C1—N1—C2—C4	−84.6 (2)	C1—N2—C5—C6	115.7 (4)
C1—N1—C2—C3	151.0 (2)	C1—N2—C5—C7	−120.4 (3)
DPTU			
S—C1	1.681 (5)	N1—C2	1.419 (5)
C1—N1	1.349 (4)		
$N1^i$—C1—N1	113.9 (4)	C1—N1—C2	124.6 (3)
$N1^i$—C1—S	123.0 (2)	C7—C2—N1	119.2 (4)
N1—C1—S	123.0 (2)	C3—C2—N1	120.6 (4)

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

The structures were solved by direct methods and refined by a full-matrix least-squares technique. The H atoms were geometrically fixed in the case of DETU and located from difference maps for both DIPTU and DPTU. The large R factors for DETU and DPTU result from the partly disordered structure and/or large displacement factors.

For all compounds, data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990*a*); program(s) used to refine structures: *SHELXL*93 (Sheldrick, 1993); molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); software used to prepare material for publication: *SHELXL*93; geometric calculations: *PARST* (Nardelli, 1983).

One of the authors (KS) thanks the Universiti Sains Malaysia for a Visiting Post Doctoral Research Fellowship.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1179). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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A 2:1 Solid Solution of 6-Chloro-2,3,6-trideoxy-D-*erythro*-hex-2-enono-1,5-lactone and its 6-Bromo Analogue

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Abstract

The structure of an unusual 1:2 mixture of isomorphous bromo and chloro derivatives of a 1,5-lactone, $0.34C_6H_7BrO_3.0.66C_6H_7ClO_3$, is reported, together with the absolute configuration of the molecules. The lactone ring adopts a conformation between sofa and half-chair. The crystal structure is stabilized by O—H···O hydrogen bonds between the hydroxy and carbonyl groups.

Comment

1,5-Lactones are substructures of many natural products (El-Zayat, Ferrigni, McCloud, McKenzie, Byrn, Cassady, Chang & McLaughlin, 1985). Our research group is interested in their synthesis with a view to further expanding them into some of these natural products. We reported previously the synthesis and crystal structure of 2,3-dideoxy-D-*erythro*-hex-2-enono-1,5-lactone, (1), from tri-*O*-acetyl-D-glucal (Fun, Sivakumar, Ang, Sam & Gan, 1995). We are now interested in preparing halides of (1), since they are important intermediates in

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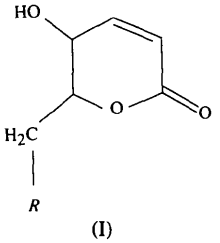
the organic synthesis of various natural pyran-2-ones. Treatment of compound (1) with bromotrichloromethane in anhydrous pyridine (distilled over potassium carbonate) at room temperature for 4 h gave a crystalline product. This product was thought to be the chloro derivative and a single crystal of suitable quality was chosen for X-ray diffraction analysis in order to establish the absolute structure. The structure determination not only established the absolute configuration, but also revealed the compound to be a 1:2 mixture of the bromo and chloro derivatives, (2). The X-ray analysis supports the NMR and gas chromatographic results, which indicated a possible 1:2 mixture of bromo and chloro derivatives. The presence of the two derivatives in a single crystal is intriguing.



(I)

(1) R = OH
(2) R = Br/Cl

An *ORTEP* plot (Johnson, 1965) of the title compound is shown in Fig. 1. The bond lengths and angles observed in the title structure are comparable with those observed in its precursor (1) and other related naturally occurring δ-lactones, such as asperlin, asperlinol (Fukuyama, Katsube, Noda, Hamasaki & Hatsuda, 1978) and goniotriol (Alkofahi, Ma, McKenzie, Byrn & McLaughlin, 1989). In general, the observed bond lengths are shorter than normal values; for example, the C1—C2 single-bond distance of 1.452 (5) Å is much less than the usual value and may be attributed to the effect of the neighbouring C=O and C=C bonds. The Br/Cl—C6 distance of 1.858 (3) Å lies between the C_{sp^3}—Br (1.910 Å) and C_{sp^3}—Cl (1.790 Å) bond lengths (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The lactone ring adopts a conformation intermediate between sofa and half-chair; the corresponding asymmetry parameters are ΔC_s(C2) = 0.077 (2) and ΔC_2(C1–C2) = 0.068 (2) (Nardelli, 1983*a*). This intermediate conformation of the lactone ring is observed in the parent lactone (1), in asperlin and in the chloro derivative of asperlinol, but the sofa conformation is favoured in asperlinol and goniotriol. The introduction of heavy atoms does not change either the conformation or the geometric parameters of the molecule with respect to its precursor molecule (1), but the molecular packing and the crystal system are different, *i.e.* (1) crystallizes in the monoclinic space group $P2_1$.

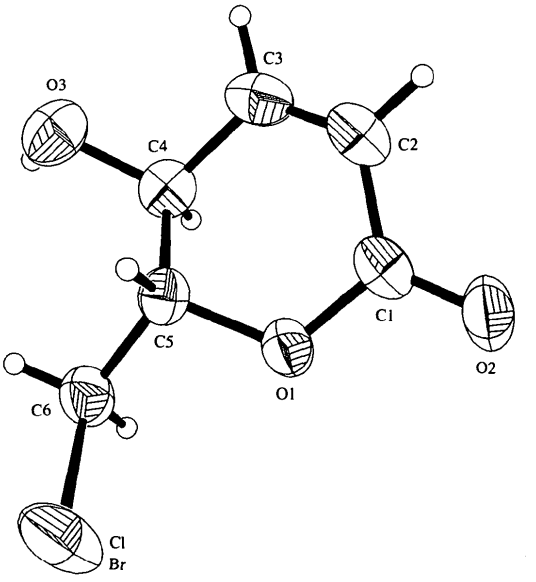


Fig. 1. The structure of the title compound showing the numbering scheme and 50% probability displacement ellipsoids.

In the crystal lattice, the molecules of the title compound are linked by O—H···O hydrogen bonds between the hydroxy and carbonyl groups to form chains along the crystallographic *b* axis, as seen in Fig. 2 [O3—H3O 0.73 (4), O3···O2^{i} 2.848 (4), H3O···O2^{i} 2.13 (4) Å and O3—H3O···O2^{i} 169 (4)°; symmetry code: (i) $-x, y-\frac{1}{2}, -z+\frac{3}{2}$]. In the case of (1), both the hydroxy groups are joined by O—H···O hydrogen bonds, while the carbonyl O2 atom is associated through C—H···O hydrogen bonds with the C4, C5 and C6 atoms of neighbouring molecules. No such C—H···O hydrogen bonds are present in compound (2).

The absolute structure of the molecule was established according to the method described by Flack (1983) and is consistent with the starting products.

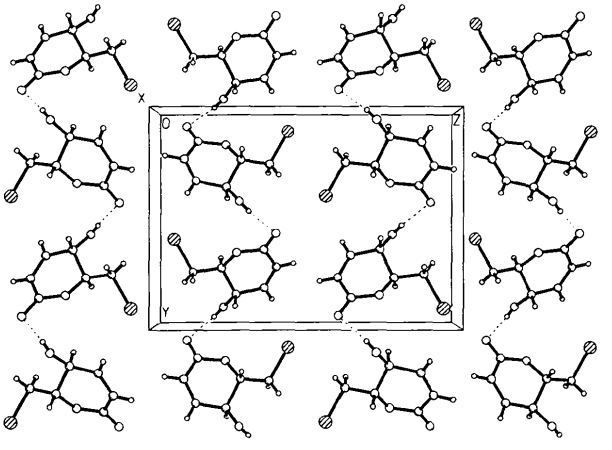


Fig. 2. The packing of molecules, with O—H···O hydrogen bonds represented by dashed lines.

Experimental

Crystals of the title compound were obtained by slow evaporation of a chloroform solution.

Crystal data

$0.34C_6H_7BrO_3.0.66C_6H_7ClO_3$
$M_r = 177.69$
Orthorhombic
$P2_12_12_1$
$a = 4.5232\ (8)$ Å
$b = 10.5764\ (10)$ Å
$c = 14.8003\ (14)$ Å
$V = 708.0\ (2)$ Å^3
$Z = 4$
$D_x = 1.667$ Mg m^{-3}
Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 8$–$20°$
$\mu = 2.270$ mm^{-1}
$T = 293\ (2)$ K
$0.32 \times 0.10 \times 0.08$ mm
Transparent, colourless

Data collection

Siemens $P4$ diffractometer
$\theta/2\theta$ scans
Absorption correction: none
1394 measured reflections
1248 independent reflections
936 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0163$
$\theta_{max} = 27.49°$
$h = -1 \rightarrow 5$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 19$
3 standard reflections monitored every 100 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.0347$
$wR(F^2) = 0.0864$
$S = 0.938$
1248 reflections
121 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0462P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.313$ e Å^{-3}
$\Delta\rho_{min} = -0.255$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0167 (30)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Absolute configuration: Flack (1983) parameter = 0.02 (3)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
Br/Cl†	0.0302 (2)	0.40231 (5)	0.56086 (4)	0.0704 (3)
O1	−0.0101 (6)	0.3414 (2)	0.76777 (11)	0.0401 (6)
O2	−0.1023 (6)	0.4304 (2)	0.89866 (15)	0.0542 (7)
O3	0.4835 (7)	0.0748 (3)	0.7145 (2)	0.0557 (7)
C1	0.0453 (8)	0.3548 (3)	0.8575 (2)	0.0414 (8)
C2	0.2613 (9)	0.2704 (4)	0.8979 (2)	0.0499 (10)
C3	0.3544 (9)	0.1690 (4)	0.8559 (2)	0.0497 (9)
C4	0.2568 (9)	0.1415 (3)	0.7608 (2)	0.0432 (8)
C5	0.1982 (8)	0.2677 (3)	0.7147 (2)	0.0366 (8)
C6	0.0583 (10)	0.2503 (3)	0.6231 (2)	0.0451 (9)

† Occupancy 34% Br + 66% Cl.

Table 2. *Selected geometric parameters* (Å, °)

Br/Cl—C6	1.858 (3)	C1—C2	1.452 (5)
O1—C1	1.358 (3)	C2—C3	1.309 (5)
O1—C5	1.453 (4)	C3—C4	1.503 (5)
O2—C1	1.207 (4)	C4—C5	1.522 (4)
O3—C4	1.421 (4)	C5—C6	1.507 (4)
C1—O1—C5	117.7 (3)	O3—C4—C5	110.2 (3)
O2—C1—O1	117.4 (3)	C3—C4—C5	107.5 (3)
O2—C1—C2	124.8 (3)	O1—C5—C6	106.2 (3)
O1—C1—C2	117.6 (3)	O1—C5—C4	109.9 (3)
C3—C2—C1	121.6 (3)	C6—C5—C4	111.6 (3)
C2—C3—C4	120.6 (3)	C5—C6—Br/Cl	111.7 (2)
O3—C4—C3	109.6 (3)		
C5—O1—C1—O2	169.5 (3)	C1—O1—C5—C4	49.8 (4)
C5—O1—C1—C2	−15.0 (4)	O3—C4—C5—O1	−173.8 (3)
O2—C1—C2—C3	161.0 (4)	C3—C4—C5—O1	−54.4 (4)
O1—C1—C2—C3	−14.0 (5)	O3—C4—C5—C6	68.6 (4)
C1—C2—C3—C4	4.6 (6)	C3—C4—C5—C6	−172.0 (3)
C2—C3—C4—O3	149.3 (4)	O1—C5—C6—Br/Cl	67.3 (3)
C2—C3—C4—C5	29.5 (5)	C4—C5—C6—Br/Cl	−172.8 (3)
C1—O1—C5—C6	170.7 (3)		

The structure was solved by heavy-atom methods and refined by a full-matrix least-squares technique. The structure was initially considered as the chloro derivative, but the refinement did not converge and a subsequent difference map showed many spurious peaks around the Cl-atom position, as well as certain abnormalities in the structural geometry. After careful consideration of the results obtained from spectroscopic analyses, the bromo derivative was also considered as an isomorphous structure, with the Br and Cl atoms occupying the same position. The occupancy of Br/Cl was refined and the final result gave 34% for Br and 66% for Cl. After introduction of the Br atom, the refinement was good and all the H atoms were located from difference Fourier maps and refined isotropically. It should be noted that location of the H atoms was impossible when only the chloro derivative was considered.

Data collection: *XSCANS* (Siemens, 1994). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*); *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL*93. Geometric calculations: *PARST* (Nardelli, 1983*b*).

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1006). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1995). C**51**, 2453–2455

1,3-Bis[4,6-bis(methylthio)-1*H*-pyrazolo[3,4-*d*]pyrimidin-1-yl]propane†

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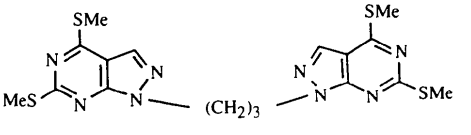
Abstract

In the crystal structure of 1,3-bis[4,6-bis(methylthio)-1*H*-pyrazolo[3,4-*d*]pyrimidin-1-yl]propane, $C_{17}H_{20}N_8S_4$, the molecules exhibit a skewed mode of stacking of the two pyrazolo[3,4-*d*]pyrimidine rings due to an intramolecular π–π interaction between the heterocyclic rings.

† CDRI communication No. 5392.

Comment

Interactions are observed between nucleic acid bases connected by polymethylene chains, particularly the trimethylene chain: *B*—$(CH_2)_3$—*B*′, where *B* and *B*′ are 9-substituted adenine or guanine, 1-substituted cytosine, thymine or uracil residues (Browne, Fisinger & Leonard, 1968). X-ray studies of the trimethylene-bridged compounds 8,8′-trimethylenebistheophylline (Rosen & Hybl, 1971) and 1,1′-trimethylenebisthymine (Frank & Paul, 1973) have revealed unusual intramolecular interactions. The importance of the trimethylene bridge as a synthetic spacer for the detection of intramolecular interactions has been reviewed previously (Leonard, 1979). Pyrazolo[3,4-*d*]pyrimidine compounds which are isomeric with purine compounds are important as they exhibit a variety of biological properties (Elion, 1978; Hupe, 1986; Avasthi *et al.*, 1993). These considerations have led us to develop a general synthesis of 1,*n*-bis-[4,6-bis(methylthio)-1*H*-pyrazolo[3,4-*d*]pyrimidin-1-yl]-alkanes of general structure *P*—$(CH_2)_n$—*P*′, where *P* and *P*′ are pyrazolo[3,4-*d*]pyrimidinyl moieties and *n* = 2–5 (Avasthi, Chandra & Bhakuni, 1995). The unusual features, exhibited by some of these compounds in their high-resolution NMR spectra (Avasthi, Chandra & Bhakuni, 1995) as compared to those of simpler 1-alkylated 4,6-bis(methylthio)-1*H*-pyrazolo[3,4-*d*]pyrimidines (Garg, Avasthi & Bhakuni, 1989), have prompted us to undertake X-ray crystallographic studies of a few of these compounds. The structure determination of the title compound, (I), reported here, is to our knowledge the first X-ray study of a bis(pyrazolo[3,4-*d*]pyrimidinyl)-alkane compound.



(I)

The conformation of the title molecule, along with the atom-numbering scheme, is shown in Fig. 1. The molecule contains two symmetrical pyrazolo[3,4-*d*]pyrimidine rings (with SMe groups substituted at the 4 and 6 positions) connected by a trimethylene bridge. Similar to the corresponding bistheophylline and bisthymine structures (Rosen & Hybl, 1971; Frank & Paul, 1973), this molecule is folded at the centre of the bridge [C(8)—C(9)—C(10) 114.1 (2)°]. The skewed mode of stacking of the two pyrazolo[3,4-*d*]pyrimidine rings occurs in such a way that only part of the six-membered rings overlap (Fig. 2). The overlapping regions are separated by an average distance of 3.4 Å, as observed in the case of stacked purinophanes (Seyama *et al.*, 1988). However, the most striking feature is the fact that the title molecule is connected by only one bridge, while purinophanes (Seyama *et al.*, 1988) are connected