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Butane-1,4-diyl bis(bromoacetate)

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.065
wR factor = 0.180
Data-to-parameter ratio = 25.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_8H_{12}Br_2O_4$, has crystallographic inversion symmetry. Molecules adopt a pleated conformation, the $OCH_2-CH_2CH_2$ torsion angles of the butanediol residue being close to 60 and −60°. The molecular packing is stabilized by a network of weak intermolecular hydrogen bonds between the methylene and the carbonyl groups of the bromoacetate units. Each molecule interacts with its four closest neighbours.

Comment

Commercially important polyesters are based mainly on the *p*-phenylene group, poly(ethylene terephthalate) (PET) and poly(butylene terephthalate) (PBT) being the most significant examples. Nowadays, increasing interest is focused on aliphatic polyesters, due to their degradable properties (Huang, 1985). These polymers can be classified into two groups, namely derivatives of hydroxyacids or lactones {*e.g.* polyglycolide, polylactide, poly[(*R*)-3-hydroxybutyrate] and poly(ε-caprolactone)}, and derivatives of diols and dicarboxylic acids. The first group has a wide range of applications in the biomedical field, due to their combination of mechanical and thermal properties, degradability and bioabsorption. In this way, glycolide derivatives constitute the main family of materials used as bioabsorbable surgical sutures (Chu, 1997).

Condensation polyesters based on diols and dicarboxylic units were first developed by Carothers (1931), but properties such as low melting point and high solubility restricted their commercial interest. In general, melting temperature increases with the methylene content of the chemical repeat unit and approaches asymptotically a value of 398 K, which is characteristic of polyethylene. Only poly(tetramethylene succinate) has been commercialized as the major component of Bionolle (Fujimaki, 1998), a product recently produced by Showa Highpolymer, due to its relatively high melting temperature (387 K; Korshak & Vinogradova, 1956). This value clearly contrasts with that found in polyesters with a similar methylene content [*e.g.* 330 K for poly(hexamethylene succinate) (Carothers, 1931)]. The crystalline structure of poly(tetramethylene succinate) has been studied because of its peculiar characteristics and two polymorphs have been characterized, namely the α-form (Chatani *et al.*, 1970), where the butanediol residue adopts a pleated conformation due to the presence of two *gauche* torsion angles with opposite senses (g and $-g$), and the less predominant β-form, characterized by an all-*trans* conformation (Ichikawa *et al.*, 1994).

The resolution of the structures of synthetic polymers is problematic, since only a small number of reflections can be observed in both X-ray diffraction patterns from fibres and electron diffraction patterns from lamellar single crystals. For

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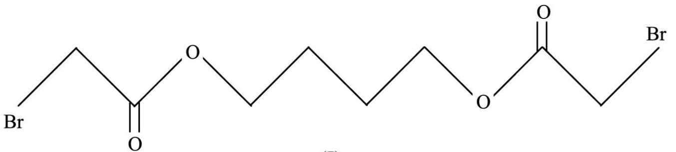
this reason, direct methods cannot be employed. Chain conformation and molecular packing are usually postulated before starting a refinement process which takes into account the calculated and experimental diffraction intensities. Additional data are useful both to select the initial molecular chain conformation and to support the refined structure. These can be provided by quantum mechanical calculations, as well as by crystallographic studies of small polymer fragments or model compounds.

Aliphatic esters of 1,4-butanediol may be adequate models to verify the conformational preferences for the corresponding segment of poly(tetramethylene succinate). Unfortunately, these compounds usually have a melting point lower than room temperature. Thus, only 12 crystalline structures corresponding to aromatic esters of 1,4-butanediol can be found in the Cambridge Structural Database (CSD; *ConQuest* Version 1.7; Allen, 2002; Bruno *et al.*, 2002). Some of these derivatives were simply studied as model compounds of poly(butylene terephthalate) (Palmer *et al.*, 1985).

We are now involved in the study of new polyesters containing glycolic acid residues which can be prepared through a polycondensation reaction between a dihalogenoacetate derivative of a diol $X\mathrm{CH_2CO{-}O(CH_2)}_n\mathrm{O{-}COCH_2}X$ and a dicarboxylate metal salt. This kind of reaction was successful in the preparation of poly(ester amide)s from *N*,*N*′-bis(chloroacetyl)diamines (Vera *et al.*, 2004). The new monomers show a significantly higher melting point for the butanediol derivatives in comparison with those constituted by similar diols [*e.g.* 349 K for butane-1,4-diyl bis(chloroacetate), 302 K for hexane-1,6-diyl bis(chloroacetate) and 296 K for ethane-1,2-diyl bis(chloroacetate)], a fact which again suggests a distinctive structure.

In this paper, we report the crystalline structure of the title compound, (I), alternatively called 1,4-bis(bromoacetoxy)butane. This study complements the data obtained for the parent bis(chloroacetate) derivative, which is currently the only linear aliphatic diester of 1,4-butanediol for which the structure has been solved (Urpí *et al.*, 2004).



(I)

The molecule of (I) is shown in Fig. 1, and selected torsion angles and the hydrogen-bond geometry are summarized in Tables 1 and 2, respectively. The structure of (I) is practically identical to that found for the chlorinated derivative. The main difference corresponds to the expected slight increase (4%) in the unit-cell volume. Thus, the β monoclinic angle remains close to the previously found value of 102°.

The ester group is planar to within experimental error, with an r.m.s. deviation of 0.0098 Å for atoms C2, C3, O3 and O4 from the mean plane passing through them. The molecular conformation is symmetric and is characterized by the *gauche* conformation of the $\mathrm{OCH_2{-}CH_2CH_2}$ torsion angles. In this way, the butanediol moiety is defined by a *tgt*(−*g*)*t* sequence of torsion angles, which is in agreement with the previously determined structure of the α-form of poly(tetramethylene succinate). It is worth mentioning that this conformation has seldom been observed when the model compound involves aromatic esters. Only the *o*-chlorobenzoate (Bocelli & Grenier-Loustalot, 1984) and *p*-nitrobenzoate (Palmer *et al.*, 1985) diester derivatives showed the same conformation, whereas the rest of the analogous compounds that appear in the CSD are characterized by all-*trans* conformations or asymmetric sequences of torsion angles.

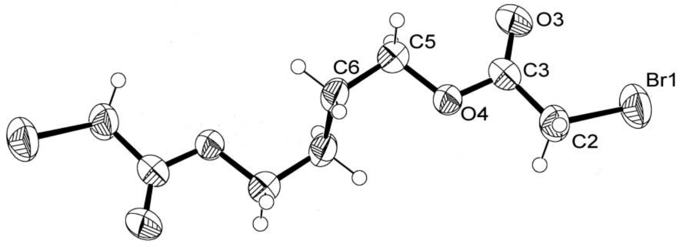


Figure 1
A drawing of the molecule of (I), with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Unlabelled atoms are related to labelled atoms by $(1-x, 1-y, 1-z)$.

The $\mathrm{BrCH_2{-}C({=}O)O}$ torsion angle corresponds to a *trans* conformation, which places the electronegative Br and O ($\mathrm{OCH_2}$) atoms as far apart as possible. Inspection of the CSD shows that only 52 crystal structures containing a total of 57 bromoacetoxy fragments have been reported, and *trans* (*t*), *gauche* (*g*) and skew (*s*) conformations have been observed in 21, 21 and 13 fragments, respectively. In the majority of cases, the bromoacetoxy units are either directly linked to aliphatic or aromatic rings or remain in an anionic form. Only six fragments are linked to acyclic C atoms, the *trans* conformation being the preferred one in three compounds [FASXAV (Uhr *et al.*, 1985), PARASB (Fukuyama *et al.*, 1975) and TLOBDH10 (Harada *et al.*, 1966)]. It must be pointed out that a *cis* conformation has been found in only two compounds, a fact that contrasts with the trend observed in some halogenoacetamide fragments [$X\mathrm{CH_2{-}C({=}O)NH}$], where the establishment of intramolecular N—H$\cdots$*X* hydrogen bonds stabilizes the conformation (Rao & Mallikarjunan, 1973; Kalyanaraman *et al.*, 1978; Urpí *et al.*, 2003).

The packing in (I) is characterized by a network of weak intermolecular $\mathrm{CH_2}\cdots\mathrm{OC}$ hydrogen bonds (Fig. 2), where each molecule interacts with its four closest neighbours (Table 2). A two-fold screw axis relates the bromoacetate units that interact. Hydrogen bonds are established along a direction parallel to the crystallographic *b* axis and they have a geometry which is slightly more favourable than that found in the chlorinated derivative, despite the lower electronegativity of the Br atom.

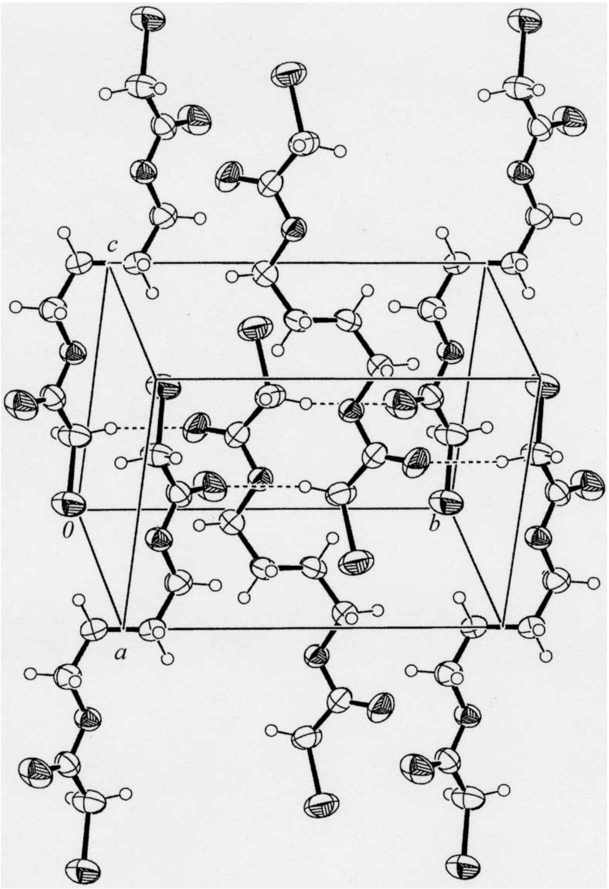


Figure 2
The crystalline packing of (I). The projection view has been selected to show both the molecular conformation and the network of weak hydrogen-bond interactions (dashed lines) between methylene and carbonyl groups.

Experimental

The title compound was synthesized by the dropwise addition of a chloroform solution of 2.2 equivalents of bromoacetyl bromide (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 solution was evaporated under reduced pressure. The white solid obtained was recrystallized from ethanol to give colourless rhombic crystals (yield 70%, m.p. 341 K). ^{1}H NMR (CDCl$_3$, TMS, internal reference, δ, p.p.m.): 4.22 (*m*, 4H, OCH$_2$), 3.84 (*s*, 4H, BrCH$_2$), 1.78 (*m*, 4H, OCH$_2$C*H*$_2$); ^{13}C NMR (CDCl$_3$, TMS, internal reference, δ, p.p.m.): 167.20 (CO), 65.52 (OCH$_2$), 25.70 (BrCH$_2$), 24.95 (OCH$_2$*C*H$_2$).

Crystal data

$C_8H_{12}Br_2O_4$
M_r = 331.98
Monoclinic, $P2_1/c$
a = 8.048 (3) Å
b = 10.039 (2) Å
c = 7.298 (2) Å
β = 100.58 (3)°
V = 579.6 (3) Å^3
Z = 2
D_x = 1.902 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 12–21°
μ = 6.98 mm^{-1}
T = 293 (2) K
Prism, colourless
0.52 × 0.17 × 0.13 mm

Data collection

Enraf-Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (*PLATON*; Spek, 2003)
$T_{\min}$ = 0.302, $T_{\max}$ = 0.463
1784 measured reflections
1684 independent reflections
764 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.086
$\theta_{\max}$ = 30.0°
$h = -11 \rightarrow 0$
$k = -14 \rightarrow 0$
$l = -10 \rightarrow 10$
1 standard reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.065$
$wR(F^2) = 0.180$
$S = 1.01$
1684 reflections
67 parameters
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0813P)^2 + 0.3508P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 0.57 e Å^{-3}
$\Delta\rho_{\min}$ = −0.84 e Å^{-3}

Table 1
Selected torsion angles (°).

C5—O4—C3—O3	−1.5 (9)	O4—C3—C2—Br1	160.3 (4)
C5—O4—C3—C2	175.2 (5)	C3—O4—C5—C6	−178.0 (5)
O3—C3—C2—Br1	−23.0 (9)	C6$^{\rm i}$—C6—C5—O4	−65.0 (9)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C2—H2A···O3$^{\rm ii}$	0.97	2.47	3.403 (9)	161

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

H atoms were placed in calculated positions and were refined isotropically as riding on their attached C atoms, with C—H distances of 0.97 Å. All H atoms belong to CH$_2$ groups. In the asymmetric unit, there are three different CH$_2$ groups. The displacement parameters of the two H atoms of each CH$_2$ group were refined as a common 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* and *WinGX-PC* (Version 1.64.05; Farrugia, 1999).

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References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.
Bocelli, G. & Grenier-Loustalot, M. F. (1984). *Acta Cryst.* C**40**, 679–683.
Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.
Carothers, W. H. (1931). *Chem. Rev.* **8**, 353–426.
Chatani, Y., Okita, H., Tadokoro, H. & Yamashita, Y. (1970). *Polym. J.* **1**, 555–562.

Chu, C. C. (1997). *Wound Closure Biomaterials and Devices*, ch. 5, pp. 65–106. Boca Raton: CRC Press.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Fujimaki, T. (1998). *Polym. Degrad. Stab.* **59**, 209–214.

Fukuyama, K., Kawai, H., Tsukihara, T., Tsukihara, K., Katsube, Y., Hamasaki, T., Hatsuda, Y. & Kuwana, H. (1975). *Bull. Chem. Soc. Jpn*, **48**, 2949–2950.

Harada, H., Sakabe, N., Hirata, Y., Tomiie, Y. & Nitta, I. (1966). *Bull. Chem. Soc. Jpn*, **39**, 1773–1775.

Huang, S. J. (1985). *Encyclopedia of Polymer Science and Engineering*, vol. 2, pp. 230–232. New York: Wiley–Interscience.

Ichikawa, Y., Suzuki, J., Washiyama, J., Moteki, Y., Noguchi, K., Okuyama, K. (1994). *Polymer*, **35**, 3338–3339.

Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kalyanaraman, B., Kispert, L. D. & Atwood, J. L. (1978). *J. Cryst. Mol. Struct.* **8**, 175–181.

Kiers, C. (1994). *CAD-4 Software*. UNIX Version. Enraf–Nonius, Delft, The Netherlands.

Korshak, V. V. & Vinogradova, S. V. (1956). *Zh. Obshch. Khim.* **26**, 539–544.

Palmer, A., Poulin-Dandurand, S. & Brisse, F. (1985). *Can. J. Chem.* **63**, 3079–3088.

Rao, S. T. & Mallikarjunan, M. (1973). *Cryst. Struct. Commun.* **2**, 257–260.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Uhr, H., Zeeck, A., Clegg, W., Egert, E., Fuhrer, H. & Peter, H. H. (1985). *J. Antibiot.* **38**, 1684–1690.

Urpí, L., Jiménez, K., Solans, X., Rodríguez-Galán, A. & Puiggalí, J. (2003). *Acta Cryst.* C**59**, o24–o25.

Urpí, L., Martínez-Palau, M., Font-Bardia, M. & Puiggalí J. (2004). *Acta Cryst.* C**60**, o847–o849.

Vera, M., Rodríguez-Galán, A. & Puiggalí, J. (2004). *Macromol. Rapid Commun.* **25**, 812–817.