

Butane-1,4-diyl bis(chloroacetate)

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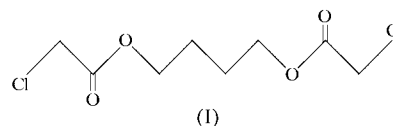
The title compound, C₈H₁₂Cl₂O₄, lies about an inversion centre. The molecular conformation is characterized by a *tḡt̄t̄* conformation for the butanedioxy moiety and a *trans* conformation for the ClCH₂—C(=O)O bond. The molecular packing is stabilized by a network of weak CH₂···O=C intermolecular hydrogen bonds, where each molecule interacts with its four closest neighbours.

Comment

Polyesters have a wide range of applications as biodegradable materials. Medical uses, such as bioabsorbable surgical sutures and drug delivery systems, are a good example. Most of the speciality polymers actually commercialized as sutures are based on glycolide, which is their major component (Chu, 1997). This group includes sutures such as Dexon or Safil (Schmitt & Polistina, 1967), Vicryl (Schneider, 1955), Maxon (Rosensaft & Webb, 1981), Monocryl (Bezwada *et al.*, 1995) and Monosyn (Erneta & Vhora, 1998), which differ slightly in composition, and obviously in properties (thermal and mechanical) and degradation rates. All of these polymers are prepared by ring-opening polymerization, with the high cost of the cyclic glycolide monomer being one of the most limiting factors.

Considerable efforts are currently focused on identifying alternative syntheses and on obtaining related polymers with enhanced properties. Thus, the solid-state polycondensation reaction of halogenated carboxylates appears to be an interesting method for the synthesis of polyglycolide (Herzberg & Epple, 2001), which could then generate the glycolide ring by pyrolysis. We have recently demonstrated that poly(ester amides) of high molecular weight could also be prepared by a condensation reaction between *N,N'*-bis(chloroacetyl) diamines and dicarboxylate salts (Vera *et al.*, 2004). The driving force of these polymerizations corresponds to the formation of metal halide salts (Epple & Kirschnick, 1997). A similar process could be extended to prepare new polyesters containing glycolic acid residues, characterized by the sequence OCH₂—COO(CH₂)_nOCOCH₂OCO(CH₂)_{m-2}CO.

The title compound, alternatively called 1,4-bis(chloroacetoxy)butane, (I), is one of the monomers that could be employed to prepare the series derived from 1,4-butanediol (*n* = 4). It is of interest to determine the crystalline structure of various monomers, since these kinds of reactions sometimes occur in the solid state. Furthermore, knowledge of their molecular conformations is a useful tool for the determination of the polymer structure, since they correspond to small fragments of its sequence.



The molecule of (I) is shown in Fig. 1, and selected torsion angles and the hydrogen-bond geometry are reported in Tables 1 and 2, respectively. The ester group is planar within experimental error, with an r.m.s. deviation of 0.0041 Å for atoms C2, C3, O3 and O4 from the best plane passing through them. The molecule lies on an inversion centre and, consequently, the molecular conformation is symmetric (symmetry code: 1 - *x*, 1 - *y*, 1 - *z*).

The conformations of the chloroacetyl unit and the butanedioxy moiety, which is a constituent of some synthetic polyesters of commercial interest, such as poly(tetramethylene terephthalate) and poly(tetramethylene succinate), are interesting. A *tḡt̄t̄* conformation was found in (I) for the tetramethylene moiety, a fact that is in agreement with structural studies carried out on poly(tetramethylene succinate). This polymer exists as two polymorphs, the *α* form (Chatani *et al.*, 1970), where the butanediol residues adopt a kinked conformation, and the less predominant *β* form, characterized by an all-*trans* conformation (Ichikawa *et al.*, 1994). However, the reported structures for poly(tetramethylene terephthalate) show different conformations for the butanediol unit, namely *gḡt̄t̄* and *ts̄ts̄t̄* for the *α* (Mencik, 1975; Yokouchi *et al.*, 1976) and *β* forms (Yokouchi *et al.*, 1976), respectively. The shorthand nomenclature (Tadokoro, 1979) refers to the sequence of torsion angles with *gauche* (*g*), *trans* (*t*) or skew (*s*) conformations. Furthermore, potential energy calculations (Palmer *et al.*, 1985) demonstrate that in the case of poly(tetramethylene terephthalate), the *gḡt̄t̄* conformation is stabilized with respect to the *tḡt̄t̄* conformation.

A survey of the Cambridge Structural Data Base (CSD, ConQuest Version 1.6; Allen, 2002; Bruno *et al.*, 2002) shows 12 crystal structures containing XCOOCH₂CH₂CH₂CH₂

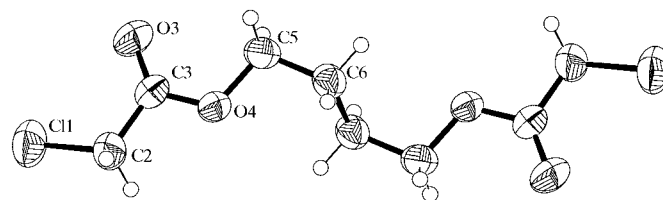


Figure 1

A view of the molecule of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

OCO X units, with X being an aromatic group (phenyl, chlorophenyl or nitrophenyl) in the majority of cases. The *tg \bar{t}* conformation was only found in two compounds, *viz.* tetramethylene glycol *o*-chlorobenzoate (Bocelli & Grenier-Loustalot, 1984) and tetramethylene glycol *p*-nitrobenzoate (Palmer *et al.*, 1985). The all-*trans* conformation was observed in four compounds, with the remainder corresponding to asymmetric conformations where, in general, one of the two O—CH₂—CH₂—CH₂ torsion angles is close to a *gauche* conformation. Among the known crystal structures of this class, compound (I) is a unique linear molecule containing aliphatic ester groups, with an observed molecular conformation in agreement with the determined structure of the α form of poly(tetramethylene succinate).

The Cl—CH₂—C(=O)—O torsion angle has a *trans* conformation, which places the electronegative Cl and O(CH₂) atoms as far apart as possible. In fact, 65 crystal structures containing a total of 96 chloroacetoxy fragments have been solved, with the *trans* conformation observed for the majority (61, 24, 13 and 2% for the *trans*, *cis*, *gauche* and skew conformations, respectively). It should be pointed out that this bond tends to a *cis* conformation in chloroacetamide fragments [ClCH₂—C(=O)NH] because of the possibility of intramolecular N—H...Cl hydrogen bonds (Rao & Mallikarjunan, 1973; Kalyanaraman *et al.*, 1978; Urpí *et al.*, 2003).

The packing in (I) is characterized by a network of weak intermolecular CH₂...O=C hydrogen bonds (Fig. 2), where each molecule interacts with its four closest neighbours (Table 2). Hydrogen bonds are established along a direction which, on average, runs parallel to the crystallographic *b* axis. The methylene and carbonyl groups that interact belong to asymmetric units related by a twofold screw axis.

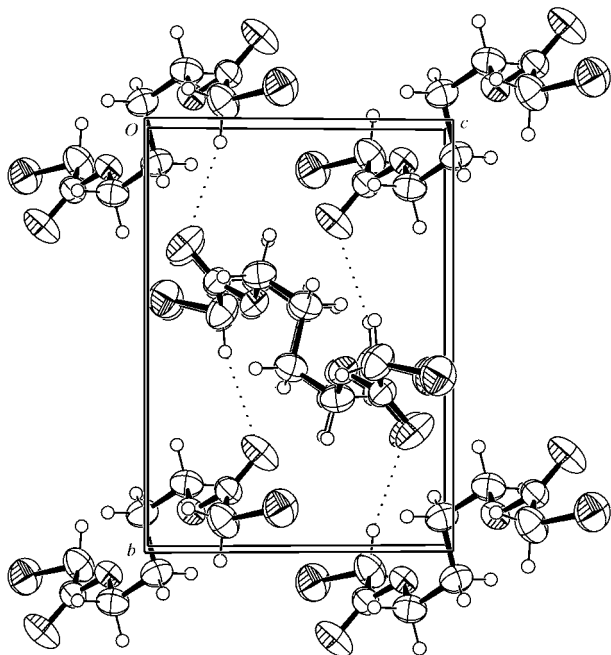


Figure 2
A view parallel to the crystallographic *a* axis, showing the crystal packing of (I). Dashed lines illustrate the weak intermolecular hydrogen-bond interactions between the methylene and carbonyl groups.

Experimental

The title compound was synthesized by the dropwise addition of a chloroform solution of 2.2 equivalents of chloroacetyl chloride (0.22 mol in 100 ml) to a chloroform solution of 1,4-butanediol (0.1 mol in 150 ml). The reaction mixture was stirred at room temperature for 3 h and then repeatedly washed with water. Finally, the chloroform solvent was evaporated under reduced pressure. The white solid obtained was recrystallized from ethanol to give colourless rhombic crystals of (I) (yield 85%, m.p. 349 K). ¹H NMR (CDCl₃, TMS, internal reference): δ 4.26 (*m*, 4H, OCH₂), 4.09 (*s*, 4H, ClCH₂), 1.81 (*m*, 4H, OCH₂CH₂); ¹³C NMR (CDCl₃, TMS, internal reference): δ 167.33 (CO), 65.53 (OCH₂), 40.84 (ClCH₂), 25.04 (OCH₂CH₂).

Crystal data

C ₈ H ₁₂ Cl ₂ O ₄	$D_x = 1.450 \text{ Mg m}^{-3}$
$M_r = 243.08$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/c$	Cell parameters from 25 reflections
$a = 7.9765 (16) \text{ \AA}$	$\theta = 12\text{--}21^\circ$
$b = 9.8921 (14) \text{ \AA}$	$\mu = 0.57 \text{ mm}^{-1}$
$c = 7.220 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$\beta = 102.22 (2)^\circ$	Prism, colourless
$V = 556.8 (2) \text{ \AA}^3$	$0.4 \times 0.3 \times 0.2 \text{ mm}$
$Z = 2$	

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{\text{max}} = 30.0^\circ$
$\omega/2\theta$ scans	$h = -11 \rightarrow 0$
1717 measured reflections	$k = -13 \rightarrow 0$
1621 independent reflections	$l = -9 \rightarrow 10$
837 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{\text{int}} = 0.032$	frequency: 120 min
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0484P)^2 + 0.2473P]$
$R[F^2 > 2\sigma(F^2)] = 0.053$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.138$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.01$	$\Delta\rho_{\text{max}} = 0.24 \text{ e \AA}^{-3}$
1621 reflections	$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$
67 parameters	
H-atom parameters constrained	

Table 1

Selected torsion angles ($^\circ$).

C5—O4—C3—O3	4.5 (4)	Cl1—C2—C3—O4	−166.40 (19)
C5—O4—C3—C2	−174.1 (2)	C3—O4—C5—C6	178.7 (2)
Cl1—C2—C3—O3	15.0 (4)	O4—C5—C6—C6 ⁱ	64.3 (3)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2

Hydrogen-bonding geometry ($\text{\AA}, ^\circ$).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
C2—H2B...O3 ⁱⁱ	0.97	2.55	3.480 (4)	160

Symmetry code: (ii) $2 - x, y - \frac{1}{2}, \frac{3}{2} - z$.

H atoms were placed in calculated positions and were refined isotropically riding on their attached C atoms, with C—H distances of 0.97 \AA . All H atoms belong to CH₂ groups, of which there are three in the asymmetric unit of (I). The displacement parameters of the two H atoms of each CH₂ group was refined as a free variable.

Data collection: *CAD-4 Software* (Kiers, 1994); cell refinement: *CAD-4 Software*; data reduction: local program; program(s) used to

solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1149). Services for accessing these data are described at the back of the journal.

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