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Ethyl 3,5-bis(allyloxy)-4-bromobenzoate

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.006 Å
R factor = 0.052
wR factor = 0.084
Data-to-parameter ratio = 19.1

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

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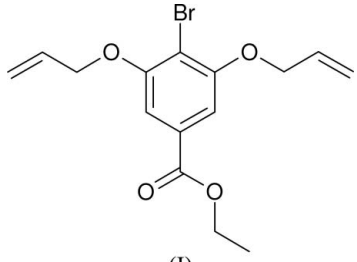
The asymmetric molecular conformation of the title compound, $C_{15}H_{17}BrO_4$, may be be influenced by an intramolecular C—H···O interaction. The molecules form π–π stacks in the crystal structure.

Comment

The title compound, (I) (Fig. 1), was prepared as part of our studies to determine the philicity of aryl radicals by competitive cyclization reactions (Kirsop *et al.*, 2004).



(I)

Compound (I) possesses normal geometrical parameters. The dihedral angle between the mean plane of the C1–C6 benzene ring and the plane of the C7/O1/O2 group is 6.0 (5)°. The two —O—CH_2—CH═CH_2 side chains have very different conformations (Fig. 1), which may be attributable, at least in part, to an intramolecular C12—H12*A*···O3 interaction (Table 1). The molecules form π–π stacks in the crystal structure (Fig. 2), with alternating centroid-to-centroid

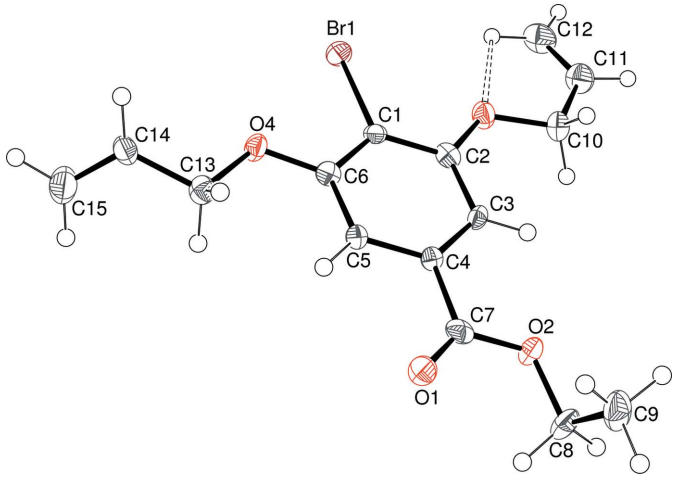


Figure 1
The molecular structure of (I), showing 50% displacement ellipsoids for non-H atoms. The intramolecular C—H···O interaction referred to in the *Comment* is indicated by a dashed line.

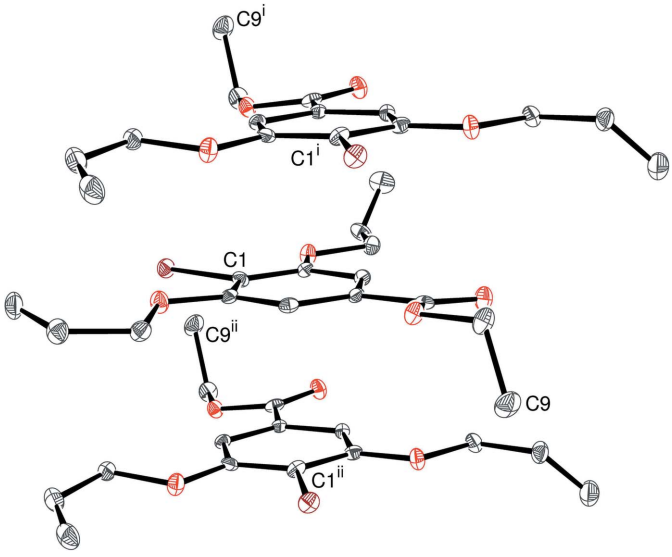


Figure 2
Part of a π–π stacked column of molecules (30% displacement ellipsoids and H atoms omitted). [Symmetry codes: (i) x, $-y$, $1-z$; (ii) x, $1-y$, $1-z$.]

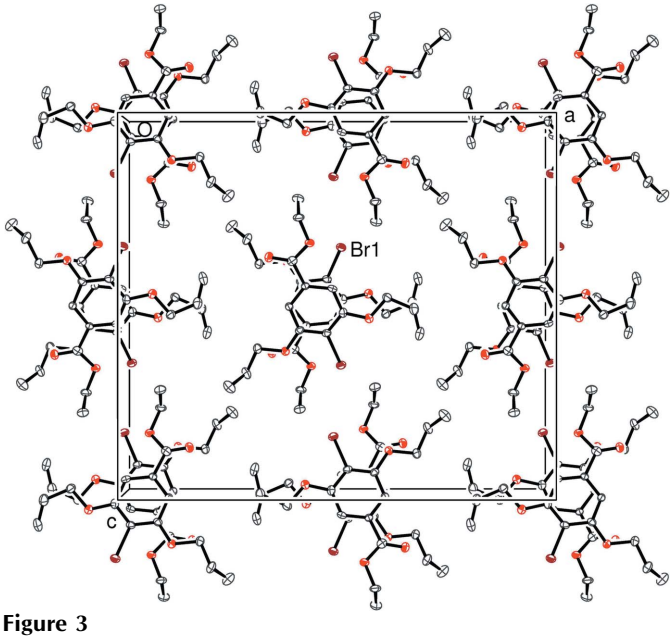


Figure 3
Unit-cell contents of (I), viewed down [010] (50% displacement ellipsoids and H atoms omitted).

separations between benzene rings [$Cg\cdots Cg^{i}$ = 3.626 (2), $Cg\cdots Cg^{ii}$ = 3.466 (2) Å; symmetry codes: (i) x, $-y$, $1-z$; (ii) x, $1-y$, $1-z$]. The stacking interactions give rise to columns of molecules along [010] (Fig. 3).

Experimental

4-Bromo-3,5-dihydroxybenzoic acid (6.8 g, 0.03 mol) was added to 100 ml of ethanol. Concentrated H_2SO_4 (1 ml) was added and the mixture was refluxed for 14 h. After cooling, the solvent was removed at reduced pressure to give a pale yellow oil. Diethyl ether (100 ml) was added and the mixture was neutralized by careful addition of a saturated $NaHCO_3$ solution (100 ml). The mixture was transferred to a separating funnel and the product extracted with diethyl ether (4 × 100 ml). The combined extracts were dried over anhydrous $MgSO_4$ and evaporated under reduced pressure to give 4-bromo-3,5-dihydroxybenzoic acid ethyl ester as a white powder (7.5 g, 96%). Ethyl 4-bromo-3,5-dihydroxybenzoate (3.00 g, 0.011 mol), allyl bromide (1.30 g, 0.011 mol) and K_2CO_3 (8.00 g, 0.0579 mol) were added to 100 ml of dry acetone. The mixture was stirred at room temperature under a nitrogen atmosphere for 14 h, then filtered and the solvent removed at reduced pressure to give a dark brown oil. Thin layer chromatography (4:1 hexane–ethyl acetate eluent) showed the title compound as a sharp spot at R_F = 0.52. The crude product was purified by flash column chromatography to yield a white powder (1.42 g, 38%). A sample of this powder was recrystallized from hot hexane to give translucent needles of (I) (m.p. 315–317 K).

Crystal data

$C_{15}H_{17}BrO_4$
M_r = 341.20
Orthorhombic, $C222_1$
a = 22.1421 (2) Å
b = 7.0559 (13) Å
c = 19.5604 (11) Å
V = 3056.0 (6) Å^3
Z = 8
D_x = 1.483 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 2.70 mm^{-1}
T = 120 (2) K
Needle, colourless
0.22 × 0.04 × 0.02 mm

Data collection

Nonius KappaCCD diffractometer
ω and φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
T_{min} = 0.588, T_{max} = 0.948
10933 measured reflections
3495 independent reflections
2604 reflections with $I > 2\sigma(I)$
R_{int} = 0.084
θ_{max} = 27.5°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.084
S = 1.01
3495 reflections
183 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.47 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), 1500 Friedel pairs
Flack parameter: 0.106 (13)

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

D—H···A	D—H	H···A	D···A	D—H···A
C12—H12A···O3	0.95	2.39	2.715 (6)	100

H atoms were placed in idealized locations (C—H = 0.95–0.99 Å) and refined as riding atoms, with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *SCALEPACK* and *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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