The Crystal Structure of a Cyclic Ester-acetal of Glycolic Acid and 2-Methyl-4,5,6-trichloro-cyclohex-2-en-1-one = $C_9H_9O_3Cl_3$

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$C_9H_9O_3Cl_3$ is orthorhombic with cell dimensions: $a=6.96$, $b=29.62$, and $c=5.32$ Å; the space group is $P2_12_12_1$ (No.19, D_2^4) and there are 4 molecules in the unit cell.

The structure has been determined by two-dimensional Patterson projections and refined by difference fourier syntheses and by the systematic variation of atomic coordinates and thermal parameters to minimise the R-value. Atomic coordinates, temperature factors and bond lengths are reported together with their estimated standard deviations.

Chlorination of *o*-cresoxyacetic acid in an organic solvent gives 4-chloro-2-methyl-phenoxyacetic acid as the main product and simultaneously a small amount of other compounds which seem to be isomers corresponding to the formula $C_9H_9O_3Cl_3$. Lund[1] proposed the following constitution:
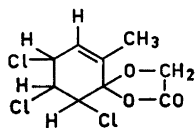
This formula contains 4 asymmetric carbon atoms in the homocyclic ring which explains the existence of the large number of isomers. One of these isomers was isolated as needle-shaped crystals having m.p. 137°C.

This paper presents the results of the crystal structure analysis of this compound.

EXPERIMENTAL

Crystal data. Chemical analysis of the compound is given in Ref.[1] The crystals are orthorhombic. The unit cell has the following dimensions:

$$a = 6.96 \text{ Å}$$
$$b = 29.62 \text{ Å}$$
$$c = 5.32 \text{ Å}$$

These values were determined from a Guinier powder pattern using highly purified sodium chloride as a reference, $CuK\alpha$ radiation being used. The density, measured by flotation, is 1.61 g $\cdot$ ml^{-1} corresponding to 4 formula units in the cell; the calculated density is 1.65 g $\cdot$ ml^{-1}. Systematic absences show that the space group must be $P2_12_12_1$ (No. 19, D_2^4). The crystals are needle-shaped, elongated in the [001] direction.

Intensity data. For the intensity measurements a crystal, of cross-section approximately 0.1×0.1 mm, mounted about the needle axis was used. The $0kl$ intensities were measured from precession photographs taken with $MoK\alpha$ radiation and using the multiple time exposure technique, the $hk0$ intensities were determined from both integrated and non-integrated Weissenberg photographs taken with $CuK\alpha$ radiation with multiple film technique. The intensities of the integrated Weissenberg photographs were measured photometrically, all other intensities were estimated visually by means of a calibration strip, made with the same crystal. 185 $hk0$ and 92 $0kl$ non-zero reflections were recorded. Corrections for Lorentz-polarisation factors were carried out on a GIER computer with ALGOL programmes written in these laboratories.

No corrections for extinction or absorption were made; the linear absorption coefficient is 45.0 cm^{-1} for $CuK\alpha$ and 8.4 cm^{-1} for $MoK\alpha$.

STRUCTURE DETERMINATION

The parameters of the chlorine atoms were obtained from xy-and yz-Patterson projections. Information on the positions of the remaining atoms was obtained from Fourier projections along the c- and a-axes. The signs of the structure factors $F(hk0)$ and $F(0kl)$ were calculated from the contributions of the chlorine atoms. The signs of 139 (75 %) $hk0$ structure factors and 59 (64 %) $0kl$ structure factors were determined in this way. The structure was refined by aid of a few successive difference Fourier projections along the c- and a-axes. The R-values $\Sigma||F_o|-k|F_c||/\Sigma|F_o|$ were reduced to R $(hk0)=18.6$ % and $R(0kl)=21.4$ %. One overall isotropic temperature factor was used. Most of these computations were carried out on the electronic digital computer DASK of Regnecentralen, Copenhagen.

At this stage a further refinement was started using the method suggested by Bhuiya and Stanley [2] since this method seems to work well for projections with overlapping atoms. The geometric and the thermal parameters of each atom of the structure are varied in turn and the parameters yielding the lowest R-value are chosen. For the computations we used an Algol programme written for the computer GIER. The programme refines, in projection, two geometric parameters and one individual isotropic B-factor for each atom of the structure. The programme varies a given parameter three steps in the negative and three steps in the positive directions and chooses the parameter value which gives the lowest R-value. For the geometric parameters we started with steps of 0.03 Å and finished with steps of 0.003 Å. For the thermal parameter the corresponding steps were 0.5 and 0.1 Å^2.

Atomic scattering factors were calculated using an approximation suggested by Bassi:[3]

$$f_n = Z_n - s^2/(a_n + b_n \cdot s + c_n \cdot s^2 + d_n \cdot s^3 + e_n \cdot s^4), \text{ where } s = \sin\Theta/\lambda$$

The coefficients were calculated using tabulated f_n values from *Intern. Tables*, Vol. III, p. 202—207. The numerical values are given in Table 1.

The residual factor $R = \Sigma||F_o|-k|F_c||/\Sigma|F_o|$ was reduced to $R(hk0)=$ 12.2 % and $R(0kl)=8.9$ %. Another refinement of the yz-projection was

Table 1. Coefficients employed in structure factor calculations.

	Cl	O	C
Z	17	8	6
a	5.300624×10^{-3}	1.190571×10^{-2}	9.566876×10^{-3}
b	3.104569×10^{-3}	5.198300×10^{-3}	6.580848×10^{-3}
c	2.022904×10^{-2}	8.168161×10^{-2}	9.869528×10^{-2}
d	1.906431×10^{-1}	9.526727×10^{-2}	2.463541×10^{-1}
e	-1.599024×10^{-1}	-4.287454×10^{-2}	-1.662073×10^{-1}

made with fixed y-coordinates taken from the xy-projection. Residual factor of this refinement was $R'(0kl)=10.6$ %.

The atomic parameters, temperature factors and estimated standard deviations are listed in Table 2. We have taken the y-parameters from the xy-refinement and the z-parameters from the yz-refinement with $R'(0kl)=10.6$ %, which seems to give the best parameters.

Table 3 gives bond lengths and bond angles with estimated standard deviations. Table 4 gives van der Waals' distances with estimated standard deviations.

The calculated and observed structure factors are not printed. The authors will gladly send copies of a table of these values to other crystallographers on request.

DISCUSSION

The X-ray analysis of the compound verifies the chemical constitution proposed by Lund [1] and gives a more detailed picture of the stereochemistry and conformation of the compound.
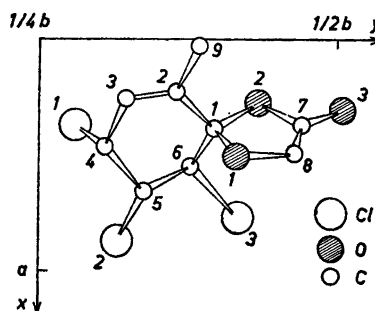
Fig. 1 shows a projection of the molecule along [001].

Fig. 1. xy-projection of the molecule.

Table 2. Atomic coordinates, temperature factors, and estimated standard deviations.

	x/a	y/b	z/c	$B(hk0)$ Å²	$B(0kl)$ Å²	$\sigma(x)$ Å	$\sigma(y)$ Å	$\sigma(z)$ Å	$\sigma(B(hk0))$ Å²	$\sigma(B(0kl))$ Å²
Cl_1	0.4615	0.2731	0.1890	4.5	2.6	0.012	0.011	0.016	0.3	0.4
Cl_2	0.8905	0.3106	0.2612	3.2	4.4	0.010	0.009	0.021	0.2	0.5
Cl_3	0.8052	0.4158	0.2618	2.6	2.5	0.009	0.008	0.016	0.2	0.4
O_1	0.5747	0.4144	0.7425	3.0	3.6	0.023	0.022	0.045	0.6	1.1
O_2	0.3822	0.4334	0.4086	2.6	1.6	0.022	0.020	0.034	0.6	0.9
O_3	0.4047	0.5078	0.4036	5.5	1.2	0.029	0.029	0.034	0.9	0.8
C_1	0.4736	0.3949	0.5240	3.3	3.2	0.038	0.034	0.064	0.9	1.8
C_2	0.3373	0.3622	0.6148	1.9	0.5	0.031	0.029	0.048	0.7	1.1
C_3	0.3637	0.3178	0.6161	2.1	1.8	0.032	0.029	0.059	0.7	1.4
C_4	0.5447	0.2997	0.5066	3.4	2.4	0.038	0.035	0.060	0.9	1.4
C_5	0.7066	0.3337	0.4558	2.2	3.5	0.033	0.028	0.065	0.7	1.9
C_6	0.6157	0.3741	0.3489	2.5	0.8	0.034	0.031	0.048	0.8	1.2
C_7	0.4601	0.4721	0.4880	2.8	4.4	0.035	0.033	0.076	0.8	2.2
C_8	0.5673	0.4648	0.7082	4.5	2.8	0.042	0.039	0.062	1.2	1.6
C_9	0.1660	0.3816	0.7558	2.9	5.4	0.035	0.032	0.083	0.9	2.2

Table 3. Bond lengths with estimated standard deviations and bond angles.

	Length (Å)	e.s.d. (Å)		Angle (°)
C_1-C_2	1.44	0.05	$O_1-C_1-O_2$	103.7
C_2-C_3	1.33	0.04	$O_1-C_1-C_2$	108.3
C_3-C_4	1.49	0.06	$O_1-C_1-C_6$	109.7
C_4-C_5	1.54	0.05	$O_2-C_1-C_2$	112.6
C_5-C_6	1.47	0.05	$O_2-C_1-C_6$	110.7
C_1-C_6	1.49	0.06	$C_2-C_1-C_6$	111.6
C_7-C_8	1.41	0.09	$C_1-C_2-C_3$	125.2
C_2-C_9	1.52	0.06	$C_1-C_2-C_9$	115.3
O_1-C_1	1.48	0.07	$C_3-C_2-C_9$	118.7
O_1-C_8	1.50	0.05	$C_2-C_3-C_4$	118.2
O_2-C_1	1.44	0.05	$Cl_1-C_4-C_3$	103.5
O_2-C_7	1.34	0.05	$Cl_1-C_4-C_5$	109.3
O_3-C_7	1.21	0.05	$C_3-C_4-C_5$	117.0
Cl_1-C_4	1.95	0.06	$Cl_2-C_5-C_4$	112.2
Cl_2-C_5	1.78	0.05	$Cl_2-C_5-C_6$	113.4
Cl_3-C_6	1.87	0.04	$C_4-C_5-C_6$	106.7
			$Cl_3-C_6-C_1$	110.5
			$Cl_3-C_6-C_5$	109.3
			$C_1-C_6-C_5$	112.4
			$O_2-C_7-O_3$	120.2
			$O_2-C_7-C_8$	110.3
			$O_3-C_7-C_8$	127.7
			$O_1-C_8-C_7$	105.8
			$C_1-O_1-C_8$	106.0
			$C_1-O_2-C_7$	111.4

In the cyclohexene ring five of the carbon atoms are in one plane. The methyl group is in the same plane while C_6 in the ring is outside the plane. This plane is at nearly right angle to the plane of the five membered ring. The chlorine atom at C_4 is in axial position and the other chlorine atoms are in equatorial positions.

The standard deviations of the geometric parameters in Table 2 indicate that the chlorine atoms are located quite accurately (r.m.s. about $0.01-0.02$ Å) while the lighter atoms are subject to r.m.s. errors of $0.02-0.08$ Å. The standard deviations in the z-direction are rather high.

Table 4. Van der Waals' distances with estimated standard deviations.

	Length (Å)	e.s.d. (Å)
Cl_1-Cl_2	3.87	0.02
Cl_1-Cl_2	3.48	0.02
Cl_2-C_9	3.88	0.06
Cl_2-C_9	3.91	0.06
Cl_3-O_1	3.20	0.04
Cl_3-C_8	3.68	0.06
Cl_3-C_8	3.66	0.04
Cl_3-C_9	3.82	0.06
Cl_3-C_9	3.77	0.06
O_3-C_8	3.54	0.05
O_3-C_9	3.41	0.05

From Table 3 it is seen that the carbon-carbon double bond must be located between C_2 and C_3. The deviations from generally accepted values of all bond lengths of the molecule are within one or two standard deviations and are therefore hardly significant.

Interatomic distances between 2.0 and 4.0 Å were calculated to analyse the packing of the molecules. The van der Waals' contacts are given in Table 4. Fig. 2 shows the packing of molecules and van der Waals' distances in the yz-projection.
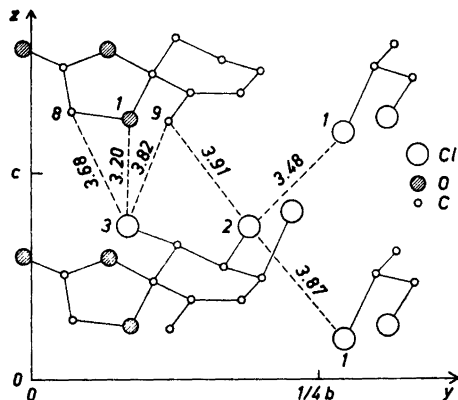

Fig. 2. yz-projection showing the packing of the molecules and van der Waals' distances.

The chlorine atoms, the methyl and the methylene groups play important roles in the packing of the molecules. Two rather short Cl—Cl distances of 3.5 and 3.9 Å indicate van der Waals' bondings. Van der Waals' bonds are probably formed between chlorine atoms and methyl and methylene groups between 3.8 and 3.9 Å. Finally we have found one Cl—O distance of 3.2 Å which indicates a rather strong bonding while the CH_3—O and CH_2—O distances indicate weak bondings. The result obtained for this structure agree, within the experimental error, with the commonly accepted values of the van der Waals' radii, 1.8 Å for Cl, 2.0 Å for CH_3 and 1.5 Å for O. The methylene group may be assigned the same van der Waals' radius as the methyl group.

REFERENCES

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Received January 16, 1964.