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On the Crystal Structures of Methylamine

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At −150° C. methylamine forms orthorhombic crystals in the space group D_{2h}^{15}–*Pcab*, with eight molecules in a unit cell of dimensions $a = 5{\cdot}75$, $b = 6{\cdot}18$ and $c = 13{\cdot}61$ Å. Hydrogen bonds extend in almost planar sheets parallel to the (001) plane. The C–N bond distance is 1·48 Å, and the N · · · N hydrogen-bond distances are 3·18 and 3·27 Å. Interatomic distances suggest that the methyl group is staggered with respect to the hydrogen bonds. The transition at −172° C. is characterized only by slight lattice contractions, and might be associated with methyl group correlations. There is no residual entropy in the crystal.

Introduction

Besides the question of possible residual entropy in crystalline methylamine (Aston, Siller & Messerly, 1937), the substance undergoes a λ-point transition at −171·7° C. and shows a slight hysteresis loop from about −158° C. nearly up to the melting point of −93·46° C. In addition to these problems of thermodynamic interest, the nature of the hydrogen bonding in the solid, the relation to the structures of methanol (Tauer & Lipscomb, 1952), and the configuration of the methyl group relative to the amino group all add to the interest in a structural study of the solid. Some of our results of interest in relation to these problems, are described below.

Experimental

Pure methylamine, melting point −93° C. as compared with the expected value of −93·46° C., was obtained from a 20% aqueous solution by repeated fractional distillations and fractional crystallizations. Samples were sealed into small capillaries about 0·5 mm. in diameter by the usual procedure (Reed & Lipscomb, 1953). Buerger precession, Weissenberg and oscillation photographs were taken with Mo $K\alpha$ radiation from single crystals at −150° C. and at −185° C. Multiple-film methods were employed in which the films were interleaved with 0·001 in. brass foil. After visual estimation of the intensities with the use of a standard scale of single-crystal reflections, and after application of the usual Lorentz and polarization factors (Lu, 1943; Waser, 1951), the observed structure factors were obtained.

Structure of the −150° C. modification

The photographs indicated reciprocal-lattice symmetry D_{2h}, and the dimensions

$$a = 5{\cdot}75_3 \pm 0{\cdot}01,\ b = 6{\cdot}17_7 \pm 0{\cdot}01 \text{ and } c = 13{\cdot}61_2 \pm 0{\cdot}02 \text{ Å}$$

for the orthorhombic unit cell. The volume, 484 Å^3, of the unit cell and the observed density* of 0·85 g.cm.$^{-3}$ give a calculated density of 0·852 g.cm.$^{-3}$ if one assumes eight molecules in the unit cell. Although (hkl) reflections were observed in all orders, the extinctions of ($hk0$) when k is odd, ($0kl$) when l is odd, and ($h0l$) when h is odd lead uniquely to the space group D_{2h}^{15}–*Pcab*.

The intensity distribution indicates that all atoms are in the general eightfold positions, and therefore no molecular symmetry is required. The normal decline of ($h00$) and ($0k0$) reflections and the appearance of the Patterson projection $P(x, z)$ led to the assignment of x and y parameters for carbon and nitrogen at either 0 or $\frac{1}{4}$. Further trial-and-error methods led to a trial structure, and the electron-density projections along c (Fig. 1), a (Fig. 3), and b (Fig. 5) were refined until no further sign changes occurred. Backshift corrections, obtained by comparison with Fourier series in which coefficients were the calculated F's, were made. These corrections were less than 0·01 Å in all carbon and nitrogen parameters. Final values of these parameters are

$$x_C = 0{\cdot}216,\ y_C = 0{\cdot}004,\ z_C = 0{\cdot}106;$$
$$x_N = 0{\cdot}257,\ y_N = 0{\cdot}065,\ z_N = 0{\cdot}210.$$

The C–N distance is 1·48 Å, with an estimated probable error of $\pm 0{\cdot}01_4$ Å. The value of 1·47 Å appears in tables of distances (Pauling, 1948, p. 164; Schomaker & Stevenson, 1941), and the more recent published values* are in the range from 1·46 to 1·51 Å.

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* This value of the density was obtained from the density of the liquid and the observed volume contraction upon solidification.

* Some of these values are 1·46$_5$ Å in methylamine hydrochloride (Hughes & Lipscomb, 1946), 1·50 Å in mono- and trimethylamine boron trifluorides (Geller & Hoard, 1950, 1951), 1·50 Å in DL-alanine (Donohue, 1950), 1·49 Å in geranylamine hydrochloride (Jeffrey, 1945), 1·49 Å in L-threonine (Shoemaker, Donohue, Schomaker & Corey, 1950), 1·51 Å and 1·48 Å in β-glycylglycine (Hughes & Moore, 1948), 1·46 Å and 1·47 Å in potassium benzyl penicillin (Pitt, 1952).

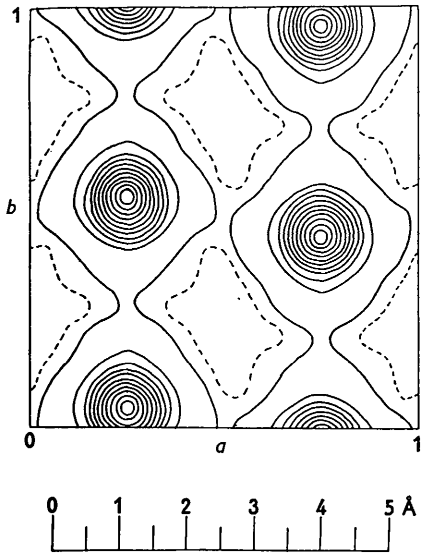

Fig. 1.

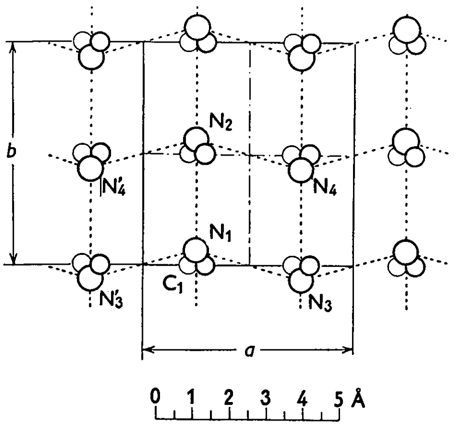

Fig. 2.

Fig. 1. Electron-density projection along the *c* axis. Each contour line represents a density increment of 2 e.Å^{-2}, the one-electron line being broken.

Fig. 2. Arrangement of the molecules in the *c* axis projection. Hydrogen bonds are indicated by broken lines. Two nitrogen atoms overlap almost completely.

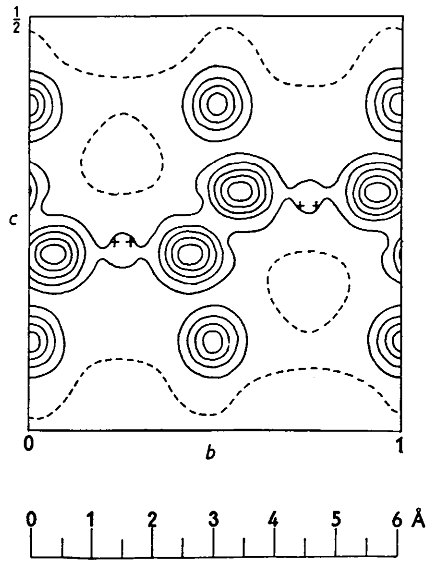

Fig. 3.

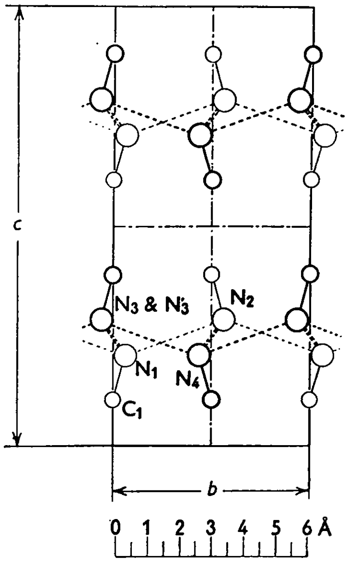

Fig. 4.

Fig. 3. Electron-density projection along the *a* axis. Each contour line represents a density increment of 1 e.Å^{-2}, the one-electron line being broken. The crosses show the positions of half of the hydrogen atoms in the amino groups.

Fig. 4. Arrangements of the molecules in the *a* axis projection. Hydrogen bonds are indicated by broken lines.

Close non-bonded distances are (Figs. 2, 4 and 6) $N_1 \cdots N_3$ and $N_1 \cdots N_3' = 3{\cdot}18$ Å, $N_1 \cdots N_2$ and $N_1 \cdots N_2' = 3{\cdot}27$ Å, and $N_1 \cdots N_4$ and $N_1 \cdots N_4' = 3{\cdot}67$ Å. We presume that the 3·18 and 3·27 Å distances involve hydrogen bonding. Bond angles are $C_1N_1N_2 = 123{\cdot}8°$, $C_1N_1N_2' = 94{\cdot}4°$, $C_1N_1N_3 = 113{\cdot}8°$, $C_1N_1N_3' = 96{\cdot}8°$, $N_2N_1N_3 = 97{\cdot}2°$, $N_2'N_1N_3 = 69{\cdot}4°$, $N_2N_1N_2' = 141{\cdot}3°$ and $N_3N_1N_3' = 129{\cdot}7°$. Now although packing effects and crystalline fields may influence hydrogen-bond angles, it seems unlikely that these deviations are more than ±20° from the tetrahedral angles. If so, the most reasonable hydrogen-bonding schemes for H_1 and H_2 bonded to N_1 are $N_1H_1 \cdots N_2$ (or $N_1H_1 \cdots N_2'$) and $N_1H_2 \cdots N_3$ (or $N_1H_2 \cdots N_3'$). The possibilities in parentheses seem less likely because of their greater deviations from the tetrahedral angle.

It is of interest to compare this interpretation of the hydrogen bonds with a Fourier projection (Fig. 7) along the *b* axis from which spherically symmetrical carbon and nitrogen atoms have been subtracted. Except for the peak approximately between the carbon and nitrogen positions the peaks seem to support the $N_1H_1 \cdots N_2$ and $N_1H_2 \cdots N_3$ positions for the hydrogen bonds. In addition the *a*-axis projection (Fig. 3) supports the positions, shown by crosses, of the H_1 type of hydrogen atoms. More exact hydrogen-atom positions were obtained with the aid of the assumption of N–H = 1·01 Å, the value in the ammonia molecule (Sheng, Barker & Dennison, 1941). The hydrogen parameters of the amino group are

$$x_{H_1} = 0{\cdot}257,\ y_{H_1} = 0{\cdot}220,\ z_{H_1} = 0{\cdot}235;$$
$$x_{H_2} = 0{\cdot}416,\ y_{H_2} = 0{\cdot}024,\ z_{H_2} = 0{\cdot}235.$$

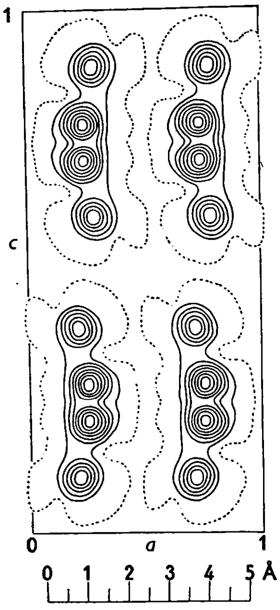

Fig. 5.

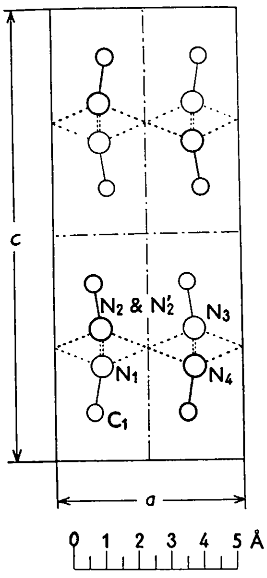

Fig. 6.

Fig. 5. Electron-density projection along the *b* axis. Each contour line represents a density increment of 1 e.Å.$^{-2}$, the one-electron line being broken.

Fig. 6. Arrangement of the molecules in the *b* axis projection. Hydrogen bonds are indicated by broken lines.

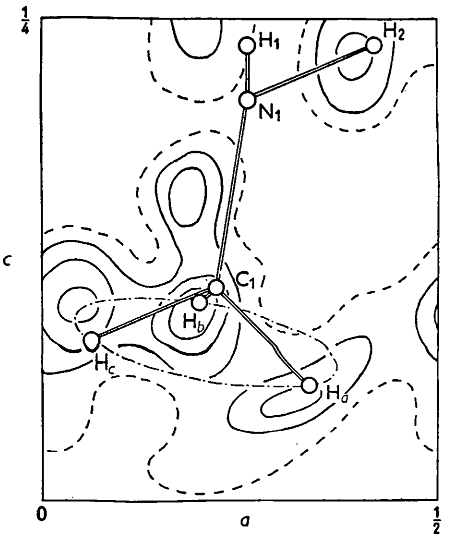

Fig. 7. Electron-density map of hydrogen contributions in the *b* axis projection. Each contour line represents a density increment of 0·2 e.Å^{-2} the zero-electron line being broken. The chain lines show the trace of rotation of the hydrogen atoms in the methyl group.

Thus, on the basis of close intermolecular distances, bond angles and electron-density maps, the hydrogen bonds occur in sheets approximately parallel to the *a b* plane. This behavior of methylamine seems remarkable in comparison with the one-dimensional chains or spirals which occur in methanol (Tauer & Lipscomb, 1952), hydrazine (Collin & Lipscomb, 1951) and hydrogen peroxide (Abrahams, Collin & Lipscomb, 1951). Nevertheless, we feel that this two-dimensional array cannot give rise to a residual entropy in the methylamine crystal, because the possible configurations for the hydrogen atoms give structures which can hardly be expected to have equal energy because of the widely different distances and bond angles.

The positions of the hydrogen atoms in the methyl group are also of interest. Since the closest $N \cdots C$ distances are 3·66–4·01 Å and the closest $C \cdots C$ distances are 3·81–4·36 Å in methylamine, we might expect some steric effects which may restrict the rotation of the methyl group. If we choose C–H = 1·09 Å, the value in methane (Ginsburg & Barker, 1935), and a van der Waals radius of 1·2 Å (Pauling, 1948, p. 189) for the hydrogen atoms, the most favorable steric situation has hydrogen atoms in the positions

$$x_{H_a} = 0{\cdot}36,\ y_{H_a} = 0{\cdot}07,\ z_{H_a} = 0{\cdot}06;$$
$$x_{H_b} = 0{\cdot}21,\ y_{H_b} = -0{\cdot}17,\ z_{H_b} = 0{\cdot}10;$$
$$x_{H_c} = 0{\cdot}05,\ y_{H_c} = 0{\cdot}07,\ z_{H_c} = 0{\cdot}08.$$

These positions give $H \cdots H$ distances of 2·4–2·5 Å between different methyl groups. Although the corre-

Table 1. *The comparison of structure factors of various models*

F_o: observed structure factor.
F_1: calculated structure factor without hydrogens.
F_2: calculated structure factor assuming free rotation of methyl groups.
F_3: calculated structure factor for staggered model.

hkl	F_o	F_1	F_2	F_3
002	35·7	−32·8	−36·0	−35·6
006	24·0	−14·1	−25·4	−25·8
220	26·2	−30·9	−26·2	−25·8
022	10·2	13·9	10·6	9·7
014	13·2	10·9	12·5	12·0
016	13·4	− 9·2	−13·1	−13·0
203	13·4	− 9·4	−12·7	−12·1
205	5·2	1·9	4·5	4·9
112	49·6	−43·9	−50·2	−50·1
124	11·0	− 9·1	−11·7	−11·5
424	2·8	− 1·2	− 2·1	− 1·9

Table 2. *Comparison of structure factors for the* −150° C. *modification of methylamine*

hkl	F_o	F_c	*hkl*	F_o	F_c	*hkl*	F_o	F_c
200	56·2	−56·6	066	2·4	− 2·5	4,0,14	< 1·8	1·0
400	19·2	19·9	018	6·7	6·4	601	5·0	− 1·9
600	7·4	− 6·9	028	< 1·7	1·3	602	5·3	5·5
020	46·4	51·1	038	9·6	9·7	603	6·6	− 6·2
040	11·8	10·6	048	3·4	4·5	604	2·4	− 2·0
060	< 2·8	0·8	058	5·4	5·5	605	< 2·8	1·4
080	< 2·3	0·1	068	3·2	3·4	606	< 1·9	1·5
002	35·7	−36·2	0,1,10	3·6	− 3·3	607	4·7	4·7
004	5·1	− 1·5	0,2,10	12·5	13·0	608	< 1·8	0·9
006	24·0	−25·4	0,3,10	4·8	− 4·5	609	< 2·6	0·6
008	< 1·6	0·3	0,4,10	4·8	4·6	6,0,10	4·0	− 3·7
0,0,10	20·8	19·6	0,5,10	2·4	− 2·7	111	3·6	5·6
0,0,12	11·2	− 9·8	0,6,10	< 2·4	0·9	122	18·6	19·6
0,0,14	< 2·3	0·2	0,1,12	< 1·9	1·3	133	< 2·4	− 0·8
0,0,16	4·5	− 4·4	0,2,12	5·4	− 5·4	144	4·4	− 5·0
120	24·5	21·7	0,3,12	< 2·2	0·6	155	< 3·0	− 1·1
220	26·2	−26·2	0,4,12	< 2·2	− 0·3	166	< 3·0	0·8
320	10·1	−11·8	0,5,12	< 2·4	0·0	177	< 2·7	− 0·2
420	12·0	11·7	0,1,14	< 2·2	0·6	211	< 2·1	0·2
520	4·9	4·9	0,2,14	< 2·2	− 1·2	222	7·9	6·9
620	3·9	− 4·0	0,3,14	< 2·3	1·3	233	< 2·5	− 0·7
720	< 2·4	− 2·0	0,4,14	3·0	− 3·2	244	6·2	6·4
140	17·0	15·0	201	5·7	− 0·2	255	< 3·0	0·8
240	7·0	− 7·4	202	18·6	23·4	266	3·0	2·2
340	9·0	−10·2	203	13·4	−12·7	277	< 2·5	− 0·1
440	4·0	3·5	204	< 2·0	− 0·9	311	3·8	− 4·9
540	4·9	4·6	205	5·2	4·5	322	10·6	− 9·5
640	< 2·6	− 0·8	206	9·8	10·7	333	< 2·7	1·8
160	9·2	4·2	207	6·4	5·3	411	< 2·7	− 0·1
260	< 2·9	− 0·2	208	< 2·6	0·2	422	4·9	− 3·9
360	4·0	− 3·2	209	< 2·8	1·0	433	< 2·9	0·7
460	< 2·6	− 0·5	2,0,10	14·9	−16·0	112	49·6	−50·2
012	9·3	− 9·0	2,0,11	< 2·0	− 2·7	212	5·4	6·2
022	10·2	−10·6	2,0,12	8·6	9·0	312	17·8	17·5
032	10·0	−11·0	2,0,13	3·3	− 2·4	412	3·1	− 2·6
042	3·8	2·5	2,0,14	< 2·1	− 0·4	512	7·5	− 6·8
052	5·4	− 5·2	2,0,15	< 2·0	1·4	612	< 2·3	1·0
062	5·6	5·8	2,0,16	3·0	3·8	124	11·0	−11·7
072	< 2·3	− 1·1	401	5·0	3·0	224	5·3	5·6
014	13·2	12·5	402	8·5	−10·8	324	4·6	5·0
024	7·9	− 8·3	403	8·5	7·7	424	2·8	− 2·1
034	10·4	13·7	404	< 2·7	1·0	524	2·4	− 2·6
044	7·2	− 8·6	405	2·7	− 1·8	624	< 1·9	− 0·5
054	5·8	6·1	406	4·4	− 4·5	136	3·0	3·3
064	6·9	− 7·2	407	6·0	− 6·5	236	9·8	11·0
074	< 2·4	0·6	408	< 2·8	− 0·5	336	2·2	− 2·1
016	13·4	−13·1	409	< 2·9	− 0·1	436	4·9	− 6·2
026	10·4	−10·2	4,0,10	8·2	9·4	536	< 2·9	0·1
036	12·8	−13·8	4,0,11	< 2·9	2·6	148	3·5	3·2
046	5·0	− 5·0	4,0,12	5·1	− 5·6	248	3·4	− 3·8
056	5·8	− 5·8	4,0,13	3·7	3·0			

sponding distances for the freely rotating methyl group are only about 0·1 Å less than these values, there is further support for these hydrogen positions from the difference Fourier projection (Fig. 7).

The methyl group thus appears to be staggered with respect to the amino group. The greater stability of this configuration is to be expected, for it is the usual stable configuration except possibly when unusual constraints in the solid phase occur, as in hydrazine (Collin & Lipscomb, 1950). Indeed, a barrier of 1520 cal. mole^{-1} is indicated in a spectroscopic study of methylamine (Aston & Doty, 1940). It is therefore not surprising that the rotation of the methyl group is very probably strongly hindered in the solid phase.

Finally these conclusions were tested by calculation of structure factors. A comparison of those most sensitive to the hydrogen contributions is shown in Table 1, and a complete list is shown in Table 2 for the model having a rotating methyl group. The overall reliability factor $\Sigma||F_o|-|F_c||\div\Sigma|F_o|$ is 0·163 when hydrogen contributions are omitted, 0·131 when the methyl group is axially disordered and 0·138 when the hydrogens of the methyl group are placed in the staggered configuration. Thus the inclusion of hydrogen atoms markedly improves the agreement, but the differences for the axially rotating or orientationally fixed methyl groups are not significant, and we feel that the above non-crystallographic arguments are therefore of some value.

The temperature factors, which have been multiplied into the calculated structure factors of Table 2, are $B = 3{\cdot}0_4$ Å^{-2} for $\{h0l\}$, $B = 3{\cdot}6_0$ Å^2 for $\{hkk\}$ and $B = 3{\cdot}8_5$ Å^2 for all other zones. The slight differences among these values are of interest in the following section.

The transition, and the —185° C. modification

Precession photographs were taken of the $\{hk0\}$, $\{h0l\}$, $\{hkk\}$ and $\{h,k,2k\}$ zones with the crystal at $-185\pm5°$ C., and also at $-150\pm5°$ C. under the same conditions for direct comparison. No appreciable change of the relative intensities was observable. However the lattice constants at $-185°$ C. are

$$a = 5{\cdot}73_3\pm0{\cdot}01,\ b = 6{\cdot}10_9\pm0{\cdot}01 \text{ and } c = 13{\cdot}51_3\pm0{\cdot}02 \text{ Å}.$$

The fractional contractions from $-150°$ to $-185°$ C. are thus

$$\Delta a/a = 0{\cdot}003_5,\ \Delta b/b = 0{\cdot}011_2 \text{ and } \Delta c/c = 0{\cdot}007_3\,.$$

The total volume contraction is 10 Å^3. The larger fractional contraction along the b direction is in agreement with the slight anisotropy of the temperature factor, which is higher for those reflections containing a second, (k), index greater than zero in the $-150°$ C. modification. As is expected, the fractional contraction is least along the a axis in which direction the shorter type of hydrogen bonds occur.

Additional data which pertain to the transition are the frequency dependence of the dielectric constant (McNeight & Smyth, 1936), and the nuclear magnetic resonance studies of Andrew & Bersohn (1950) and Gutowsky & Pake (1950). The second moment of the proton resonance at $-183°$ C. is 20 gauss, intermediate between 40 gauss expected for a rigid lattice and 13 gauss expected for rotation about the C–N axis. There is a small decrease in line width from 7 gauss at $-183°$ C. to 6 gauss at $-148°$ C. It seems probable to us that both the lattice contractions and decrease in line width of nuclear resonance are associated with further hindering of the methyl-group interactions with neighboring methyl groups. In addition a shortening of the longer hydrogen bond also may occur, and it would therefore be of interest to study the isotope effect on the lengths of these hydrogen bonds (Nordman & Lipscomb, 1951) and its relation to the expansion coefficients. However, probably the methyl-group interactions are of such importance that the interpretation of the nature of the transition in terms of these changes in lattice parameters is not simple.

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