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2,3,10,11-Tetraphenyl-1,4,9,12-tetraoxadi-spiro[4.2.4.2]tetradeca-6,13-diene

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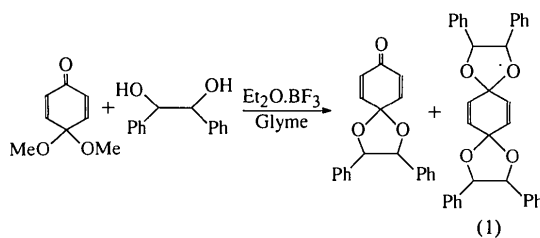
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Abstract

The crystal structure of the title compound, C₃₄H₂₈O₄, consists of discrete molecules held together by normal van der Waals interactions. The molecule possesses a crystallographic twofold axis passing through the midpoints of the two double bonds of the cyclohexadiene ring. The asymmetric C atoms in the dioxolane rings have an *S,S* configuration.

Comment

The title compound, (1), was obtained as a minor product (14% yield, m.p. 475–477 K) from the reaction of 4,4-dimethoxycyclohexadienone (0.015 mol) and (*S,S*)-hydrobenzoin (0.0163 mol) in the presence of Et₂O·BF₃ (0.031 mol) in glyme at 258 K. The product was separated from the major component, 1,4-dioxo-2,3-diphenylspiro[5.4]deca-6,9-dien-8-one (32% yield, m.p. 457 K), and purified by column chromatography (neutral silica) using gradient elution starting with 100% petroleum spirit (313–333 K) to 100% dichloromethane. Both compounds were characterized by IR, ¹H and ¹³C NMR spectroscopy and mass spectral analysis.



The structure of (1) was confirmed by an X-ray study. The absolute configuration could not be determined from this study because of the absence of significant anomalous scattering, but it was implied from the known chirality of the materials used in the synthesis [Flack (1983) parameter = −2.3 (13)]. The molecular structure

of (1) is shown in Fig. 1, which also indicates the atom labelling in the asymmetric unit. The molecule possesses a crystallographic twofold axis passing through the midpoints of the C(16)—C(16') and C(17)—C(17') bonds of the central cyclohexadiene ring. This ring and the terminal phenyl groups are planar within 0.013 (3) Å and have normal geometric parameters, but the dioxolane ring, as expected, is non-planar. The orientations of the phenyl rings relative to their particular OCC moieties of the dioxolane ring are somewhat different, as indicated by the torsion angles O(1)—C(1)—C(3)—C(4) 31.2 (2) and O(2)—C(2)—C(9)—C(10) 42.0 (2)°.

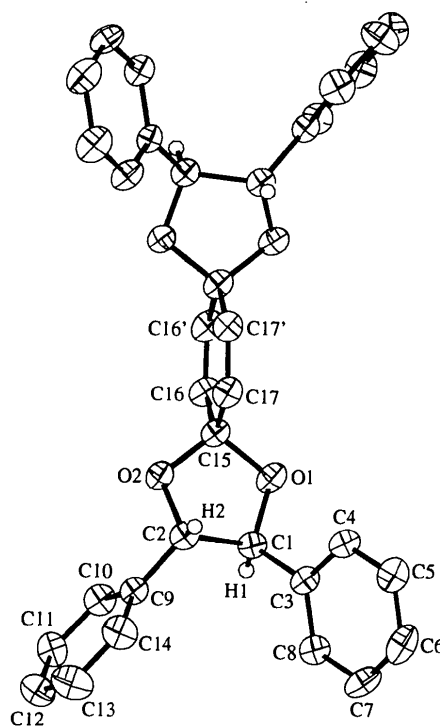


Fig. 1. The molecular structure of (1) showing the atom labelling in the asymmetric unit. Ellipsoids are plotted at the 50% probability level.

It is pertinent to note that the *cis* configuration and *C*₂ symmetry of this molecule, which is of course a direct consequence of the incorporation of the two (*S,S*)-hydrobenzoin, contrasts with the *trans* configuration of the unsubstituted centrosymmetric achiral compound 1,4,9,12-tetraoxadispiro[4.2.4.2]tetradecane, (2) (Chadwick, Dunitz & Schweizer, 1977). These differences are highlighted in Fig. 2. The conformation of the five-membered dioxolane ring is best described as a slightly twisted envelope (Altona, Geize & Romers, 1968) and resembles that in compound (2). The torsion angles in the ring are O(1)—C(1)—C(2)—O(2) 29.6 (2), C(1)—C(2)—O(2)—C(15) −38.1 (2), C(2)—O(2)—C(15)—O(1) 31.8 (2), C(1)—O(1)—C(15)—O(2) −11.8 (2) and

C(2)—C(1)—O(1)—C(15) —11.2(2)°; the corresponding values in the unsubstituted saturated compound (2) are 27.7, -31.9, 23.9, -5.8 and -13.4°, respectively. The two sets of values show a common trend and the differences (2–8°) may be attributed to the presence of the bulky phenyl substituents in compound (1). Other structural parameters are as expected for this type of compound. The intermolecular distances are appropriate for van der Waals interactions.

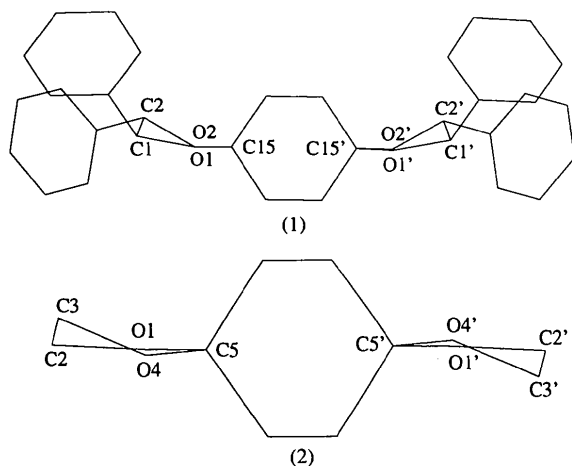


Fig. 2. The structures of compounds (1) and (2) showing the *cis* and *trans* conformations of the C—C ends of the dioxolane rings.

Experimental

Crystal data

C₃₄H₂₈O₄
M_r = 500.56
 Trigonal
*P*3₂21
a = 9.691(2) Å
c = 24.841(6) Å
V = 2020.2(8) Å³
Z = 3
D_x = 1.234 Mg m⁻³
D_m not measured

Mo *K*α radiation
 λ = 0.71069 Å
 Cell parameters from 250 reflections
 θ = 2.43–24.86°
 μ = 0.080 mm⁻¹
T = 140(2) K
 Parallelepiped
 0.30 × 0.20 × 0.10 mm
 Light orange

Data collection

Delft Instruments FAST
 area-detector diffractometer
 Measurement method: Darr,
 Drake, Hursthouse &
 Malik (1993)
 Absorption correction:
 none

8689 measured reflections
 2164 independent reflections
 1728 observed reflections
 $[I > 2\sigma(I)]$
 $R_{\text{int}} = 0.0857$
 $\theta_{\text{max}} = 24.86^\circ$
 $h = -10 \rightarrow 10$
 $k = -11 \rightarrow 11$
 $l = -29 \rightarrow 19$

Refinement

Refinement on *F*²
 $R(F) = 0.0309$
 $wR(F^2) = 0.0629$

$(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.148 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.156 \text{ e } \text{Å}^{-3}$

S = 0.892
 2164 reflections
 228 parameters
 H atoms refined isotropically
 $w = 1/[\sigma^2(F_o^2) + (0.0195P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$

Atomic scattering factors
 from *International Tables
 for Crystallography* (1992,
 Vol. C, Tables 4.2.6.8 and
 6.1.1.4)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U_{eq}</i>
O(1)	0.38457 (15)	0.89924 (14)	0.06650 (5)	0.0335 (3)
O(2)	0.28960 (15)	0.70660 (13)	0.13176 (4)	0.0324 (3)
C(1)	0.3362 (2)	0.7499 (2)	0.03983 (7)	0.0280 (4)
C(2)	0.3295 (2)	0.6406 (2)	0.08617 (7)	0.0285 (4)
C(3)	0.4498 (2)	0.7706 (2)	-0.00524 (7)	0.0267 (4)
C(4)	0.6105 (2)	0.8854 (2)	-0.00196 (8)	0.0325 (5)
C(5)	0.7148 (2)	0.9055 (2)	-0.04297 (8)	0.0396 (5)
C(6)	0.6608 (3)	0.8082 (3)	-0.08825 (8)	0.0405 (5)
C(7)	0.5018 (3)	0.6924 (3)	-0.09192 (8)	0.0377 (5)
C(8)	0.3972 (2)	0.6740 (2)	-0.05079 (7)	0.0321 (5)
C(9)	0.2092 (2)	0.4661 (2)	0.08189 (7)	0.0276 (5)
C(10)	0.0483 (2)	0.4107 (2)	0.08956 (8)	0.0332 (5)
C(11)	-0.0606 (3)	0.2491 (2)	0.08699 (8)	0.0377 (5)
C(12)	-0.0108 (3)	0.1419 (3)	0.07689 (8)	0.0409 (5)
C(13)	0.1492 (3)	0.1962 (2)	0.06840 (9)	0.0469 (6)
C(14)	0.2582 (3)	0.3574 (2)	0.07111 (8)	0.0405 (5)
C(15)	0.3748 (2)	0.8750 (2)	0.12464 (7)	0.0301 (5)
C(16)	0.2799 (2)	0.9429 (2)	0.14825 (7)	0.0323 (5)
C(17)	0.5389 (2)	0.9448 (2)	0.14762 (7)	0.0308 (4)

Table 2. Selected geometric parameters (Å, °)

O(1)—C(1)	1.440 (2)	C(7)—C(8)	1.386 (3)
O(1)—C(15)	1.459 (2)	C(9)—C(14)	1.382 (3)
O(2)—C(15)	1.424 (2)	C(9)—C(10)	1.385 (3)
O(2)—C(2)	1.445 (2)	C(10)—C(11)	1.385 (3)
C(1)—C(3)	1.512 (2)	C(11)—C(12)	1.370 (3)
C(1)—C(2)	1.544 (2)	C(12)—C(13)	1.382 (3)
C(2)—C(9)	1.502 (2)	C(13)—C(14)	1.382 (3)
C(3)—C(4)	1.392 (3)	C(15)—C(16)	1.493 (3)
C(3)—C(8)	1.392 (2)	C(15)—C(17)	1.495 (3)
C(4)—C(5)	1.379 (3)	C(16)—C(16')	1.325 (4)
C(5)—C(6)	1.391 (3)	C(17)—C(17')	1.325 (3)
C(6)—C(7)	1.383 (3)		
C(1)—O(1)—C(15)	109.34 (12)	C(14)—C(9)—C(10)	118.7 (2)
C(15)—O(2)—C(2)	106.23 (13)	C(14)—C(9)—C(2)	120.2 (2)
O(1)—C(1)—C(3)	110.98 (14)	O(10)—C(9)—C(2)	121.1 (2)
O(1)—C(1)—C(2)	103.14 (13)	C(9)—C(10)—C(11)	120.4 (2)
C(3)—C(1)—C(2)	114.90 (15)	C(12)—C(11)—C(10)	120.5 (2)
O(2)—C(2)—C(9)	108.96 (14)	C(11)—C(12)—C(13)	119.6 (2)
O(2)—C(2)—C(1)	102.09 (13)	C(12)—C(13)—C(14)	120.1 (2)
C(9)—C(2)—C(1)	117.53 (15)	C(9)—C(14)—C(13)	120.7 (2)
C(4)—C(3)—C(8)	118.2 (2)	O(2)—C(15)—O(1)	105.15 (13)
C(4)—C(3)—C(1)	120.8 (2)	O(2)—C(15)—C(16)	108.91 (15)
C(8)—C(3)—C(1)	121.0 (2)	O(1)—C(15)—C(16)	108.80 (15)
C(5)—C(4)—C(3)	121.2 (2)	O(2)—C(15)—C(17)	110.33 (14)
C(4)—C(5)—C(6)	120.1 (2)	O(1)—C(15)—C(17)	109.67 (14)
C(7)—C(6)—C(5)	119.5 (2)	C(16)—C(15)—C(17)	113.6 (2)
C(6)—C(7)—C(8)	120.2 (2)	C(16')—C(16)—C(15)	123.20 (11)
C(7)—C(8)—C(3)	120.9 (2)	C(17')—C(17)—C(15)	123.15 (10)

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

The unit-cell and intensity data were recorded at 140 K on a FAST area-detector diffractometer using the routines *ENDEX*, *REFINE* and *MADONL* in the *MADNES* software (Pflugrath & Messerschmidt, 1989); detailed procedures are described by Darr, Drake, Hursthouse & Malik (1993). The H atoms were all located from a difference map and refined isotropically. All calculations were performed on a 486DX2/66 personal computer.

Data reduction: *ABSMAD* (Karaulov, 1992). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SNOOPI* (Davies, 1983). Software used to prepare material for publication: *SHELXL93*.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: SZ1047). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2,3,4,5-Tetra-*O*-acetyl-1,6-di-*O*-(triphenylmethyl)-*D*-mannitol

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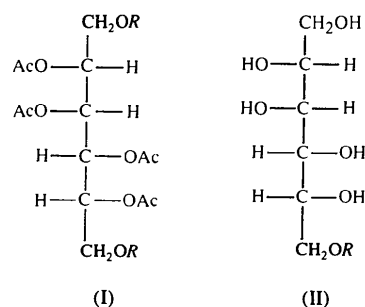
Abstract

The central six-C-atom chain of the title compound, C₅₂H₅₀O₁₀, adopts a nearly planar extended conformation free from C//C, C//O and O//O 1,3-parallel interactions. The three torsion angles formed by these atoms have values of 177.4 (2), 174.2 (2) and –178.0 (2)°. The bulky triphenylmethyl groups, which are oriented *gauche* to their neighboring acetoxy groups with O—

C—C—O torsion angles of –69.8 (2) and –63.0 (2)°, cause no distortion of the bond lengths and bond angles of the sugar moiety.

Comment

The title compound, 2,3,4,5-tetra-*O*-acetyl-1,6-di-*O*-(triphenylmethyl)-*D*-mannitol, (I), is one of the acyclic alditol derivatives which have shown, by crystal structure analyses, to possess some interesting conformational features (Kopf, Morf, Zimmer, Bischoff & Koll 1992). The structure of (I) was determined in order to confirm the identity of the reaction product and to observe to what extent the conformation of its parent compound, *D*-mannitol, (II) (Kim, Jeffrey & Rosenstein 1968; Kanters, Roelofsen & Smiths 1977), might be affected by the presence of the two bulky triphenylmethyl groups.



R = triphenylmethyl

The molecular structure of (I) (Fig. 1) reveals that the molecule does not possess crystallographic twofold symmetry as observed in the parent compound (II). Approximate twofold symmetry is present, however, and the mannitol core has an extended conformation with no 1,3-parallel interactions between the heavy atoms. This conformation is described by the three *anti* torsion angles given in the *Abstract*, as well as O1—C1—C2—C3 and C4—C5—C6—O6 [47.7 (2) and 53.9 (2)°, respectively]. The C—C bond distances in the sugar moiety are in the range 1.514 (3)–1.526 (3) Å while the C—O bonds are in the range 1.411 (2)–1.445 (2) Å, in good agreement with the corresponding values for (II) and other related carbohydrate structures (Jeffrey & French, 1978; Allen, 1986; Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The orientation of the triphenylmethyl groups at the terminal positions (C1 and C6) are *gauche* to their neighbouring acetoxy O atoms, as are the primary hydroxy groups in the parent compound (II), the torsion angles O1—C1—C2—O2 and O6—C6—C5—O5 being –69.8 (2) and –63.0 (2)°, respectively. The four acetoxy groups, on C2, C3, C4, and C5, are oriented in the sequence *trans, gauche, trans*; the torsion angles O2—C2—C3—O3, O3—C3—C4—O4 and O5—C5—C4—O4 are 178.5 (2), 49.9 (2)