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Abstract

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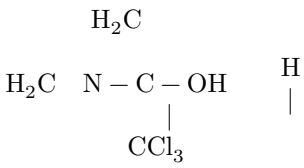
R. P. Shibaeva, L. O. Atovmyan

Crystal Structure of α-Trichloromethyl-N-methylolethylenimine $C_4H_6ONCl_3$

(Presented by Academician N. V. Belov, 7 VIII 1964)

α-Trichloromethyl-N-methylolethylenimine



, one of the most active chemical mutagens, is a derivative of ethylenimine—a three-membered nitrogen-containing heterocycle.*

Very unstable single crystals of $C_4H_6ONCl_3$ were grown from a saturated solution in ether by slow evaporation at constant temperature. Crystals of $C_4H_6ONCl_3$ readily sublime in air and dissolve well in all common organic solvents, on the basis of which adhesives are prepared; therefore, to protect them from sublimation and decomposition during X-ray photography, the single crystals were first coated with a thin layer of paraffin and then with a layer of BF adhesive. The experimental X-ray diffraction material, obtained in a Weissenberg camera using Cu radiation, consists of a set of goniometric records of three equatorial layers of the lines $hk0$, $h0l$, $0kl$ and four nonzero layer lines $h1l$–$h4l$ (345 reflections with $F \neq 0$ in all).

The reflection intensities were estimated visually according to the usual ($\sqrt[4]{2}$) blackening scale. From rotation and Weissenberg photographs the unit-cell parameters were established: $a = 10.50 \pm 0.05$ Å; $b = 9.25 \pm 0.03$ Å; $c = 7.75 \pm 0.03$ Å. Systematic absences (among reflections of the type $h00$, $0k0$, $00l$ only those for which $h, k, l = 2n$ were present) fixed for $C_4H_6ONCl_3$ the enantiomorphic space group $D_2^4 = P2_{12_12}1$. With molecular weight $M = 190.47$ for $z = 4$, the calculated density is $d = 1.69$ g/cm^3.

The structural study was begun with an analysis of the Patterson projections $P(xz)$ and $P(xy)$. The presence in the composition of the compound $C_4H_6ONCl_3$ of relatively heavy chlorine atoms ($z = 17$) made it possible to apply the superposition method ([2,3]) for solving the structure. The projection

Fig. 1. Interatomic distances and bond angles in the structure of C4H6ONCl3 (projection of the molecule along the b axis)

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$P(yz)$ was excluded from consideration at the first stage of the study, since it showed a regular arrangement of bands of maxima. The Patterson projection $P(xz)$ had first been modified by the function $M = \sin^2 \vartheta/\lambda^2$. Since in the group $P2_{12_{12}}1$ all projections are centrosymmetric, the analysis of the Patterson projections $P(xz)$ and $P(xy)$ for "centrosymmetric triplets" of peaks ([4]) made it possible to isolate peaks for minimization. Minimization functions $M_2(xz)$ and $M_2(xy)$ were constructed, and then, using the sliding-reflection lines, we obtained $M_4(xz)$ and $M_4(xy)$. As a result, the positions of three Cl atoms were roughly localized, after which we proceeded to the three-dimensional distribution of electron density. First, an electron-density synthesis was calculated for 3Cl with factor $R = 44.1\%$; then, by the method of successive approximations, a very rough model of the structure was obtained. Refinement of this model by the least-

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* The compound $C_4H_6ONCl_3$ was synthesized at the Institute of Chemical Physics of the Academy of Sciences of the USSR by P. G. Kostyanovskii and kindly provided to us for the X-ray structural investigation.

···least squares reduced the R-factor only to 33.7% with extremely unsatisfactory interatomic distances. The next substantial step in determining the structure of α-trichloromethyl-N-methylolethyleneimine was made through the use of a procedure for refining structures by the least-squares method with additional conditions, described by Waser ([5]) and programmed at the Institute of Chemical Physics of the Academy of Sciences of the USSR by V. I. Andrianov.

Additional conditions are understood to mean *a priori* known information on interatomic distances and bond angles in the structure being refined. (In the present article only the results obtained are reported, without a detailed description of the application of the least-squares method with additional conditions for refining the structure of $C_4H_6ONCl_3$.)

Fig. 1. Interatomic distances and bond angles in the structure of $C_4H_6ONCl_3$ (projection of the molecule along the b axis)

The study of this program for the structure described gave striking success. In the course of refinement the coordinates of all atoms changed substantially (for the Cl atoms along the a axis the maximum displacement proved to be 0.536 Å). The R-factor, calculated only for the three Cl atoms with the new coordinates, was 34.1%, i.e., 10.0% lower than the previously calculated R-factor, also for 3Cl. Therefore a three-dimensional electron-density distribution was con-

structed from the three Cl atoms. From this synthesis we practically obtained a reasonable model of the structure with quite satisfactory interatomic distances. Subsequently, for refinement of the structure, a combination of the ordinary least-squares method and the least-squares method with additional conditions was used. The final atomic coordinates, individual isotropic temperature corrections B_j, and heights of the electron-density maxima ρ are given in Table 1.

Table 1

Atom	x/a	y/b	z/c	B_j, Å^2	ρ, el/Å^3
Cl (1)	0.3090	0.8572	0.4245	−3.54	17.8
Cl (2)	0.4620	0.5998	0.4223	−3.31	18.6
Cl (3)	0.2512	0.6245	0.6577	−3.51	19.2
C (1)	0.3747	0.7194	0.5538	−3.43	5.6
C (2)	0.4639	0.7866	0.6900	−3.26	5.1
C (3)	0.6030	0.7101	0.9472	−3.25	5.5
C (4)	0.4611	0.6596	0.9861	−3.15	5.9
N	0.5149	0.6741	0.8027	−3.07	6.5
O	0.4043	0.9006	0.7847	−3.06	8.6

The reliability factor, calculated from the final coordinates for all nonzero reflections, is equal to 15.7%. The errors in the determination of the atomic coordinates, calculated according to the formulas of B. K. Vainshtein ([6]) and M. A. Porai-Koshits ([7]), are: ε(Cl) = ±0.004 Å; ε(O) = ±0.011 Å; ε(N) = ±0.013 Å; ε(C) = ±0.016 Å.

The interatomic distances and bond angles in the structure of α-trichloromethyl-*N*-methylolethyleneimine are shown in Fig. 1. The accuracy of determination of the bond angles, calculated according to Darlow' s formulas ([8]), is ±0°50′,

and the maximum standard deviation in the determination of interatomic distances for light atoms is Δr = ±0.023 Å. The structural motif of $C_4H_6ONCl_3$ is clearly seen from its projection onto the yz plane (Fig. 2). The $C_4H_6ONCl_3$ molecules are connected with one another by hydrogen bridges O—H ... N into chains parallel to the b axis, with two such chains per period c. The length of the hydrogen bond O—H ... N is 2.75 Å; the angle that it makes with the C—O bond is 114°12′. Within the molecule itself, the angle between the C—N bond and the plane of the three-membered ring is 126°18′.

Fig. 2. Projection of the structure of α-trichloromethyl-N-methylolethyleneimine $C_4H_6ONCl_3$ onto the yz plane

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Institute of Chemical Physics
Academy of Sciences of the USSR

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Note: Figure translations are in progress. See original paper for figures.