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2,3-Dimethylbutane-2,3-diyl 1,2-phenylene orthocarbonate

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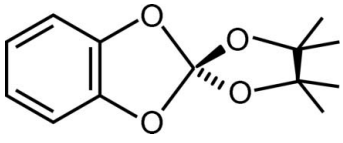
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.004 Å; R factor = 0.070; wR factor = 0.145; data-to-parameter ratio = 17.5.

The title compound, $C_{13}H_{16}O_4$, is a mixed orthocarbonic acid ester derived from the alcohol components benzene-1,2-diol and 2,3-dimethylbutane-2,3-diol (pinacol). The spirocyclic molecules exhibit noncrystallographic C_2 symmetry. The C—O bonds between the spiro centre and the aliphatic dioxy fragment are markedly shorter than the bonds to the aromatic residue. Neither steric strain, which equalizes the bond lengths in a glucoside analogue, nor the packing of the molecules in the crystal structure are responsible for the large C—O bond-length range, which obviously is a molecular property.

Related literature

The orthocarbonate was prepared in analogy to a published procedure (Mues & Buysch, 1990). Related mixed aliphatic–aromatic spirocyclic orthocarbonates have been described recently; a bicyclic aliphatic component shows the same marked bond-length differences as the title compound (Betz & Klüfers, 2007*a*), whereas one with a glucoside as the aliphatic diol does not (Betz & Klüfers, 2007*b*).



Experimental

Crystal data

$C_{13}H_{16}O_4$
M_r = 236.26
Monoclinic, $P2_1/n$
a = 12.165 (2) Å
b = 8.2420 (12) Å
c = 13.321 (2) Å
β = 114.146 (16)°
V = 1218.8 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.10 mm^{-1}
T = 200 (2) K
0.28 × 0.27 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
6937 measured reflections
2797 independent reflections
1892 reflections with $I > 2\sigma(I)$
R_{int} = 0.050

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.070
$wR(F^2)$ = 0.145
S = 1.13
2797 reflections
160 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{max}$ = 0.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O12—C10	1.372 (3)	O21—C10	1.432 (3)
O13—C10	1.361 (3)	O22—C10	1.428 (3)
O12—C12—C13—O13	34.0 (2)		

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2005); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2005); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2330).

References

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  doi:10.1107/S1600536807046405

supplementary materials

Acta Cryst. (2007). E**63**, o4152 [**doi:10.1107/S1600536807046405**]

2,3-Dimethylbutane-2,3-diyl 1,2-phenylene orthocarbonate

R. Betz, N. Jahn and P. Klüfers

Comment

The spirocyclic orthocarbonate derived from benzene-1,2-diol and 2,3-dimethylbutane-2,3-diol (pinacol) has been prepared to obtain NMR data and structural details for comparison with analogous spirocyclic silicon compounds.

The overall molecular symmetry of (I) is close to C_2. In the spiro centre of the molecules of (I), a carbon atom is bonded to a 1,2-dioxybenzene moiety and to the chelating alkylenedioxy fragment derived from pinacol. The spiro centre exhibits two kinds of C—O bonds: shorter bonds to the aliphatic dioxy group and longer bonds to the aromatic fragment (Table 1). The bond-length difference obviously is not caused by packing effects. Accordingly, the crystal structure does not show any specific intermolecular interactions. Instead, a typical van der Waals packing is observed (Figure 2). A similar situation has been found and analyzed by means of DFT calculations for a related orthocarbonic-acid spiroester of the bicyclic norbornane-2,7-diol as the aliphatic alcohol (Betz & Klüfers, 2007*a*). With their similar C—O bond patterns, both (I) and the norbornane compound appear to be the unstrained normal cases.

A related glucose derivative desribed recently (Betz & Klüfers, 2007*b*), which does not show the obviously characteristic bond-length difference, now appears as a special case whose molecular structure is determined by internal strain: though the diol torsion angle of *ca* 42° of the *trans*-pyranoidic diol function that is forced into a five-membered ring is markedly compressed compared with the free sugar (*trans*-pyranose diol angles typically exceed 60°), it does not reach the even smaller value of the open-chain chain title compound of 34°.

Experimental

To a solution of 1 eq of pinacol and 2 eq of pyridine in dry dichloromethane was added a solution of 1 eq. of 2,2-dichlorobenzo[1.3]dioxol. The solution was stirred for several hours at room temperature, the organic layer washed with water, dried over Na_2SO_4, filtered and evaporated to dryness. The solid obtained was recrystallized from boiling ethylacetate.

Refinement

All H atoms were located in a difference map and refined as riding on their parent atoms. One common isotropic displacement parameter for the methyl H atoms and one common U_{iso} for the phenyl H atoms were refined.

Figures

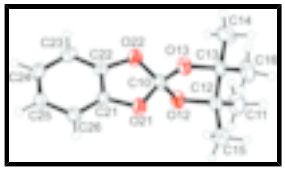

Fig. 1. The molecular structure of (I), with atom labels and anisotropic displacement ellipsoids (drawn at 50% probability level) for non-H atoms.

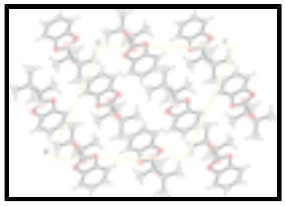

Fig. 2. The packing of (I), viewed along [0 1 0].

2,3-Dimethylbutane-2,3-diyl 1,2-phenylene orthocarbonate

Crystal data

$C_{13}H_{16}O_4$	$Z = 4$
$M_r = 236.26$	$F_{000} = 504$
Monoclinic, $P2_1/n$	$D_x = 1.288$ Mg m^{-3}
Hall symbol: -P 2yn	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 12.165$ (2) Å	$\theta = 4.2$–27.5º
$b = 8.2420$ (12) Å	$\mu = 0.10$ mm^{-1}
$c = 13.321$ (2) Å	$T = 200$ (2) K
$\beta = 114.146$ (16)º	Block, colourless
$V = 1218.8$ (4) Å^3	0.28 × 0.27 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer	1892 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.050$
Monochromator: graphite	$\theta_{max} = 27.5$º
$T = 200$(2) K	$\theta_{min} = 4.2$º
ω scans	$h = -15\rightarrow15$
Absorption correction: none	$k = -10\rightarrow10$
6937 measured reflections	$l = -17\rightarrow7$
2797 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.070$	Only H-atom displacement parameters refined
$wR(F^2) = 0.145$	$w = 1/[\sigma^2(F_o^2) + (0.0522P)^2 + 0.0465P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.13$	$(\Delta/\sigma)_{max} < 0.001$
2797 reflections	$\Delta\rho_{max} = 0.23$ e Å^{-3}
160 parameters	$\Delta\rho_{min} = -0.18$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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. refU for H atoms: 2 parameters refined, one for methyl-H U and one for phenyl-H U.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O12	0.48066 (13)	0.26004 (18)	0.24474 (12)	0.0348 (4)
O13	0.62337 (13)	0.09153 (18)	0.35363 (12)	0.0366 (4)
O21	0.52256 (13)	0.02093 (18)	0.17456 (12)	0.0341 (4)
O22	0.42256 (14)	0.01756 (19)	0.28749 (12)	0.0387 (4)
C10	0.51416 (19)	0.1005 (3)	0.26671 (18)	0.0314 (5)
C11	0.5443 (3)	0.5229 (3)	0.3242 (2)	0.0547 (8)
H111	0.4966	0.5779	0.2547	0.066 (2)*
H112	0.6139	0.5902	0.3679	0.066 (2)*
H113	0.4944	0.5053	0.3653	0.066 (2)*
C12	0.5875 (2)	0.3614 (3)	0.30062 (18)	0.0343 (6)
C13	0.6568 (2)	0.2544 (3)	0.40176 (18)	0.0349 (6)
C14	0.6143 (3)	0.2719 (3)	0.4931 (2)	0.0569 (8)
H141	0.5262	0.2657	0.4622	0.066 (2)*
H142	0.6406	0.3770	0.5295	0.066 (2)*
H143	0.6485	0.1845	0.5468	0.066 (2)*
C15	0.6508 (2)	0.3813 (3)	0.2243 (2)	0.0504 (7)
H151	0.5945	0.4270	0.1541	0.066 (2)*
H152	0.6791	0.2753	0.2114	0.066 (2)*
H153	0.7197	0.4546	0.2580	0.066 (2)*
C16	0.7923 (2)	0.2652 (3)	0.4455 (2)	0.0539 (8)
H161	0.8183	0.2337	0.3876	0.066 (2)*
H162	0.8287	0.1922	0.5086	0.066 (2)*
H163	0.8179	0.3769	0.4686	0.066 (2)*
C21	0.43220 (18)	−0.0945 (2)	0.13746 (17)	0.0271 (5)
C22	0.37234 (19)	−0.0959 (3)	0.20499 (17)	0.0286 (5)
C23	0.2770 (2)	−0.1976 (3)	0.18734 (19)	0.0365 (6)
H23	0.2355	−0.1981	0.2342	0.036 (3)*
C24	0.2445 (2)	−0.3000 (3)	0.0967 (2)	0.0388 (6)
H24	0.1790	−0.3727	0.0810	0.036 (3)*
C25	0.3050 (2)	−0.2987 (3)	0.02915 (19)	0.0369 (6)
H25	0.2806	−0.3708	−0.0317	0.036 (3)*
C26	0.4016 (2)	−0.1935 (3)	0.04813 (17)	0.0327 (5)
H26	0.4434	−0.1912	0.0016	0.036 (3)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O12	0.0300 (8)	0.0307 (8)	0.0367 (9)	0.0013 (7)	0.0065 (7)	−0.0025 (7)
O13	0.0339 (9)	0.0291 (8)	0.0362 (9)	0.0008 (7)	0.0034 (7)	−0.0029 (7)
O21	0.0328 (8)	0.0381 (9)	0.0358 (9)	−0.0090 (7)	0.0185 (7)	−0.0104 (7)
O22	0.0408 (9)	0.0411 (10)	0.0408 (9)	−0.0114 (8)	0.0235 (8)	−0.0132 (8)
C10	0.0300 (12)	0.0314 (12)	0.0319 (12)	−0.0026 (10)	0.0117 (10)	−0.0051 (10)
C11	0.0606 (19)	0.0356 (14)	0.0572 (17)	0.0052 (13)	0.0133 (15)	−0.0067 (13)
C12	0.0327 (13)	0.0303 (12)	0.0354 (13)	−0.0036 (10)	0.0091 (11)	−0.0042 (10)
C13	0.0383 (13)	0.0277 (12)	0.0329 (13)	−0.0010 (10)	0.0089 (11)	−0.0057 (10)
C14	0.078 (2)	0.0561 (18)	0.0372 (15)	−0.0022 (16)	0.0240 (15)	−0.0071 (13)
C15	0.0564 (17)	0.0503 (16)	0.0461 (15)	−0.0119 (13)	0.0226 (14)	−0.0017 (13)
C16	0.0401 (15)	0.0474 (16)	0.0539 (17)	−0.0011 (13)	−0.0013 (13)	−0.0115 (13)
C21	0.0240 (11)	0.0248 (11)	0.0290 (11)	−0.0006 (9)	0.0075 (9)	0.0016 (9)
C22	0.0289 (11)	0.0289 (11)	0.0284 (11)	0.0014 (9)	0.0121 (10)	0.0008 (9)
C23	0.0354 (13)	0.0393 (14)	0.0405 (14)	−0.0033 (11)	0.0214 (11)	0.0034 (11)
C24	0.0306 (12)	0.0372 (14)	0.0457 (14)	−0.0107 (10)	0.0126 (11)	−0.0010 (11)
C25	0.0397 (14)	0.0318 (12)	0.0345 (13)	−0.0076 (10)	0.0104 (11)	−0.0078 (10)
C26	0.0337 (12)	0.0360 (13)	0.0294 (12)	−0.0019 (10)	0.0138 (10)	−0.0043 (10)

Geometric parameters (Å, °)

O12—C10	1.372 (3)	C14—H143	0.9800
O12—C12	1.466 (3)	C15—H151	0.9800
O13—C10	1.361 (3)	C15—H152	0.9800
O13—C13	1.471 (3)	C15—H153	0.9800
O21—C21	1.383 (2)	C16—H161	0.9800
O21—C10	1.432 (3)	C16—H162	0.9800
O22—C22	1.381 (2)	C16—H163	0.9800
O22—C10	1.428 (3)	C21—C26	1.363 (3)
C11—C12	1.510 (3)	C21—C22	1.369 (3)
C11—H111	0.9800	C22—C23	1.371 (3)
C11—H112	0.9800	C23—C24	1.392 (3)
C11—H113	0.9800	C23—H23	0.9500
C12—C15	1.514 (3)	C24—C25	1.375 (3)
C12—C13	1.541 (3)	C24—H24	0.9500
C13—C16	1.509 (3)	C25—C26	1.397 (3)
C13—C14	1.511 (3)	C25—H25	0.9500
C14—H141	0.9800	C26—H26	0.9500
C14—H142	0.9800		
C10—O12—C12	108.26 (16)	H141—C14—H143	109.5
C10—O13—C13	108.72 (17)	H142—C14—H143	109.5
C21—O21—C10	107.25 (16)	C12—C15—H151	109.5
C22—O22—C10	107.25 (16)	C12—C15—H152	109.5
O13—C10—O12	109.57 (18)	H151—C15—H152	109.5
O13—C10—O22	112.13 (18)	C12—C15—H153	109.5

O12—C10—O22	108.24 (17)	H151—C15—H153	109.5
O13—C10—O21	108.50 (17)	H152—C15—H153	109.5
O12—C10—O21	112.04 (18)	C13—C16—H161	109.5
O22—C10—O21	106.37 (16)	C13—C16—H162	109.5
C12—C11—H111	109.5	H161—C16—H162	109.5
C12—C11—H112	109.5	C13—C16—H163	109.5
H111—C11—H112	109.5	H161—C16—H163	109.5
C12—C11—H113	109.5	H162—C16—H163	109.5
H111—C11—H113	109.5	C26—C21—C22	122.7 (2)
H112—C11—H113	109.5	C26—C21—O21	128.1 (2)
O12—C12—C11	107.21 (19)	C22—C21—O21	109.24 (18)
O12—C12—C15	108.03 (18)	C21—C22—C23	122.2 (2)
C11—C12—C15	111.1 (2)	C21—C22—O22	109.63 (18)
O12—C12—C13	99.91 (17)	C23—C22—O22	128.2 (2)
C11—C12—C13	115.79 (19)	C22—C23—C24	116.1 (2)
C15—C12—C13	113.7 (2)	C22—C23—H23	122.0
O13—C13—C16	106.63 (18)	C24—C23—H23	122.0
O13—C13—C14	108.3 (2)	C25—C24—C23	121.7 (2)
C16—C13—C14	111.3 (2)	C25—C24—H24	119.2
O13—C13—C12	100.74 (16)	C23—C24—H24	119.2
C16—C13—C12	115.1 (2)	C24—C25—C26	121.4 (2)
C14—C13—C12	113.8 (2)	C24—C25—H25	119.3
C13—C14—H141	109.5	C26—C25—H25	119.3
C13—C14—H142	109.5	C21—C26—C25	116.0 (2)
H141—C14—H142	109.5	C21—C26—H26	122.0
C13—C14—H143	109.5	C25—C26—H26	122.0
C13—O13—C10—O12	8.1 (2)	O12—C12—C13—C16	148.18 (19)
C13—O13—C10—O22	−112.1 (2)	C11—C12—C13—C16	−97.1 (3)
C13—O13—C10—O21	130.69 (18)	C15—C12—C13—C16	33.3 (3)
C12—O12—C10—O13	16.1 (2)	O12—C12—C13—C14	−81.7 (2)
C12—O12—C10—O22	138.60 (17)	C11—C12—C13—C14	33.1 (3)
C12—O12—C10—O21	−104.42 (19)	C15—C12—C13—C14	163.5 (2)
C22—O22—C10—O13	−123.52 (19)	C10—O21—C21—C26	176.2 (2)
C22—O22—C10—O12	115.50 (18)	C10—O21—C21—C22	−2.9 (2)
C22—O22—C10—O21	−5.1 (2)	C26—C21—C22—C23	0.0 (3)
C21—O21—C10—O13	125.73 (18)	O21—C21—C22—C23	179.2 (2)
C21—O21—C10—O12	−113.18 (18)	C26—C21—C22—O22	−179.52 (19)
C21—O21—C10—O22	4.9 (2)	O21—C21—C22—O22	−0.3 (2)
C10—O12—C12—C11	−152.62 (19)	C10—O22—C22—C21	3.4 (2)
C10—O12—C12—C15	87.6 (2)	C10—O22—C22—C23	−176.1 (2)
C10—O12—C12—C13	−31.5 (2)	C21—C22—C23—C24	0.2 (3)
C10—O13—C13—C16	−147.44 (19)	O22—C22—C23—C24	179.6 (2)
C10—O13—C13—C14	92.7 (2)	C22—C23—C24—C25	0.0 (3)
C10—O13—C13—C12	−27.0 (2)	C23—C24—C25—C26	−0.4 (4)
O12—C12—C13—O13	34.0 (2)	C22—C21—C26—C25	−0.4 (3)
C11—C12—C13—O13	148.7 (2)	O21—C21—C26—C25	−179.4 (2)
C15—C12—C13—O13	−80.9 (2)	C24—C25—C26—C21	0.5 (3)

Fig. 1

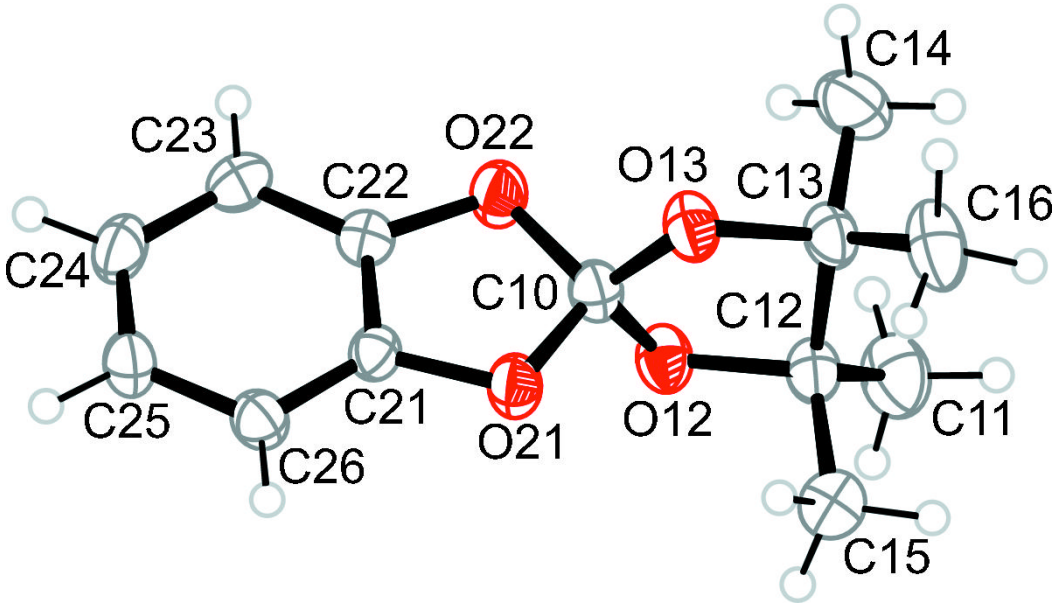
C14
C23
O22
O13
C13
C16
C22
C24
C10
C12
C25
C21
O21
O12
C11
C26
C15

Fig. 2