

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.026$
 $wR(F^2) = 0.073$
 $S = 1.077$
 2549 reflections
 248 parameters
 H atoms treated by a
 mixture of independent
 and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0481P)^2$
 $+ 0.2260P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.006$

$\Delta\rho_{\max} = 0.224 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.166 \text{ e } \text{\AA}^{-3}$
 Extinction correction:
 SHELXL97 (Sheldrick,
 1997)
 Extinction coefficient:
 0.0071 (5)
 Scattering factors from
International Tables for
Crystallography (Vol. C)
 Absolute structure:
 Flack (1983)
 Flack parameter = 0.09 (14)

Table 1. Selected geometric parameters (\AA , $^\circ$)

O1—C1	1.2853 (16)	C3—C4	1.5382 (18)
O2—C1	1.2299 (16)	N9—C22	1.5085 (16)
O3—C2	1.4063 (16)	O7—C21	1.4208 (16)
O4—C3	1.4193 (15)	C21—C22	1.5234 (18)
O5—C4	1.2356 (16)	C22—C23	1.5369 (18)
O6—C4	1.2781 (16)	C23—C24	1.524 (2)
C1—C2	1.5417 (18)	C23—C25	1.5289 (19)
C2—C3	1.5318 (17)		
O2—C1—C2—O3	-2.4 (2)	C2—C3—C4—O5	121.2 (1)
O1—C1—C2—O3	176.6 (1)	O4—C3—C4—O6	-179.5 (1)
O2—C1—C2—C3	122.9 (1)	C2—C3—C4—O6	-59.1 (1)
O1—C1—C2—C3	-58.1 (1)	O7—C21—C22—N9	-61.7 (1)
O3—C2—C3—O4	72.9 (1)	O7—C21—C22—C23	61.2 (1)
C1—C2—C3—O4	-51.8 (1)	N9—C22—C23—C24	-51.6 (2)
O3—C2—C3—C4	-47.9 (1)	C21—C22—C23—C24	-172.1 (1)
C1—C2—C3—C4	-172.6 (1)	N9—C22—C23—C25	-174 (1)
O4—C3—C4—O5	0.8 (2)	C21—C22—C23—C25	65.4 (2)

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

D—H...A	D—H	H...A	D...A	D—H...A
O1—H10...O6 ⁱ	1.15 (3)	1.33 (3)	2.4622 (13)	169 (3)
O8—H81...O3 ⁱⁱ	0.93 (3)	1.77 (3)	2.6987 (14)	175 (2)
O8—H82...O2 ⁱⁱⁱ	0.78 (3)	2.01 (3)	2.7805 (15)	170 (2)
O3—H30...O7 ^{iv}	0.81 (2)	1.85 (2)	2.6493 (15)	170 (2)
O4—H40...O8 ^v	0.81 (2)	2.33 (2)	2.9007 (16)	128.9 (18)
O7—H7...O8 ^{vi}	0.85 (2)	1.80 (2)	2.6424 (15)	176 (2)
N9—H91...O4 ^{vii}	0.92 (2)	1.90 (2)	2.8183 (15)	174.0 (16)
N9—H92...O5 ^{viii}	0.91 (2)	1.97 (2)	2.8689 (15)	169.3 (19)
N9—H93...O2 ^{ix}	0.894 (17)	1.975 (18)	2.8358 (15)	161.0 (16)

Symmetry codes: (i) $x - 1, y, z$; (ii) $2 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $\frac{3}{2} - x, 1 - y, z - \frac{1}{2}$; (v) $x, 1 + y, z$; (vi) $\frac{3}{2} - x, -y, \frac{1}{2} + z$; (vii) $\frac{1}{2} + x, \frac{3}{2} - y, 1 - z$; (viii) $x - \frac{1}{2}, \frac{3}{2} - y, 1 - z$; (ix) $\frac{3}{2} - x, 1 - y, \frac{1}{2} + z$.

After anisotropic displacement parameters were introduced for all the non-H atoms, all H atoms were introduced in the positions calculated from the difference Fourier map. The hydrogen positional parameters were included in the refinement and given isotropic displacement parameters equal to $1.2U_{\text{eq}}$ or $1.5U_{\text{eq}}$ of the parent C or O atoms, respectively. The absolute configuration of the optically active diastereomer was determined by refinement of the absolute structure parameter (Flack, 1983).

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *DREADD* (Blessing, 1987). Program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: OS1047). Services for accessing these data are described at the back of the journal.

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1-D-3,4-Anhydro-1,2:5,6-di-O-isopropylidene-*allo*-inositol

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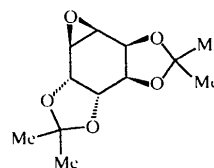
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Abstract

The title compound was isolated from the reaction of the 3,4-bis-*O*-mesylate of 1-D-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol with lithium diphenylphosphide in tetrahydrofuran. The structure consists of independent molecules of 1-D-3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-*allo*-inositol, C₁₂H₁₈O₅. The two fused dioxolane rings adopt identical envelope conformations around the inositol ring.

Comment

The current interest in the use of carbohydrate molecules as asymmetric ligand fragments for homoge-



(I)

neous catalysis (Gilbertson & Chang, 1995; RajanBabu *et al.*, 1994) prompted us to investigate the use of *D-chiro*-inositol as a precursor for chiral phosphorus ligands (Falshaw *et al.*, 1999). In the course of this work, we attempted the preparation of a bis-phosphine by reacting the 3,4-bis-*O*-mesylate of 1-*D*-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol with lithium diphenylphosphide in tetrahydrofuran. Instead of the anticipated bis(phosphine), we isolated crystals of the title compound, (I). Its structure consists of independent molecules of 1-*D*-3,4-anhydro-1,2:5,6-di-*O*-isopropylidene-*allo*-inositol (Fig. 1), held in the lattice by weak van der Waals interactions, *e.g.* O3...H1(*x* - 1, *y*, *z*) 2.48 (3) Å.

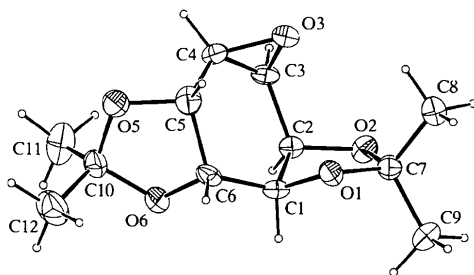


Fig. 1. View of the independent molecule of (I), showing the labelling of the non-H atoms [ORTEP (Johnson, 1976) in PLATON98 (Spek, 1998)]. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as small circles of an arbitrary radius.

The bond lengths and angles shown in Table 1 are normal (*International Tables for X-ray Crystallography*, 1992, Vol. C, pp. 691–706), *e.g.* C3—C4 1.470 (5) Å. The epoxide C—O bonds are at the longer end of the range, with a mean of 1.455 (4) Å (*cf.* 1.452 and 1.449 Å in Latvala *et al.*, 1995). The 3,4-anhydro-inositol ring, defined by atoms C1–C6, can be described as a half chair: atoms C2, C3, C4 and C5 are coplanar (± 0.010 Å), with C1 and C6 0.307 (3) and -0.192 (3) Å from the plane, respectively. A ‘parent’ inositol ring structure, $\pm 1,2:5,6$ -di-*O*-isopropylidene-*myo*-inositol, hereinafter PINMII, has been reported as a skew-boat with the Cremer & Pople (1975) parameters $Q = 0.749$ Å and $\theta = 83.6^\circ$ (Chung *et al.*, 1994). A very similar conformation was also observed in the 3,4-di-*O*-tosyl structure (McConnell *et al.*, 1972).

The two dioxolane rings have very similar envelope conformations, with flap atoms C6 and C1 0.553 (5) and 0.554 (6) Å, respectively, from the other four coplanar atoms (± 0.010 Å); the respective parameters (Cremer & Pople, 1975) for Q_2 and ϕ are 0.355 (2) and 0.358 (3) Å, and 69.2 (6) and 32.4 (6)°, for the C6- and C1-containing rings, respectively. The mean planes of the dioxolane rings make angles of about 70° with the fused cyclohexane ring and are at 81.9 (2)° to each other. The dioxolane rings in the two ‘parent’ structures are in twist forms about different ring bonds; for example, the C1-containing ring in PINMII is twisted about the C7—O1

bond, with $Q_2 = 0.327$ Å and $\phi = 341^\circ$. In PINMII, an O3—O2 intramolecular hydrogen bond (2.70 Å) is postulated, but this seems highly unlikely given the observed ring conformations.

Experimental

The title compound was isolated in small yield from the reaction of the 3,4-bis-*O*-mesylate of 1-*D*-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol with lithium diphenylphosphide in tetrahydrofuran. Unfortunately, this reaction is not very well understood and does not always produce (I) in isolatable yields. Synthesis of the enantiomer of this compound from the 3,4-bis-*O*-tosylate of 1-*L*-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol has been reported by Angyal & Matheson (1955).

Crystal data

C₁₂H₁₈O₅
 $M_r = 242.26$
 Orthorhombic
 $P2_12_12_1$
 $a = 6.264$ (2) Å
 $b = 9.035$ (4) Å
 $c = 22.362$ (9) Å
 $V = 1265.6$ (9) Å³
 $Z = 4$
 $D_x = 1.271$ Mg m⁻³
 D_m not measured

Mo K α radiation
 $\lambda = 0.71073$ Å
 Cell parameters from 24 reflections
 $\theta = 9.67$ – 23.74°
 $\mu = 0.099$ mm⁻¹
 $T = 152$ (2) K
 Block
 0.48 × 0.25 × 0.20 mm
 Colourless

Data collection

Siemens P4 diffractometer
 ω scans
 Absorption correction: none
 1995 measured reflections
 1819 independent reflections
 1245 reflections with
 $I > 2\sigma(I)$
 $R_{int} = 0.021$

$\theta_{max} = 26^\circ$
 $h = -1 \rightarrow 7$
 $k = -1 \rightarrow 11$
 $l = -1 \rightarrow 26$
 3 standard reflections
 every 97 reflections
 intensity decay: 2.13%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.093$
 $S = 1.042$
 1819 reflections
 226 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.036P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{max} = 0.001$
 $\Delta\rho_{max} = 0.204$ e Å⁻³
 $\Delta\rho_{min} = -0.205$ e Å⁻³
 Extinction correction: none
 Scattering factors from
International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.436 (4)	C1—C2	1.520 (5)
O1—C1	1.438 (4)	C1—C6	1.524 (4)
O2—C7	1.453 (4)	C2—C3	1.522 (5)
O2—C2	1.457 (4)	C3—C4	1.470 (5)
O3—C4	1.453 (4)	C4—C5	1.519 (5)
O3—C3	1.456 (4)	C5—C6	1.535 (5)
O5—C10	1.440 (5)	C7—C8	1.516 (5)
O5—C5	1.446 (4)	C7—C9	1.529 (5)
O6—C10	1.447 (4)	C10—C12	1.518 (6)
O6—C6	1.452 (4)	C10—C11	1.522 (6)

C7—O1—C1	106.0 (2)	C4—C3—C2	121.0 (3)
C7—O2—C2	108.3 (3)	C3—C4—C5	122.5 (3)
C4—O3—C3	60.7 (2)	O6—C6—C5	101.8 (3)
O1—C1—C2	102.7 (3)	C1—C6—C5	116.9 (3)
C2—C1—C6	116.5 (3)	O1—C7—O2	106.2 (2)
O2—C2—C1	102.4 (3)	C8—C7—C9	112.5 (3)
C1—C2—C3	115.1 (3)	C12—C10—C11	113.8 (4)

C7—O1—C1—C2	-37.6 (3)	O3—C4—C5—O5	166.3 (3)
C7—O1—C1—C6	-162.6 (3)	C3—C4—C5—O5	-125.4 (4)
C7—O2—C2—C1	-19.9 (3)	O3—C4—C5—C6	-78.3 (4)
C7—O2—C2—C3	103.4 (3)	C3—C4—C5—C6	-10.1 (5)
O1—C1—C2—O2	34.9 (3)	C10—O6—C6—C1	-157.9 (3)
C6—C1—C2—O2	155.7 (3)	C10—O6—C6—C5	-35.3 (3)
O1—C1—C2—C3	-85.7 (3)	O1—C1—C6—O6	-174.8 (3)
C6—C1—C2—C3	35.1 (4)	C2—C1—C6—O6	68.6 (4)
C4—O3—C3—C2	-112.4 (3)	O1—C1—C6—C5	72.7 (4)
O2—C2—C3—O3	-62.4 (4)	C2—C1—C6—C5	-43.9 (4)
C1—C2—C3—O3	53.4 (4)	O5—C5—C6—O6	35.4 (3)
O2—C2—C3—C4	-130.8 (3)	C4—C5—C6—O6	-84.7 (3)
C1—C2—C3—C4	-15.0 (4)	O5—C5—C6—C1	150.2 (3)
C3—O3—C4—C5	115.0 (4)	C4—C5—C6—C1	30.1 (5)
C2—C3—C4—O3	103.3 (3)	C1—O1—C7—O2	25.6 (3)
O3—C3—C4—C5	-100.5 (4)	C2—O2—C7—O1	-2.5 (4)
C2—C3—C4—C5	2.8 (5)	C5—O5—C10—O6	2.1 (4)
C10—O5—C5—C4	99.4 (4)	C6—O6—C10—O5	21.7 (4)
C10—O5—C5—C6	-23.4 (4)		

Data collection: XSCANS (Siemens, 1993). Cell refinement: XSCANS. Data reduction: XSCANS. Program(s) used to solve structure: SHELXS86 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL93 (Sheldrick, 1993). Molecular graphics: ORTEPII (Johnson, 1976) in PLATON98 (Spek, 1990, 1998). Software used to prepare material for publication: SHELXL93.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1231). Services for accessing these data are described at the back of the journal.

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N-(Isopropyl)norbornane-endo-2,3-dicarboximide

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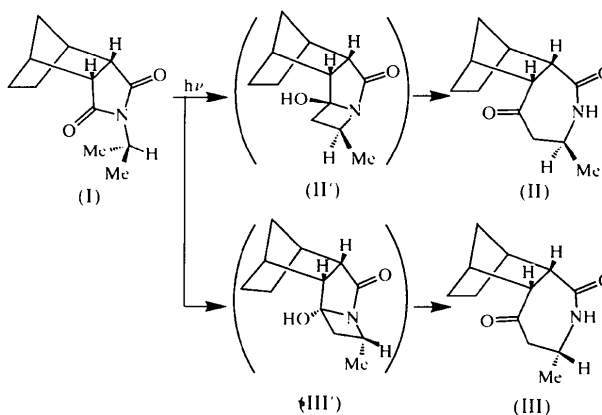
(Received 13 October 1998; accepted 9 February 1999)

Abstract

The geometry of the title molecule, *N*-isopropylbicyclo[2.2.1]heptane-endo-2,3-dicarboximide, C₁₂H₁₇NO₂, has been confirmed as the *endo* conformation. The orientation of the isopropyl (ⁱPr) group relative to the succinimide moiety is a little unsymmetric and the ⁱPr group rotates *ca* 6° around the N—C bond from the perpendicular configuration. This causes the stereoselectivity of the photoreaction in the solid state. The diastereomeric excess of the ring expansion products indicates that the carbonyl-O atom predominantly abstracts the nearest γ -hydrogen in the molecule.

Comment

By photoirradiation of the title compound, (I), the ring expansion products, (II) and (III), were obtained. The reaction may proceed via intramolecular γ -hydrogen abstraction by the carbonyl-O atom to yield the 2-azetidino derivatives, (II') and (III').



When one of the H atoms bonded to C14 in (I) is abstracted by the carbonyl atom O2, compound (II) is obtained. Compound (III) is obtained if an H atom on C15 in (I) is abstracted by O2. In the solid-state reaction