

Conformational Studies of Oligomethylene Glycol Derivatives and Related Compounds. IV. The Crystal and Molecular Structure of Trimethylene Glycol Di-*p*-chlorobenzoate, $C_{17}H_{14}O_4Cl_2$

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The diester $C_{17}H_{14}O_4Cl_2$ crystallizes in space group $C2/c$ with 4 molecules per unit cell of dimensions $a = 31.499$ (22), $b = 4.530$ (3), $c = 11.587$ (8) Å and $\beta = 95.37$ (10)°. The intensity measurements were made on an automatic diffractometer and the structure was solved by direct methods. Anisotropic least-squares refinement was concluded with a final R value of 0.042 for 1238 reflexions with $I/\sigma(I) \geq 2.5$. The molecule lies on a crystallographic twofold axis of rotation. The carboxylic plane is tilted by only 1.4° from the aromatic plane. The conformational angles within the 'trimethylene' part of the molecule are both *gauche*. Van der Waals interactions maintain the molecules together in the crystal.

Introduction

As a continuation of our systematic studies of oligomethylene glycol derivatives, we present here the crystal structure determination of the trimethylene glycol di-*p*-chlorobenzoate molecule. The knowledge of the geometry of this molecule will be a very useful starting point in the study of the conformation of polytrimethylene terephthalate, $[O-(CH_2)_3-O-CO-C_6H_4-CO]_n$.

Experimental

Trimethylene glycol di-*p*-chlorobenzoate was prepared in a manner similar to that described by Heim & Poe (1944). Recrystallization in chloroform gave crystals suitable for X-ray diffraction studies. Weissenberg and precession photographs indicated a monoclinic unit cell. The systematic absences (hkl , $h+k \neq 2n$; $h0l$, $l \neq 2n$) are compatible with both Cc and $C2/c$ space groups. Further measurements were made on a Picker FACS-I diffractometer. The unit-cell dimensions and their standard deviations, determined by least-squares refinement of twelve high-angle carefully centred reflexions, are given in Table 1.

Table 1. *Crystal data*

$C_{17}H_{14}O_4Cl_2$, F.W. 353.39, m.p. 100°C, $F(000) = 728$.
Monoclinic: $C2/c$, $d_{obs} = 1.44$, $d_{cal} = 1.426$ g cm⁻³, $Z = 4$.
 $a = 31.499$ (22), $b = 4.530$ (3), $c = 11.587$ (8) Å, $\beta = 95.37$ (10)°,
 $V = 1646.1$ Å³, $\mu(Mo K\alpha) = 2.9$ cm⁻¹, $\lambda(Mo K\alpha) = 0.71069$ Å,
 $T = 20^\circ C$

Intensity data were collected from a crystal of dimensions $0.17 \times 0.30 \times 0.32$ mm, using a scintillation counter and graphite-monochromatized Mo $K\alpha$ radiation, for two octants within the sphere limited by $2\theta \leq 52^\circ$. Peaks were scanned by the $\theta-2\theta$ technique at a rate of $1^\circ (2\theta) \text{ min}^{-1}$ and with a minimum width of $1.75^\circ (2\theta)$. Background counts of 20s were taken at

each end of the scan range. The intensities of three reference reflexions, monitored every 30 reflexions, decreased by 10% over the duration of the intensity measurements. This decrease was taken into account during the data reduction which was performed using the programs of Ahmed, Hall, Pippy & Huber (1966).

Of the 1635 reflexions measured, 1238 (75%) have been kept for the structure refinement. These reflexions have $I/\sigma(I) \geq 2.5$, where $\sigma(I)$ is calculated by a relation described by Pérez & Brisse (1976c). Because of the smallness of the crystal and the low value of the absorption coefficient, no absorption correction was applied. The X-ray scattering factors were obtained from Cromer & Waber (1965) for Cl, O and C and from Stewart, Davidson & Simpson (1965) for H. The real and imaginary parts of the anomalous dispersion for Cl were taken from Cromer (1965).

Structure determination and refinement

A set of normalized structure factors $|E|$ was obtained after isotropic temperature factor correction. Analysis of the $|E|$ statistics (Table 2) strongly indicated a centrosymmetric space group. However it was decided to try to solve the structure in the non-centrosymmetric space group Cc .

The structure was solved using the multiresolution method described by Germain, Main & Woolfson (1970). 129 reflexions with $|E| > 1.70$ (6 reflexions per non-hydrogen atom to be found) were used to generate 642 \sum_2 relations. Two origin-defining reflexions 512, ($E = 3.07$, $\varphi = 0$) and 22,2,9, ($E = 2.17$, $\varphi = 0$), one enantiomorph-fixing reflexion 25,1,2 ($E = 4.73$, $\varphi = \pi/4$, $3\pi/4$) and three symbolic reflexions 14,0,10 ($E = 3.40$, $\varphi = \pm\pi/4$, $\pm 3\pi/4$), 428 ($E = 2.65$, $\varphi = \pm\pi/4$) and 641 ($E = 1.88$, $\varphi = \pm\pi/4$) were used for the phasing of the reflexions. The various indicators for the choice of the best set of phases are presented in Table 3. The E -map calculated with the best set of phases revealed the 23

non-hydrogen atoms of the molecule. Four cycles of full-matrix isotropic least-squares refinement led to a conventional *R* value of 0.16. The correlation matrix computed at the same time indicated that there was a fairly strong correlation between the coordinates of chemically equivalent atoms of the molecule.

Table 2. *E* statistics

	Centro-symmetric	Experimental	Non centro-symmetric
$\langle E ^2 - 1 \rangle$	0.968	1.020	0.736
$\langle E \rangle$	0.798	0.789	0.886

Table 3. *Figures of merit (FOM) of the best set of phases and extreme values*

	Absolute FOM	ψ_0^* ($\times 10^3$)	Residual	Combined FOM
Best set of phases	1.027	0.485	19.09	2.96
Maximum value	1.027	0.649	24.76	
Minimum value	0.916	0.483	18.95	

* $\psi_0 = \sum_H |E_H \cdot E_{-H}|$ for all *H*'s with $E_H = 0$, or nearly 0.

Thus it was confirmed that the compound belongs to the centrosymmetric space group *C2/c* and the molecule had to lie either on a twofold axis of rotation at $x=0$, $z=\frac{1}{4}$ or on a centre of symmetry. The conformation revealed by the *E*-map can only be arrived at with a twofold axis of rotation. After a change of origin to comply with space group *C2/c*, the full-matrix refinement proceeded smoothly as indicated in Table 4. The symmetry restrictions on anisotropic tem-

perature factor components for the atom situated on the twofold axis were taken from Peterse & Palm (1966). Each reflexion was assigned a weight $w=1/\sigma^2(F)$ derived from $\sigma(I)$. At the end of the refinement, the average shift to σ ratio was less than 0.2. A final electron density map showed no significant residual density, the extreme fluctuations being -0.15 , $+0.14$ e \AA^{-3} .*

Table 4. *Refinement summary*

$R = \sum \Delta F / F_0$; $R_w = [\sum w \Delta F^2 / \sum w F^2]^{1/2}$; $\sigma_F = [\sum w \Delta F^2 / (m-n)]^{1/2}$; $m = \text{number of reflexions}$; $n = \text{number of parameters refined}$.

Cycle	<i>n</i>	<i>R</i>	<i>R_w</i>	σ_F	Comments
1	47	0.218		15.86	Isotropic refinement
2-4	47	0.158		12.60	Isotropic refinement
5-7	105	0.088		7.77	Anisotropic refinement; 7 hydrogen atoms found
8-11	133	0.056		4.97	Anisotropic refinement for Cl, O, C; isotropic for H
12-15	133	0.042	0.043	2.70	Weighting and anomalous scattering included
		0.061	0.062		For all measured reflexions

Results and discussion

The positional and thermal parameters and their standard deviations are presented in Table 5 while the stereochemical structure of the trimethylene glycol di-*p*-chlorobenzoate molecule is shown in Fig. 1.

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31482 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5. *Fractional coordinates, thermal parameters and their e.s.d.'s*

The thermal parameters are the coefficients of the expression $T = \exp [-2\pi^2(U_{11}a^*h^2 + \dots + 2U_{12}a^*b^*hk + \dots)]$. The coordinates are in fractions of unit-cell edges $\times 10^5$ for Cl, O and C and $\times 10^4$ for H atoms. The thermal parameters are given $\times 10^4$ for Cl, C and O atoms and $\times 10^5$ for H atoms. The standard deviations refer to the least significant digit.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U₁₁</i>	<i>U₂₂</i>	<i>U₃₃</i>	<i>U₁₂</i>	<i>U₁₃</i>	<i>U₂₃</i>
Cl(1)	23120 (2)	4141 (16)	37766 (6)	798 (4)	1075 (6)	904 (4)	-193 (4)	-91 (3)	-105 (4)
C(38)	0	101816 (64)	25000	639 (17)	583 (20)	875 (21)	0	-5 (16)	0
O(11)	6554 (4)	-49587 (39)	3415 (11)	733 (9)	1380 (16)	444 (7)	-37 (9)	0 (7)	84 (9)
O(12)	5442 (4)	-68496 (32)	20682 (10)	578 (7)	763 (10)	501 (7)	-30 (7)	31 (6)	3 (7)
C(11)	11405 (5)	-38034 (43)	19800 (15)	523 (10)	624 (13)	454 (10)	120 (10)	76 (8)	-11 (10)
C(12)	12485 (6)	-42548 (49)	31581 (16)	651 (12)	812 (16)	464 (11)	-36 (11)	96 (9)	17 (11)
C(13)	16084 (6)	-29539 (56)	37033 (17)	755 (13)	826 (17)	481 (11)	-20 (12)	22 (9)	-35 (12)
C(14)	18594 (6)	-12058 (50)	30826 (17)	591 (11)	703 (15)	641 (12)	23 (11)	43 (10)	-53 (11)
C(15)	17562 (7)	-6982 (49)	19090 (18)	668 (12)	786 (16)	651 (13)	-21 (12)	94 (10)	94 (12)
C(16)	13971 (6)	-20108 (50)	13750 (15)	646 (12)	778 (15)	488 (11)	57 (12)	84 (9)	83 (11)
C(17)	7594 (5)	-52323 (43)	13636 (15)	526 (10)	708 (15)	500 (10)	145 (10)	97 (9)	-17 (10)
C(18)	1697 (6)	-83887 (52)	15522 (16)	601 (12)	710 (15)	605 (12)	55 (11)	11 (10)	-101 (11)

Table 5 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
H(121)	1068 (5)	-5498 (37)	3522 (14)	64 (2)
H(131)	1691 (6)	-3352 (49)	4533 (17)	93 (3)
H(151)	1933 (5)	561 (40)	1509 (16)	76 (3)
H(161)	1318 (5)	-1752 (41)	573 (14)	64 (2)
H(181)	272 (5)	-9710 (38)	960 (15)	67 (2)
H(182)	-30 (5)	-6899 (40)	1208 (15)	64 (2)
H(381)	238 (5)	11505 (42)	2883 (14)	70 (2)

Bond distances and angles†

The interatomic distances and angles are presented in Fig. 2. The standard deviations of these quantities, derived from the calculated e.s.d.'s of the final coordinates, amount to 0.003 Å and 0.2° for non-hydrogen

† Primed atoms are derived by twofold rotation from the non-primed atoms having the same number.

atom bond distances and angles respectively and amount to 0.02 Å for C–H distances. All bond distances and angles are reasonable and compare extremely well with those obtained for ethylene glycol dibenzoate (Pérez & Brisse, 1976*c*) and ethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1976*a*). As noted in those two structures, the distances and angles of the 'glycol' part of the molecule depart significantly from the values expected between C(*sp*³) atoms. Here again the C(18)–C(38) distance is 1.504 (3) Å while the O(12)–C(18)–C(38) and the C(18)–C(38)–C'(18) angles are 106.8 and 114.6° respectively. Such a short distance is close to that found, for example, in bis-(2-hydroxyethyl) terephthalate, 1.499 Å (Kashino & Haisa, 1975), in 3-carbethoxy-4-oxo-6-methylhomopyrimidazole, 1.489 Å (Sasvári, Horvai & Simon, 1972) and in 4-carbethoxyanilinium bis-*p*-nitrophenylphosphate, 1.471 Å (Pletcher, Sax & Yoo, 1972).

Molecular conformation

The equations for the aromatic mean plane (plane *A*) and for the carboxylic group (plane *B*) are given in Table 6. The carboxylic plane is tilted by only 1.4° from the aromatic ring plane. The two aromatic planes of the molecule form between them an angle of 105.9°.

The torsional angles of interest are listed in Table 7. The *p*-chlorobenzoate parts of the molecule up to the C(18) or C'(18) atoms are quasi planar. The torsional angles within the 'trimethylene' part of the molecule are identical (–66.3°) and indicate a *gauche* conformation. A similar conformation has also been found for trimethylene dibenzoate (Pérez & Brisse, 1976*b*).

It is worth mentioning that the length of this molecule, from atom C(11) to C'(14) is 9.52 Å and this very nearly coincides with half the fibre repeat of polytrimethylene terephthalate (Pérez & Brisse, 1976*b*).

Table 6. Mean planes

The planes are expressed by $lX+mY+nZ-p=0$ with XYZ and p in Å. The orthogonal system of axes has $X||a$ axis, $Y||b$ axis and Z along the c^* axis.

Plane <i>A</i>	Deviation from plane		Plane <i>B</i>	Deviation from plane	
	Atoms	Deviation		Atoms	Deviation
$\chi^2=9.02$	C(11)	+0.003 (2) Å	$\chi^2=2.10$	O(11)	–0.001 (2) Å
	C(12)	–0.003 (3)		O(12)	–0.001 (2)
	C(13)	–0.001 (3)		C(11)	–0.001 (2)
	C(14)	0.004 (2)		C(17)	0.004 (2)
	C(15)	–0.003 (3)			
	C(16)	–0.002 (3)			
	Cl(1)†	0.008 (1)			
Plane <i>A</i> :		0.564 <i>X</i> +0.797 <i>Y</i> +0.214 <i>Z</i> +2.78=0			
Plane <i>B</i> :		0.569 <i>X</i> +0.799 <i>Y</i> +0.191 <i>Z</i> +2.87=0			

† Not included in the mean plane calculation.

Table 7. Torsional angles (°)

C(17)–O(12)–C(18)–C(38)	$\phi_1 = -176.7$
O(12)–C(18)–C(38)–C'(18)	$\phi_2 = -66.3$
C(18)–O(12)–C(17)–C(11)	$\omega = 179.1$
C(18)–O(12)–C(17)–O(11)	–1.3

Packing of the molecules

The intermolecular distances shorter than 3.60 Å are presented in Table 8. None of the contacts is less than 3.30 Å, consequently the molecules are held in the crystal by van der Waals forces only. The packing of the trimethylene glycol di-*p*-chlorobenzoate molecules is shown in Fig. 3. It is noteworthy to observe that contrary to what was observed in the structure of ethylene glycol di-*p*-chlorobenzoate (Pérez & Brisse, 1976*a*), the aromatic rings do not place themselves parallel to each other.



Fig. 1. A stereoscopic view of the structure of one molecule of trimethylene glycol di-*p*-chlorobenzoate. The twofold axis of rotation is vertical.

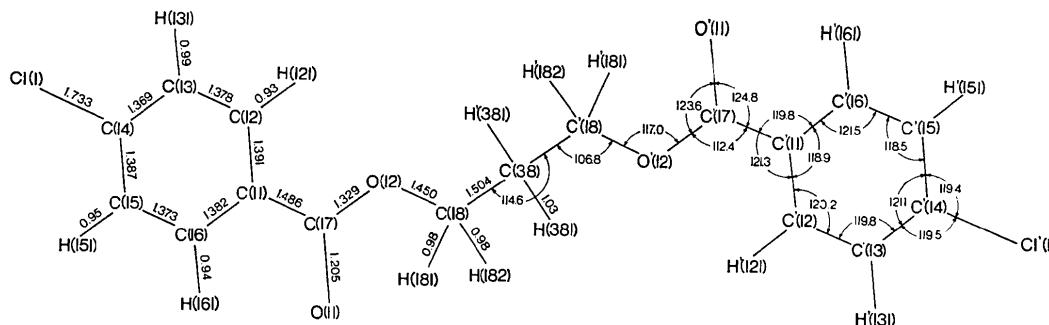


Fig. 2. Bond distances and angles.

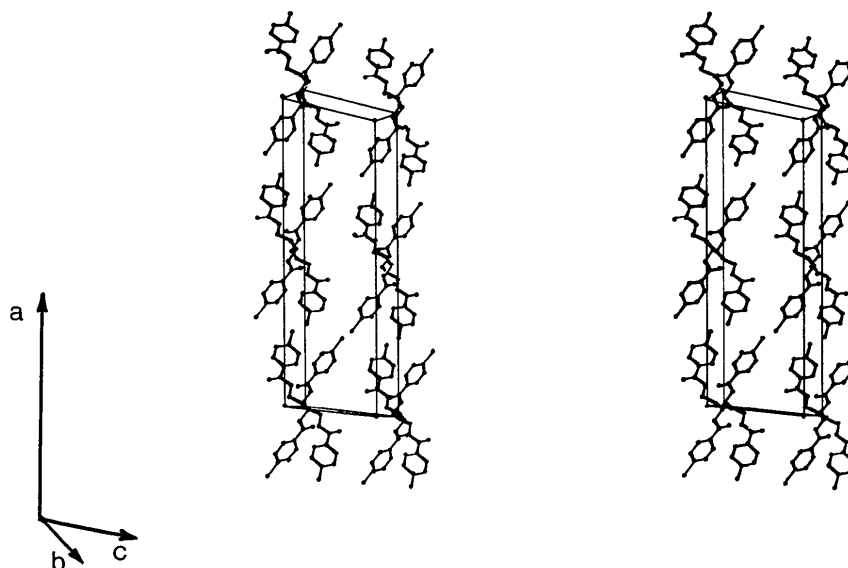
Fig. 3. Molecular packing of trimethylene glycol di-*p*-chlorobenzoate.

Table 8. Intermolecular contacts (Å) shorter than 3.60 Å

	Position	
Cl(1) ... Cl(1)	$\frac{1}{2}-x, \frac{1}{2}-y, 1-z$	3.519
Cl(1) ... C(15)	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$	3.575
O(11) ... C(12)	$x, -1+y, z-\frac{1}{2}$	3.302
O(11) ... C(18)	$-x, -1+y, -z$	3.578
O(12) ... C(38)	$x, 1+y, z$	3.522

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