

## 1-Allyloxy-2-bromo-3-(3-phenylallyloxy)benzene

Peter Kirsop, John M. D. Storey  
and William T. A. Harrison\*Department of Chemistry, University of  
Aberdeen, Meston Walk, Aberdeen AB24 3UE,  
ScotlandCorrespondence e-mail:  
w.harrison@abdn.ac.uk

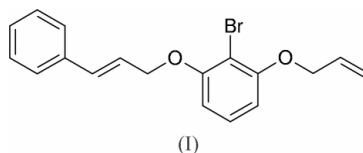
## Key indicators

Single-crystal X-ray study  
 $T = 293$  K  
Mean  $\sigma(\text{C}-\text{C}) = 0.006$  Å  
 $R$  factor = 0.041  
 $wR$  factor = 0.111  
Data-to-parameter ratio = 16.5For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The title compound,  $\text{C}_{18}\text{H}_{17}\text{BrO}_2$ , possesses normal geometrical parameters. A possible intramolecular  $\text{C}-\text{H}\cdots\text{O}$  interaction is present. The crystal packing is influenced by  $\pi-\pi$  stacking.

## Comment

The title compound, (I) (Fig. 1), arose during our studies to determine the philicity of aryl radicals by competitive cyclization (Kirsop *et al.*, 2004a,b).



Compound (I) possesses normal geometrical parameters. A *PLATON* (Spek, 2003) analysis of (I) indicated that an intramolecular  $\text{C}-\text{H}\cdots\text{O}$  interaction (Table 1) may occur between an *exo* methylene  $\text{C}1-\text{H}1A$  group and acceptor  $\text{O}1$ , which may help to stabilize an essentially planar arrangement of the atoms  $\text{C}1$ ,  $\text{C}2$ ,  $\text{C}3$  and  $\text{O}1$  [ $\text{C}1-\text{C}2-\text{C}3-\text{O}1 = -3.0(6)^\circ$ ]. The acute  $\text{C}-\text{H}\cdots\text{O}$  bond angle of  $100^\circ$  is consistent with the intramolecular nature of this interaction.

As well as van der Waals forces, the crystal packing in (I) is influenced by  $\pi-\pi$  stacking interactions. Inversion symmetry results in dimeric associations of molecules of (I) with a  $\text{C}_g\cdots\text{C}_g^i$  separation of  $3.767(3)$  Å [ $\text{C}_g$  is the geometric centroid of atoms  $\text{C}13-\text{C}18$ ; symmetry code: (i)  $-1 - x, 2 - y, -z$ ]. The ring planes are exactly parallel and separated by  $3.55(3)$  Å. The lateral displacement of  $\text{C}_g^i$  relative to the perpendicular from  $\text{C}_g$  to the mean plane for the atoms  $\text{C}13^i-\text{C}18^i$  is  $1.25(8)$  Å. The packing of (I) is shown in Fig. 2.

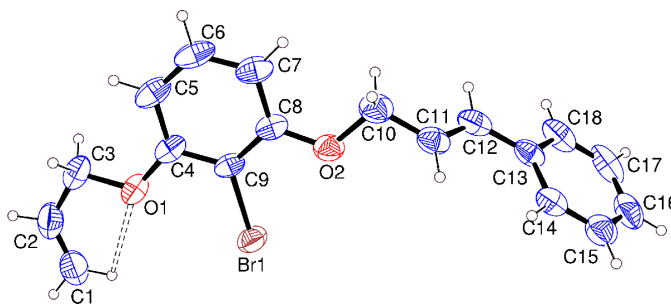


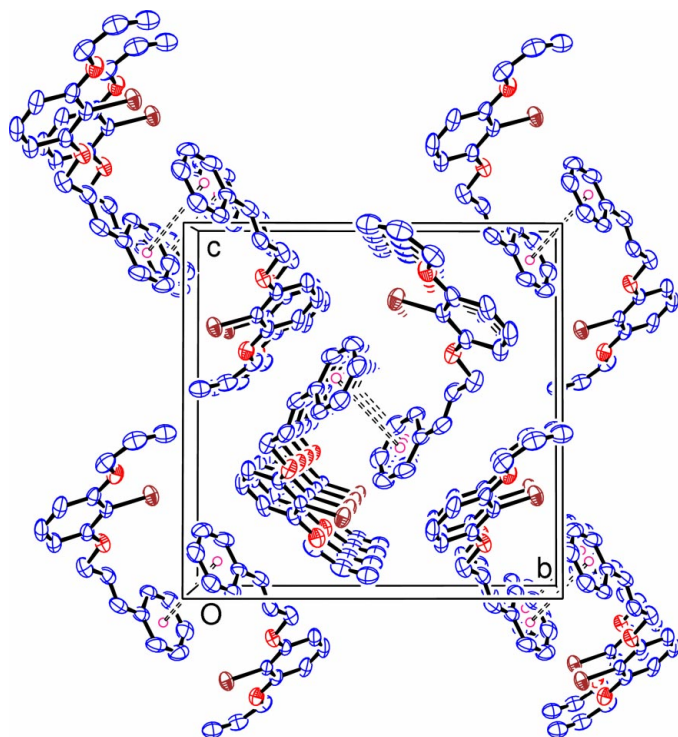
Figure 1

The molecular structure of (I) (30% displacement ellipsoids). H atoms are drawn as small spheres of arbitrary radius and the possible intramolecular  $\text{C}-\text{H}\cdots\text{O}$  interaction is shown as a dashed lines.

Received 24 May 2004

Accepted 1 June 2004

Online 12 June 2004



**Figure 2**  
The packing in (I) projected on to (100), with  $\pi$ - $\pi$  stacking interactions involving the C13–C18 phenyl rings indicated by dashed lines and all C–H H atoms omitted for clarity (30% displacement ellipsoids).

## Experimental

2-Bromobenzene-1,3-diol (Kirsop *et al.*, 2004b; 5.00 g, 0.026 mol), allyl bromide (3.20 g, 0.026 mol) and potassium carbonate (8.00 g, 0.0579 mol) were added to 100 ml of dry acetone. The mixture was stirred at reflux under a nitrogen atmosphere for 3 h. After cooling, the mixture was filtered and the solvent removed at reduced pressure to give a dark brown oil (4.64 g, 78%). Thin-layer chromatography (4:1 hexane–ethyl acetate) showed three sharp spots: at  $R_F = 0.24$  was unreacted starting material, at  $R_F = 0.38$  was 3-allyloxy-2-bromophenol, and at  $R_F = 0.52$  was 1,3-bis(allyloxy)-2-bromobenzene. These compounds were separated using flash column chromatography to give 3-allyloxy-2-bromophenol as a clear oil (1.85 g, 31%).  $^1\text{H NMR}$ :  $\delta_H$  ( $\text{CDCl}_3$ ) 4.58 (2H, *d*,  $J = 4.9$  Hz,  $\text{CH}_2$ ), 5.30 (1H, *d*,  $J = 10.7$  Hz, CH), 5.47 (1H, *d*,  $J = 17.1$  Hz, CH) 5.74 (1H, *s*, OH), 6.05 (1H, *m*, CH), 6.45 (1H, *d*,  $J = 8.2$  Hz, Ar-H), 6.66 (1H, *d*,  $J = 9.8$  Hz, Ar-H), 7.12 (1H, *t*,  $J = 8.2$  Hz, Ar-H).  $^{13}\text{C NMR}$ :  $\delta_C$  69.8, 100.6, 105.0, 108.6, 117.8, 128.6, 132.6, 153.6, 155.5.  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 3497, 2912, 1595, 1463, 1269, 1192, 1064, 767.

A mixture of 3-allyloxy-2-bromophenol (2.00 g, 0.009 mol), cinnamyl bromide (2.06 g, 0.011 mol) and potassium carbonate (8.0 g, 0.058 mol) was added to dry acetone (100 ml). The mixture was stirred at reflux under a nitrogen atmosphere for 12 h. After cooling, the mixture was filtered and the solvent removed at reduced pressure to give a dark brown oil (1.92 g, 68%). Thin-layer chromatography (4:1 hexane–ethyl acetate) showed 1-allyloxy-2-bromo-3-(3-phenylallyloxy) benzene (I) as a sharp spot at  $R_F = 0.33$ . The crude product was purified by flash column chromatography to give (I) as a white powder (1.56 g, 51%). A sample of this powder was recrystallized from hot hexane–ethyl acetate (20:1) to give translucent rhombs and slabs (m.p. 353–355 K).  $^1\text{H NMR}$ :  $\delta_H$  ( $\text{CDCl}_3$ ) 4.58 (2H, *d*,  $J = 4.1$  Hz,

$\text{CH}_2$ ), 4.74 (2H, *d*,  $J = 3.9$  Hz,  $\text{CH}_2$ ), 5.26 (1H, *d*,  $J = 9.6$  Hz,  $\text{CH}_2$ ), 5.44 (1H, *d*,  $J = 17.0$  Hz,  $\text{CH}_2$ ), 6.01–6.08 (1H, *m*, CH), 6.37–6.41 (1H, *m*, CH), 6.53 (1H, *d*,  $J = 7.0$  Hz, Ar-H), 6.58 (1H, *d*,  $J = 7.0$  Hz, Ar-H), 6.75 (1H, *d*,  $J = 9.2$  Hz, CH), 7.14 (1H, *t*,  $J = 8.1$  Hz, CH), 7.23 (1H, *d*,  $J = 6.2$  Hz, Ar-H), 7.29 (2H, *t*,  $J = 8.3$  Hz, Ar-H), 7.38 (2H, *d*,  $J = 7.2$  Hz, Ar-H).  $^{13}\text{C NMR}$ :  $\delta_C$  70.0, 70.1, 102.7, 106.6, 106.7, 117.8, 124.2 (2 C), 126.8, 128.1, 128.2, 128.8 (2 C), 132.9, 133.1, 136.6, 156.6 (2 C).  $\nu_{\text{max}}$  (KBr)/ $\text{cm}^{-1}$ : 1644, 1591, 1470, 1375, 1255, 1116, 1062, 767.

### Crystal data

$\text{C}_{18}\text{H}_{17}\text{BrO}_2$   
 $M_r = 345.23$   
Monoclinic,  $P2_1/n$   
 $a = 7.2956$  (4) Å  
 $b = 14.8719$  (8) Å  
 $c = 14.7849$  (7) Å  
 $\beta = 95.171$  (1)°  
 $V = 1597.62$  (14) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.435$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 3898 reflections  
 $\theta = 2.7$ – $23.3$ °  
 $\mu = 2.57$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Slab, colourless  
 $0.47 \times 0.32 \times 0.18$  mm

### Data collection

Bruker SMART1000 CCD diffractometer  
 $\omega$  scans  
Absorption correction: multi-scan (SADABS; Bruker, 1999)  
 $T_{\text{min}} = 0.362$ ,  $T_{\text{max}} = 0.628$   
11903 measured reflections

3131 independent reflections  
2142 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.025$   
 $\theta_{\text{max}} = 26.0$ °  
 $h = -8 \rightarrow 8$   
 $k = -18 \rightarrow 18$   
 $l = -17 \rightarrow 18$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.041$   
 $wR(F^2) = 0.111$   
 $S = 1.06$   
3131 reflections  
190 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.058P)^2 + 0.1552P]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.31$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.35$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bonding geometry (Å, °).

$D\text{---}H\cdots A$	$D\text{---}H$	$H\cdots A$	$D\cdots A$	$D\text{---}H\cdots A$
C1–H1A $\cdots$ O1	0.93	2.39	2.715 (5)	100

All the H atoms were positioned geometrically and refined as riding on their carrier C atoms ( $\text{C—H} = 0.93$  Å for aromatic and  $sp^2$ -hybridized C atoms and  $\text{C—H} = 0.97$  Å for  $sp^3$ -hybridized C atoms) with the the constraint  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{carrier atom})$  applied.

Data collection: SMART (Bruker, 1999); cell refinement: SAINT-Plus (Bruker, 1999); data reduction: SAINT-Plus; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97; molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: SHELXL97.

## References

- Bruker (1999). SMART (Version 5.624), SAINT-Plus (Version 6.02A) and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Kirsop, P., Storey, J. M. D. & Harrison, W. T. A. (2004a). *Acta Cryst.* **E60**, o222–o224.  
Kirsop, P., Storey, J. M. D. & Harrison, W. T. A. (2004b). *Acta Cryst.* **C60**, o353–o355.  
Sheldrick, G. M. (1997). SHELXL97 and SHELXS97. University of Göttingen, Germany.  
Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.