Acta Cryst. (1997). C53, 340–342

Twinned Crystal Structure of Bis(2-hydroxy-4,4-dimethyl-6-oxo-1-cyclohexenyl)phenylmethane at 150 K

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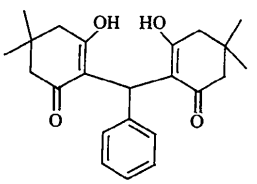
(Received 20 September 1996; accepted 18 October 1996)

Abstract

The title compound, 2,2′-(phenylmethylene)bis(3-hydroxy-5,5-dimethylcyclohex-2-en-1-one), $C_{23}H_{28}O_4$, forms tetragonal crystals twinned on (110). The two molecules in the asymmetric unit differ only in the conformation of one of the two cyclohexenone rings which both display the expected envelope conformation; while three apices are extended towards the phenyl ring, one is directed away from it. The molecules form two strong intramolecular hydrogen bonds connecting the two cyclohexenone rings. The X-ray structure analysis was undertaken in order to ascertain the nature of the reaction product.

Comment

The title compound, (I), crystallizes with two molecules in the asymmetric unit (Fig. 1). A least-squares fit (r.m.s. deviation of fitted atoms = 0.1144 Å) shows the similarities between the two molecules (Fig. 2).



(I)

All four cyclohexenone rings display envelope conformations. While the C14, C14*A* and C24*A* atoms are directed towards the phenyl ring, C24 is bent away from the aromatic residue. The two cyclohexenone rings of each molecule are connected by two strong hydrogen bonds, so that two additional eight-membered rings are formed. The geometric parameters of the moieties O12—C12—C11—C16—O16, O22—C22—C21—C26—O26, O12*A*—C12*A*—C11*A*—C16*A*—O16*A* and O22*A*—C22*A*—C21*A*—C26*A*—O26*A* indicate that each of these groups forms a conjugated π-system. All four cyclohexenone rings display envelope conformations, with the C11, C12, C13, C15 and C16 (r.m.s. deviation = 0.024 Å), C21, C22, C23, C25 and C26 (r.m.s. deviation = 0.061 Å), C11*A*, C12*A*, C13*A*, C15*A* and C16*A* (r.m.s. deviation = 0.028 Å), and C21*A*, C22*A*, C23*A*, C25*A* and C26*A* (r.m.s. deviation = 0.039 Å) sets of atoms in common planes, while the

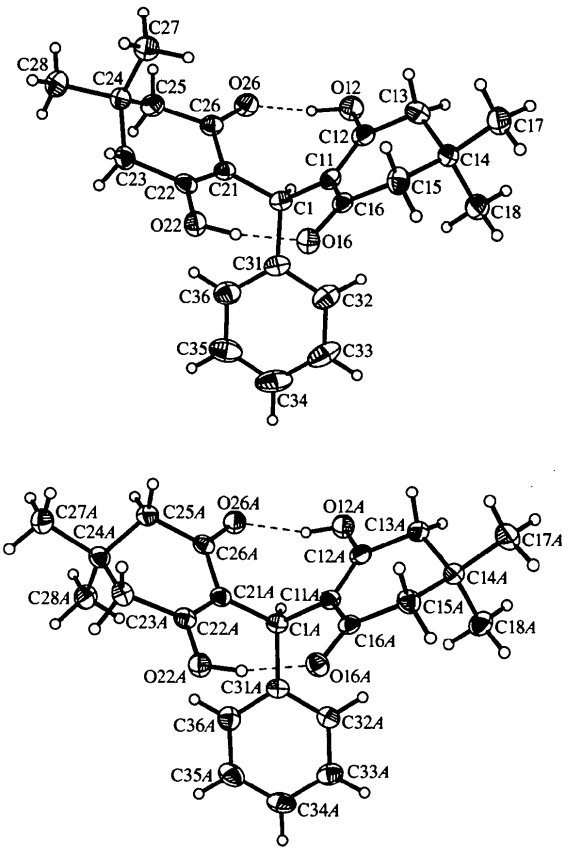


Fig. 1. Perspective view of the two molecules of the title compound with the atom-numbering schemes. Displacement ellipsoids are shown at the 50% probability level.

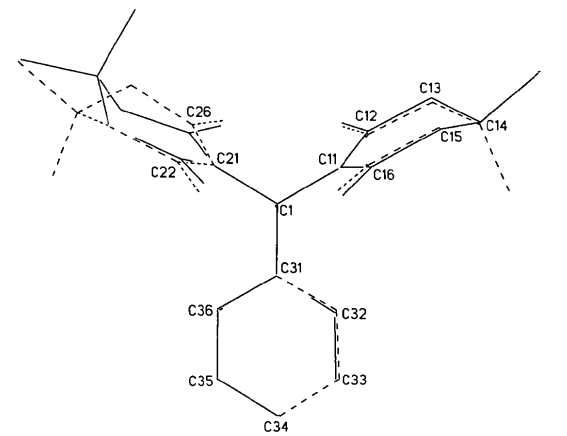


Fig. 2. Least-squares fit of the two molecules in the asymmetric unit, with fitted atoms labelled.

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C14, C24, C14*A* and C24*A* atoms deviate from their respective planes by 0.629 (3), 0.594 (3), 0.608 (2) and 0.658 (2) Å. No significant intermolecular contacts could be found.

Experimental

The title compound was obtained by mixing a solution of 0.6 g (4.3 mmol) 5,5-dimethyl-1,3-cyclohexanedione in 8 ml 50% ethanol with 0.2 ml (2 mmol) benzaldehyde. After addition of a catalytic quantity of piperidine, the reaction mixture was heated to boiling. After 10 min of reflux, the solution was cooled to 273 K. The white crystalline solid which formed was collected by filtration. The crude product was purified by recrystallization from ethanol/water (1:1). Suitable crystals were obtained by slow evaporation of a diethyl ether solution.

Crystal data

$C_{23}H_{28}O_4$
M_r = 368.45
Tetragonal
$I4_1/a$
a = 20.7727 (2) Å
c = 36.6751 (1) Å
V = 15825.5 (2) Å^3
Z = 32
D_x = 1.237 Mg m^{-3}
D_m not measured
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 8192 reflections
θ = 2.0–26.0°
μ = 0.083 mm^{-1}
T = 150 K
Block
0.80 × 0.40 × 0.30 mm
Colourless

Data collection

Siemens CCD three-circle diffractometer
ω scans
Absorption correction: none
74 624 measured reflections
7940 independent reflections
7442 reflections with $I > 2\sigma(I)$
R_{int} = 0.0483
θ_{max} = 26.45°
$h = -25 \rightarrow 25$
$k = -25 \rightarrow 24$
$l = -44 \rightarrow 45$
1049 standard reflections
frequency: 480 min
intensity decay: negligible

Refinement

Refinement on F^2
$R(F)$ = 0.0392
$wR(F^2)$ = 0.0855
S = 1.180
7940 reflections
504 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0292P)^2 + 9.3976P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.119 (U_{12} of C36*A*)
$\Delta\rho_{max}$ = 0.180 e Å^{-3}
$\Delta\rho_{min}$ = −0.188 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

C1—C21	1.525 (2)	C1*A*—C21*A*	1.527 (2)
C1—C11	1.526 (2)	C1*A*—C11*A*	1.527 (2)
C11—C12	1.370 (2)	C11*A*—C12*A*	1.362 (2)
C11—C16	1.439 (2)	C11*A*—C16*A*	1.445 (2)
C12—O12	1.335 (2)	C12*A*—O12*A*	1.343 (2)
C12—C13	1.493 (3)	C12*A*—C13*A*	1.497 (3)
C13—C14	1.533 (3)	C13*A*—C14*A*	1.531 (2)
C14—C15	1.533 (3)	C14*A*—C15*A*	1.528 (2)
C15—C16	1.507 (2)	C15*A*—C16*A*	1.504 (2)
C16—O16	1.252 (2)	C16*A*—O16*A*	1.247 (2)
C21—C22	1.364 (2)	C21*A*—C22*A*	1.371 (2)
C21—C26	1.447 (2)	C21*A*—C26*A*	1.446 (2)
C22—O22	1.328 (2)	C22*A*—O22*A*	1.328 (2)
C22—C23	1.504 (2)	C22*A*—C23*A*	1.495 (2)
C23—C24	1.533 (2)	C23*A*—C24*A*	1.529 (2)
C24—C25	1.525 (3)	C24*A*—C25*A*	1.526 (2)
C25—C26	1.511 (3)	C25*A*—C26*A*	1.510 (2)
C26—O26	1.246 (2)	C26*A*—O26*A*	1.250 (2)
C21—C1—C11	113.95 (14)	C21*A*—C1*A*—C11*A*	113.02 (13)
C12—C11—C16	118.11 (16)	C12*A*—C11*A*—C16*A*	117.86 (15)
C12—C11—C1	120.98 (15)	C12*A*—C11*A*—C1*A*	122.29 (14)
C16—C11—C1	120.78 (15)	C16*A*—C11*A*—C1*A*	119.70 (14)
O12—C12—C11	123.59 (17)	O12*A*—C12*A*—C11*A*	123.65 (16)
O12—C12—C13	112.60 (16)	O12*A*—C12*A*—C13*A*	111.99 (15)
C11—C12—C13	123.80 (16)	C11*A*—C12*A*—C13*A*	124.34 (15)
C12—C13—C14	114.54 (15)	C12*A*—C13*A*—C14*A*	114.78 (14)
C16—C15—C14	114.96 (15)	C16*A*—C15*A*—C14*A*	115.78 (14)
O16—C16—C11	121.90 (15)	O16*A*—C16*A*—C11*A*	121.69 (15)
O16—C16—C15	117.78 (15)	O16*A*—C16*A*—C15*A*	118.21 (14)
C11—C16—C15	120.27 (15)	C11*A*—C16*A*—C15*A*	120.06 (15)
C22—C21—C26	118.25 (15)	C22*A*—C21*A*—C26*A*	117.82 (15)
C22—C21—C1	124.89 (14)	C22*A*—C21*A*—C1*A*	125.48 (15)
C26—C21—C1	116.82 (15)	C26*A*—C21*A*—C1*A*	116.60 (14)
O22—C22—C21	124.17 (15)	O22*A*—C22*A*—C21*A*	123.94 (15)
O22—C22—C23	112.06 (15)	O22*A*—C22*A*—C23*A*	112.30 (14)
C21—C22—C23	123.73 (15)	C21*A*—C22*A*—C23*A*	123.76 (15)
C22—C23—C24	113.95 (15)	C22*A*—C23*A*—C24*A*	114.54 (14)
C26—C25—C24	113.16 (15)	C26*A*—C25*A*—C24*A*	114.03 (14)
O26—C26—C21	122.36 (16)	O26*A*—C26*A*—C21*A*	122.02 (16)
O26—C26—C25	119.44 (15)	O26*A*—C26*A*—C25*A*	118.44 (15)
C21—C26—C25	118.19 (16)	C21*A*—C26*A*—C25*A*	119.45 (15)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O12—H12···O26	1.02 (3)	1.65 (3)	2.656 (2)	170 (3)
O22—H22···O16	0.93 (3)	1.66 (3)	2.571 (2)	164 (3)
O12*A*—H12*A*···O26*A*	0.92 (3)	1.76 (3)	2.645 (2)	160 (2)
O22*A*—H22*A*···O16*A*	0.91 (3)	1.69 (3)	2.572 (2)	161 (2)

The data collection nominally covered over a sphere of reciprocal space by a combination of six sets of exposures; each set had a different φ angle for the crystal and each exposure covered 0.3° in ω. The crystal-to-detector distance was 5.95 cm. Coverage of the unique set was over 99% complete to at least 26° in θ. Crystal decay was monitored by repeating the initial frames at the end of data collection and analyzing the duplicate reflections. Despite the excellent reflection profiles and promising R_{int} = 0.048 and R_{sigma} = 0.021 values, the data displayed some suspicious signs, *i.e.* R_{int} for Laue group *4/mmm* (0.052) was only insignificantly higher than that for *4/m* and the mean value of $|E^2 - 1|$ was 0.772, but the systematic absence exceptions were pointing to space group $I4_1/a$, which is centrosymmetric. The structure could only be solved with difficulty by direct methods using *SHELXS*86 (Sheldrick, 1990). Anisotropic refinement with *SHELXL*93 (Sheldrick, 1993) by full-matrix least-squares methods remained stuck at $R1$ = 0.31, yielding non-sensible anisotropic displacement parameters. It was therefore assumed that the crystal was twinned and applying the twin law (010/100/00$\bar{1}$) provided the ultimate success ($R1$ dropped below 0.1). All H atoms could now be located by difference Fourier synthesis. While the four hydroxyl H atoms were refined isotropically, the others were refined with fixed individual displacement parameters [U(H) = 1.5U_{eq}(C_{methyl}) or 1.2U_{eq}(C)] using a riding model with aromatic C—H = 0.95, methyl C—H = 0.98, secondary C—H = 0.99 and tertiary C—H = 1.0 Å. The twin ratio refined to 0.5200 (8).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Molecular graphics: *XP* in *SHELXTL-Plus* (Sheldrick, 1991).

Lists of atomic coordinates, displacement parameters, structure factors and complete geometry have been deposited with the IUCr (Reference: SK1062). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Acta Cryst. (1997). C**53**, 342–343

Bis(*p*-methoxyphenyl) Telluride

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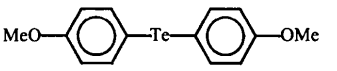
(*Received 26 July 1996; accepted 21 October 1996*)

Abstract

The title compound, $C_{14}H_{14}O_2Te$, displays an angular geometry at tellurium, with a C—Te—C angle of 99.5 (1)° and Te—C distances of 2.110 (3) and 2.112 (3) Å. The Te atom is displaced by 0.1963 (3) and 0.0044 (3) Å out of the planes of the aromatic rings. These rings are approximately perpendicular to one another [dihedral angle 70.4 (1)°], while each methoxy group is almost coplanar with the phenyl ring to which it is bonded [dihedral angles 3.3 (2) and 1.5 (3)°].

Comment

Aside from the pioneering work of Blackmore & Abrahams (1955) on $(p\text{-}MeC_6H_4)_2Te$, based on a partial data set, only three other diaryl tellurides, Ar—Te—Ar′, have been structurally characterized, *viz.* $(p\text{-}EtOC_6H_4)Te[o\text{-}C_6H_4(o\text{-}C_5NH_4)]$ (Al-Salim, West & McWhinnie, 1988), $[o\text{-}(p\text{-}MeOC_6H_4N{:}CH)C_6H_4]_2Te$ (Sadekov *et al.*, 1989) and $(o\text{-}PhC_6H_4)_2Te$ (Chen, Hamor, Singh & McWhinnie, 1996). As part of our synthetic and structural studies on organotellurium compounds (Farran, Alvarez-Larena, Piniella, Germain & Torres-Castellanos, 1995*a*,*b*; Matheus, Torres, Piniella, Briansó & Miravitlles, 1991; Matheus, Torres, Cabiativa, Fuertes & Miravitlles, 1991; Matheus, Torres, Piniella & Miravitlles, 1991; Torres, 1990), we report here the structure of bis(*p*-methoxyphenyl) telluride, (I).



(I)

The crystals of (I) contain discrete $(p\text{-}MeOC_6H_4)_2Te$ molecules (Fig. 1) which display an angular geometry at tellurium, as predicted by the valence-shell electron-pair repulsion (VSEPR) model for an AX_2E_2 molecule (Gillespie & Hargittai, 1991, and references therein). The Te—C distances are equal within experimental error and their values are comparable with that of 2.116 (20) Å tabulated by Allen *et al.* (1987) for Te—C(aryl) bonds, and with those of 2.105 (5) and 2.125 (5) Å observed in $(o\text{-}PhC_6H_4)_2Te$ (Chen *et al.*, 1996). As expected, the C—Te—C angle is substantially smaller than the tetrahedral value (109.5°) due to the repulsion of bonded electron pairs by lone pairs. This angle, however, is somewhat larger than those observed in the above-mentioned diaryl tellurides; 94.8 (2) in $(p\text{-}EtOC_6H_4)Te[o\text{-}C_6H_4(o\text{-}C_5NH_4)]$ (Al-Salim *et al.*, 1988), 96.3 (2) in $[o\text{-}(p\text{-}MeOC_6H_4N{:}CH)C_6H_4]_2Te$ (Sadekov *et al.*, 1989) and 96.2 (2)° in $(o\text{-}PhC_6H_4)_2Te$ (Chen *et al.*, 1996).

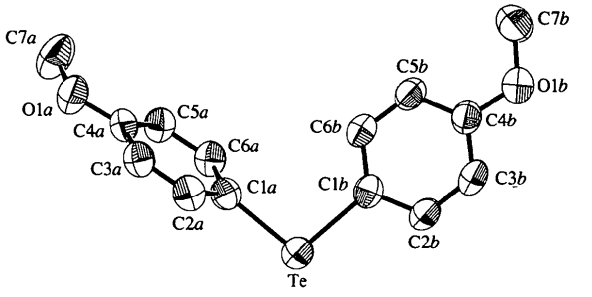


Fig. 1. The molecular structure of the title compound showing the displacement ellipsoids drawn at the 50% probability level. H atoms have been omitted for clarity.

Each aromatic ring is planar [to within 0.007 (3) Å]. The Te atom lies 0.1963 (3) and 0.0044 (3) Å from the planes of rings *a* and *b*, respectively. The angles between the C—Te—C plane and those of the phenyl rings differ [70.8 (1) and 2.0 (1)° for rings *a* and *b*] and the phenyl rings are approximately perpendicular to one another [inter-ring dihedral angle 70.4 (1)°].

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