fluoride but twice as much Freon 11 is required compared with Freon 12 thus making it less attractive as a method of synthesis. At 400° $CFCl_3$ presumably reacts with uranium trioxide according to the equation

$$4CFCl_3 + UO_3 \xrightarrow{400°} UF_4 + 3COCl_2 + CCl_4 + Cl_2$$

This reaction appears to begin at 350–360°.

The authors wish to express their thanks to the Wisconsin Alumni Research Foundation for providing financial assistance during the period that the work was being completed at the University of Wisconsin. We are indebted for the supply of Freon 11 and 12 to the kindness of the Kinetic Mfg. Co., Inc.

## Summary

Difluorodichloromethane reacts quantitatively with uranium trioxide to produce pure anhydrous uranium tetrafluoride at elevated temperatures. Monofluorotrichloromethane reacts similarly but its use has the disadvantage of needing twice as much as in the case of Freon 12.

CLEVELAND, OHIO JANUARY[12] 13, 1943

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(12) The publication of this paper was delayed for war-time security reasons.—*The Editor.*

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1037]

# The Crystal Structure of Methylammonium Chloride

BY EDWARD W. HUGHES[1] AND WILLIAM N. LIPSCOMB

Values of the carbon–nitrogen single-bond distance in various compounds are of special interest because of the occurrence of this bond in amino acids, proteins and related substances. Numerous electron diffraction studies[2] of gas molecules have yielded values of about 1.47 Å., which are consistent with the usual table of covalent radii.[3] On the other hand, distances ranging from 1.39 to 1.49 Å. have recently been reported in X-ray crystal structure investigations of compounds containing tetracovalent nitrogen.[2] Because of these many different values it was thought desirable to investigate the carbon–nitrogen distance in a simple crystal in which a minimum number of parameters needed determination; methylammonium chloride appeared to be such a crystal.

Methylammonium chloride crystallizes in the tetragonal system.[4] A determination of its crystal structure has been reported by Hendricks.[5] The smallest unit of structure which he found compatible with his data had the dimensions $a$ = 4.28 Å. (obtained from powder data) and $c$ = 5.13 Å. (obtained from oscillation photographs); this unit contains one molecule of $CH_3NH_3Cl$. The atomic positions were $Cl^-$ at 000, N at $\frac{1}{2}\frac{1}{2}z_1$, and C at $\frac{1}{2}\frac{1}{2}z_2$, with the most probable values of the parameters given as $z_1 = 0.24$ and $z_2 = 0.50$.

When the present investigation was begun it was thought necessary only to refine the above parameter values, but it soon became evident that the structure proposed by Hendricks is incorrect. The value of $a_0$ was found to be larger by $\sqrt{2}$ and its direction to be at 45° to that given by him; hence the unit cell actually contains two molecules of $CH_3NH_3Cl$.

**The Unit Cell and Space Group.**—The material used for this investigation was Eastman Kodak Co. Red Label Grade methylamine hydrochloride. Suitable crystals were grown from aqueous solutions by allowing the water to evaporate slowly. A needle-like specimen approximately 0.2 mm. in thickness and 1.5 mm. in length was selected for the single-crystal photographs. Early experiments indicated that the compound is somewhat deliquescent; hence the crystal which was selected was dipped in a mixture of paraffin wax and vaseline. This mixture not only provided a film which protected the crystal from the atmosphere but was also found suitable for attaching the crystal to a quartz fiber mounted on the goniometer head. The crystal was oriented by means of preliminary oscillation photographs or Laue photographs.

The dimensions of the unit cell were determined approximately from layer-line separations and more accurately from the equatorial reflections on oscillation photographs taken with filtered CuK$\alpha$ radiation. Oscillations about the $a$, $c$ and [110] axes gave the values $a_0$ = 6.04 Å. and $c_0$ = 5.05 Å. with probable errors of 0.01 Å. These dimensions of the unit cell together with the observed density value,[5] 1.23 g./cc., require two molecules of $CH_3NH_3Cl$ per unit cell. The calculated value of the density, 1.216 g./cc., is in satisfactory agreement with the observed value. A set of powder photographs was taken with filtered CuK$\alpha$ radiation by means of the multiple-film technique.[6] These photographs were successfully indexed on the new unit cell.

The only systematic extinction which occurs on

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(1) Noyes Fellow.

(2) A partial list of values obtained for this distance in various compounds is given in Table V.

(3) L. Pauling, "The Nature of the Chemical Bond," second edition, Cornell University Press, Ithaca, N. Y., 1940, p. 164. The value 1.465 Å. is given by the slightly modified values of covalent radii proposed by V. Schomaker and D. P. Stevenson, THIS JOURNAL, **63**, 37 (1941).

(4) P. Groth, "Chemische Krystallographie," Vol. I, Wilhelm Engelmann, Leipzig, 1906, p. 168.

(5) S. B. Hendricks, *Z. Krist.*, **67**, 106 (1928).

(6) J. J. deLange, J. M. Robertson, and I. Woodward, *Proc. Roy. Soc.* (London), **A171**, 398 (1939).

the oscillation and powder photographs is *hk*0 with $h + k$ odd. The Laue symmetry as found from photographs both parallel and perpendicular to $c_0$ is $4/mmm$. These data indicate[7] that the space group is $D_{4h}^7 - P4/nmm$.

If for the present we disregard the hydrogen atoms we have, with two atoms of each kind in the unit cell, the following possible point positions[7]

(a) $000; \frac{1}{2}\frac{1}{2}0$
(b) $00\frac{1}{2}; \frac{1}{2}\frac{1}{2}\frac{1}{2}$
(c) $0\frac{1}{2}z; \frac{1}{2}0\bar{z}$

Neither the C nor N atoms can be in (a) or (b) and still form covalent bonds; consequently we chose (c), with point symmetry $C_{4v}$, and locate $NH_3^+$ at $0\frac{1}{2}z_1; \frac{1}{2}0\bar{z}_1$, and $CH_3$ at $0\frac{1}{2}z_2; \frac{1}{2}0\bar{z}_2$. If we assume the normal van der Waals radii for the atoms and a normal C–N distance, the dimensions of the unit cell do not allow sufficient room for the $Cl^-$ ions along the four-fold axis; hence the $Cl^-$ ions must be in (a) or (b). The choice between these positions is arbitrary. A rough consideration of the *hk*0 intensities (*cf.* Table III) also requires that the positions for $Cl^-$ be either (a) or (b).

It must be pointed out that the hydrogen atoms of the $CH_3NH_3^+$ groups cannot conform to this space group unless the group is rotating about the carbon–nitrogen axis or unless the hydrogens are randomly oriented with respect to rotation about this axis. A consideration of the rotation of these groups is presented in a subsequent section.

A further test of the structure, and one which distinguishes our structure from the one proposed by Hendricks, is the pyroelectric test. His structure, which has no center of symmetry, consists of alternate layers of $Cl^-$ ions, $NH_3^+$ groups, and $CH_3$ groups and is therefore strongly polar; it would show a strong pyroelectric effect. Our proposed structure, shown in Fig. 1, has a center of symmetry at $\frac{1}{4}\frac{1}{4}0$, etc., and hence could show no pyroelectric effect. In order to test for pyroelectricity the crystal was attached to a single fiber of silk by means of a microscopic drop of cement. The crystal was suspended in liquid air and then removed. Since the crystal then showed no tendency to be attracted to the neck of the Dewar and since no anisotropic growth of ice crystals was observed, it was concluded that the pyroelectric test was negative.

**Determination of the Parameters.**—Complete sets of oscillation photographs were taken with filtered MoK$\alpha$ radiation about the *a* axis and the [110] axis, and with filtered CuK$\alpha$ radiation about the *c* axis. The multiple-film technique[6] was used; when MoK$\alpha$ radiation was used, 0.001-inch copper sheets were interleaved between the films in order to reduce the intensities by a suitable factor. The peak densities of reflections in the density range 0.3 to 0.8 (including background) were measured with the aid of an Eastman Densitometer, Model B, fitted with an opening 0.012-inch in diameter, and then all of the reflections were estimated visually using the densitometered values as a basis. In the densitometered range the intensity was taken proportional to the peak density of a reflection minus the density of the neighboring background. Structure factors were calculated from these estimated intensities after correction for Lorentz and polarization factors and, on the powder photographs, for the multiplicity factors. In the photographs about the *a* axis and [110] axis, for which the needle axis was horizontal, the intensities were estimated of only those reflections for which the incident and reflected rays passed through relatively short paths in the crystal. The various oscillation photographs about a given axis were placed on the same relative scale by comparison of corresponding structure factors with those obtained from the powder photographs. The observed structure factors, $F_{hkl}$, in a given zone were placed on the proper absolute scale by determination of the scale factor $\alpha$ such that $\Sigma w_{hkl}\ (\alpha F'_{hkl} - F_{hkl})^2$ is a minimum, where $w_{hkl}$ is the weighting factor referred to below and $F'_{hkl}$ is the structure factor calculated from the final values of the parameters. The resulting structure factors are listed in Tables I, II and

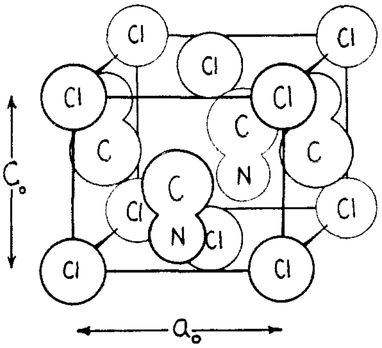

Fig. 1.—The unit cell of methylammonium chloride.

TABLE I

STRUCTURE FACTORS OF THE *h*0*l* REFLECTIONS

| *h*0*l* | $F_{obs.}$ | $F_{calcd.}$ |
|---|---|---|
| 001 | 19.7 | 21.5 |
| 101 | 11.6 | 10.1 |
| 200 | 39.2 | 39.0 |
| 201 | 17.1 | 17.4 |
| 002 | 18.9 | 19.8 |
| 102 | 5.4 | 5.2 |
| 202 | 14.6 | 14.7 |
| 301 | 5.8 | 5.0 |
| 003 | 3.2 | 4.4 |
| 103 | 2.4 | −1.9 |
| 302 | <1.3 | 1.3 |
| 400 | 20.6 | 18.7 |
| 203 | 4.5 | 4.8 |

TABLE II

STRUCTURE FACTORS OF THE *hhl* REFLECTIONS

| *hhl* | $F_{obs.}$ | $F_{calcd.}$ |
|---|---|---|
| 001 | 19.7 | 21.5 |
| 110 | 5.5 | 5.5 |
| 111 | 29.4 | 28.7 |
| 002 | 18.9 | 19.8 |
| 112 | 17.6 | 16.5 |
| 220 | 28.8 | 28.0 |
| 221 | 15.2 | 14.6 |
| 003 | 3.2 | 4.4 |
| 222 | 12.4 | 12.5 |
| 113 | 17.3 | 16.7 |
| 330 | 8.4 | 7.1 |
| 331 | 12.7 | 12.5 |
| 223 | 5.5 | 4.6 |

(7) "Internationale Tabellen zur Bestimmung von Kristallstrukturen," Gebrüder Borntrāger, Berlin, 1935.

III; the observed intensities of the powder lines, corrected for Lorentz and polarization factors, are listed in Table IV.

TABLE I (*Concluded*)

| $h0l$ | $F_{obs.}$ | $F_{calcd.}$ |
|---|---|---|
| 401 | 11.6 | 11.0 |
| 402 | 3.6 | 9.6 |
| 303 | <1.3 | −0.9 |
| 004 | 9.2 | 9.1 |
| 104 | 2.8 | −2.5 |
| 501 | 3.5 | 2.0 |
| 204 | 8.2 | 8.3 |
| 403 | 4.1 | 4.1 |
| 502 | <1.3 | 0.7 |
| 304 | <1.3 | −1.9 |
| 005 | 4.2 | 4.0 |
| 600 | 9.6 | 10.0 |
| 105 | <1.3 | 0.3 |
| 601 | 6.7 | 6.1 |
| 503 | <1.3 | −0.5 |
| 404 | 6.1 | 5.8 |
| 205 | 3.9 | 3.6 |
| 602 | 4.9 | 5.7 |
| 305 | <1.2 | 0.4 |
| 504 | 2.2 | −1.0 |
| 603 | 2.6 | 2.7 |
| 701 | <1.2 | 0.8 |
| 006 | 2.8 | 2.8 |
| 405 | 2.5 | 2.6 |
| 106 | 1.2 | 0.3 |
| 702 | <1.2 | 0.3 |
| 206 | 2.6 | 2.5 |
| 604 | 3.1[a] | 3.3 |
| 306 | <1.2 | 0.3 |
| 505 | <1.2 | 0.2 |
| 703 | <1.2 | −0.2 |
| 800 | 3.8 | 4.4 |
| 801 | 3.1 | 3.0 |
| 406 | 1.6 | 1.8 |
| 802 | 2.8 | 2.8 |
| 007 | <1.2 | 0.3 |
| 107 | <1.2 | 0.4 |
| 704 | 1.6 | −0.5 |
| 605 | 1.9 | 1.5 |

[a] Limit of CuK$\alpha$ radiation.

TABLE II (*Concluded*)

| $hkl$ | $F_{obs.}$ | $F_{calcd.}$ |
|---|---|---|
| 004 | 9.2 | 9.1 |
| 332 | 10.2 | 9.1 |
| 114 | 4.6 | 4.4 |
| 333 | 8.4 | 9.3 |
| 224 | 7.6 | 7.3 |
| 440 | 10.8 | 11.1 |
| 441 | 8.4 | 6.8 |
| 005 | 4.2 | 4.0 |
| 442 | 6.0 | 6.4 |
| 115 | 3.2 | 3.4 |
| 334 | 3.7 | 3.0 |
| 225 | 3.9 | 3.2 |
| 443 | 3.4 | 2.9 |
| 550 | 3.6 | 3.5 |
| 551 | 4.5 | 5.2 |
| 006 | 2.8 | 2.8 |
| 116 | 1.6 | 1.0 |
| 335 | 2.7 | 2.3 |
| 444 | 3.7 | 3.7 |
| 552 | 5.4 | 3.8 |
| 226 | 2.5[b] | 2.2 |
| 553 | 4.1 | 3.7 |
| 445 | 2.0 | 1.8 |
| 007 | <1.7 | 0.3 |
| 660[a] | | 3.5 |
| 117 | <1.7 | 1.4 |
| 554 | <1.7 | 1.4 |
| 661 | 3.4 | 2.5 |
| 227 | <1.7 | 0.2 |
| 662 | 2.2 | 2.2 |

[a] Not observed because of experimental arrangement. [b] Limit of CuK$\alpha$ radiation.

TABLE III

STRUCTURE FACTORS OF THE $hk0$ REFLECTIONS

| $hk0$ | $F_{obs.}$ | $F_{calcd.}$ |
|---|---|---|
| 110 | 5.5 | 5.5 |
| 200 | 39.2 | 39.0 |
| 220 | 28.8 | 28.0 |
| 310 | 8.9 | 8.8 |
| 400 | 20.6 | 18.7 |
| 330 | 8.4 | 7.1 |
| 420 | 16.4 | 16.1 |
| 510 | 6.9 | 5.9 |
| 440 | 10.8 | 11.1 |
| 530 | 5.8 | 5.0 |
| 600 | 9.6 | 10.0 |
| 620 | 9.3 | 8.7 |
| 550 | 3.6 | 3.5 |
| 710 | 3.6 | 3.5 |
| 640 | 6.2 | 6.2 |
| 730 | 3.1 | 2.9 |

TABLE IV

INTENSITY DATA FROM THE POWDER PHOTOGRAPHS

| $hkl$ | $\frac{\sin\theta}{\lambda}$ | $(mF^2_{hkl})_{obs.}$[a] | $(mF^2_{hkl})_{calcd.}$ |
|---|---|---|---|
| 001 | 0.099 | 780 | 920 |
| 110 | .117 | 120 | 120 |
| 101 | .129 | 1080 | 820 |
| 111 | .153 | 6920 | 6580 |
| 200 | .166 | 6150 | 6080 |
| 201 | .193 | 2340 | 2420 |
| 002 | .198 | 710 | 780 |
| 211 | .210 | 730 | 780 |
| 102 | .215 | 230 | 220 |
| 112 | .230 | 2480 | 2180 |
| 220 | .234 | 3320 | 3130 |
| 221 | .254 | 1850 | 1700 |
| 202 | .258 | 1710 | 1730 |
| 310 | .262 | 630 | 620 |
| 301 | .267 | 270 | 200 |
| 212 | .271 | 160 | 120 |
| 311 | .280 | 5120 | 4520 |
| 003 | .297 | <200 | 40 |
| 222 | .307 | 1230 | 1250 |
| 103 | .308 | <190 | 30 |
| 321 | .314 | 370 | 240 |
| 302 | .318 | <200 | 10 |
| 113 | .319 | 2390 | 2230 |
| 312 | .328 | 2550 | 2380 |
| 400 | .331 | 1700 | 1400 |
| 203 | .340 | 160 | 180 |
| 401 | .346 | 1070 | 970 |
| 213 | .350 | 370 | 230 |
| 330 | .351 | | |
| 411 | .356 | 280 | 140 |
| 322 | .358 | <240 | 20 |
| 331 | .364 | 1290 | 1250 |
| 420 | .370 | 2150 | 2070 |
| 223 | .378 | 240 | 170 |
| 421 | .384 | 1420 | 1410 |
| 402 | .386 | 490 | 740 |
| 303 | .387 | | |
| 412 | .394 | 3000 | 2440 |
| 004 | .396 | | |
| 313 | .396 | | |
| 332 | .403 | 830 | 660 |
| 104 | .405 | <310 | 50 |
| 114 | .413 | 170 | 160 |
| 422 | .420 | 1240 | 1220 |
| 323 | .420 | | |
| 510 | .422 | 380 | 280 |
| 501 | .425 | <350 | 100 |
| 431 | .425 | | |
| 204 | .429 | 540 | 550 |
| 511 | .433 | 1400 | 1570 |

[a] The values of $(mF^2_{hkl})_{obs.}$, where $m$ is the multiplicity factor, were obtained by correcting the observed intensities for Lorentz and polarization factors. Very few reflections were resolved for values of sin $\theta/\lambda$ greater than 0.433.

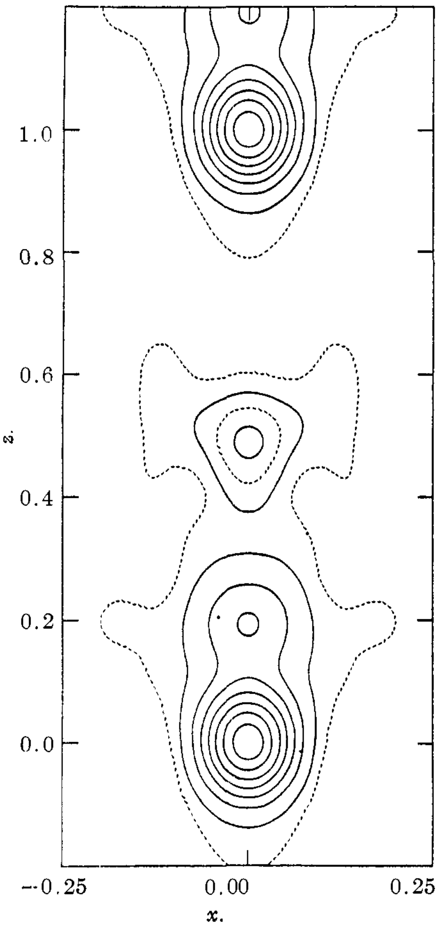

Fig. 2.—Fourier projection on (010). The function calculated was $A_{xz}\,\rho\,(x, z) = \sum_{h,l} A_{h0l} \cos 2\pi\,(hx + lz) + B_{h0l} \sin 2\pi\,(hx + lz)$. Solid contours are drawn at intervals of $100\,n$, where $n = 1, 2, \ldots, 7$; dotted contours are drawn for $n = 1/2$ and $3/2$.

The Fourier projections on (010) and (1$\bar{1}$0) as shown in Fig. 2 and 3 were calculated from the observed absolute values of the structure factors with signs which were determined from structure factors calculated from preliminary values of the parameters. Although one line of each of the two-dimensional projections would have served for the parameter determinations, the complete projections were prepared in order to investigate any possible anisotropy of thermal vibrations. The calculations were carried out using the punched card method[8] and International Business Machines. The series were summed at intervals of $a_0/100$ and $c_0/125$ ($h0l$ projection), and $a'/50$ and $c_0/100$ ($hhl$ projection). The small negative areas which occurred in the Fourier projections are not shown; the lowest level of these areas is −4 for the $h0l$ projection (height of $Cl^-$ peak, 770), and −4 for the $hhl$ projection (height of the 2 $Cl^-$ peak, 1117).

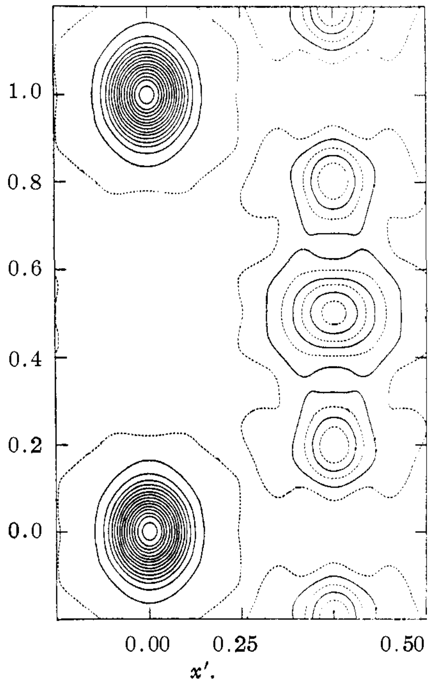

Fig. 3.—Fourier projection on (1$\bar{1}$0). The function calculated was $A_{x'z}\,\rho\,(x'z) = \sum_{h,l} F_{hhl} \cos 2\pi\,(hx' + lz)$. Solid contours are drawn at intervals of $(100\,n)/\sqrt{2}$ where $n = 1, 2, \ldots, 15$; dotted contours are drawn for $n = 1/2$ and, in part, for $n = 3/2$ and $5/2$.

The values of the carbon and nitrogen parameters may be obtained, respectively, from the corresponding resolved peaks on the (010) and (1$\bar{1}$0) projections. The carbon parameter is 0.489; the nitrogen parameter is 0.198. The nitrogen parameter may also be determined, but with less certainty, from the projection on (100). If, along the line $x = 0$, the electron density $\rho\,(0,z)$ in the region from $z = 1.0$ to $z = 0.7$, is subtracted from that in the region from $z = 0.0$ to $z = 0.3$, the resulting electron density represents approximately that of the $NH_3^+$ group; the resulting maximum, at 0.199, is in good agreement with the value observed on the (1$\bar{1}$0) projection.

The probable error assigned to each of these two parameters is ±0.001. In order to calculate these probable errors, the probable error $r$ for the observation of an $F_{hkl}$ of unit weight was determined from the residuals, $F_{\text{obs.}} - F_{\text{calcd.}}$, in the usual way.[9] Division of this probable error by $\sqrt{w_{hkl}}$ where $w_{hkl}$ is the weighting factor for each $F_{hkl}$, yields the probable error $r_{hkl}$ in $F_{hkl}$. The choice of weights was the same as for the least-squares calculation described below.[10] From these $r_{hkl}$ the probable error in the parameter $z_i$ was derived by straightforward application of the

[8] P. A. Shaffer, Jr., Ph.D. Thesis, California Institute of Technology (1942).

[9] E. T. Whittaker and G. Robinson, "Calculus of Observations," Chapter IX, Blackie and Son, London, 1929. The values of $r$ determined from average deviations and mean error were the same to within less than 1%. The average value of $r$ (0.40) was used in both the Fourier and least-squares calculations of $r_{hkl}$.

theory of propagation of errors to the Fourier equation relating the electron density $\rho$ $(x,y,z)$ to the $F_{hkl}$. The resulting probable error $r_{z_i}$ is given for our specific case by the equation

$$r_{z_i}^2 = \frac{2\pi^2}{\left[\frac{\partial^2(\rho V)}{\partial z^2}\right]_i^2} \sum_{hkl} r_{hkl}^2 l^2 (1 \pm \cos 4\pi l z_i)$$

where $V$ is the volume of the unit cell, and where the choice of signs is + if $h + k$ is odd and − if $h + k$ is even; the values of the second partial derivative were estimated from the Fourier projection in the region of the maximum at $z_i$. These matters will be discussed in detail elsewhere.

Several preliminary comparisons (not included here) of calculated and observed structure factors indicated that satisfactory agreement of observed and calculated structure factors could not be obtained without the introduction of a separate temperature factor for the $CH_3NH_3^+$ group and an anisotropic temperature factor for the $Cl^-$ atom with the direction of maximum vibration along the $c$ axis, as is suggested by the two Fourier projections. The temperature factor constants $B_1$, $B_2$ and $B_3$ in the expressions

$$f_{Cl^-} = f_{0Cl^-} \exp - (B_1 + B_2 \cos^2\varphi) \frac{\sin^2\theta}{\lambda^2} \text{ and}$$

$$f_{CH_3 \cdot NH_3^+} = f_{0CH_3 \cdot NH_3^+} \exp\left(-B_3 \frac{\sin^2\theta}{\lambda^2}\right)$$

were determined by the method of least squares.[10] The final result of a least squares treatment in which the distance parameters and temperature factors were allowed to vary simultaneously was $z_1 = 0.198 \pm 0.002$, $z_2 = 0.485 \pm 0.004$, $B_1 = 2.8$, $B_1 + B_2 = 5.4$, and $B_3 = 4.3$. The probable errors for the distance parameters were determined on the assumption that the structure factors calculated from the final parameters were the most probable values. The probable error for the parameter was calculated from the probable error of the observation of unit weight (obtained from the residuals, $F_{calcd.} - F_{obs.}$, as described above) by multiplication by $1/w_{z_i}^{1/2}$ as determined from the normal equations in the usual manner.[9]

In addition significant improvement between observed and calculated structure factors for planes of large spacing, particularly (103) and (003), was obtained by introduction of the contributions of the hydrogen atoms, which were assumed to be rotating about the C–N axis.[11]

The introduction of these modifications reduced the sum of squares of residuals for the $h0l$, $hkl$ and $hk0$ zones from 208 to 40.

If we take into account the values and probable errors of the distance parameters as determined by the Fourier method and the least squares method the final parameters $z_1 = 0.198 \pm 0.001$ and $z_2 = 0.488 \pm 0.001$ are obtained.

The calculated structure factors listed in Tables I, II and III and the calculated values of $mF_{hkl}^2$ listed in Table IV were obtained with the use of these final values of the parameters, which, together with the dimensions of the unit cell, yield the following interatomic distances and probable errors (calculated to the nearest 0.005 Å.)

C—N = 1.465 ± 0.010 Å.
C...Cl⁻ = 3.900 ± 0.005 Å.
C...Cl⁻ = 3.975 ± 0.005 Å.
N...Cl⁻ = 3.180 ± 0.005 Å.

It is thus very unlikely that the C–N distance is in error by more than ± 0.03 Å., or that the other distances are wrong by more than ± 0.015 Å.

**Discussion.**—One unit cell of the structure is shown in Fig. 1. Layers of $Cl^-$ ions are inter-

TABLE V

VALUES OF THE CARBON-NITROGEN SINGLE-BOND DISTANCE IN VARIOUS COMPOUNDS

| Distance in Å. | Compound |
|---|---|
| | X-Ray Investigations |
| 1.465 | Methylammonium chloride[a] |
| 1.49 | Geranylamine hydrochloride[b] |
| 1.45 | Hexamethylenetetramine[c] |
| 1.42 | *dl*-Alanine[d] |
| 1.39 | Glycine[e] |
| 1.41 | Diketopiperazine[f] |
| 1.48 | Tetramethylammonium chloride[g] |
| | Electron Diffraction Investigations |
| 1.48 | Hexamethylenetetramine[c] |
| 1.44 | Methyl isocyanide[h] |
| 1.49 | Trimethylamine oxide[i] |
| 1.47 | Dimethylchloroamine[j] |
| 1.47 | Tetranitromethane[k] |
| 1.46 | Dimethylamine[l] |
| 1.53 | Borinetrimethylamine[m] |
| 1.47 | Methyl azide[n] |
| 1.47 | Trimethylamine[o] |
| 1.46 | Nitromethane[p] |

[a] This determination. [b] G. A. Jeffrey, *Proc. Roy. Soc.*, **A183,** 388 (1945); L. Bateman and G. A. Jeffrey, *Nature*, **152,** 446 (1945). [c] Reference 8. [d] H. A. Levy and R. B. Corey, THIS JOURNAL, **63,** 2095 (1941). [e] G. A. Albrecht and R. B. Corey, *ibid.*, **61,** 1087 (1939). [f] R. B. Corey, *ibid.*, **60,** 1598 (1938). [g] L. Vegard and K. Sollesnes, *Phil. Mag.*, **4,** 985 (1927, VII). [h] L. Pauling and W. Gordy, THIS JOURNAL, **64,** 2952 (1942). [i] R. E. Rundle, Ph.D. Thesis, California Institute of Technology (1939). [j] D. P. Stevenson and V. Schomaker, THIS JOURNAL, **62,** 1913 (1940). [k] A. J. Stosick, Ph.D. Thesis, California Institute of Technology (1939). [l] S. H. Bauer, THIS JOURNAL, **60,** 524 (1938). [m] S. H. Bauer, *ibid.*, **59,** 1804 (1937). [n] L. Pauling and L. O. Brockway, *ibid.*, **59,** 13 (1937). [o] L. O. Brockway and H. O. Jenkins, *ibid.*, **58,** 2036 (1936). [p] L. O. Brockway, J. Y. Beach and L. Pauling, *ibid.*, **57,** 2693 (1935).

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(10) E. W. Hughes, THIS JOURNAL, **63,** 1737 (1941).

(11) When the contribution of a hydrogen atom to the structure factor is averaged over a circle of radius $\rho$ the result $f_{jhkl} = f_j \exp(2\pi i\mathbf{h}\cdot\mathbf{r}_0)\, J_0(u)$ is obtained, where $\mathbf{r}_0$ is the vector to the center of the circle, $u = 2\pi \frac{\rho}{a_0} (h^2 + k^2)^{1/2}$, and $J_0(u)$ is the zero-order Bessel function. This calculation assumes in effect that the rotating atoms are smeared out uniformly over the circle; possible phase relationships between moving atoms in the same or different cells are ignored. This refinement was suggested by Professor V. Shomaker (see also D. Coster, *Verlag. Akad. Wetenschappen Amsterdam*, **28,** 391 (1919); N. H. Kolkmejer, *ibid.*, **28**, 767 (1920); J. M. Bijvoet and J. A. A. Ketelaar, THIS JOURNAL, **54,** 625 (1932)).

leaved with layers of methylammonium ions. The methylammonium ions are arranged along the four-fold axes so that half are directed with $NH_3^+$ up and and half with $NH_3^+$ down; each $Cl^-$ is surrounded by a bisphenoid of $NH_3^+$ groups.

The predicted value of the C–N distance[2] is 1.47 Å. if we ignore the formal charge correction,[3] or 1.44 Å. if we take it into account. If we consider the ionic radius[12] for $Cl^-$ (1.81 Å.), the van der Waals radius[12] for the methyl group (2.0 Å.) and the ionic radius for the $NH_4^+$ ion (1.4 Å.) corrected for the effect of change of coördination number[13] we calculate the non-bonded distances $C\ldots Cl^- = 3.8$ Å. and $N\ldots Cl^- = 3.2$ Å. Thus the observed values are in satisfactory agreement with those predicted on the basis of previous structural determinations in other compounds. The formal charge of the $NH_3^+$ group does not seem to shorten the C–N bond appreciably below the normal covalent value of 1.47 Å.

A partial summary of carbon–nitrogen single-bond distances obtained in the most recent X-ray and electron diffraction studies of various compounds is shown in Table V.

**Acknowledgment.**—We are indebted to Professor Verner Schomaker for helpful discussions and to Mary S. Lipscomb for assistance with the calculations.

## Summary

The crystal structure of methylammonium chloride has been redetermined. The unit cell was found to be tetragonal with the dimensions $a_0 = 6.04$ Å. and $c_0 = 5.05$ Å.; this cell contains two molecules of $CH_3NH_3Cl$. The space group is $D_{4h}^7 - P4/nmm$; the $Cl^-$ ions are placed at 000 and $\frac{1}{2}\frac{1}{2}0$, the nitrogen atoms at $0\frac{1}{2}z_1$ and $\frac{1}{2}0\bar{z}_1$, and the carbon atoms at $0\frac{1}{2}z_2$ and $\frac{1}{2}0\bar{z}_2$. The $z$ parameters of the carbon and nitrogen atoms were determined by the methods of Fourier projection and least-squares with the results $z_1 = 0.198 \pm 0.001$ and $z_2 = 0.488 \pm 0.001$. The carbon–nitrogen distance is 1.465 ± 0.010Å.

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(12) Reference 3, pp. 352 and 189.

(13) The $NH_4^+\ldots Cl^-$ distance found in "low" ammonium chloride (3.35 Å.) by R. J. Havighurst, E. Mack, Jr., and F. C. Blake, THIS JOURNAL, **46**, 2368 (1924) yields an ionic radius of 1.54 Å. for $NH_4^+$ when the ionic radius for $Cl^-$ is subtracted. This value may be corrected for change of coördination number from eight to four (reference 3, p. 368) to give the $NH_4^+$ ionic radius of 1.41 Å.

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[CONTRIBUTION NO. 603 FROM THE DEPARTMENTS OF CHEMISTRY AND PHYSICS, UNIVERSITY OF PITTSBURGH]

# X-Ray Investigation of Glycerides. IV. Diffraction Analysis of 1-Monoarachidin (1-Monoeicosanoate)

BY S. S. SIDHU AND B. F. DAUBERT

The only reference in the literature to the preparation of a 1-monoarachidin was that recorded by Berthelot[1] in 1856. The constants on this compound were incomplete and of doubtful value. In the course of our program on the study of the physical properties of glycerides, it became desirable to synthesize this compound in a high degree of purity. Therefore, the purpose of this communication is to report the method of preparation and the physical data obtained on a highly purified 1-monoarachidin.

## Experimental

**Preparation of Intermediates.**—The arachidic acid was prepared from a mixture of hydrogenated fish oil fatty acids[2] by fractional distillation of the methyl esters and subsequent repeated fractional crystallization of the arachidic acid from ethyl ether. The arachidic acid so obtained had the following constants: m. p. 75.1° (cor.); sap. eq., 312.2 (theory 312.5); iodine value (Wijs), 0.0. The acetone–glycerol was prepared by the method of Malkin and Shurbagy.[3]

**Preparation of 1-Monoarachidin.**—The monoglyceride was prepared by a modification of the method of Malkin and Shurbagy[3] and is as follows: Dry hydrogen chloride was passed into a mixture, cooled to 15°, of arachidic acid (30 g.) and sufficient acetone–glycerol (*ca.* 75 g.) to make a paste. Completion of the reaction required approximately six hours, during which time the mixture liquefied. The liquid product was dissolved in an equal volume of ethyl ether and filtered. The filtrate was cooled to 5° in an ice-bath and the product hydrolyzed with cold hydrochloric acid (36%). After one-half hour, 500 ml. of ice water was added to the mixture. The precipitated monoglyceride was washed repeatedly with cold water to remove the mineral acid. The monoglyceride was then suction filtered and dried *in vacuo*. After several crystallizations of the product from ethyl ether, it was dried *in vacuo* over phosphorus pentoxide; m. p. 83.5–84.0°; mol. wt.[4] 385.5 (calcd. 386.6). *Anal.*[5] Calcd. for $C_{13}H_{46}O_4$: C, 71.45; H, 11.99. Found: C, 71.74, 71.62; H, 12.07, 12.09.

By the capillary tube method and thermometric techniques previously described[6,7] crystalline modifications of the monoglyceride melted at 77.0, 81.5 and 83.5°, respectively.

**X-Ray Diffraction Analysis.**—The X-ray diffraction patterns of the 1-monoarachidin were made with filtered CuK$\alpha$ radiation, $\lambda = 1.5386$ Å. A finely powdered specimen of the solvent-crystallized material was packed into a nylon tube and the tube was mounted first in a cylindrical

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(1) M. Berthelot, *Ann. chim. phys.*, [3] **47**, 355 (1856).

(2) The fish oil fatty acids were hydrogenated by Dr. Alton E. Bailey at the Southern Regional Research Laboratory, New Orleans, La.

(3) Malkin and Shurbagy, *J. Chem. Soc.*, 1628 (1936).

(4) Hanson and Bowman, *Ind. Eng. Chem., Anal. Ed.*, **11**, 440 (1939).

(5) The microchemical analyses were performed by Mr. George Stragand.

(6) Daubert and Clark, THIS JOURNAL, **66**, 690 (1944).

(7) Daubert and Clark, *Oil and Soap*, **22**, 113 (1945).