# 6-[Bis(ethoxycarbonyl)methyl]-6-deoxy-1,2;3,4-di-O-isopropylidene-D-galacto-pyranose

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The title compound, $C_{19}H_{30}O_9$, was prepared by substitution at the C6 position in 1,2;3,4-di-O-isopropylidene-6-O-trifluoromethanesulfonyl-D-galactose using sodium ethoxy-malonate in dimethylformamide. The conformation is skew-boat $^0S_2$, slightly distorted towards boat $B_{2,5}$. The inflexible pyranose structure makes the title compound a suitable intermediate for further synthetic work by keeping stereo-genic carbon atoms safe from inversion. Several short intramolecular C—H$\cdots$O contacts may stabilize the confor-mation of the molecule. Intermolecular C—H$\cdots$O inter-actions also occur.

## Related literature

For syntheses of this and similar compounds, see: Bouhlal et al. (2001); Doboszewski et al. (1987); Honeyman & Stening (1958); Sugihara et al. (1963); Tipson (1953); Cipolla et al. (1996). For the structures of diisopropylidene-galactopyranose and related compounds, see: Krajewski et al. (1990, 1994); Coutrot et al. (2001); Weaver et al. (2004, 2006); Boeyens et al. (1978); Berces et al. (2001). For conformations of small rings, see: Schwarz (1973); Cremer & Pople (1975); Boeyens (1978); Hill & Reilly (2007); Köll et al. (1994). For analysis of absolute structure, see: Flack (1983); Hooft et al. (2008).
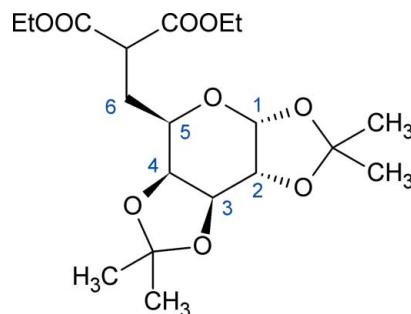


## Experimental

### Crystal data

| | |
|---|---|
| $C_{19}H_{30}O_9$ | $V$ = 2155.9 (2) Å$^3$ |
| $M_r$ = 402.43 | $Z$ = 4 |
| Orthorhombic, $P2_12_12_1$ | Cu $K\alpha$ radiation |
| $a$ = 8.3287 (4) Å | $\mu$ = 0.83 mm$^{-1}$ |
| $b$ = 10.8895 (4) Å | $T$ = 292 K |
| $c$ = 23.7706 (16) Å | 0.38 × 0.26 × 0.21 mm |

### Data collection

| | |
|---|---|
| Rigaku R-AXIS RAPID II imaging plate diffractometer | 9353 measured reflections |
| | 3745 independent reflections |
| Absorption correction: multi-scan (ABSCOR; Higashi,1995) | 2824 reflections with $I > 2\sigma(I)$ |
| $T_{min}$ = 0.822, $T_{max}$ = 0.840 | $R_{int}$ = 0.075 |

### Refinement

| | |
|---|---|
| $R[F^2 > 2\sigma(F^2)]$ = 0.040 | $\Delta\rho_{max}$ = 0.19 e Å$^{-3}$ |
| $wR(F^2)$ = 0.096 | $\Delta\rho_{min}$ = −0.15 e Å$^{-3}$ |
| $S$ = 1.02 | Absolute structure: Flack (1983), |
| 3745 reflections | 1607 Friedel pairs |
| 275 parameters | Flack parameter: 0.06 (18) |
| H atoms treated by a mixture of independent and constrained refinement | |

**Table 1**
Hydrogen-bond geometry (Å, °).

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C1—H1$A\cdots$O9$^i$ | 0.98 | 2.43 | 3.381 (3) | 163 |
| C5—H5$A\cdots$O7 | 1.01 | 2.59 | 3.185 (3) | 117 |
| C8—H8$B\cdots$O7$^i$ | 1.03 | 2.56 | 3.577 (3) | 169 |
| C12—H12$A\cdots$O5 | 1.02 | 2.42 | 2.811 (3) | 102 |
| C13—H13$A\cdots$O1 | 0.96 | 2.43 | 2.814 (3) | 103 |
| C16—H16$B\cdots$O1$^{ii}$ | 0.99 | 2.51 | 3.422 (3) | 153 |

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 1, y + \frac{1}{2}, -z + \frac{1}{2}$.

Data collection: *CrystalClear-SM Expert* (Rigaku, 2009); cell refinement: *HKL-2000* (Otwinowski & Minor, 1997); data reduction: *CrystalClear-SM Expert*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2009).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZL2327).

# organic compounds

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**supplementary materials**

## 6-[Bis(ethoxycarbonyl)methyl]-6-deoxy-1,2;3,4-di-*O*-isopropylidene-D-galactopyranose

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### Comment

The title compound is an intermediate for the synthesis of a wide range of chain-extended galactopyranoses, which in turn are considered as precursors of chiral α-hydroxycarboxylic acids. The stereogenic atom C5 is retained in the target compounds. Knowledge of exact geometry of the intermediate is helpful for better understanding of upcoming steps in this ongoing synthetic project.

To realise these objectives we (BD & PRS) have prepared the title compound by substitution at the C6 position in 1,2;3,4-di-*O*-isopropylidene-6-*O*-trifluoromethanesulfonyl-D-galactose using sodium ethoxymalonate. Substitutions at this atom in diisopropylidene-galactose are rather difficult and require prolonged reaction times and/or elevated temperatures (Tipson, 1953, Honeyman & Stening, 1958, Sugihara *et al.*, 1963, Bouhlal *et al.*, 2001). Howeever, by using the best available leaving group, a trifluoromethanesulfonate, smooth nucleophilic substitution can been accomplished in less than 10 min (Doboszewski *et al.*, 1987).

The absolute structure of 6-deoxy-6-(diethylmalonyl)-1,2;3,4-di-*O* -isopropylidene-D-galactopyranose is certain from the synthetic route which does not affect asymmetric atoms of the starting compound. Nevertheless, we preferred to receive a direct experimental confirmation using X-ray diffractometry data. Because there are no heavy atoms in a chiral molecule of title compound, Cu *K*α radiation was necessary for determination of the absolute structure.

In the crystal structure of title compound (Fig.1), all bond lengths and bond angles have standard dimensions.

Fig. 2 shows that the pyranose ring adopts a skew-boat with atoms C1, C3, C4, and C5 being within 0.03–0.08 Å from their mean plane, and O1 and C2 atoms being at 0.633 (2) and -0.557 (2) Å, respectively. Such conformation is named $^OS_2$ in the IUPAC notation (Schwarz, 1973). A quantitative analysis of the ring conformations in the titlw compound was performed using the method of Cremer and Pople (Cremer & Pople, 1975, Boeyens, 1978) for the calculation of parameters of puckering. The polar parameters for the pyranose ring are $Q$ = 0.639 (2) Å, $\Phi$ = 325.1 (2)°, and $\theta$ = 80.3 (2)°. These suggest the conformation as skew-boat $^0S_2$ ($\Phi$ = 330°, $\theta$ = 90°), slightly distorted towards boat $B_{2,5}$, ($\Phi$ = 300°, $\theta$ = 90°); the same conformation is designated as a twist-boat $^OT_2$ when using the Boeyenes nomenclature. This conformation is similar to many other known galactopyranoses with two substituent isopropylidene rings (see, for example, POCSUV (Krajewski *et al.*, 1994): $Q$ = 0.632 (5) Å, $\theta$ = 82.8 (5)°, $\Phi$ = 327.4 (4)°; JERJIUL (Krajewski *et al.*, 1990): $Q$ = 0.631 (5) Å, $\theta$ = 79.7 (5)°, $\Phi$ = 324.9 (5)°; ICALED (Coutrot *et al.*, 2001): $Q$ = 0.646 (4) Å, $\theta$ = 83.9 (4)°, $\Phi$ = 334.2 (3)°; BIHZUO (Weaver *et al.*, 2004): $Q$ = 0.661 (2) Å, $\theta$ = 81.3 (2)°, $\Phi$ = 327.1 (2)°; ADXPOP (Boeyens, Rathbone & Woolard,1978): $Q$ = 0.65 Å, $\Phi$ = 329°, $\theta$ = 81°). All conformations of substituted compounds are radically different from the chair conformation of unsubstituted α -D-galactopyranose. This is caused by the presence of the two isopropylidene substituents that make the geometry of the pyranose ring more rigid and less sensitive towards any effects of substituents at the remaining C5 position. A detailed discussion of terminology and different puckering coordinates being used to describe six-membered non-aromatic cycles can be found in Hill & Reilly (2007) and Köll *et al.* (1994).

# supplementary materials

The same approach yielded the parameters of puckering Q(2) = 0.279 (2) Å, Φ = 283.3 (4)° and Q(2) = 0.234 (2) Å, Φ = 177.1 (7)° for the 1,2- and 3,4- isopropylidene rings. These values correspond to the envelope conformations $^4E$ (Φ = 288°) and $E_1$ (Φ = 180°) with atoms O3 and O4 being out of their corresponding planes by 0.426 (2) and 0.357 (2) Å correspondingly (Fig. 3 and 4). All other atoms in both five-membered rings are located within 0.01 Å from their mean planes.

No classic hydrogen bonds are possible for the title compound. However, several short C—H··· O contacts were detected that possibly stabilize the existing conformation of the molecule (Table 1).

The inflexible pyranose structure makes the title compound a suitable intermediate for further synthetic work by keeping the stereogenic carbon atoms C1—C5 safe from inversion. For the same reason, it is very probable that in solution this molecule will keep almost the same geometry as in the molecular crystal.

## Experimental

Synthesis of the title compound was accomplished similar to previuosly published fluorination reaction (Doboszewski *et al.*, 1987). We treated 1,2;3,4-di-*O*-isopropylidene-6-*O*-trifluoromethanesulfonyl-D- galactose with sodium ethoxymalonate in dimethylformamide at 333 K; the title compound was isolated in 80% yield (Figure 5). The compound is identical to previously obtained *via* a free-radical process in low yield (Cipolla *et al.*, 1996). Spontaneous crystallization from a hexane-ethyl acetate system yielded colourless crystals suitable for single-crystal diffractometry (m.p. 331–334 K).

## Refinement

The chirality of the title compound was known from the synthetic route; it was also examined using anomalous scattering. Analysis of the absolute structure using likelihood methods (Hooft *et al.*, 2008) was performed using *PLATON* (Spek, 2003); 1570 Bijvoet pairs were employed. The results confirmed that the absolute structure had been correctly assigned: the probability that the structure is inverted is smaller than $10^{-9}$ with probability of racemic twinning at 0.002. Because no atom heavier than O is present, the standard deviation of the Flack parameter is relatively high. All H atoms were positioned geometrically and refined using a riding model, with C–H = 0.99–1.03 Å and $U_{iso}$(H) = 1.2 or 1.5 $U_{eq}$(C). The rotating group model was applied for the methyl groups.

## Figures
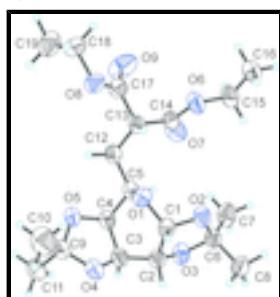


Fig. 1. The title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitary radius.
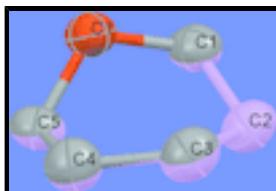
Fig. 2. Conformation of the six-membered ring: mean plane drawn through C1—C3—C4—C5.
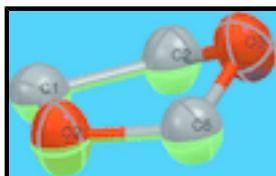


Fig. 3. Conformation of the five-membered isopropylidene ring: plane through C1 C2 C6 O2.
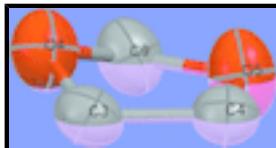


Fig. 4. Conformation of the five-membered isopropylidene ring: plane through C3 C9 O5 C4.
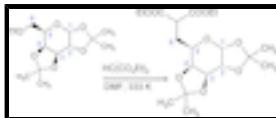


Fig. 5. Synthetic route towards the title compound.

## 6-[Bis(ethoxycarbonyl)methyl]-6-deoxy-1,2;3,4-di-*O*-isopropylidene- D-galactopyranose

*Crystal data*

| | |
|---|---|
| $C_{19}H_{30}O_9$ | $D_x = 1.240$ Mg m$^{-3}$ |
| $M_r = 402.43$ | Melting point: 322 K |
| Orthorhombic, $P2_12_12_1$ | Cu $K\alpha$ radiation, $\lambda = 1.54187$ Å |
| Hall symbol: P 2ac 2ab | Cell parameters from 9579 reflections |
| $a = 8.3287$ (4) Å | $\theta = 6.7–68.2°$ |
| $b = 10.8895$ (4) Å | $\mu = 0.83$ mm$^{-1}$ |
| $c = 23.7706$ (16) Å | $T = 292$ K |
| $V = 2155.9$ (2) Å$^3$ | Prism, colourless |
| $Z = 4$ | $0.38 \times 0.26 \times 0.21$ mm |
| $F(000) = 864$ | |

*Data collection*

| | |
|---|---|
| Rigaku R-AXIS RAPID II imaging plate diffractometer | 3745 independent reflections |
| Radiation source: fine-focus sealed tube | 2824 reflections with $I > 2\sigma(I)$ |
| graphite | $R_{int} = 0.075$ |
| Detector resolution: 10 pixels mm$^{-1}$ | $\theta_{max} = 66.5°$, $\theta_{min} = 6.7°$ |
| $\omega$ scans | $h = -6 \rightarrow 9$ |
| Absorption correction: multi-scan (*ABSCOR*; Higashi,1995) | $k = -12 \rightarrow 10$ |
| $T_{min} = 0.822$, $T_{max} = 0.840$ | $l = -28 \rightarrow 19$ |
| 9353 measured reflections | |

*Refinement*

| | |
|---|---|
| Refinement on $F^2$ | Hydrogen site location: inferred from neighbouring sites |
| Least-squares matrix: full | H atoms treated by a mixture of independent and constrained refinement |
| $R[F^2 > 2\sigma(F^2)] = 0.040$ | $w = 1/[\sigma^2(F_o^2) + (0.0285P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ |
| $wR(F^2) = 0.096$ | $(\Delta/\sigma)_{max} < 0.001$ |
| $S = 1.02$ | $\Delta\rho_{max} = 0.19$ e Å$^{-3}$ |
| 3745 reflections | $\Delta\rho_{min} = -0.15$ e Å$^{-3}$ |
| 275 parameters | Extinction correction: *SHELXL*, Fc$^*$=kFc[1+0.001xFc$^2\lambda^3$/sin(2θ)]$^{-1/4}$ |
| 0 restraints | Extinction coefficient: 0.0057 (5) |
| Primary atom site location: structure-invariant direct methods | Absolute structure: Flack (1983), 1607 Friedel pairs |
| Secondary atom site location: difference Fourier map | Flack parameter: 0.06 (18) |

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å$^2$)*

| | $x$ | $y$ | $z$ | $U_{iso}*/U_{eq}$ |
|---|---|---|---|---|
| O1 | 0.30842 (18) | 0.05824 (11) | 0.37716 (6) | 0.0531 (4) |
| O2 | 0.2263 (2) | 0.25329 (12) | 0.35151 (6) | 0.0653 (5) |
| O3 | 0.2044 (2) | 0.30221 (12) | 0.44385 (6) | 0.0646 (5) |
| O4 | 0.0989 (2) | −0.00622 (15) | 0.48415 (7) | 0.0747 (5) |
| O5 | 0.3563 (2) | −0.07330 (14) | 0.48515 (7) | 0.0817 (6) |
| O6 | 0.6685 (2) | 0.16820 (13) | 0.27264 (7) | 0.0718 (5) |
| O7 | 0.7237 (2) | 0.22413 (15) | 0.36113 (7) | 0.0852 (6) |
| O8 | 0.7062 (2) | −0.17738 (13) | 0.31233 (6) | 0.0666 (5) |
| O9 | 0.8976 (2) | −0.03812 (18) | 0.32008 (11) | 0.1155 (9) |
| C1 | 0.1819 (3) | 0.14252 (17) | 0.37891 (9) | 0.0523 (6) |
| H1A | 0.088 (2) | 0.1070 (8) | 0.3597 (4) | 0.063* |
| C2 | 0.1329 (3) | 0.18443 (17) | 0.43770 (9) | 0.0573 (6) |
| H2A | 0.012 (3) | 0.1918 (2) | 0.43999 (11) | 0.069* |
| C3 | 0.1939 (3) | 0.10213 (19) | 0.48485 (10) | 0.0600 (6) |

| | | | | |
|---|---|---|---|---|
| H3A | 0.1836 (4) | 0.1456 (10) | 0.5227 (8) | 0.072* |
| C4 | 0.3665 (3) | 0.0557 (2) | 0.47632 (9) | 0.0566 (6) |
| H4A | 0.4367 (16) | 0.0921 (8) | 0.5044 (6) | 0.068* |
| C5 | 0.4315 (3) | 0.0817 (2) | 0.41783 (9) | 0.0490 (5) |
| H5A | 0.4630 (7) | 0.1708 (18) | 0.41554 (10) | 0.059* |
| C6 | 0.2124 (3) | 0.35512 (18) | 0.38911 (9) | 0.0580 (6) |
| C7 | 0.3592 (3) | 0.4335 (2) | 0.38497 (12) | 0.0860 (10) |
| H7A | 0.3572 (11) | 0.4945 (14) | 0.4142 (7) | 0.129* |
| H7B | 0.3615 (12) | 0.4733 (15) | 0.3489 (6) | 0.129* |
| H7C | 0.4532 (15) | 0.3831 (8) | 0.3892 (8) | 0.129* |
| C8 | 0.0607 (3) | 0.4254 (2) | 0.37542 (11) | 0.0742 (8) |
| H8A | 0.0457 (11) | 0.4951 (13) | 0.4040 (6) | 0.111* |
| H8B | −0.0360 (13) | 0.3671 (8) | 0.3773 (7) | 0.111* |
| H8C | 0.0694 (9) | 0.4617 (14) | 0.3357 (6) | 0.111* |
| C9 | 0.1971 (3) | −0.1063 (2) | 0.49989 (10) | 0.0657 (7) |
| C10 | 0.1486 (5) | −0.2177 (2) | 0.46606 (14) | 0.1124 (13) |
| H10A | 0.034 (2) | −0.2405 (13) | 0.4754 (7) | 0.169* |
| H10B | 0.222 (2) | −0.2886 (14) | 0.4756 (8) | 0.169* |
| H10C | 0.157 (3) | −0.1985 (8) | 0.4246 (7) | 0.169* |
| C11 | 0.1883 (4) | −0.1306 (3) | 0.56235 (11) | 0.0901 (10) |
| H11A | 0.0735 (17) | −0.1545 (17) | 0.5730 (2) | 0.135* |
| H11B | 0.221 (2) | −0.0531 (13) | 0.5838 (3) | 0.135* |
| H11C | 0.265 (2) | −0.2007 (15) | 0.5725 (2) | 0.135* |
| C12 | 0.5762 (3) | 0.00309 (19) | 0.40257 (9) | 0.0557 (6) |
| H12A | 0.5494 (4) | −0.0868 (13) | 0.40954 (15) | 0.067* |
| H12B | 0.6699 (14) | 0.0260 (3) | 0.4279 (4) | 0.067* |
| C13 | 0.6261 (3) | 0.01977 (16) | 0.34089 (9) | 0.0510 (6) |
| H13A | 0.535 (2) | 0.0017 (4) | 0.3179 (5) | 0.061* |
| C14 | 0.6788 (3) | 0.1493 (2) | 0.32781 (11) | 0.0585 (6) |
| C15 | 0.7163 (4) | 0.2883 (2) | 0.25156 (13) | 0.0870 (10) |
| H15A | 0.826 (2) | 0.3111 (5) | 0.2665 (3) | 0.104* |
| H15B | 0.6368 (15) | 0.3532 (13) | 0.2641 (3) | 0.104* |
| C16 | 0.7196 (4) | 0.2807 (2) | 0.18966 (12) | 0.0887 (10) |
| H16A | 0.799 (2) | 0.2184 (16) | 0.1779 (2) | 0.133* |
| H16B | 0.750 (2) | 0.3614 (13) | 0.1739 (3) | 0.133* |
| H16C | 0.6122 (18) | 0.2572 (17) | 0.1757 (3) | 0.133* |
| C17 | 0.7604 (3) | −0.0665 (2) | 0.32388 (10) | 0.0608 (6) |
| C18 | 0.8256 (3) | −0.2666 (2) | 0.29360 (12) | 0.0725 (8) |
| H18A | 0.9058 (14) | −0.2830 (3) | 0.3248 (5) | 0.087* |
| H18B | 0.8859 (11) | −0.2336 (6) | 0.2598 (5) | 0.087* |
| C19 | 0.7401 (4) | −0.3825 (2) | 0.27835 (11) | 0.0828 (10) |
| H19A | 0.6860 (18) | −0.4159 (10) | 0.3119 (5) | 0.124* |
| H19B | 0.8182 (11) | −0.4430 (10) | 0.2641 (7) | 0.124* |
| H19C | 0.6597 (18) | −0.3651 (4) | 0.2490 (6) | 0.124* |

*Atomic displacement parameters ($Å^2$)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|

| | | | | | | |
|---|---|---|---|---|---|---|
| O1 | 0.0620 (10) | 0.0461 (7) | 0.0511 (9) | 0.0023 (8) | −0.0101 (7) | −0.0076 (7) |
| O2 | 0.0976 (13) | 0.0470 (8) | 0.0515 (9) | 0.0008 (8) | 0.0044 (9) | 0.0014 (6) |
| O3 | 0.0955 (13) | 0.0472 (8) | 0.0510 (9) | 0.0018 (9) | −0.0093 (9) | −0.0041 (7) |
| O4 | 0.0744 (13) | 0.0687 (10) | 0.0811 (13) | −0.0030 (10) | 0.0129 (9) | 0.0232 (9) |
| O5 | 0.0809 (13) | 0.0615 (9) | 0.1028 (14) | 0.0083 (10) | 0.0273 (11) | 0.0349 (9) |
| O6 | 0.0982 (15) | 0.0526 (8) | 0.0645 (11) | −0.0142 (9) | 0.0074 (10) | 0.0135 (8) |
| O7 | 0.1065 (16) | 0.0676 (10) | 0.0814 (13) | −0.0359 (11) | 0.0086 (12) | −0.0092 (9) |
| O8 | 0.0630 (11) | 0.0515 (8) | 0.0854 (12) | −0.0037 (9) | 0.0082 (10) | −0.0091 (8) |
| O9 | 0.0547 (12) | 0.0826 (12) | 0.209 (3) | −0.0130 (11) | 0.0071 (14) | −0.0325 (14) |
| C1 | 0.0597 (15) | 0.0464 (11) | 0.0508 (13) | −0.0018 (12) | −0.0106 (12) | −0.0010 (9) |
| C2 | 0.0730 (18) | 0.0486 (12) | 0.0504 (14) | 0.0037 (12) | 0.0039 (12) | −0.0024 (10) |
| C3 | 0.0764 (18) | 0.0570 (12) | 0.0466 (14) | 0.0017 (14) | 0.0079 (13) | 0.0032 (10) |
| C4 | 0.0679 (17) | 0.0551 (12) | 0.0467 (13) | −0.0024 (13) | −0.0017 (12) | 0.0068 (11) |
| C5 | 0.0588 (15) | 0.0430 (10) | 0.0452 (13) | −0.0078 (11) | −0.0057 (11) | 0.0016 (9) |
| C6 | 0.0759 (18) | 0.0446 (11) | 0.0534 (14) | 0.0025 (13) | −0.0021 (13) | 0.0002 (10) |
| C7 | 0.087 (2) | 0.0612 (15) | 0.110 (2) | −0.0130 (16) | −0.0115 (17) | 0.0115 (15) |
| C8 | 0.0827 (19) | 0.0598 (14) | 0.0800 (19) | 0.0081 (15) | −0.0057 (14) | 0.0083 (13) |
| C9 | 0.0756 (19) | 0.0581 (13) | 0.0635 (16) | 0.0010 (14) | 0.0195 (15) | 0.0125 (11) |
| C10 | 0.146 (4) | 0.0824 (19) | 0.108 (3) | −0.020 (2) | 0.013 (2) | −0.0156 (18) |
| C11 | 0.109 (2) | 0.0972 (19) | 0.0644 (17) | 0.015 (2) | 0.0238 (17) | 0.0259 (15) |
| C12 | 0.0600 (15) | 0.0517 (11) | 0.0555 (15) | −0.0035 (13) | −0.0012 (12) | 0.0091 (10) |
| C13 | 0.0539 (14) | 0.0458 (11) | 0.0534 (14) | −0.0058 (11) | 0.0009 (11) | 0.0032 (10) |
| C14 | 0.0595 (17) | 0.0515 (12) | 0.0645 (16) | −0.0050 (12) | 0.0059 (13) | 0.0027 (11) |
| C15 | 0.113 (3) | 0.0524 (13) | 0.096 (2) | −0.0125 (16) | 0.026 (2) | 0.0189 (14) |
| C16 | 0.091 (2) | 0.0784 (17) | 0.096 (2) | 0.0061 (17) | 0.0249 (19) | 0.0356 (16) |
| C17 | 0.0568 (17) | 0.0571 (13) | 0.0684 (16) | −0.0068 (13) | 0.0037 (13) | −0.0003 (12) |
| C18 | 0.0680 (19) | 0.0702 (15) | 0.0794 (18) | 0.0135 (16) | 0.0072 (15) | −0.0077 (13) |
| C19 | 0.109 (3) | 0.0585 (14) | 0.0807 (19) | 0.0077 (16) | −0.0041 (17) | −0.0091 (13) |

*Geometric parameters (Å, °)*

| | | | |
|---|---|---|---|
| O1—C1 | 1.398 (2) | C7—H7C | 0.9614 |
| O1—C5 | 1.432 (2) | C8—H8A | 1.0264 |
| O2—C1 | 1.420 (2) | C8—H8B | 1.0264 |
| O2—C6 | 1.429 (2) | C8—H8C | 1.0264 |
| O3—C2 | 1.422 (2) | C9—C11 | 1.510 (3) |
| O3—C6 | 1.425 (2) | C9—C10 | 1.511 (4) |
| O4—C9 | 1.413 (3) | C10—H10A | 1.0094 |
| O4—C3 | 1.421 (2) | C10—H10B | 1.0094 |
| O5—C9 | 1.418 (3) | C10—H10C | 1.0094 |
| O5—C4 | 1.423 (3) | C11—H11A | 1.0229 |
| O6—C14 | 1.330 (3) | C11—H11B | 1.0229 |
| O6—C15 | 1.456 (2) | C11—H11C | 1.0229 |
| O7—C14 | 1.196 (3) | C12—C13 | 1.535 (3) |
| O8—C17 | 1.317 (3) | C12—H12A | 1.0171 |
| O8—C18 | 1.460 (3) | C12—H12B | 1.0171 |
| O9—C17 | 1.187 (3) | C13—C14 | 1.509 (3) |
| C1—C2 | 1.526 (3) | C13—C17 | 1.515 (3) |
| C1—H1A | 0.9878 | C13—H13A | 0.9571 |

| | | | |
|---|---|---|---|
| C2—C3 | 1.523 (3) | C15—C16 | 1.474 (4) |
| C2—H2A | 1.0091 | C15—H15A | 1.0130 |
| C3—C4 | 1.537 (3) | C15—H15B | 1.0130 |
| C3—H3A | 1.0200 | C16—H16A | 0.9879 |
| C4—C5 | 1.518 (3) | C16—H16B | 0.9879 |
| C4—H4A | 0.9713 | C16—H16C | 0.9879 |
| C5—C12 | 1.522 (3) | C18—C19 | 1.494 (3) |
| C5—H5A | 1.0065 | C18—H18A | 1.0133 |
| C6—C7 | 1.494 (3) | C18—H18B | 1.0133 |
| C6—C8 | 1.513 (3) | C19—H19A | 0.9857 |
| C7—H7A | 0.9614 | C19—H19B | 0.9857 |
| C7—H7B | 0.9614 | C19—H19C | 0.9857 |
| | | | |
| C1—O1—C5 | 113.72 (15) | O4—C9—C10 | 108.9 (2) |
| C1—O2—C6 | 110.56 (16) | O5—C9—C10 | 108.8 (2) |
| C2—O3—C6 | 106.90 (15) | C11—C9—C10 | 111.7 (2) |
| C9—O4—C3 | 108.33 (17) | C9—C10—H10A | 109.5 |
| C9—O5—C4 | 110.03 (18) | C9—C10—H10B | 109.5 |
| C14—O6—C15 | 117.44 (19) | H10A—C10—H10B | 109.5 |
| C17—O8—C18 | 116.12 (19) | C9—C10—H10C | 109.5 |
| O1—C1—O2 | 110.33 (18) | H10A—C10—H10C | 109.5 |
| O1—C1—C2 | 115.16 (18) | H10B—C10—H10C | 109.5 |
| O2—C1—C2 | 103.64 (15) | C9—C11—H11A | 109.5 |
| O1—C1—H1A | 109.2 | C9—C11—H11B | 109.5 |
| O2—C1—H1A | 109.2 | H11A—C11—H11B | 109.5 |
| C2—C1—H1A | 109.2 | C9—C11—H11C | 109.5 |
| O3—C2—C3 | 108.38 (19) | H11A—C11—H11C | 109.5 |
| O3—C2—C1 | 104.60 (18) | H11B—C11—H11C | 109.5 |
| C3—C2—C1 | 114.14 (18) | C5—C12—C13 | 112.06 (17) |
| O3—C2—H2A | 109.8 | C5—C12—H12A | 109.2 |
| C3—C2—H2A | 109.8 | C13—C12—H12A | 109.2 |
| C1—C2—H2A | 109.8 | C5—C12—H12B | 109.2 |
| O4—C3—C2 | 107.09 (19) | C13—C12—H12B | 109.2 |
| O4—C3—C4 | 104.26 (18) | H12A—C12—H12B | 107.9 |
| C2—C3—C4 | 114.1 (2) | C14—C13—C17 | 108.06 (19) |
| O4—C3—H3A | 110.4 | C14—C13—C12 | 112.71 (17) |
| C2—C3—H3A | 110.4 | C17—C13—C12 | 112.42 (17) |
| C4—C3—H3A | 110.4 | C14—C13—H13A | 107.8 |
| O5—C4—C5 | 109.92 (18) | C17—C13—H13A | 107.8 |
| O5—C4—C3 | 104.44 (18) | C12—C13—H13A | 107.8 |
| C5—C4—C3 | 113.11 (19) | O7—C14—O6 | 124.5 (2) |
| O5—C4—H4A | 109.7 | O7—C14—C13 | 126.2 (2) |
| C5—C4—H4A | 109.7 | O6—C14—C13 | 109.2 (2) |
| C3—C4—H4A | 109.7 | O6—C15—C16 | 107.3 (2) |
| O1—C5—C4 | 109.26 (18) | O6—C15—H15A | 110.2 |
| O1—C5—C12 | 107.79 (17) | C16—C15—H15A | 110.2 |
| C4—C5—C12 | 113.28 (17) | O6—C15—H15B | 110.2 |
| O1—C5—H5A | 108.8 | C16—C15—H15B | 110.2 |
| C4—C5—H5A | 108.8 | H15A—C15—H15B | 108.5 |
| C12—C5—H5A | 108.8 | C15—C16—H16A | 109.5 |

| | | | |
|---|---|---|---|
| O3—C6—O2 | 105.14 (15) | C15—C16—H16B | 109.5 |
| O3—C6—C7 | 109.3 (2) | H16A—C16—H16B | 109.5 |
| O2—C6—C7 | 109.6 (2) | C15—C16—H16C | 109.5 |
| O3—C6—C8 | 111.2 (2) | H16A—C16—H16C | 109.5 |
| O2—C6—C8 | 109.00 (19) | H16B—C16—H16C | 109.5 |
| C7—C6—C8 | 112.36 (18) | O9—C17—O8 | 123.5 (2) |
| C6—C7—H7A | 109.5 | O9—C17—C13 | 124.7 (2) |
| C6—C7—H7B | 109.5 | O8—C17—C13 | 111.8 (2) |
| H7A—C7—H7B | 109.5 | O8—C18—C19 | 108.2 (2) |
| C6—C7—H7C | 109.5 | O8—C18—H18A | 110.1 |
| H7A—C7—H7C | 109.5 | C19—C18—H18A | 110.1 |
| H7B—C7—H7C | 109.5 | O8—C18—H18B | 110.1 |
| C6—C8—H8A | 109.5 | C19—C18—H18B | 110.1 |
| C6—C8—H8B | 109.5 | H18A—C18—H18B | 108.4 |
| H8A—C8—H8B | 109.5 | C18—C19—H19A | 109.5 |
| C6—C8—H8C | 109.5 | C18—C19—H19B | 109.5 |
| H8A—C8—H8C | 109.5 | H19A—C19—H19B | 109.5 |
| H8B—C8—H8C | 109.5 | C18—C19—H19C | 109.5 |
| O4—C9—O5 | 106.31 (17) | H19A—C19—H19C | 109.5 |
| O4—C9—C11 | 111.6 (2) | H19B—C19—H19C | 109.5 |
| O5—C9—C11 | 109.4 (2) | | |
| | | | |
| C5—O1—C1—O2 | 78.7 (2) | C2—O3—C6—C7 | −146.7 (2) |
| C5—O1—C1—C2 | −38.2 (2) | C2—O3—C6—C8 | 88.7 (2) |
| C6—O2—C1—O1 | −122.13 (19) | C1—O2—C6—O3 | 16.5 (3) |
| C6—O2—C1—C2 | 1.7 (3) | C1—O2—C6—C7 | 133.8 (2) |
| C6—O3—C2—C3 | 152.18 (19) | C1—O2—C6—C8 | −102.8 (2) |
| C6—O3—C2—C1 | 30.0 (2) | C3—O4—C9—O5 | −26.3 (2) |
| O1—C1—C2—O3 | 101.3 (2) | C3—O4—C9—C11 | 93.0 (3) |
| O2—C1—C2—O3 | −19.2 (2) | C3—O4—C9—C10 | −143.3 (2) |
| O1—C1—C2—C3 | −16.9 (3) | C4—O5—C9—O4 | 17.1 (3) |
| O2—C1—C2—C3 | −137.5 (2) | C4—O5—C9—C11 | −103.5 (2) |
| C9—O4—C3—C2 | 145.74 (19) | C4—O5—C9—C10 | 134.2 (2) |
| C9—O4—C3—C4 | 24.4 (2) | O1—C5—C12—C13 | 51.9 (2) |
| O3—C2—C3—O4 | 169.21 (18) | C4—C5—C12—C13 | 172.91 (19) |
| C1—C2—C3—O4 | −74.7 (3) | C5—C12—C13—C14 | 62.8 (2) |
| O3—C2—C3—C4 | −76.0 (2) | C5—C12—C13—C17 | −174.81 (18) |
| C1—C2—C3—C4 | 40.2 (3) | C15—O6—C14—O7 | 0.4 (4) |
| C9—O5—C4—C5 | −123.7 (2) | C15—O6—C14—C13 | −179.3 (2) |
| C9—O5—C4—C3 | −2.1 (3) | C17—C13—C14—O7 | −104.0 (3) |
| O4—C3—C4—O5 | −13.5 (2) | C12—C13—C14—O7 | 20.9 (4) |
| C2—C3—C4—O5 | −129.97 (19) | C17—C13—C14—O6 | 75.7 (3) |
| O4—C3—C4—C5 | 106.0 (2) | C12—C13—C14—O6 | −159.4 (2) |
| C2—C3—C4—C5 | −10.5 (3) | C14—O6—C15—C16 | 171.0 (2) |
| C1—O1—C5—C4 | 69.3 (2) | C18—O8—C17—O9 | −0.5 (4) |
| C1—O1—C5—C12 | −167.25 (15) | C18—O8—C17—C13 | 177.98 (19) |
| O5—C4—C5—O1 | 74.9 (2) | C14—C13—C17—O9 | 23.8 (3) |
| C3—C4—C5—O1 | −41.4 (2) | C12—C13—C17—O9 | −101.2 (3) |
| O5—C4—C5—C12 | −45.3 (3) | C14—C13—C17—O8 | −154.6 (2) |
| C3—C4—C5—C12 | −161.60 (18) | C12—C13—C17—O8 | 80.4 (2) |

| C2—O3—C6—O2 | −29.2 (3) | C17—O8—C18—C19 | −175.6 (2) |
|---|---|---|---|

*Hydrogen-bond geometry (Å, °)*

| $D$—H$\cdots A$ | $D$—H | H$\cdots A$ | $D\cdots A$ | $D$—H$\cdots A$ |
|---|---|---|---|---|
| C1—H1A$\cdots$O9[i] | 0.98 | 2.43 | 3.381 (3) | 163 |
| C5—H5A$\cdots$O7 | 1.01 | 2.59 | 3.185 (3) | 117 |
| C8—H8B$\cdots$O7[i] | 1.03 | 2.56 | 3.577 (3) | 169 |
| C12—H12A$\cdots$O5 | 1.02 | 2.42 | 2.811 (3) | 102 |
| C13—H13A$\cdots$O1 | 0.96 | 2.43 | 2.814 (3) | 103 |
| C16—H16B$\cdots$O1[ii] | 0.99 | 2.51 | 3.422 (3) | 153 |

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+1, y+1/2, -z+1/2$.

**Fig. 1**

**Fig. 2**

**Fig. 3**

**Fig. 4**

**Fig. 5**