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trans-5-(4-Bromobenzoyloxy)-2-phenyl-1,3-dioxane

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Key indicators

Single-crystal X-ray study
T = 300 K
Mean σ(C–C) = 0.012 Å
R factor = 0.054
wR factor = 0.099
Data-to-parameter ratio = 13.7

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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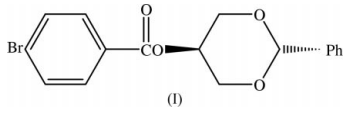
The structure of the major product from the treatment of benzaldehyde with glycerol, derivatized as its crystalline 4-bromobenzoate, is shown to be the title compound, $C_{17}H_{15}BrO_4$, by a room-temperature single-crystal X-ray structure determination, providing a rare example of a structurally characterized 1,3-dioxane system.

Comment

The treatment of glycerol with benzaldehyde yields benzylidene glycerol as a mixture of four possible isomers (Baggett *et al.*, 1960). On esterification of the mixture with 4-bromobenzoyl chloride, the *trans*-1,3-dioxane (I) was readily obtained as a pure and substantial crop from the reaction mixture, the needles being characterized by a room-temperature single-crystal X-ray structure determination.



(I)

Compound (I) crystallizes in triclinic space group $P\overline{1}$, a single molecule, devoid of crystallographic symmetry, comprising the asymmetric unit of the structure. Bond lengths and angles in the molecule are unexceptional; the carboxylate CCO_2 array is approximately coplanar with its parent six-C-atom aromatic ring [interplanar dihedral angle = 11.7 (3)°], the latter in turn having a dihedral angle of 80.0 (3)° with the other aromatic plane. The aromatic planes, parallel and close to their inversion images, appear to be a significant determinant of crystal packing. The carboxylate and phenyl pendants lie equatorial to the dioxane ring, which adopts a chair conformation, with ring torsion angles in the bonds, sequentially beginning with O1—C2, closely ranged about 60°, being −61.2 (8), 58.7 (8), −58.6 (8), 56.0 (9), −55.3 (9) and 58.7 (8)°. Well defined structurally characterized examples of the 1,3-dioxane ring (in contrast to 1,4-dioxane) are very few; examples are found, *O*,*O*′-bridging pairs of Ag^I atoms, in $AgAsF_6\cdot 3C_4H_8O_2$ (Jones *et al.*, 1984) and, less precisely, as solvents of crystallization or clathrates of larger organic molecules (Caira *et al.*, 1999; Gdaniec *et al.*, 1995).

Experimental

4–Bromobenzoyl chloride (260 mg, 1.2 mmol) was added to a solution containing a mixture of four isomers of benzylidene glycerol (180 mg, 1.0 mmol) in dichloromethane/pyridine (9:1, 10 ml) and the solution was stirred (room temperature, 6 h). Excess acid chloride was decomposed by the addition of water (0.5 ml) and, after an hour, the solvent was removed. Normal workup (Et_2O), followed by

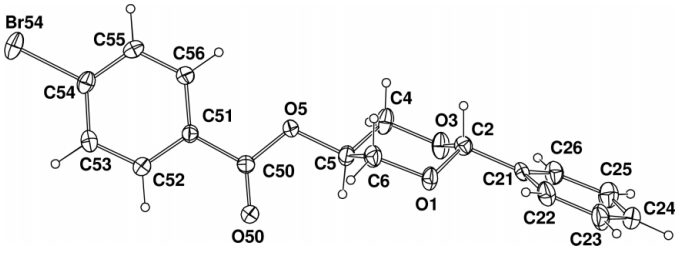


Figure 1
Projection of the molecule. Non-H-atom displacement ellipsoids are shown at the 50% probability level and H atoms are represented by spheres of arbitrary radii of 0.1 Å.

chromatography (EtOAc/hexane, 2:8), allowed the isolation of pure (I) (45 mg) as needles (m.p. 427–429 K). ^{1}H NMR (80 MHz): δ 3.70–3.97 (*m*, H4ax,6ax), 4.53 (*ddd*, $J_{4,4}$ = 9.9 Hz, $J_{4eq,5}$ = 5.1 Hz, $J_{4eq,6eq}$ = 1.2 Hz, H4eq,6eq), 5.27 (*tt*, $J_{4ax,5}$ = 9.9 Hz, H5), 5.53 (*s*, H2), 7.37–8.10 (*m*, 9H, Ar).

Crystal data

$C_{17}H_{15}BrO_4$
M_r = 363.22
Triclinic, $P\overline{1}$
a = 8.117 (4) Å
b = 9.977 (7) Å
c = 10.737 (6) Å
α = 113.47 (4)°
β = 90.49 (4)°
γ = 93.98 (5)°
V = 795.0 (9) Å^3
Z = 2
D_x = 1.517 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 6 reflections
θ = 9.0–12.7°
μ = 2.6 mm^{-1}
T = 300 (2) K
Plate, colourless
0.40 × 0.21 × 0.09 mm

Data collection

Syntex $P\overline{1}$ diffractometer
2θ–ω scans
Absorption correction: Gaussian (*Xtal*3.5; Hall *et al.*, 1995)
T_{min} = 0.55, T_{max} = 0.81
2718 measured reflections
2718 independent reflections
1251 reflections with $I > 2\sigma(I)$
θ_{max} = 25.0°
$h = -9 \rightarrow 0$
$k = -10 \rightarrow 10$
$l = -11 \rightarrow 11$
9 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.099
S = 1.17
2718 reflections
199 parameters
H-atom parameters not refined
$w = 1/(\sigma^2(F^2) + 2.4F^2)$
$(\Delta/\sigma)_{max}$ = 0.002
$\Delta\rho_{max}$ = 1.27 e Å^{-3}
$\Delta\rho_{min}$ = −0.86 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C2	1.402 (9)	C5—C6	1.498 (11)
O1—C6	1.430 (9)	C5—O5	1.445 (8)
C2—O3	1.401 (9)	O5—C50	1.361 (8)
C2—C21	1.495 (9)	C50—O50	1.184 (11)
O3—C4	1.427 (9)	C54—Br54	1.890 (7)
C4—C5	1.515 (12)		
C2—O1—C6	112.2 (6)	C4—C5—O5	107.7 (7)
O1—C2—O3	110.9 (5)	C6—C5—O5	111.9 (6)
O1—C2—C21	108.0 (7)	O1—C6—C5	108.6 (6)
O3—C2—C21	109.3 (5)	C5—O5—C50	115.1 (6)
C2—O3—C4	111.1 (6)	O5—C50—O50	123.7 (6)
O3—C4—C5	109.3 (8)	O5—C50—C51	111.6 (7)
C4—C5—C6	108.6 (6)	O50—C50—C51	124.7 (6)

H atoms were located from difference Fourier maps and placed at idealized positions [C—H = 0.95 Å and U_{iso}(H) = 1.25 times U_{eq}(C)]. The maximum electron-density peak is located 0.088 Å from the Br atom.

Data collection: *Syntex Software* (Syntex, 1974); cell refinement: *Syntex Software*; data reduction: *Xtal*3.5 (Hall *et al.*, 1995); program(s) used to solve structure: *Xtal*3.5; program(s) used to refine structure: *CRYLSQ* in *Xtal*3.5; molecular graphics: *Xtal*3.5; software used to prepare material for publication: *BONDLA* and *CIFIO* in *Xtal*3.5.

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