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Crystal data of acetyl choline chloride.* By K. W. ALLEN,† *The Crystallography Laboratory, The University of Pittsburgh, Pittsburgh 13, Pennsylvania, U.S.A.*

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While the crystal structures of acetyl choline bromide and iodide (Sørum, 1956, 1959) have both been investigated, that of the chloride has not. This is almost certainly due to the difficulty of preparing satisfactory crystals. Acetyl choline chloride ((CH₃)₃N.C₂H₄OOCCH₃.Cl) is very hygroscopic and extremely soluble, giving a solution of high viscosity. At 25 °C. a saturated solution contains approximately 0.962 g.ml.⁻¹, has a density of 1.19 g.ml.⁻¹ and has a viscosity rather greater than that of glycerine.

When a solution nearly saturated at room temperature is cooled to approximately -10 °C. the anhydrous salt crystallizes slowly as clusters of needles. There was no evidence of hydrate formation, which was the original cause of the investigation. Single crystals, mounted and sealed in glass capillaries were examined about the needle axis [α] by oscillation and Weissenberg methods using filtered copper radiation and by the precession method using molybdenum radiation. Provided that the sealing was satisfactory these mounted crystals remained unchanged for a period of several weeks.

The crystal data obtained were as follows:

Acetyl choline chloride. (CH₃)₃N.C₂H₄.OOCCH₃.Cl.
Orthorhombic. Formula weight 181.5.
 $a = 6.28 \text{ \AA}$, Unit cell volume 952 Å³.
 $b = 9.93 \text{ \AA}$,
 $c = 15.26 \text{ \AA}$.
Space group $P2_12_12_1$.

Systematic extinctions observed:

$h00$ for $h = 2n$, $0k0$ for $k = 2n$, $00l$ for $l = 2n$.

Density: observed 1.202 g.ml.⁻¹; calculated 1.27 g.ml.⁻¹.
Molecules per unit cell 4.

The density of the crystals was estimated by floatation in benzene/chloroform mixtures. It is recognized that the value is not very accurate and is almost certainly lower than the true value because of the difficulty of freeing the crystals completely from the viscous mother liquor. However it is sufficient to confirm the number of molecules per unit cell.

There are no apparent similarities between this structure and that of the other acetyl choline halides. No further work on this structure is contemplated.

References

- SØRUM, H. (1956). *Acta Chem. Scand.* **10**, 1669.
SØRUM, H. (1959). *Acta Chem. Scand.* **13**, 345.

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† On leave from Northampton College, London.

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Refinement of the crystal structure of trimethylamine oxide hydrochloride, (CH₃)₃NO.HCl.

By AIMERY CARON and JERRY DONOHUE, *Department of Chemistry, University of Southern California, Los Angeles 7, California, U.S.A.*

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During the course of the determination of the structure of trimethylamine oxide (Caron & Donohue, 1962), we felt that it would be desirable to carry out additional refinement of the structure of trimethylamine oxide hydrochloride (Rérat, 1960) by making full allowance for thermal anisotropy and by including the effect of the hydrogen atoms. This refinement was carried out on Rérat's observed structure factors by both least-squares and Fourier methods. The complete details of the results of these calculations (Caron, 1962) will not be presented here.

The full matrix was used in the least-squares treatment. The weighting function used was that of Hughes (1941), with $4F_{\min}$ assigned a value of 2.4. The unobserved F 's, listed by Rérat as zero, and F_{002} , which apparently suffers from extinction, were not included in the calculations. The F_c were calculated with the form factor curves of Berghuis *et al.* (1956) for C, N, O, and Cl⁻, and the curve of McWeeny (1951) for H.

The refinement was started at Rérat's final parameter values, omitting the hydrogen atoms. Thus, the published F_c and R value (of 24.4%) were duplicated. Convergence was reached after the computation of a few cycles, during which R dropped to 15.6%. The coordinates of the hydrogen atoms were then estimated by assuming C-H bond lengths of 1.0 Å, H-C-H angles of 110°,

staggered conformations of the methyl groups, and the presence of a proton on the oxygen atom along the direction of the shortest O...Cl distance (2.95 Å). These coordinates, together with isotropic B values of 6.0 Å², were introduced in the computations as variables, and the refinement was resumed. The ultimate R value, including the hydrogen contributions, was 14.0%. The final values of the various parameters are shown in Tables 1, 2, and 3.

Table 1. *Coordinates for the heavy atoms**

		All values have been multiplied by 10 ⁴				
		Least squares				
Atom	Rérat	Fourier	Final	(σ)		
Cl	x	3967	3967	3966	(2)	
	y	6394	6386	6388	(6)	
O	x	2237	2228	2232	(8)	
	y	3441	3422	3422	(9)	
N	x	1439	1436	1437	(4)	
	y	5015	5015	5017	(12)	
C ₁	x	619	633	631	(6)	
	y	3287	3301	3303	(14)	
C ₂	x	1442	1445	1449	(8)	
	y	6575	6557	6544	(27)	
	z	9136	9111	9115	(10)	

* For the molecule lying on the mirror plane at $z = \frac{1}{2}$.

Table 2. *Anisotropic temperature factors for the heavy atoms*All values have been multiplied by 10^4

Atom	<i>B</i>	Rérat	Least squares	(σ)
Cl	11	49	23	(1)
	22	343	315	(10)
	33	173	169	(6)
	12	—	-17	(3)
O	11	50	20	(2)
	22	351	272	(19)
	33	177	205	(12)
	12	—	33	(10)
N	11	39	29	(3)
	22	274	228	(20)
	33	138	99	(10)
	12	—	25	(10)
C ₁	11	48	23	(3)
	22	334	232	(23)
	33	168	190	(15)
	12	—	11	(13)
C ₂	11	52	35	(3)
	22	360	316	(21)
	33	181	136	(11)
	12	—	-7	(10)
	13	—	-0	(7)
	23	—	-125	(24)

Table 3. *Hydrogen coordinates and temperature factors*Positional parameters have been multiplied by 10^3

Atom*	Assumed	Least squares		Final	(σ)
		Fourier	Final		
H ₀	<i>x</i>	282	266	—	266 (19)
	<i>y</i>	445	453	—	453 (42)
	<i>B</i>	6.0	9.3	—	9.3 (6.0)
H ₁₁	<i>x</i>	4	10	1	5 (17)
	<i>y</i>	426	407	431	419 (39)
	<i>B</i>	6.0	4.9	—	4.9 (3.6)
H ₁₂	<i>x</i>	66	73	71	72 (6)
	<i>y</i>	222	225	174	200 (54)
	<i>z</i>	857	877	849	863 (30)
	<i>B</i>	6.0	3.0	—	3.0 (1.6)
H ₂₁	<i>x</i>	204	203	211	207 (9)
	<i>y</i>	756	739	745	742 (14)
	<i>z</i>	911	902	916	909 (16)
	<i>B</i>	6.0	1.1	—	1.1 (1.1)
H ₂₂	<i>x</i>	90	95	88	91 (8)
	<i>y</i>	765	779	792	786 (18)
	<i>z</i>	911	887	889	888 (7)
	<i>B</i>	6.0	0.2	—	0.2 (1.1)
H ₂₃	<i>x</i>	144	141	156	148 (16)
	<i>y</i>	546	530	527	528 (11)
	<i>z</i>	1018	1004	1009	1007 (10)
	<i>B</i>	6.0	0.7	—	0.7 (1.0)

* H₀ is the proton bonded to the oxygen atom. The first subscript of the remaining hydrogen atoms designates the carbon atom to which they are bonded.

The rather small decrease of *R* upon the introduction of the hydrogen scattering as well as the *B* values obtained for the hydrogen atoms and their standard deviations indicate that the intensity data do not allow clear demonstration of the presence of the hydrogen atoms.

In order to obtain a better idea of the state of resolution of the hydrogen atoms, the three-dimensional electron density function and the corresponding difference map were prepared by using the parameters and phase angle values of the last least-squares cycle. The positions of the

heavy atoms were located in the usual way. The final values of the coordinates, including back shift corrections, are given in Table 1. Examination of the difference map showed that, except for the proton presumably bonded to the oxygen atom, peaks could be found for all hydrogen atoms at or near the least-squares positions. Unfortunately, the 'hydrogen peaks' had heights varying between 0.25 and 1.25 e.Å⁻³ and, in addition, many spurious peaks of comparable heights could be found elsewhere.

The final values for the atomic coordinates, presented in Tables 1 and 3, represent the average of the Fourier and least-squares results. The standard deviations were derived according to the relation: $\sigma = (\sigma_{LS}^2 + \Delta^2)^{1/2}$, where σ_{LS} is the least-squares standard deviation and Δ is the difference between the coordinate values as obtained by the Fourier and the least-squares methods. The temperature factors and their standard deviations were obtained from the least-squares treatment only. Corrections to the bond lengths implied by the anisotropies derived from the *B_{ij}* of Table 2 are much less than the standard errors in those lengths.

Table 4. *Intramolecular distances and angles*

Atoms	Rérat	Present work	σ
N-O	1.424 Å	1.425 Å	0.011 Å
N-C ₁	1.495	1.475	0.010
N-C ₂	1.504	1.480	0.011
Cl...O	2.94	2.948	0.010
Cl...O-N	110.4°	109.9°	0.7°
O-N-C ₁	104.7	103.9	1.1
O-N-C ₂	109.2	109.1	1.3
C ₁ -N-C ₂	110.7	111.0	1.5
C ₂ -N-C ₂	111.8	112.3	1.4

Bond distances and angles, before and after the present refinement, are given in Table 4. The differences are not large, with the exception of both C-N bond lengths, which have become shorter. Rérat's longer C-N values do not result from his neglect of the hydrogen atoms since essentially the same short values were obtained in this investigation after the two first least-squares cycles in which hydrogen scattering was also omitted. The comparison of these results, including the abnormally small O-N-C₁ bond angle, with those obtained for trimethylamine oxide will be discussed elsewhere (Caron & Donohue, 1962).

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References

- BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1956). *Acta Cryst.* **8**, 478.
 CARON, A. (1962). Dissertation, University of Southern California.
 CARON, A. & DONOHUE, J. (1962). *Acta Cryst.* (To be published.)
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737.
 MCWEENY, R. (1951). *Acta Cryst.* **4**, 513.
 RÉRAT, C. (1960). *Acta Cryst.* **13**, 63.