

(±)-6-*tert*-Butyl-8-hydroxymethyl-2-phenyl-4*H*-1,3-benzodioxin and 2,2,2',2',6,6'-hexamethyl-8,8'-methylenebis(4*H*-1,3-benzodioxin)

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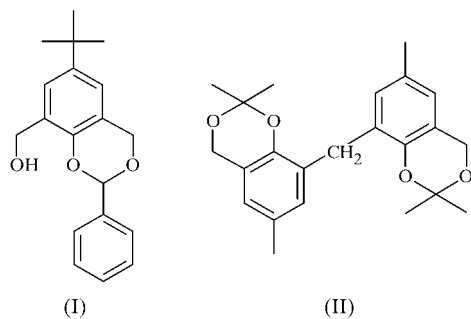
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Two compounds containing 1,3-benzodioxin groups are reported, namely (±)-6-*tert*-butyl-8-hydroxymethyl-2-phenyl-4*H*-1,3-benzodioxin, C₁₉H₂₂O₃, (I), and 2,2,2',2',6,6'-hexamethyl-8,8'-methylenebis(4*H*-1,3-benzodioxin), C₂₃H₂₈O₄, (II). The hydroxy groups of neighbouring molecules in (I) are hydrogen bonded to each other, giving rise to double-row chains. The molecule in (II) adopts a 'butterfly' conformation, with the O atoms in distal positions. In both compounds, the dioxin rings are in distorted half-chair conformations.

Comment

In the course of the synthesis of homooxalixarene compounds, the two cyclic acetals (I) and (II) were obtained from bishydroxymethylated phenols, as a result of a protection step in the case of compound (I) and of a spurious reaction in the case of (II). In both compounds, a heterocyclic 1,3-dioxin ring is fused to an aromatic ring, giving the 1,3-benzodioxin moiety.



The asymmetric unit in (I) comprises two molecules, denoted *A* and *B*, which have almost identical geometries and conformation. The two aromatic rings are nearly parallel in

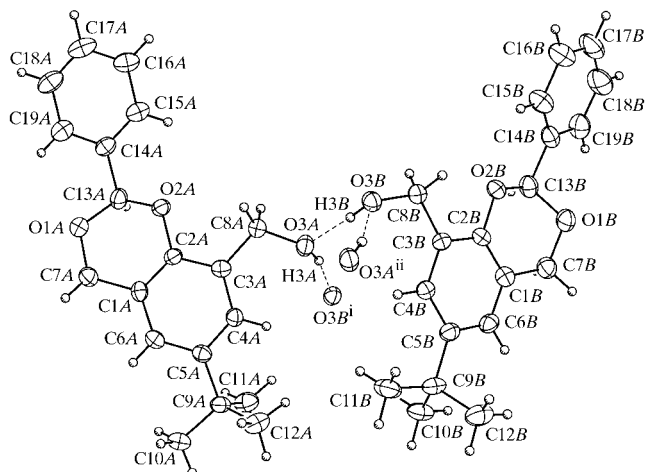
molecule *A* and more tilted in molecule *B*, with dihedral angles of 6.8 (2) and 25.0 (1)°, respectively.

In both molecules, the dioxin ring is in a distorted half-chair conformation, but the deviations of atoms O1 and C13 with respect to the mean plane defined by atoms O2, C1, C2 and C7 are different in the two molecules; in molecule *A*, atoms O1*A* and C13*A* are 0.270 (5) and −0.492 (5) Å from the mean plane (r.m.s. deviation 0.008 Å), whereas in molecule *B*, the situation is reversed, with O1*B* 0.433 (5) Å and C13*B* −0.294 (6) Å from the mean plane (r.m.s. deviation 0.002 Å). Such distortions have been reported in related compounds, such as 6,8-dichloro-1,3-benzodioxin (Irving & Irving, 1989).

Atoms O3*A* and O3*B* are each close to the mean plane of the aromatic ring to which they belong, at distances of 0.088 (5) and 0.092 (6) Å, respectively. Both are involved in hydrogen bonds as both donors and acceptors, which gives rise to chains of alternating *A* and *B* molecules along the *c* axis (Table 1). These chains consist of strings of hydroxy groups, while the planes of the molecules themselves lie approximately perpendicular to the chain direction such that they form two stacks of alternately upside-down molecules around the central string of hydrogen-bonded hydroxy groups. Each of these two stacks corresponds either to the *A* molecule and its symmetry equivalents or to the *B* molecule and its symmetry equivalents.

Due to the small differences between the geometry of the two molecules, as indicated above, the packing in the two hydrogen-bonded rows is somewhat different, which in turn results in different intermolecular interactions. The aromatic ring defined by atoms C1*A*–C6*A* (centroid denoted Cg1) is possibly involved in two C–H... π interactions with neighbouring molecules along the *c* axis, on one side with atom H13*A*ⁱ [H13*A*ⁱ...Cg1 = 2.470 Å and C13*A*ⁱ–H13*A*ⁱ...Cg1 = 167°; symmetry code: (i) $\frac{3}{2} - x, y, z + \frac{1}{2}$], and on the other side with atom H8*A*ⁱⁱ [H8*A*ⁱⁱ...Cg1 = 2.636 Å and C8*A*ⁱⁱ–H8*A*ⁱⁱ...Cg1 = 143°; symmetry code: (ii) $\frac{3}{2} - x, y, z - \frac{1}{2}$]. The aromatic ring defined by atoms C14*A*–C19*A* (centroid denoted Cg2) is possibly involved in a very loose C–H... π interaction with atom H18*B*ⁱⁱⁱ of a molecule in the other row [H18*B*ⁱⁱⁱ...Cg2 = 2.776 Å and C18*B*ⁱⁱⁱ–H18*B*ⁱⁱⁱ...Cg2 = 138°; symmetry code: (iii) $x, y - 1, z$].

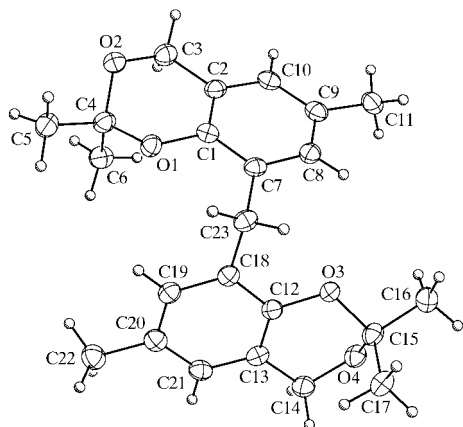
The repeat unit in (II) comprises a single molecule possessing a pseudo-binary axis containing the central methylene C atom. A search of the Cambridge Structural Database (Version 5.23; Allen & Kennard, 1993) gives only one related molecule, also obtained as a by-product during the synthesis of bisphenols, namely 6,6',7,7'-tetrachloro-8,8'-methylenebis(4*H*-1,3-benzodioxin) (Ferguson *et al.*, 1989). Both compounds comprise two methylene-linked aromatic rings bearing acetal rings, but they differ in the substituents on these rings. The compound previously reported possesses a crystallographic binary axis, its aromatic rings bear two Cl substituents each and the central C atoms of the acetal groups are unsubstituted. The aromatic rings in (II) bear one methyl substituent and the central C atoms of the acetal groups each have two methyl substituents. In both compounds, the molecule adopts a 'butterfly' shape with the two phenol-derived O


Figure 1

A view of molecules *A* and *B* in (I) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii. Hydrogen bonds are shown as dashed lines. Only the hydroxy groups of symmetry-equivalent molecules involved in hydrogen bonding are shown [symmetry codes: (i) $\frac{3}{2} - x, y, z - \frac{1}{2}$; (ii) $\frac{3}{2} - x, y, z + \frac{1}{2}$].

atoms in distal positions, which minimizes steric interactions. The two torsion angles defined by the methylene bridge in (II) are C1—C7—C23—C18 of 84.4 (3)° and C12—C18—C23—C7 of 83.5 (3)°, whereas their counterpart in the previously reported compound is 88.2°. The dihedral angle between the aromatic rings in (II) is 72.17 (8)°, which is comparable with values reported for bisphenols (Thuéry *et al.*, 2000).

As in compound (I), the two dioxin rings in (II) are in distorted half-chair conformations, with, in the first ring, deviations of atoms O2 and C4 with respect to the mean plane defined by atoms O1, C1, C2 and C3 (r.m.s. deviation 0.001 Å) of 0.306 (5) and −0.419 (5) Å, respectively, and in the second ring, deviations of atoms O4 and C15 with respect to the mean plane defined by atoms O3, C12, C13 and C14 (r.m.s. deviation


Figure 2

A view of compound (II) with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as small spheres of arbitrary radii.

0.001 Å) of 0.312 (5) and −0.374 (5) Å, respectively. This conformation is close to that described in the previously reported compound as a ‘puckered plane’ (Ferguson *et al.*, 1989).

The packing in (II) brings the side of the molecule containing atoms C3 and C10 close to the ‘cup’ defined by a neighbouring molecule. The shortest C—H... π contact associated with this ‘self-inclusion’ arrangement involves the aromatic ring defined by atoms C12, C13, C18, C19, C20 and C21 (centroid denoted *Cg*3) and atom H10^{iv} [H10^{iv}...*Cg*3 = 2.950 Å and C10^{iv}—H10^{iv}...*Cg*3 = 140°; symmetry code: (iv) $\frac{3}{2} - x, \frac{1}{2} - y, z - \frac{1}{2}$]. Another C—H... π contact involves the ring defined by atoms C1, C2, C7, C8, C9 and C10 (centroid denoted *Cg*4) and atom H14B^v of a neighbouring molecule along the *c* axis [H14B^v...*Cg*4 = 2.822 Å and C14^v—H14B^v...*Cg*4 = 141°; symmetry code: (v) $x, y, z + 1$]. These H...*Cg* distances are much larger than the usual values for such bonds (Jeffrey & Saenger, 1994) and do not indicate the presence of significant C—H... π interactions.

Experimental

Compound (I) was obtained from 4-*tert*-butyl-1,6-bis(hydroxymethyl)phenol and benzaldehyde dimethyl acetal (144 mmol) in dimethylformamide (100 ml) and *p*-toluenesulfonic acid (2.1 mmol). The compound was recrystallized from ethyl acetate–hexane (1:1) (m.p. 389–390 K). Spectroscopic analysis, ¹H NMR (300 MHz, CDCl₃, δ , p.p.m.): 1.09 (*s*, 9H), 2.06 (*s*, 1H), 4.43 (*s*, 2H), 4.77 (*d*, *J* = 14.5 Hz), 4.98 (*d*, *J* = 14.5 Hz), 5.80 (*s*, 1H), 6.76 (*d*, *J* = 1.7 Hz), 7.04 (*d*, *J* = 1.7 Hz, 1H), 7.19–7.26 (*m*, 3H), 7.35–7.39 (*m*, 2H). Compound (II) was an unexpected by-product obtained while carrying out the methylation of 5,5′-di-*tert*-butyl-2,2′-dihydroxy-3,3′-methanedioldibenzyl alcohol (35 mmol) with dimethyl sulfate (76 mmol) in acetone (110 ml) and K₂CO₃ (109 mmol). Acidic impurities in the dimethyl sulfate apparently promoted the formation of the acetal before being neutralized by the heterogeneous base. The compound was recrystallized from acetone (m.p. 403–404 K). Spectroscopic analysis, ¹H NMR (300 MHz, CDCl₃, δ , p.p.m.): 1.48 (*s*, 12H), 2.20 (*s*, 6H), 3.78 (*s*, 2H), 4.80 (*s*, 4H), 6.60 (*d*, *J* = 1.6 Hz, 2H), 6.83 (*d*, *J* = 1.6 Hz, 2H).

Compound (I)

Crystal data

C₁₉H₂₂O₃
M_r = 298.37
 Orthorhombic, *Pcca*2₁
a = 25.6945 (15) Å
b = 16.0188 (11) Å
c = 7.9750 (4) Å
V = 3282.5 (3) Å³
Z = 8
D_x = 1.208 Mg m^{−3}

Mo *K* α radiation
 Cell parameters from 24 138 reflections
 θ = 2.7–25.7°
 μ = 0.08 mm^{−1}
T = 100 (2) K
 Parallelepiped, colourless
 0.3 × 0.2 × 0.1 mm

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans
 24 138 measured reflections
 3349 independent reflections
 2589 reflections with *I* > 2 σ (*I*)

*R*_{int} = 0.058
 θ_{\max} = 25.7°
h = −31 → 31
k = −19 → 19
l = −9 → 9

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.051$
 $wR(F^2) = 0.107$
 $S = 1.09$
 3349 reflections
 403 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0267P)^2 + 1.6239P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.18 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O3B-H3B \cdots O3A$	0.91	1.77	2.674 (3)	174
$O3A-H3A \cdots O3B^i$	0.93	1.79	2.705 (3)	167

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

Compound (II)

Crystal data

$C_{23}H_{28}O_4$
 $M_r = 368.45$
 Tetragonal, $I\bar{4}$
 $a = 20.5349 (10) \text{ \AA}$
 $c = 9.3356 (5) \text{ \AA}$
 $V = 3936.7 (3) \text{ \AA}^3$
 $Z = 8$
 $D_x = 1.243 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
 Cell parameters from 14 507 reflections
 $\theta = 2.8\text{--}25.7^\circ$
 $\mu = 0.08 \text{ mm}^{-1}$
 $T = 100 (2) \text{ K}$
 Parallelepiped, colourless
 $0.30 \times 0.15 \times 0.15 \text{ mm}$

Data collection

Nonius KappaCCD area-detector diffractometer
 φ scans
 14 507 measured reflections
 1992 independent reflections
 1642 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.042$
 $\theta_{\text{max}} = 25.7^\circ$
 $h = -25 \rightarrow 24$
 $k = -17 \rightarrow 17$
 $l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.044$
 $wR(F^2) = 0.097$
 $S = 1.06$
 1992 reflections
 250 parameters
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0333P)^2 + 3.4238P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.20 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.19 \text{ e } \text{\AA}^{-3}$

The hydroxy H atoms in compound (I) were found in a difference Fourier map and were introduced as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O})$. All other H atoms in both compounds were introduced at calculated positions as riding atoms, with C–H distances of 0.93 (CH), 0.97 (CH₂) and 0.96 Å (CH₃), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent})$ for CH and CH₂, or $1.5U_{\text{eq}}(\text{parent})$ for CH₃. In the absence of suitable anomalous scatterers, Friedel equivalents could not be used to determine the absolute structure. Refinement of the Flack parameter (Flack, 1983) led to inconclusive values (Flack & Bernardinelli, 2000) of 0.3 (15) for (I) and -1.8 (14) for (II). Therefore, the 2688 and 1726 Friedel equivalents for (I) and (II), respectively, were merged before the final refinement, resulting in the absolute direction of the polar axis being chosen arbitrarily.

For both compounds, data collection: *KappaCCD Server Software* (Nonius, 1997); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PARST97* (Nardelli, 1995).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LN1148). Services for accessing these data are described at the back of the journal.

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