Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

5,5′-Di-*tert*-butyl-2,2′-dihydroxy-3,3′-methylenedibenzaldehyde and 6,6′-di-*tert*-butyl-8,8′-methylenebis(spiro[4*H*-1,3-benzodioxin-2,1′-cyclohexane])

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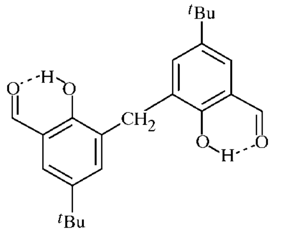
Received 20 November 2003
Accepted 3 December 2003
Online 10 January 2004

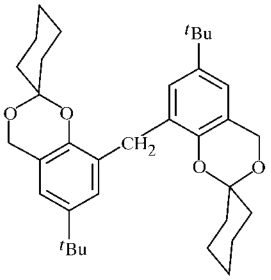
Two related compounds containing *p*-*tert*-butyl-*o*-methylene-linked phenol or phenol-derived subunits are described, namely 5,5′-di-*tert*-butyl-2,2′-dihydroxy-3,3′-methylenedibenzaldehyde, $C_{23}H_{28}O_4$, (I), and 6,6′-di-*tert*-butyl-8,8′-methylenebis(spiro[4*H*-1,3-benzodioxin-2,1′-cyclohexane]), $C_{35}H_{48}O_4$, (II). Both compounds adopt a 'butterfly' shape, with the two phenol or phenol-derived O atoms in distal positions. Phenol and aldehyde groups in (I) are involved in intramolecular hydrogen bonds and the two dioxin rings in (II) are in distorted half-chair conformations.

Comment

In the course of our studies of homooxacalixarenes and related compounds, we obtained single crystals of two species containing two equivalent *p*-*tert*-butyl-*o*-methylene-linked phenol or phenol-derived subunits, *ortho*-formyl groups being also present in (I), and spiro systems involving 1,3-benzodioxin and cyclohexane being featured in (II), which is the diacetal compound obtained by condensation of a bis(hydroxymethyl)diphenol with cyclohexanone.



(I)



(II)

The asymmetric unit in (I) (Fig. 1) contains one-half of the molecule, with methylene atom C12 located on a binary axis. The two aromatic rings define a dihedral angle of 61.68 (4)°, similar to that in 2,2′-methylenediphenol [61.81 (8)°] and somewhat lower than the values generally observed in uncomplexed diphenols in 'butterfly' conformations (Thuéry *et al.*, 2000, and references therein) [$C2-C3-C12-C3^{i} = 101.23\ (16)°$; symmetry code: (i) $2 - x, \frac{3}{2} - y, z$]. However, in contrast to the previously reported diphenol, the phenol O atoms in (I) are in distal positions; this difference can be ascribed to the absence of a hydrogen bond between the two phenol O atoms, such a bond being observed frequently in diphenols. The two intramolecular hydrogen bonds in (I) involve the phenol and aldehyde groups in each half-molecule (Table 1). Atoms O2 and H1 are displaced by only 0.053 (3) and 0.022 (3) Å from the plane of the aromatic ring. The latter plane and the $O1-H1\cdots O2-C7-C1-C2$ six-membered ring are thus nearly coplanar. The packing does not involve intermolecular hydrogen bonds, or π–π or CH–π interactions, in contrast to the situation that is frequently observed in such compounds (Masci *et al.*, 2002), but instead is effected by normal van der Waals forces.

Compound (II) (Fig. 2) possesses a pseudo-binary axis only, as does the related compound 2,2,2′,2′,6,6′-hexamethyl-8,8′-methylenebis(4*H*-1,3-benzodioxin), (III) (Masci *et al.*, 2002). Each half-molecule contains a cyclic acetal group in the form of a heterocyclic 1,3-dioxin ring, which is fused to an aromatic ring, giving the 1,3-benzodioxin moiety. Compound (II) differs from (III) by replacement of the 6-methyl groups by 6-*tert*-butyl substituents and of the 2,2-dimethyl substituents by the pentamethylene unit, giving rise to the spiro system. A 'butterfly' conformation, with the dioxin rings in distal positions, is observed in both (II) and (III). The dihedral angle between the two aromatic rings in (II) is 65.67 (6)°, slightly larger than that in (I) and smaller than that in (III) [72.17 (8)°]. The $C2-C3-C18-C19$ and $C3-C18-C19-C20$ torsion angles in (II) are 82.0 (3) and 81.2 (3)°, respectively, which are close to the values in (III) and in 6,6′,7,7′-tetrachloro-8,8′-methylenebis(4*H*-1,3-benzodioxin) (88.2°; Ferguson *et al.*, 1989). As in the previous benzodioxin derivatives, the 1,3-dioxin rings in (II) are in distorted half-chair conformations. In the first ring, atoms O1 and C12 lie

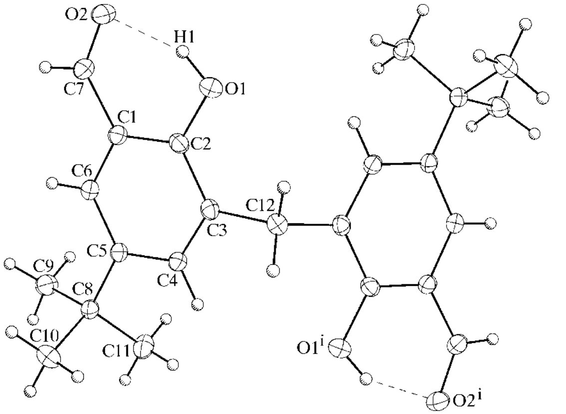


Figure 1
A view of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as small spheres of arbitrary radii. [Symmetry code: (i) $2 - x, \frac{3}{2} - y, z$.]

DOI: 10.1107/S0108270103027859

−0.340 (4) and 0.373 (4) Å from the mean plane defined by atoms O2, C1, C2 and C11 (r.m.s. deviation 0.004 Å), and in the second ring, atoms O4 and C30 lie 0.201 (4) and −0.505 (4) Å from the mean plane defined by atoms O3, C20, C21 and C29 (r.m.s. deviation 0.0008 Å). It has been noted previously that the single C—O bonds in such compounds are not of equal length, the bonds analogous to O1—C12 in (II) being shorter by about 0.03–0.05 Å than those analogous to O1—C11 (and possibly also O2—C12) (Hamada *et al.*, 1987; Ferguson *et al.*, 1989; Irving & Irving, 1989*a*,*b*). The same trend seems to apply to the 1,3-benzodioxin compounds that we reported recently (Masci *et al.*, 2002) and to (II), in spite of the different substituents present, with an overall mean value of 1.415 (9) Å for the O1—C12 bond and its counterparts, and a mean of 1.436 (8) Å for the O1—C11 and O2—C12 bonds and their counterparts [for (II), O1—C12 = 1.422 (3) Å, O1—C11 = 1.432 (3) Å, O2—C12 = 1.439 (3) Å, O4—C30 = 1.420 (3) Å, O4—C29 = 1.430 (3) Å and O3—C30 = 1.436 (3) Å]. The C12–C17 and C30–C35 rings both have chair conformations, although with a difference in their linking to the 1,3-dioxin ring; the C12–C17 ring is bound in such a way that alcohol-derived atom O1 is in an equatorial position, whereas the C30–C35 ring has phenol-derived atom O3 in an equatorial position. This difference is not surprising, since there is no size difference between these two groups and hence no increase in stability is expected upon location of one or the other in an equatorial position. No significant π–π interaction is present in the packing and only two very weak C—H···π interactions are observed, both of them involving *tert*-butyl H atoms [$H9A\cdots Cg1^{ii}$ = 2.88 Å and C9—$H9A\cdots Cg1^{ii}$ = 163°, and $H28C\cdots Cg2^{iii}$ = 2.73 Å and C28—$H28C\cdots Cg2^{iii}$ = 143°; *Cg*1 and *Cg*2 are the centroids of the C1–C6 and C19–C24 rings, respectively; symmetry codes: (ii) $-x, 2-y, -z$; (iii) $1-x, 1-y, -z$]. The latter interaction corresponds to the formation of loosely associated dimers, with the *tert*-butyl group containing atom C28 in each molecule included in the 'cup' formed by the other molecule.

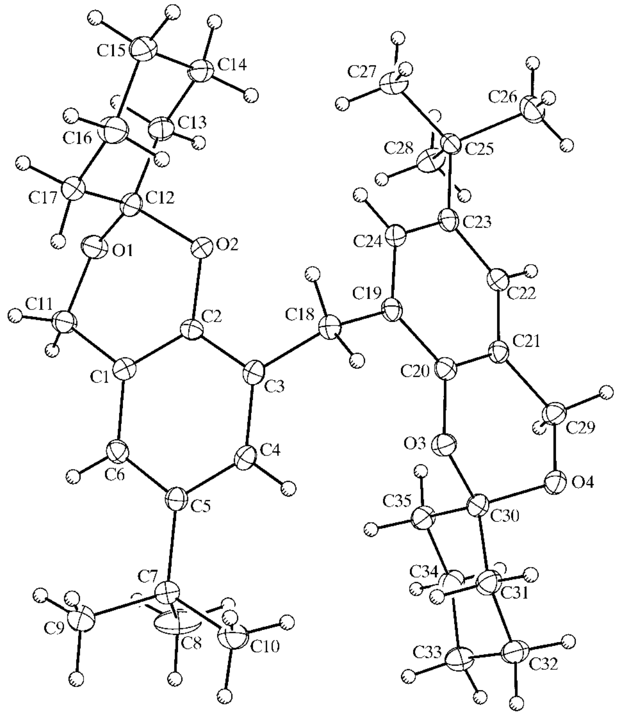


Figure 2
A view of (II), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are drawn as small spheres of arbitrary radii.

Experimental

Compound (I) was obtained as reported previously (Barreira Fontecha *et al.*, 2002) and recrystallized from methanol. Compound (II) was obtained from 5,5′-di-*tert*-butyl-2,2′-dihydroxy-3,3′-methanediyldibenzyl alcohol and cyclohexanone in the presence of *p*-toluenesulfonic acid, and was recrystallized from acetone (m.p. 427.5–429.0 K). ^{1}H NMR (300 MHz, CDCl$_3$, p.p.m.): 1.22 (*s*, 18H), 1.36–1.50 (*m*, 2H), 1.54–1.64 (*m*, 4H), 1.69–1.79 (*m*, 2H), 1.80–1.90 (*m*, 2H), 3.89 (*s*, 2H), 4.82 (*s*, 2H), 6.77 (*d*, *J* = 1.8 Hz, 2H), 7.08 (*d*, *J* = 1.8 Hz, 2H).

Compound (I)

Crystal data

$C_{23}H_{28}O_4$
M_r = 368.45
Tetragonal, $I4_1/a$
a = 12.7655 (5) Å
c = 24.1122 (11) Å
V = 3929.3 (3) Å^3
Z = 8
D_x = 1.246 Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 15 112 reflections
θ = 2.8–25.7°
μ = 0.08 mm^{-1}
T = 100 (2) K
Irregular, colourless
0.40 × 0.35 × 0.30 mm

Data collection

Nonius KappaCCD diffractometer
φ scans
15 112 measured reflections
1874 independent reflections
1437 reflections with $I > 2\sigma(I)$

R_{int} = 0.066
θ_{max} = 25.7°
$h = 0 \rightarrow 15$
$k = -10 \rightarrow 11$
$l = 0 \rightarrow 29$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.130
S = 0.97
1874 reflections
126 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0774P)^2 + 2.6466P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.16 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.87	1.85	2.6461 (18)	151

Compound (II)

Crystal data

$C_{35}H_{48}O_4$
M_r = 532.73
Monoclinic, $P2_1/n$
a = 12.7635 (10) Å
b = 10.0278 (9) Å
c = 23.2629 (13) Å
β = 91.496 (5)°
V = 2976.4 (4) Å^3
Z = 4

D_x = 1.189 Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 22 732 reflections
θ = 3.0–25.7°
μ = 0.08 mm^{-1}
T = 100 (2) K
Irregular, colourless
0.18 × 0.15 × 0.09 mm

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Data collection

Nonius KappaCCD diffractometer
φ scans
22 732 measured reflections
5621 independent reflections
3467 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.063$
$\theta_{\rm max} = 25.7°$
$h = 0 \rightarrow 15$
$k = 0 \rightarrow 12$
$l = -28 \rightarrow 28$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.056$
$wR(F^2) = 0.147$
$S = 1.02$
5621 reflections
358 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0648P)^2 + 0.6047P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.22$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}

The hydroxy H atom in (I) was found in a difference Fourier map and introduced as a riding atom, with an isotropic displacement parameter equal to 1.2 times that of the parent atom. All other H atoms in both compounds were introduced at calculated positions as riding atoms, with C—H bond lengths of 0.93 (CH), 0.97 (CH_2) and 0.96 Å (CH_3), and isotropic displacement parameters equal to 1.2 (CH and CH_2) or 1.5 (CH_3) times that of the parent atom.

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: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1999); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2000).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1630). Services for accessing these data are described at the back of the journal.

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