uw)$ the three-dimensional position of the bromine atom was determined. Comparison of observed structure factors with calculated contributions of bromine atoms gave signs of 80% of the structure factors with $|F_{obs}|>10$. Using these structure factors and all structure factors less than 10 with $2|F_{obs}|<|F_{Br}|$ a three-dimensional difference Fourier synthesis with $(F_{obs}-F_{Br})$ as coefficients was calculated, from which the configuration of the molecule was obtained (Fig. 1).

Refinement of the structure

As a first step the positions of all atoms in the xz projection were refined by means of three difference Fourier syntheses with values $(F_{obs}-F_{cal})$ as coefficients. As a next step the y coordinates were refined on the one hand by generalized Fourier syntheses and on the other hand by the method of linear structure-factor equations (Kutschabsky, 1965) using the $F_{obs}(h3l)$ and $F_{obs}(h4l)$. Both methods gave similar results. Comparison with the positional parameters obtained by a three-dimensional least-squares refinement (see below) showed that the coordinates obtained by systems of linear structure-factor equations were considerably more accurate than coordinates obtained from generalized Fourier syntheses.

The final refinement of the structure was carried out by means of a block-diagonal least-squares program.

The quantity minimized was $\sum w(|F_{obs}|-|F_{cal}|)^2$. The weighting scheme was that of Cruickshank (1961). The positional parameters, the individual isotropic B_j values of the light atoms and the anisotropic b_{ij} values of the bromine atom were refined. (b_{ij} are the coefficients in the expression: $\exp\{-[b_{11}h^2+b_{22}k^2+b_{33}l^2+b_{12}hk+b_{13}hl+b_{23}kl]\}$.) The R value for all 1341 reflexions dropped from 0·230 at the beginning to 0·132 at the end of refinement. The last average shift/σ ratio of the positional parameters of the light atoms was 0·1.

The Freeman (1959) f curve was assumed for carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) for nitrogen, and those of Freeman & Watson (1961) for bromine.

After the least-squares refinement a three-dimensional difference Fourier synthesis using ($F_{obs}-F_{cal}$) as coefficients was calculated which verified the correctness of the refinement but the positions of the hydrogen atoms could not be determined unambiguously. Therefore their positions were left out.

The calculations of the three-dimensional difference Fourier syntheses and the least-squares calculations were performed on the NE 503 computer, and the two-dimensional syntheses and the systems of linear structure-factor equations were calculated on the ZRA 1 computer.

The resulting atomic coordinates and the thermal parameters are listed in Table 2, the atomic distances and bond angles in Table 3. The observed and calculated structure factors are compared in Table 1.

Description of the structure

The X-ray analysis showed that the carbon atom C(3) inclines to the side of the molecule carrying the *gem*-dimethyl group, *e.g.* the atoms C(1) to C(6) form a boat. The dihedral angle between the planes C(1)–C(2)–C(4)–C(5) and C(2)–C(3)–C(4) is 161·1° whereas the angle between C(1)–C(2)–C(4)–C(5) and C(1)–C(5)–C(6) is 114·3°. This difference is evidently caused by the influence of the cyclobutane ring which reduces the distance between C(1) and C(5) to 2·07 Å whereas the distance between C(2) and C(4) amounts to 2·60 Å. Therefore the arrangement of the atoms C(1) to C(5) is similar to a plane cyclopentane ring. The large value of the dihedral angle between C(1)–C(2)–C(4)–C(5) and C(2)–C(3)–C(4) is presumably also the result of the non-bonding interactions between the hydrogen atom on C(3) and the CH_3(9) group. These interactions also cause the dihedral angle between C(1)–C(2)–C(4)–C(5) and C(1)–C(5)–C(6) to be 9° larger than the dihedral angle between C(1)–C(2)–C(4)–C(5) and C(1)–C(5)–C(7) and the bond angles C(9)–C(6)–C(1) and C(9)–C(6)–C(5) to be on average 11° larger than the angles C(8)–C(6)–C(1) and C(8)–C(6)–C(5) (Table 3).

The *N*-methylaminomethyl group on C(3) and the CH_3(10) group on C(2) occupy equatorial positions. The carbon atoms C(11), C(3), C(6), C(7), C(8) and C(9) lie near a plane described by the equation:

$$-0{\cdot}1451\ X-0{\cdot}0292\ Y-0{\cdot}9890\ Z+2{\cdot}9872=0$$

(referred to the orthogonal axes *abc**).

The average deviation from this plane is 0·03 Å. The distances of the atoms C(1), C(5), C(2) and C(4) from this plane are 1·01, 1·06, 1·29 and 1·31 Å.

A similar molecular conformation was found in the crystal structure of 3-*N*-dimethylaminomethyl-2(10)-pinene hydrobromide (Kutschabsky, 1969). As in the structure studied here, C(3) lies on the same side of the plane of C(1)–C(2)–C(4)–C(5) as C(6) whereas in the molecules of 3-bromo-6,6-dimethylnorpinan-2-one and 3-chloro-6,6-dimethylnorpinan-2-one (Barrans,

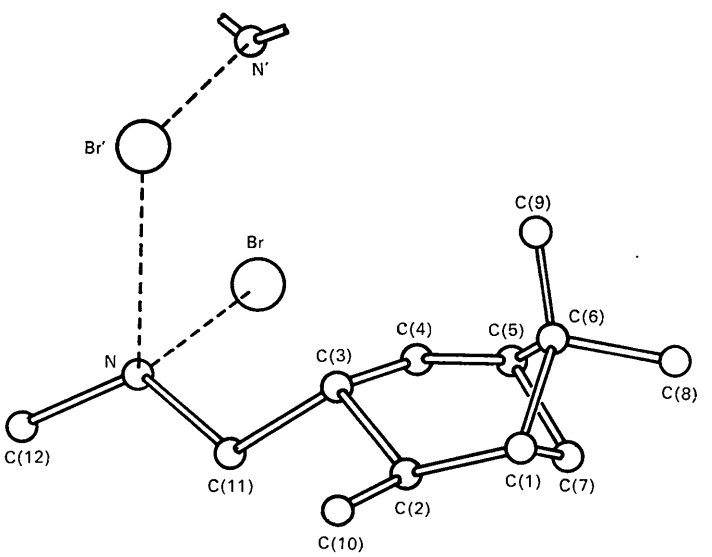

Fig. 1. The molecule of 3-*N*-methylaminomethylpinane hydrobromide and the hydrogen bonds between the nitrogen and bromine atoms (broken lines).

1964) it lies on the other side. But in all cases the dihedral angles between the planes C(1)–C(2)–C(4)–C(5) and C(2)–C(3)–C(4) are larger than 148°. The relations between the structures of 3-*N*-methylaminomethylpinane hydrobromide, 3-*N*-dimethylaminomethyl-2(10)-pinene hydrobromide (Kutschabsky, 1969) and 2-bromo-6-*N*-dimethylaminomethylfenchane hydrobromide (Reck, 1969) especially the relations between the intermolecular bonds of these structures, will be discussed in a separate paper.

The angle C(11)–N–C(12) in the structure of 3-*N*-methylaminomethylpinane hydrobromide is equal to the tetrahedral angle within the limit of error. The distances N–Br of 3·27 Å and N–Br′ of 3·28 Å corres-

Table 1. *Observed and calculated values of structure factors*

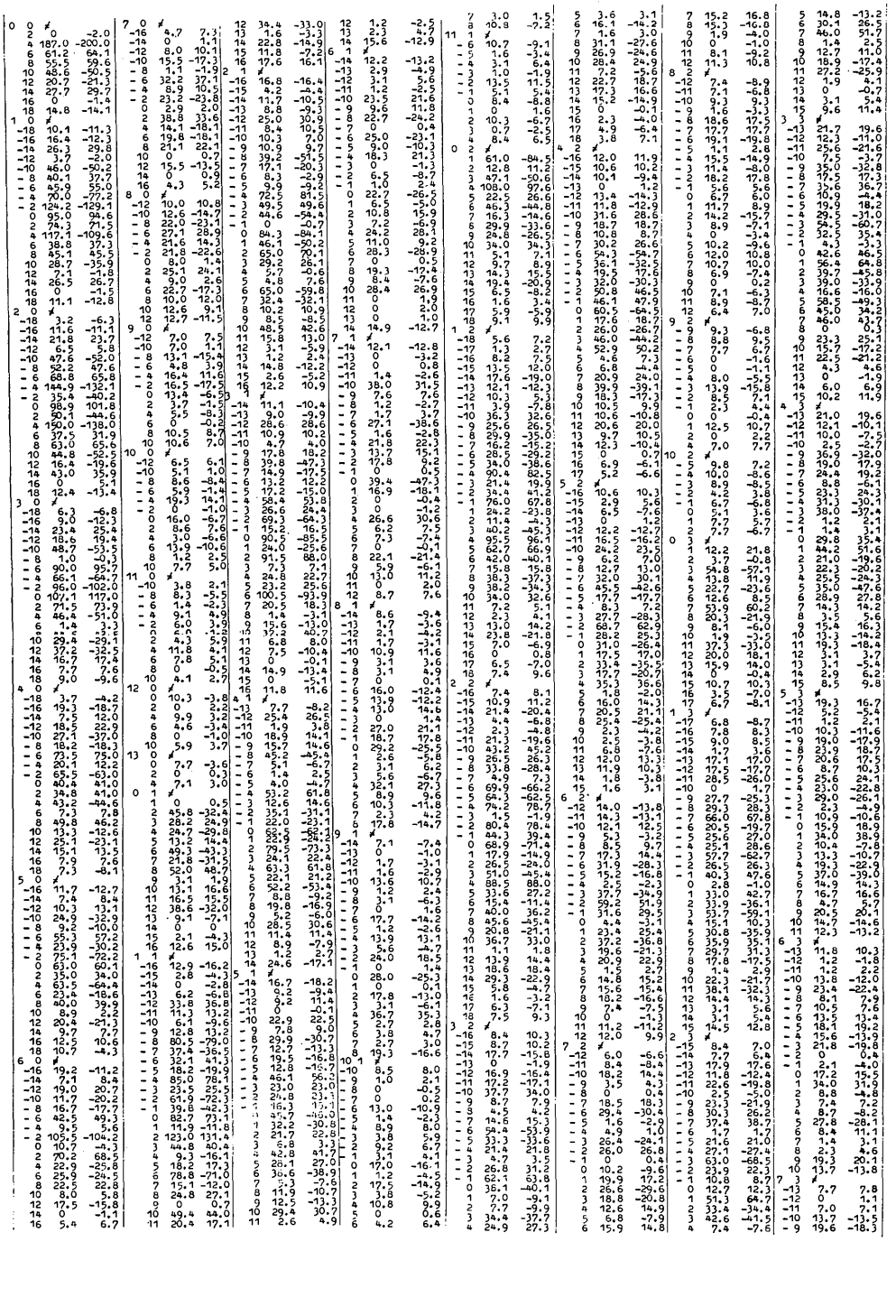

Table 1 (*cont.*)

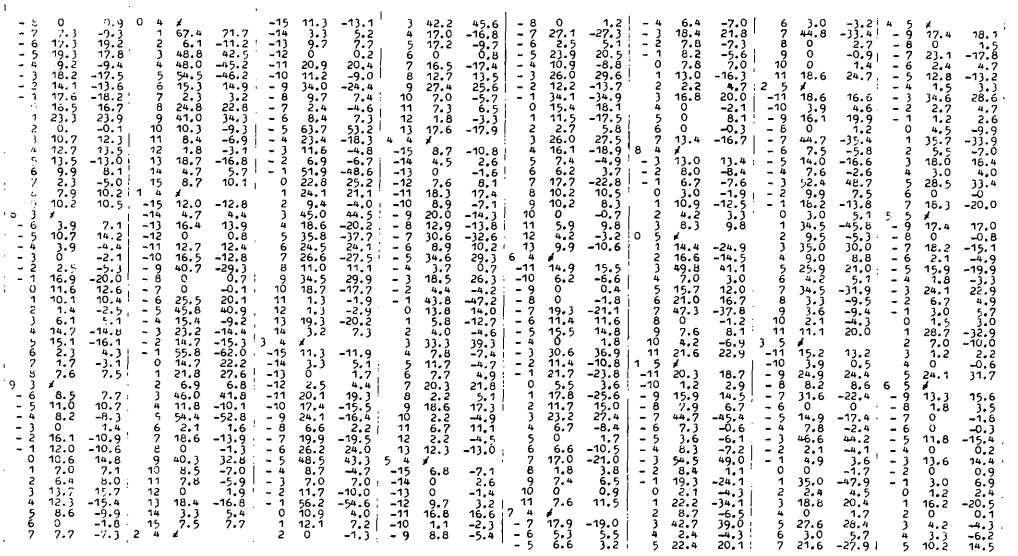

Table 2. *Positional and thermal parameters*

E.s.d. in parentheses.

	x/a	*y/b*	*z/c*	*B*
Br	0·0364 (1)	0·1984 (2)	0·3579 (1)	–
N	0·0076 (10)	0·2715 (16)	0·1481 (8)	5·9 (3)
C(1)	0·6193 (15)	0·1443 (23)	0·0573 (11)	7·0 (4)
C(2)	0·7322 (14)	0·1859 (22)	0·0252 (11)	6·7 (4)
C(3)	0·8103 (14)	0·2582 (20)	0·1006 (10)	6·0 (3)
C(4)	0·7719 (15)	0·2062 (23)	0·1931 (11)	6·9 (4)
C(5)	0·6520 (16)	0·1522 (26)	0·1911 (13)	8·1 (5)
C(6)	0·5780 (13)	0·2650 (21)	0·1276 (11)	6·5 (4)
C(7)	0·6351 (17)	0·9933 (28)	0·1279 (13)	8·9 (5)
C(8)	0·4523 (19)	0·2268 (28)	0·1385 (15)	9·6 (6)
C(9)	0·5944 (21)	0·4620 (32)	0·1252 (16)	10·8 (6)
C(10)	0·7226 (23)	0·1741 (34)	0·4506 (19)	11·7 (7)
C(11)	0·9234 (13)	0·1812 (21)	0·0860 (10)	6·1 (3)
C(12)	0·1238 (16)	0·2154 (24)	0·1249 (12)	7·5 (4)

Anisotropic thermal parameters (× 10⁴) of bromine

b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
179 (2)	228 (4)	50 (1)	−9 (4)	10 (2)	−15 (3)

pond closely to similar distances found in other structures of hydrohalides (Bryan & Tomita, 1962; Przybylska, 1963). The angles C(11)–N–Br, C(11)–N–Br′, C(12)–N–Br′ and Br–N–Br′ lie between 97 and 125°. It is very likely, therefore that Br and Br′ are attached to the N atom through hydrogen bridges. Assuming the hydrogen bonds to the nitrogen atom to form approximately tetrahedral angles between themselves and with the N–C(11) and N–C(12) bonds, and that the hydrogen atoms are located at the usual distance of about 1·0 Å from the nitrogen atom, then the hydrogen bridge to Br′ deviates by only 4° from linearity, whereas the bridge to Br is more kinked (23°). This is probably due to steric hindrance: a straight bridge in the direction determined by the tetrahedral angles would reduce the Br–C(4) distance to an impossibly low value of 2·8 Å. The direction of the anisotropic vibration of bromine was found to be perpendicular to the plane formed by atoms Br′, N and N′ (Fig. 1). This is to be expected if the bromine atom is linked to these atoms by hydrogen bonds, so the assumption of hydrogen bonding is confirmed. The hydrogen bonds connect the molecules of 3-*N*-methylaminomethylpinane hydrobromide along the *b* axis and form chains around the screw axis. In the **a** and **c** directions the molecules are connected by van der Waals bonds. In Fig. 2 all distances between the bromine atom and the light atoms and all intermolecular distances shorter than 4·25 Å are shown.

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Table 3. *Bond lengths and angles*

E.s.d. in parentheses.

C(1)–C(2)	1·51 (2) Å	C(6)—C(8)	1·56 (3) Å
C(2)–C(3)	1·55 (2)	C(6)—C(9)	1·51 (3)
C(3)–C(4)	1·57 (2)	C(2)—C(10)	1·56 (3)
C(4)–C(5)	1·51 (3)	C(3)—C(11)	1·52 (2)
C(5)–C(6)	1·54 (3)	C(11)–N	1·52 (2)
C(6)–C(1)	1·52 (2)	C(12)–N	1·53 (2)
C(1)–C(7)	1·58 (3)	N · · · Br	3·27 (1)
C(7)–C(5)	1·55 (3)	N · · · Br′	3·28 (1)
C(1)–C(2)–C(3)	111 (1)°	C(5)—C(6)—C(9)	120 (2)°
C(2)–C(3)–C(4)	113 (1)	C(8)—C(6)—C(9)	108 (2)
C(3)–C(4)–C(5)	113 (1)	C(1)—C(2)—C(10)	110 (2)
C(4)–C(5)–C(6)	113 (2)	C(10)–C(2)—C(3)	109 (2)
C(5)–C(6)–C(1)	85 (1)	C(2)—C(3)—C(11)	106 (1)
C(6)–C(1)–C(2)	116 (1)	C(11)–C(3)—C(4)	110 (1)
C(7)–C(1)–C(2)	107 (1)	C(3)—C(11)–N	108 (1)
C(4)–C(5)–C(7)	109 (2)	C(11)–N——C(12)	109 (1)
C(6)–C(1)–C(7)	89 (1)	C(11)–N · · · Br	125 (1)
C(1)–C(7)–C(5)	83 (1)	C(11)–N · · · Br′	109 (1)
C(7)–C(5)–C(6)	89 (1)	C(12)–N · · · Br	98 (1)
C(1)–C(6)–C(8)	109 (1)	C(12)–N · · · Br′	115 (1)
C(1)–C(6)–C(9)	122 (2)	Br · · · N · · · Br′	102 (1)
C(5)–C(6)–C(8)	111 (2)		

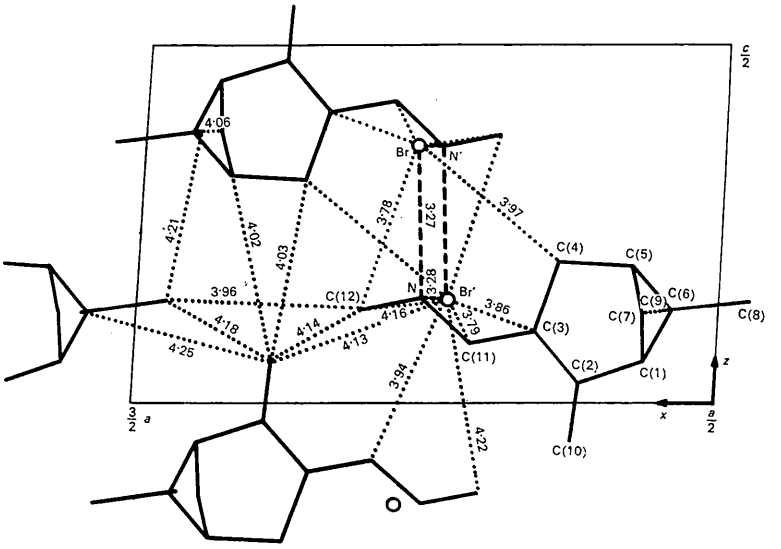

Fig. 2. Arrangement of molecules in *xz* projection. The distances between the bromine and the light atoms and all intermolecular distances under 4·25 Å are marked by dashed lines and the hydrogen bonds by broken lines.

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