Refinement

Refinement on F^2
$R(F) = 0.041$
$wR(F^2) = 0.129$
$S = 1.424$
2526 reflections
300 parameters
H atoms: see text
$w = 1/[\sigma^2(F_o^2)$
$+ 0.00203(F_o^2)^2]$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.16$ e Å^{-3}
$\Delta\rho_{\min} = -0.16$ e Å^{-3}
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.060 (4)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C11	1.451 (4)	O2*—C11	1.30 (1)
O1′—C11′	1.434 (4)	O2*—C12	1.45 (1)
O2—C11	1.385 (6)	O2′—C11′	1.367 (5)
O2—C12	1.340 (7)	O2′—C12′	1.401 (6)
C11—O2—C12	117.1 (6)	O1—C11—O2	111.2 (4)
C11—O2*—C12	115.0 (8)	O1—C11—O2*	111.0 (6)
C11′—O2′—C12′	115.2 (4)	O1′—C11′—O2′	112.3 (3)

The O atom in the disordered methoxymethyl group was refined over two sites (O2 and O2*, occupancies of 0.7 and 0.3, respectively). H atoms, except those of the disordered methoxymethyl group [C11—O2(O2*)—C12] were found by difference Fourier synthesis and constrained with $U(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$, including H atoms of the major disorder component.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *TEXSAN* and *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *TEXSAN LS* and *SAPI*91. Molecular graphics: *TEXSAN* and *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN* and *SAPI*91.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1308). Services for accessing these data are described at the back of the journal.

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1-D-1,2:5,6-Di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol, a hydrogen-bonded dimeric structure

ANDREW FALSHAW, GRAEME J. GAINSFORD AND CORNELIS LENSINK

Industrial Research Limited, PO Box 31-310, Lower Hutt, New Zealand. E-mail: c.lensink@irl.cri.nz

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Abstract

The title compound ($C_{24}H_{29}O_7P$) was prepared from the reaction of chlorodiphenylphosphine with 1-D-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol in pyridine. The structure consists of two independent molecules of 1-D-1,2:5,6-di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol hydrogen bonded to each other, so that the dimer has close to centrosymmetric symmetry in space group *P*1. Subtle twisting in the fused cyclohexane rings and at the P atoms breaks the centrosymmetry, allowing the formation of strong hydrogen bonds (P═O···H—O 1.9 and 2.0 Å).

Comment

The current interest in the use of carbohydrate molecules as asymmetric ligand fragments for homogeneous catalysis (Gilbertson & Chang, 1995; RajanBabu *et al.*, 1994) prompted us to investigate the use of D-*chiro*-inositol for this purpose. In the course of our work, we isolated the title compound, (I), and report its molecular structure here. The structure consists of two independent molecules of 1-D-1,2:5,6-di-*O*-isopropylidene-3-*O*-(diphenylphosphinoyl)-*chiro*-inositol hydrogen bonded to each other *via* the free phosphate O atoms and

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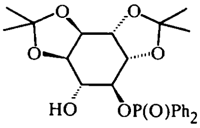
α-hydroxyl groups. This is achieved by a conformational twist about the phosphorus P—O bonds: O7—P1—O1—C1 −25.0 (8) and O7′—P1′—O1′—C1′ 81.2 (3)°.



(I)

Although constructed from molecules with the same chirality, the resulting 'dimer' unit (Fig. 1) has pseudo-centrosymmetric symmetry; the two molecules have other subtle differences in conformation shown by the dihedral angles, particularly around atoms C3, C5 and C6, and C3′, C5′ and C6′. These differences were confirmed by the failure of an attempted refinement in the centrosymmetric space group ($P\bar{1}$), with these three atoms split into two sites, giving higher *R* factors. As there are no close intermolecular contacts, the closest being H32′···H121 and H2···H3′ 2.2 Å, it is presumed that the differences in the two molecules are related to the formation of two strong hydrogen bonds (P1═O7···H2O′—O2′ 2.0 and P1′═O7′···H2O—O2 1.9 Å; s.u.'s are estimated as 0.1 Å). Note that the hydrogen-bond interaction is between molecules in different (adjacent) cells along the *b* axis.

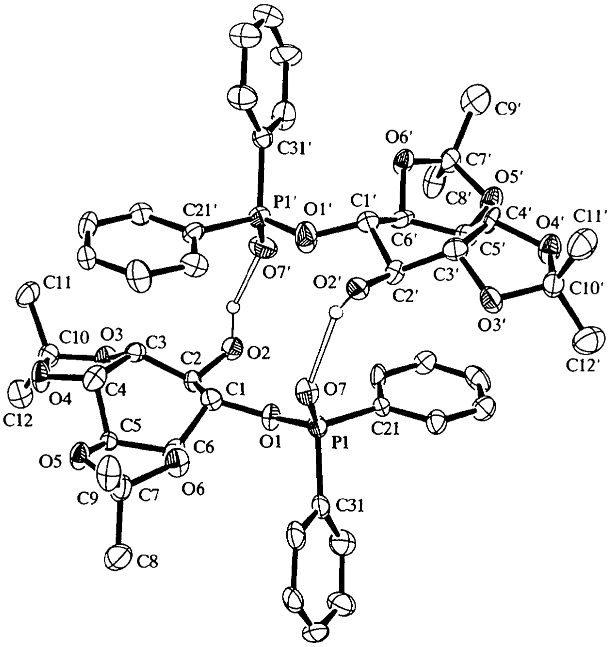


Fig. 1. View of the two independent molecules of (I) showing the labelling of the non-H atoms (*ORTEP*II; Johnson, 1976). Displacement ellipsoids are shown at 30% probability levels; H atoms have been omitted for clarity, except for H2O and H2O′. The hydrogen bonds are indicated with empty bonds. The second molecule (based on *P*1) has been shifted by +1.0 in *y*.

The bond lengths and angles are normal (*International Tables for Crystallography*, Vol. C, 1992) and self-consistent (Table 1). Except for atom P1 [0.175 (4) Å from the C31–C36 plane], the P atoms are statistically coplanar with their pendant planar phenyl rings; again, small angular differences are noted around the two P atoms which break the apparent 'dimer' centrosymmetry and suggest the phosphorus P1 atom is slightly disturbed from its expected tetrahedral geometry [*e.g.* O1—P1—C31 105.0 (2) and O1′—P1′—C31′ 110.0 (2)°].

Both fused cyclohexane rings adopt approximate boat conformations [$Q(2)/Q$ = 0.71 (1)/0.72 (2) Å and θ = 100 (1)° for C1–C6; $Q(2)/Q$ = 0.77 (1)/0.77 (2) Å and θ = 97 (1)° for C1′–C6′ (Cremer & Pople, 1975)], with atoms C1 and C4 0.69 (1) and 0.41 (1) Å, respectively, from the plane through atoms C2, C3, C5 and C6. The two fused dioxalane rings in each molecule are slightly different: C3—C4—O4—C10—O3 and C3′—C4′—O4′—C10′—O3′ are close to envelope conformations [Q = 0.28 (1) and 0.31 (1) Å, and Φ = 188 (2) and 167 (2)°, respectively (Cremer & Pople, 1975)]; atom O3 is 0.42 (1) Å from the C3—C4—O4—C10 plane [mean deviations of ±0.017 (4) Å]. In contrast, the C5—C6—O6—C7—O5 and C5′—C6′—O6′—C7′—O5′ rings are closer to a pure twist (half-boat) form [Q = 0.32 (1) and 0.33 (1) Å, and Φ = 310 (2) and 270 (2)°, respectively (Cremer & Pople, 1975); mean deviations of ±0.040 (5) Å from the best four-atom plane]. The closest pucker descriptor for all four dioxalane rings involves twists about different bonds in each of the rings (Spek, 1998).

Experimental

The title compound was prepared by the reaction of 1-D-1,2:5,6-di-*O*-isopropylidene-*chiro*-inositol with chlorodiphenylphosphine in pyridine. Isolation was achieved *via* silica-gel chromatography after exposure to air.

Crystal data

$C_{24}H_{29}O_7P$
M_r = 460.44
Triclinic
$P1$
a = 9.556 (3) Å
b = 11.007 (3) Å
c = 12.713 (4) Å
α = 111.67 (2)°
β = 107.02 (2)°
γ = 99.25 (2)°
V = 1132.6 (6) Å^3
Z = 2
D_x = 1.350 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 17 reflections
θ = 4.72–12.46°
μ = 0.165 mm^{-1}
T = 158 (2) K
Irregular block
0.40 × 0.34 × 0.20 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: empirical (*SHELXTL*; Sheldrick, 1984)
$T_{\min} = 0.912$, $T_{\max} = 0.968$
4631 measured reflections
2039 independent reflections (plus 2592 Friedel-related reflections)
3456 reflections with $I > 2\sigma(I)$
$\theta_{\max} = 25°$
$h = -10 \rightarrow 7$
$k = -11 \rightarrow 11$
$l = -15 \rightarrow 14$
3 standard reflections every 297 reflections intensity decay: 8.60%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.068$
$wR(F^2) = 0.181$
$S = 0.998$
4631 reflections
528 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1164P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.429$ e Å^{-3}
$\Delta\rho_{\min} = -0.284$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.2 (2)

Table 1. *Selected geometric parameters (Å, °)*

P1—O7	1.473 (6)	P1′—O7′	1.477 (7)
P1—O1	1.574 (6)	P1′—O1′	1.565 (8)
P1—C31	1.782 (5)	P1′—C21′	1.801 (5)
P1—C21	1.805 (4)	P1′—C31′	1.803 (5)
O1—C1	1.443 (9)	O1′—C1′	1.450 (11)
O7—P1—O1	115.2 (3)	O7′—P1′—O1′	114.8 (3)
O7—P1—C31	113.9 (3)	O7′—P1′—C21′	114.7 (3)
O1—P1—C31	105.0 (2)	O1′—P1′—C21′	99.0 (2)
O7—P1—C21	115.6 (3)	O7′—P1′—C31′	110.6 (3)
O1—P1—C21	99.6 (3)	O1′—P1′—C31′	110.0 (2)
C31—P1—C21	106.1 (3)	C21′—P1′—C31′	107.1 (3)
C1—O1—P1	127.2 (5)	C1′—O1′—P1′	133.7 (7)
O1—C1—C6	110.9 (7)	O1′—C1′—C6′	114.5 (3)
O7—P1—O1—C1	−25.0 (8)	O7′—P1′—O1′—C1′	81.2 (3)
C31—P1—O1—C1	101.1 (7)	C21′—P1′—O1′—C1′	−156.2 (3)
C21—P1—O1—C1	−149.3 (7)	C31′—P1′—O1′—C1′	−44.2 (2)
P1—O1—C1—C6	−77.4 (8)	P1′—O1′—C1′—C6′	−42.9 (4)
P1—O1—C1—C2	164.3 (5)	P1′—O1′—C1′—C2′	−163.4 (3)
C7—O5—C5—C4	−136.2 (7)	C7′—O5′—C5′—C4′	−110.7 (7)
C7—O5—C5—C6	−13.5 (8)	C7′—O5′—C5′—C6′	10.2 (8)
O1—C1—C6—O6	78.7 (8)	O1′—C1′—C6′—O6′	93.2 (6)
C2—C1—C6—O6	−164.1 (6)	C2′—C1′—C6′—O6′	−148.2 (6)
C2—C1—C6—C5	−45.4 (9)	C2′—C1′—C6′—C5′	−31.6 (8)
O5—C5—C6—O6	−8.4 (8)	O5′—C5′—C6′—O6′	−28.3 (8)
C4—C5—C6—O6	111.1 (8)	C4′—C5′—C6′—O6′	91.4 (8)
O5—C5—C6—C1	−131.3 (7)	O5′—C5′—C6′—C1′	−149.8 (6)
C4—C5—C6—C1	−11.8 (10)	C4′—C5′—C6′—C1′	−30.1 (10)
O1—P1—C21—C26	16.3 (4)	O1′—P1′—C21′—C26′	−9.3 (3)

The phenyl rings were constrained to be regular hexagons (C—C 1.39 Å). Methyl, tertiary carbon, phenyl and hydroxyl H atoms were constrained to calculated positions (C—H = 0.98, 1.00, 0.95 and O—H = 0.84 Å, respectively). All H-atom isotropic displacement parameters were set at 1.2 times the equivalent isotropic displacement parameter of their parent atom.

Data collection: *XSCANS* (Siemens, 1993). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976) and *ORTEP*-3 (Farrugia, 1997). Software used to prepare material for publication: *CIFTAB* in *SHELXL*93 and *PLATON*98 (Spek, 1998).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1226). Services for accessing these data are described at the back of the journal.

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1-Acetyl-1,2,3,4-tetrahydro-4-methyl-2,4-diphenyl-5*H*-1,5-benzodiazepine

P. Laavanya,[a] K. Panchanatheswaran,[a] M. Venkatraj,[a] R. Jeyaraman[a] and W. Marshall[b]

[a]*Department of Chemistry, Bharathidasan University, Tiruchirappalli 620 024, India, and* [b]*duPont Central Research and Development, Wilmington, DE 19880-0328, USA. E-mail: pan@bdu.ernet.in*

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Abstract

The single-crystal X-ray diffraction study of the title compound, $C_{24}H_{24}N_2O$, confirms the boat conformation of the benzodiazepine ring. The equatorial and axial orientations of the phenyl and methyl groups, respectively, are also confirmed. The *N*-acetyl group is non-coplanar with the fused benzene ring. There are two independent molecules in the asymmetric unit.

Comment

The configuration and conformation of molecules containing a benzodiazepine ring are of interest to the understanding of their drug action. The structure of the title compound, (I), has been determined to assign the