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Crystal structure of 2α-(1,1-diphenylethyl)-4-methyl-4α,5α-diphenyl-1,3-dioxolane: the result of a non-acid pinacol rearrangement

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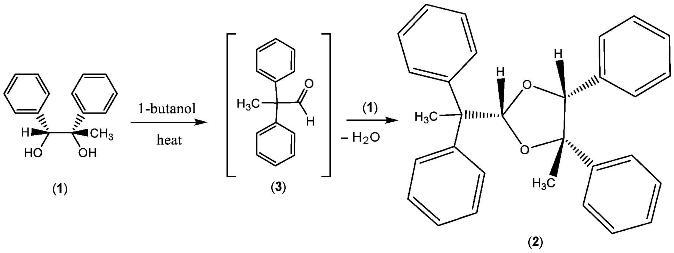
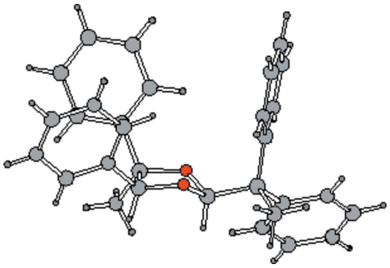
The title compound, $C_{30}H_{28}O_2$, was obtained during recrystallization of (±)-1,2-diphenyl-1,2-propanediol in 1-butanol, from an unexpected non-acid-catalyzed pinacol rearrangement followed by acetal formation of the newly formed aldehyde with the diol. The tri-substituted dioxolane ring has a twist conformation on the C—O bond opposite the methyl-substituted C atom. There is an intramolecular C—H⋯π interaction present involving one of the diphenylethyl rings and an H atom of the phenyl ring in position 4 of the dioxolane ring. In the crystal, molecules are linked by weak C—H⋯O hydrogen bonds, forming chains along [001]. The chains are linked by a second C—H⋯π interaction, forming sheets parallel to the *bc* plane.

1. Chemical context

The pinacol rearrangement is a well-documented reaction (Collins, 1960) that converts substituted 1,2-diols into aldehydes or ketones (pinacolone derivatives), usually with the aid of mineral or Lewis acid catalysis. In the present work, a pinacol rearrangement has occurred during recrystallization **in the absence of a catalyst**, thus transforming the intended object of our study (**1**), into the pinacol rearrangement aldehyde (**3**), which then reacts (by acetal formation) with another molecule of (**1**) to form the unexpected product (**2**) presented in this paper, as shown in the scheme below.



The pseudo-equatorial orientation of the diphenylethane group at C2 likely follows from thermodynamic control during the acetalization step. For the reaction conditions of our recrystallization, the acetalization step must proceed faster than pinacol rearrangement. A similar reaction has been described by Ciminale *et al.* (2005). There are very few other reports of the pinacol rearrangement occurring in the absence of catalysts: for example, the thermal rearrangement of pinacol to pinacolone in supercritical H_2O (Ikushima *et al.*, 2000), the conversion of 1,1,2-triphenylethane-1,2-diol to 1,2,2-triphenylethan-1-one when heated above its melting



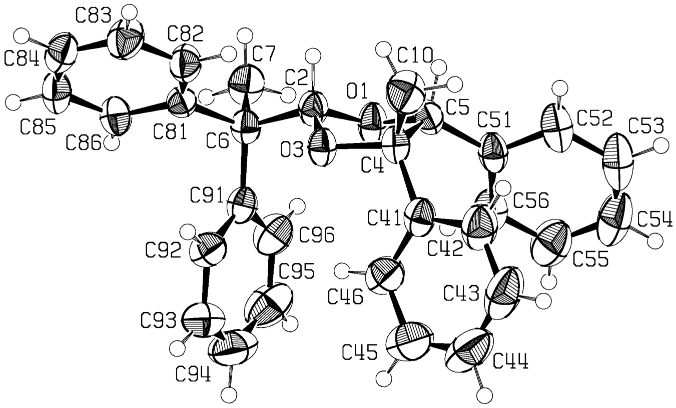


Figure 1
The molecular structure of the title compound, (**2**), with atom labeling. Displacement ellipsoids are drawn at the 50% probability level. One of the H atoms on the methyl group C10 was omitted for clarity.

point (Collins, 1960), and a vinylogous pinacol rearrangement thermally induced in the solid state (Sekiya *et al.*, 2000).

2. Structural commentary

The molecular structure of the title compound, (**2**), is illustrated in Fig. 1. The dioxolane five-membered ring has a twist configuration on bond O1—C2, with atoms O1 and C2 at distances of 0.314 (4) and −0.330 (3) Å above and below the plane through atoms O3/C4/C5. The dioxolane ring has bond angles and distances that are within *ca* 3σ (using the larger s.u. values from the reported structures) of the values found in published X-ray structures (see for example: Rao & Hong Chan, 2014; Jones *et al.*, 1998). The planes of the two phenyl substituents on the dioxolane ring are inclined to one another by 44.67 (13)°. They and the diphenylethyl substituent are all *cis* to one another, in equatorial positions. The phenyl rings of the diphenylethyl substituent are inclined to one another by 68.16 (12)°. There is an intramolecular C—H$\cdots\pi$ interaction present involving one of the diphenylethyl rings (C91–C96) and an H atom of the phenyl ring in position 4 of the dioxolane ring (Table 1).

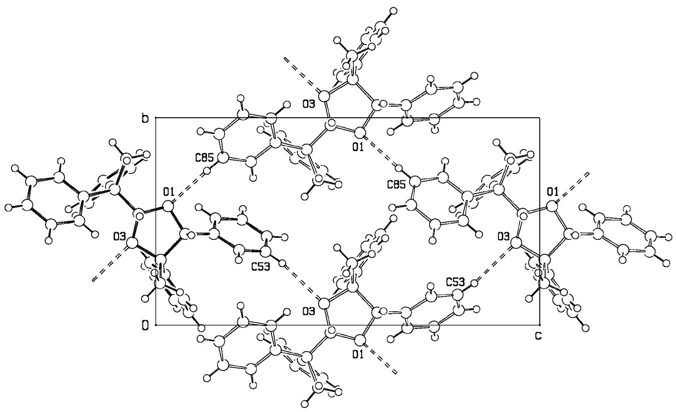


Figure 2
A view in projection along the *a* axis of the crystal packing of the title compound, (**2**). The C—H$\cdots$O hydrogen bonds are shown as double dashed lines.

Table 1
Hydrogen-bond geometry (Å, °).

*Cg*3 and *Cg*5 are the centroids of the C51–C56 and C91–C96 rings, respectively.

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
C53—H53$\cdots$O3^{i}	0.93	2.61	3.533 (3)	170
C85—H85$\cdots$O1^{ii}	0.93	2.50	3.411 (3)	167
C46—H46$\cdots$*Cg*5	0.93	2.99	3.894 (3)	164
C86—H86$\cdots$*Cg*3^{ii}	0.93	2.91	3.799 (2)	160

Symmetry codes: (i) $x, -y+\frac{1}{2}, z+\frac{1}{2}$; (ii) $x, -y+\frac{3}{2}, z-\frac{1}{2}$.

3. Supramolecular features

In the crystal, molecules are linked by weak C—H$\cdots$O hydrogen bonds, forming chains along [001]. The chains are linked by C—H$\cdots$O bonds and by type I C—H$\cdots\pi$ interactions (Malone *et al.*, 1997), forming sheets parallel to the *bc* plane (Table 1 and Fig. 2).

4. Database survey

The Cambridge Structural Database (Version 5.36, last update February 2015; Groom & Allen 2014) was searched for structures containing the dioxolane ring. As there are several thousand dioxolane entries in the database, we selected only entries with the ring atoms plus one H atom each on C2 and C5, which includes the present structure. This search generated 594 hits, with 2227 sets of ring conformational angles that were reduced to 770 after removal of duplicates. There were 28 structures, 4% of the total, that contained near planar dioxolane rings, defined as rings where all torsional angles were less than 16°. Five-membered dioxolane rings have been described as 'puckered envelopes', 'half-chair' or 'twisted'. Arbitrarily broad criteria were used for envelope or twist conformations. Structures were identified as **envelope** when one torsional angle was less than 10° and at least 10° less than the remaining angles, or **twist** when two torsional angles were below 20°, with less than 10° difference between them. In this way, all of the remaining structures could be classified as envelope (447 structures, or 58%) or twist (295 structures, or 38%). The envelope flap was most often one of the ring oxygen atoms (309 structures). In the twist structures, the twisted bond was usually either of the O1—C2 type (145 examples), as in the structure described in this paper, or of the O1–C5 type (123 examples). Of the twist structures, there were 39 like the present structure (**2**), close to an ideal symmetric twist configuration, where the two smallest torsional angles are within 3° of each other.

The wide variety of dioxolane ring conformations found in the structural literature reflects well the conclusion from our own calculations (see: Sections 5 and 6 below) as well as in Willy *et al.* (1970), that the dioxolane ring is highly flexible.

Table 2
Substituted 1,3-dioxolanes (Å, °).

Dioxolane is the title compound (**2**). The phenyl and diphenyl substituents are replaced by H atoms in column two, and CH_3 groups in column three.

Parameter	Ring with H atoms	Ring with CH_3 groups	Dioxolane	X-ray Dioxolane
Bond length				
O1—C2	1.41	1.43	1.39	1.406 (2)
C2—O3	1.41	1.43	1.39	1.408 (2)
O3—C4	1.43	1.45	1.42	1.444 (2)
C4—C5	1.55	1.57	1.59	1.577 (2)
C5—O1	1.43	1.45	1.40	1.427 (2)
Bond angle				
O1—C2—O3	106.3	105.7	104.4	104.5 (1)
C2—O3—O4	106.3	110.0	108.6	106.9 (1)
O3—C4—C5	104.3	101.3	101.5	102.2 (1)
C4—C5—O1	103.8	101.3	102.9	103.0 (1)
C5—O1—C2	104.5	110.0	105.8	103.4 (1)
Torsion angle				
O1—C2—O3—C4	−33.1	−11.8	−35.6	37.59 (2)
C2—O3—C4—C5	13.3	28.1	15.0	−14.28 (2)
O3—C4—C5—O1	10.3	−33.2	10.1	−13.50 (1)
C4—C5—O1—C2	−29.9	28.1	−31.6	35.50 (1)
C5—O1—C2—O3	39.9	−11.8	42.4	−46.21 (2)
Distance from plane				
C2···O3/C4/C5	−0.31	−0.64	+0.34	−0.330 (3)
O1···O3/C4/C5	+0.25	−0.78	−0.24	+0.314 (4)
C4···O1/C2/O3		+0.28		
C5···O1/C2/O3		−0.28		

5. Density functional analysis

A B3LYP/6-311+G(d,p) density functional calculation (Spartan, 2006) of the present molecule in the gas phase shows minimum energy for a twist configuration with similar torsional angles to those in the structure presented here. A calculation where H atoms replace phenyl and diphenylethyl substituents on the dioxolane ring suggests that the large phenyl rings have little effect upon the ring conformation (Table 2).

6. Conformational analysis of 1,3-dioxolane rings

No organic five-membered ring is exactly planar because flat rings would have eclipsed C—C bonds that can have considerable torsional strain. Five-membered rings are usually identified as envelope or half-chair with more or less distortion. The planar part of the ring is described by a least-squares fit of three or four atoms in the ring, or by the torsional angle formed by four contingent atoms in the ring. When only one of the remaining atoms is a significant distance from the plane, this conformation is described as an 'envelope'. The non-planar atom defines the flap of the envelope. The torsional angles of an ideal half-chair configuration have two small angles of a given sign, two medium angles of opposite sign, and a single large angle of the same sign as the first. The Database Survey reveals that any atom in the ring can be the flap atom. When two atoms (one up, the other down) are a significant but different distance from the plane through the other three atoms, the conformation can be described as 'distorted envelope'. When two atoms have equal significant distances in opposite directions from the plane, the ring conformation can be described as 'twist', as shown in Fig. 3. A full range of conformations from ideal envelope to ideal twist is obtained with various substituents on the ring because the various ring conformations do not differ substantially in conformational energy (Willy *et al.* 1970).

Figure 3
Ideal five-membered ring conformations.

To illustrate the conformational properties of the five-membered 1,3-dioxolane ring of the title compound, some B3LYP/6-311+G(d,p) density functional calculation results (Spartan, 2006) are given in Table 2. The atom numbering is shown in Fig. 4. Column two of the table (Ring with H atoms)

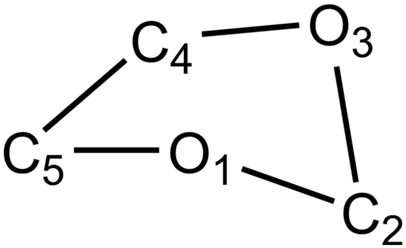


Figure 4
Atom numbering in the 1,3-dioxolane ring.

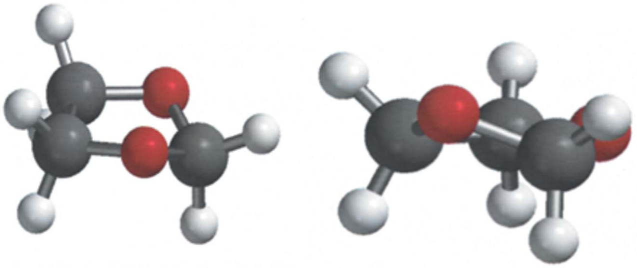


Figure 5
Perspective views of the dioxolane ring with hydrogen atoms as calculated with *Spartan*. Left: viewed as a distorted envelope. Right: viewed as twist.

shows a pattern of dihedral angles similar to the near-perfect twist found in the present crystal structure, shown in column five, where O1—C2 is the twisted bond. Fig. 5 above offers two views of the density functional theory (DFT) optimized structure. The pattern shown in column three (Ring with CH_3 groups), has a much larger (O3—C4—C5—O1) torsional angle. The calculated conformation is still that of a twist, but the twist bond in this CH_3 model is C4—C5, not O1—C2. The best plane through O1—C2—O3 has C4 + 0.28 Å above the plane and C5 − 0.28 Å below the plane, giving the CH_3 model an ideal twist conformation. The DFT-optimized CH_3-substituted structure is depicted in Fig. 6. Column four of Table 2 shows the DFT results for the title compound. The predicted conformation is similar to the conformation found in the crystal structure. The differences between columns four and five are presumably due to packing (intermolecular) forces present in the X-ray structure. The Spartan DFT calculations do not include intermolecular forces, but are calculations in the gas phase. Comparing distance and angle values in column two (dioxolane ring with only H atom substituents) to columns four and five (dioxolane rings with phenyl and diphenylethyl substituents) suggests these larger substituents have little effect upon the ring conformation. Fig. 7 views the title compound as a distorted envelope.

7. Synthesis and crystallization

A sample of (±)-1,2-diphenyl-1,2-propanediol (Ciaccio *et al.*, 2001) was recrystallized in 1-butanol, as well as 2-butanol and 1-octanol. The solutions were mildly heated to obtain saturated solutions, cooled to room temperature and layered over water in an open test tube. In attempts to better characterize the rearrangements that occurred, we also recrystallized the starting material at the reflux temperature of 1-butanol. Thin layer chromatography revealed that the non-acid-catalyzed pinacol rearrangement was substantially complete after 8 h, and that other unknown products were also present. The experimental density of a typical recrystallization product, determined by flotation, is 1.054 g ml^{-1}. The melting point range was 435.9–443.2 K. Redoing the experimental density and melting point with hand-selected crystals with the same morphology as the X-ray data crystal gave values of 1.203 g ml^{-1} and 445.4–448.4 K, respectively.

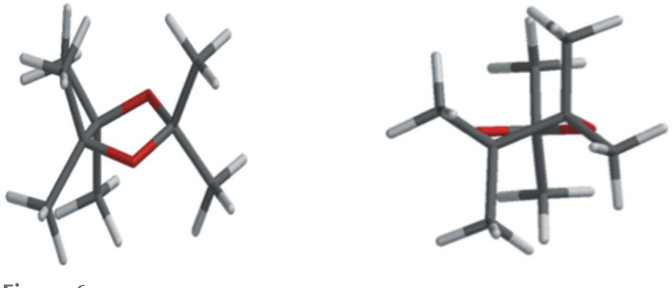


Figure 6
Perspective views of dioxolane ring with methyl groups as calculated with *Spartan*. Left: viewed as distorted envelope. Right: viewed as twist.

Table 3
Experimental details.

Crystal data	
Chemical formula	$C_{30}H_{28}O_2$
M_r	420.52
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	302
a, *b*, *c* (Å)	16.720 (3), 9.0056 (9), 16.6747 (12)
β (°)	112.040 (9)
V (Å^3)	2327.3 (5)
Z	4
Radiation type	Mo *Kα*
μ (mm^{-1})	0.07
Crystal size (mm)	0.4 × 0.4 × 0.26
Data collection	
Diffractometer	Enraf–Nonius CAD-4
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6377, 4547, 2612
R_{int}	0.025
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.616
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.047, 0.133, 1.03
No. of reflections	4547
No. of parameters	291
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.16, −0.18

Computer programs: *CAD-4 EXPRESS* (Enraf–Nonius, 1994), *SUPERFLIP* (Palatinus & Chapuis, 2007), *SHELXL97* (Sheldrick, 2008) and *ORTEPIII* (Burnett & Johnson, 1996). Data reduction followed procedures in Corfield *et al.* (1973) and data were averaged with a local version of *SORTAV* (Blessing, 1989),

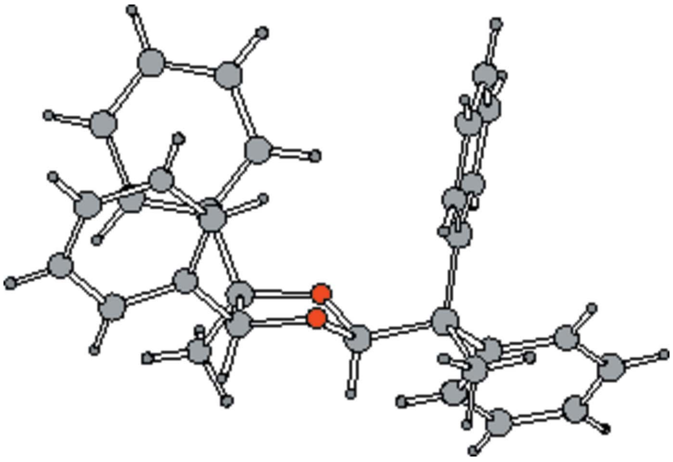


Figure 7
Perspective view of the X-ray structure of the title compound, (**2**).

The proton NMR spectrum was obtained with a Bruker AVANCE-400 NMR spectrometer using hand-picked crystals having the same morphology as the crystal used for the X-ray study. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46 (*d*, 2H), 7.39 (*d*, 2H), 7.3–7.2 (*m*, 6H), 7.0-6.6 (*m*, 8H), 6.44 (*d*, 2H), 5.83 (*s*, 1H), 4.95 (*s*, 1H), 1.97 (*s*, 3H), 1.83 (*s*, 3H).

8. Refinement details

Crystal data, data collection and structure refinement details are summarized in Table 3. The H atoms were included in calculated positions and treated as riding atoms: C—H = 0.96-0.98 Å with $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl H atoms, $U_{eq}(C)$ for methine H atoms, and $1.2U_{eq}(C)$ for other H atoms.

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Crystal structure of 2*α*-(1,1-diphenylethyl)-4-methyl-4*α*,5*α*-diphenyl-1,3-dioxolane: the result of a non-acid pinacol rearrangement

Richard M. Kirchner, Peter W. R. Corfield, Michelle Annabi, John Regan, Kevin Speina, Anthony DiProperzio, James A. Ciaccio and Joseph F. Capitani

Computing details

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); data reduction: Data reduction followed procedures in Corfield *et al.* (1973); Data were averaged with a local version of *SORTAV* (Blessing, 1989); program(s) used to solve structure: Superflip (Palatinus & Chapuis, 2007); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97* (Sheldrick, 2008).

2-(1,1-Diphenylethyl)-4-methyl-4,5-diphenyl-1,3-dioxolane

Crystal data

$C_{30}H_{28}O_2$
$M_r = 420.52$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 16.720$ (3) Å
$b = 9.0056$ (9) Å
$c = 16.6747$ (12) Å
$\beta = 112.040$ (9)°
$V = 2327.3$ (5) Å^3
$Z = 4$
$F(000) = 896$
$D_x = 1.200$ Mg m^{-3}
Melting point = 436–443 K
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 4.5$–10.1°
$\mu = 0.07$ mm^{-1}
$T = 302$ K
Block, colourless
0.4 × 0.4 × 0.26 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
$\theta/2\theta$ scans
6377 measured reflections
4547 independent reflections
2612 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.025$
$\theta_{\text{max}} = 26.0°$, $\theta_{\text{min}} = 2.5°$
$h = -20 \rightarrow 19$
$k = 0 \rightarrow 11$
$l = 0 \rightarrow 20$
3 standard reflections every 180 min
intensity decay: 3.1(8)

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.133$
$S = 1.03$
4547 reflections
291 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.020P)^2 + 0.5P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.16$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. In the monoclinic unit cell, the *a* and *c* axes are of very similar lengths, so that before data collection commenced, it was important to check that the Laue symmetry was indeed 2/m and not mmm. This was accomplished by temporarily transforming the cell to orthorhombic axes, and collecting all 8 forms of the (orthorhombic) 111 and 222 reflections. In each case, the 8 forms clearly split into two different sets of four, verifying the monoclinic symmetry.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.18420 (9)	0.57319 (14)	0.10104 (8)	0.0484 (4)
O3	0.19021 (8)	0.39714 (14)	0.00987 (8)	0.0419 (3)
C2	0.15272 (14)	0.5361 (2)	0.01270 (12)	0.0416 (5)
H2	0.0899	0.5249	−0.0083	0.042*
C4	0.19172 (13)	0.3148 (2)	0.08470 (12)	0.0419 (5)
C41	0.27953 (14)	0.2435 (2)	0.12749 (12)	0.0448 (5)
C42	0.29066 (18)	0.1231 (3)	0.18187 (15)	0.0669 (7)
H42	0.2430	0.0822	0.1897	0.080*
C43	0.3712 (2)	0.0626 (3)	0.22479 (17)	0.0879 (9)
H43	0.3775	−0.0186	0.2612	0.105*
C44	0.4421 (2)	0.1213 (4)	0.21416 (18)	0.0874 (9)
H44	0.4966	0.0810	0.2435	0.105*
C45	0.43208 (17)	0.2395 (3)	0.16012 (17)	0.0770 (8)
H45	0.4799	0.2790	0.1520	0.092*
C46	0.35148 (15)	0.3013 (3)	0.11716 (14)	0.0586 (6)
H46	0.3458	0.3826	0.0810	0.070*
C5	0.17302 (14)	0.4396 (2)	0.14164 (12)	0.0441 (5)
H5	0.1123	0.4325	0.1348	0.044*
C51	0.22718 (15)	0.4399 (2)	0.23635 (12)	0.0459 (5)
C52	0.19966 (18)	0.3615 (3)	0.29192 (14)	0.0636 (7)
H52	0.1466	0.3134	0.2707	0.076*
C53	0.2504 (2)	0.3536 (3)	0.37949 (16)	0.0801 (8)
H53	0.2321	0.2978	0.4164	0.096*
C54	0.3268 (2)	0.4272 (3)	0.41131 (16)	0.0814 (9)
H54	0.3605	0.4228	0.4701	0.098*
C55	0.35420 (18)	0.5080 (3)	0.35694 (16)	0.0758 (8)
H55	0.4063	0.5591	0.3790	0.091*
C56	0.30502 (16)	0.5139 (3)	0.26954 (14)	0.0588 (6)
H56	0.3244	0.5680	0.2329	0.071*
C6	0.17518 (13)	0.6541 (2)	−0.04152 (11)	0.0386 (5)

C7	0.13530 (15)	0.8014 (2)	−0.02620 (14)	0.0543 (6)
H7A	0.1514	0.8808	−0.0555	0.081*
H7B	0.1562	0.8222	0.0347	0.081*
H7C	0.0736	0.7926	−0.0483	0.081*
C81	0.13165 (12)	0.6192 (2)	−0.13860 (11)	0.0373 (5)
C82	0.07434 (14)	0.5033 (2)	−0.17192 (13)	0.0514 (6)
H82	0.0636	0.4371	−0.1344	0.062*
C83	0.03285 (15)	0.4846 (3)	−0.26028 (14)	0.0610 (6)
H83	−0.0060	0.4069	−0.2814	0.073*
C84	0.04836 (15)	0.5791 (3)	−0.31673 (14)	0.0560 (6)
H84	0.0199	0.5667	−0.3761	0.067*
C85	0.10630 (15)	0.6922 (2)	−0.28491 (13)	0.0554 (6)
H85	0.1182	0.7559	−0.3229	0.066*
C86	0.14699 (14)	0.7122 (2)	−0.19714 (12)	0.0478 (5)
H86	0.1858	0.7903	−0.1767	0.057*
C91	0.27312 (13)	0.6670 (2)	−0.01420 (12)	0.0417 (5)
C92	0.31673 (14)	0.5900 (2)	−0.05657 (14)	0.0518 (6)
H92	0.2862	0.5266	−0.1017	0.062*
C93	0.40453 (15)	0.6047 (3)	−0.03367 (16)	0.0679 (7)
H93	0.4322	0.5522	−0.0638	0.082*
C94	0.45124 (17)	0.6955 (3)	0.03284 (19)	0.0790 (8)
H94	0.5104	0.7064	0.0476	0.095*
C95	0.41022 (19)	0.7700 (3)	0.07731 (18)	0.0783 (8)
H95	0.4419	0.8300	0.1237	0.094*
C96	0.32217 (16)	0.7572 (3)	0.05420 (14)	0.0599 (6)
H96	0.2952	0.8099	0.0849	0.072*
C10	0.11855 (16)	0.2027 (3)	0.05553 (15)	0.0652 (7)
H10A	0.0660	0.2516	0.0205	0.098*
H10B	0.1118	0.1596	0.1053	0.098*
H10C	0.1316	0.1259	0.0223	0.098*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0752 (10)	0.0384 (8)	0.0376 (8)	0.0104 (7)	0.0280 (7)	0.0030 (6)
O3	0.0587 (9)	0.0362 (7)	0.0341 (7)	0.0042 (7)	0.0212 (6)	0.0009 (6)
C2	0.0501 (12)	0.0423 (11)	0.0353 (11)	0.0070 (10)	0.0192 (9)	0.0005 (9)
C4	0.0543 (13)	0.0391 (11)	0.0353 (10)	−0.0009 (10)	0.0201 (9)	0.0035 (9)
C41	0.0597 (14)	0.0408 (11)	0.0351 (10)	0.0052 (11)	0.0192 (10)	−0.0053 (9)
C42	0.0881 (19)	0.0587 (15)	0.0575 (14)	0.0193 (14)	0.0313 (14)	0.0118 (13)
C43	0.116 (3)	0.081 (2)	0.0603 (17)	0.043 (2)	0.0258 (18)	0.0202 (15)
C44	0.080 (2)	0.099 (2)	0.0642 (17)	0.041 (2)	0.0058 (16)	−0.0043 (17)
C45	0.0579 (17)	0.093 (2)	0.0720 (17)	0.0099 (16)	0.0146 (14)	−0.0103 (17)
C46	0.0570 (16)	0.0611 (15)	0.0532 (13)	0.0058 (13)	0.0156 (12)	−0.0017 (12)
C5	0.0502 (12)	0.0476 (12)	0.0418 (11)	0.0040 (10)	0.0256 (10)	0.0055 (10)
C51	0.0666 (15)	0.0406 (11)	0.0386 (11)	0.0077 (11)	0.0289 (11)	0.0003 (10)
C52	0.0938 (19)	0.0587 (15)	0.0499 (14)	−0.0016 (14)	0.0401 (13)	0.0036 (12)
C53	0.133 (3)	0.0688 (17)	0.0516 (15)	0.0109 (19)	0.0500 (17)	0.0131 (14)

C54	0.118 (3)	0.0799 (19)	0.0395 (14)	0.0189 (19)	0.0215 (16)	0.0017 (14)
C55	0.0838 (19)	0.0815 (19)	0.0527 (16)	0.0003 (16)	0.0148 (14)	−0.0081 (14)
C56	0.0742 (17)	0.0582 (14)	0.0469 (13)	0.0010 (13)	0.0261 (12)	0.0010 (11)
C6	0.0482 (12)	0.0341 (10)	0.0358 (10)	0.0042 (9)	0.0185 (9)	0.0009 (8)
C7	0.0690 (15)	0.0445 (12)	0.0512 (13)	0.0141 (11)	0.0246 (11)	0.0017 (10)
C81	0.0391 (11)	0.0370 (10)	0.0376 (10)	0.0061 (9)	0.0166 (9)	0.0044 (9)
C82	0.0552 (13)	0.0549 (13)	0.0423 (12)	−0.0080 (12)	0.0163 (10)	0.0081 (11)
C83	0.0616 (15)	0.0645 (15)	0.0467 (13)	−0.0164 (12)	0.0086 (11)	−0.0014 (12)
C84	0.0629 (15)	0.0630 (15)	0.0364 (11)	0.0050 (13)	0.0122 (11)	0.0030 (11)
C85	0.0750 (16)	0.0526 (14)	0.0432 (12)	0.0056 (13)	0.0275 (12)	0.0123 (11)
C86	0.0585 (14)	0.0432 (12)	0.0450 (12)	−0.0043 (11)	0.0231 (10)	0.0027 (10)
C91	0.0507 (13)	0.0354 (10)	0.0372 (10)	0.0011 (10)	0.0143 (9)	0.0040 (9)
C92	0.0471 (14)	0.0550 (13)	0.0491 (12)	0.0028 (11)	0.0131 (10)	−0.0005 (11)
C93	0.0479 (15)	0.0834 (18)	0.0709 (16)	0.0079 (14)	0.0205 (13)	0.0019 (15)
C94	0.0451 (15)	0.084 (2)	0.093 (2)	−0.0030 (15)	0.0084 (15)	0.0103 (17)
C95	0.070 (2)	0.0670 (17)	0.0729 (17)	−0.0140 (15)	−0.0023 (15)	−0.0068 (15)
C96	0.0648 (16)	0.0535 (14)	0.0530 (14)	−0.0017 (12)	0.0125 (12)	−0.0055 (11)
C10	0.0717 (17)	0.0556 (14)	0.0643 (15)	−0.0153 (13)	0.0210 (13)	0.0030 (12)

Geometric parameters (Å, º)

O1—C2	1.406 (2)	C56—H56	0.9300
O1—C5	1.427 (2)	C6—C91	1.531 (3)
O3—C2	1.408 (2)	C6—C81	1.538 (3)
O3—C4	1.444 (2)	C6—C7	1.549 (3)
C2—C6	1.531 (3)	C7—H7A	0.9600
C2—H2	0.9800	C7—H7B	0.9600
C4—C41	1.513 (3)	C7—H7C	0.9600
C4—C10	1.519 (3)	C81—C86	1.381 (3)
C4—C5	1.577 (3)	C81—C82	1.385 (3)
C41—C42	1.381 (3)	C82—C83	1.383 (3)
C41—C46	1.379 (3)	C82—H82	0.9300
C42—C43	1.379 (4)	C83—C84	1.364 (3)
C42—H42	0.9300	C83—H83	0.9300
C43—C44	1.369 (4)	C84—C85	1.368 (3)
C43—H43	0.9300	C84—H84	0.9300
C44—C45	1.364 (4)	C85—C86	1.375 (3)
C44—H44	0.9300	C85—H85	0.9300
C45—C46	1.384 (3)	C86—H86	0.9300
C45—H45	0.9300	C91—C92	1.378 (3)
C46—H46	0.9300	C91—C96	1.390 (3)
C5—C51	1.497 (3)	C92—C93	1.378 (3)
C5—H5	0.9800	C92—H92	0.9300
C51—C52	1.374 (3)	C93—C94	1.363 (4)
C51—C56	1.380 (3)	C93—H93	0.9300
C52—C53	1.388 (3)	C94—C95	1.361 (4)
C52—H52	0.9300	C94—H94	0.9300
C53—C54	1.358 (4)	C95—C96	1.379 (3)

C53—H53	0.9300	C95—H95	0.9300
C54—C55	1.368 (4)	C96—H96	0.9300
C54—H54	0.9300	C10—H10A	0.9600
C55—C56	1.380 (3)	C10—H10B	0.9600
C55—H55	0.9300	C10—H10C	0.9600

C2—O1—C5	103.44 (14)	C51—C56—H56	119.9
C2—O3—C4	106.93 (13)	C2—C6—C91	110.44 (15)
O1—C2—O3	104.48 (14)	C2—C6—C81	110.85 (15)
O1—C2—C6	112.05 (16)	C91—C6—C81	111.09 (15)
O3—C2—C6	112.72 (15)	C2—C6—C7	106.33 (15)
O1—C2—H2	109.2	C91—C6—C7	111.39 (16)
O3—C2—H2	109.2	C81—C6—C7	106.59 (15)
C6—C2—H2	109.2	C6—C7—H7A	109.5
O3—C4—C41	108.94 (15)	C6—C7—H7B	109.5
O3—C4—C10	108.30 (16)	H7A—C7—H7B	109.5
C41—C4—C10	113.07 (17)	C6—C7—H7C	109.5
O3—C4—C5	102.18 (14)	H7A—C7—H7C	109.5
C41—C4—C5	113.25 (16)	H7B—C7—H7C	109.5
C10—C4—C5	110.42 (17)	C86—C81—C82	117.24 (18)
C42—C41—C46	118.0 (2)	C86—C81—C6	118.70 (18)
C42—C41—C4	120.7 (2)	C82—C81—C6	124.00 (17)
C46—C41—C4	121.23 (19)	C83—C82—C81	120.9 (2)
C43—C42—C41	121.1 (3)	C83—C82—H82	119.5
C43—C42—H42	119.5	C81—C82—H82	119.5
C41—C42—H42	119.5	C84—C83—C82	120.7 (2)
C44—C43—C42	120.3 (3)	C84—C83—H83	119.7
C44—C43—H43	119.8	C82—C83—H83	119.7
C42—C43—H43	119.8	C83—C84—C85	119.1 (2)
C45—C44—C43	119.3 (3)	C83—C84—H84	120.4
C45—C44—H44	120.3	C85—C84—H84	120.4
C43—C44—H44	120.3	C84—C85—C86	120.4 (2)
C44—C45—C46	120.7 (3)	C84—C85—H85	119.8
C44—C45—H45	119.6	C86—C85—H85	119.8
C46—C45—H45	119.6	C85—C86—C81	121.6 (2)
C41—C46—C45	120.6 (2)	C85—C86—H86	119.2
C41—C46—H46	119.7	C81—C86—H86	119.2
C45—C46—H46	119.7	C92—C91—C96	116.9 (2)
O1—C5—C51	111.34 (17)	C92—C91—C6	121.47 (17)
O1—C5—C4	102.98 (14)	C96—C91—C6	121.64 (19)
C51—C5—C4	117.29 (17)	C91—C92—C93	121.6 (2)
O1—C5—H5	108.3	C91—C92—H92	119.2
C51—C5—H5	108.3	C93—C92—H92	119.2
C4—C5—H5	108.3	C94—C93—C92	120.6 (2)
C52—C51—C56	118.8 (2)	C94—C93—H93	119.7
C52—C51—C5	119.2 (2)	C92—C93—H93	119.7
C56—C51—C5	122.01 (18)	C95—C94—C93	119.1 (2)
C51—C52—C53	120.6 (3)	C95—C94—H94	120.4

C51—C52—H52	119.7	C93—C94—H94	120.4
C53—C52—H52	119.7	C94—C95—C96	120.7 (2)
C54—C53—C52	120.0 (2)	C94—C95—H95	119.7
C54—C53—H53	120.0	C96—C95—H95	119.7
C52—C53—H53	120.0	C95—C96—C91	121.1 (2)
C53—C54—C55	120.0 (2)	C95—C96—H96	119.4
C53—C54—H54	120.0	C91—C96—H96	119.4
C55—C54—H54	120.0	C4—C10—H10A	109.5
C54—C55—C56	120.4 (3)	C4—C10—H10B	109.5
C54—C55—H55	119.8	H10A—C10—H10B	109.5
C56—C55—H55	119.8	C4—C10—H10C	109.5
C55—C56—C51	120.2 (2)	H10A—C10—H10C	109.5
C55—C56—H56	119.9	H10B—C10—H10C	109.5

O1—C2—O3—C4	37.54 (19)	C4—C5—O1—C2	35.48 (18)
C2—O3—C4—C5	−14.20 (18)	C5—O1—C2—O3	−46.16 (18)
O3—C4—C5—O1	−13.06 (18)		

Hydrogen-bond geometry (Å, º)

Cg3 and Cg5 are the centroids of the C51–C56 and C91–C96 rings, respectively.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C53—H53···O3^{i}	0.93	2.61	3.533 (3)	170
C85—H85···O1^{ii}	0.93	2.50	3.411 (3)	167
C46—H46···*Cg*5	0.93	2.99	3.894 (3)	164
C86—H86···*Cg*3^{ii}	0.93	2.91	3.799 (2)	160

Symmetry codes: (i) *x*, −*y*+1/2, *z*+1/2; (ii) *x*, −*y*+3/2, *z*−1/2.