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# 4-(3-Allyloxy-2-bromophenoxy)but-2-enenitrile

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**Key indicators**

Single-crystal X-ray study
*T* = 120 K
Mean σ(C–C) = 0.009 Å
Disorder in main residue
*R* factor = 0.055
*wR* factor = 0.133
Data-to-parameter ratio = 18.8

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

The title compound, $C_{13}H_{12}BrNO_2$, possesses normal geometrical parameters. The molecular conformation and crystal packing appear to be influenced by intramolecular C—H···O and intermolecular C—H···N interactions, the latter resulting in centrosymmetric $R_2^2(10)$ loops.

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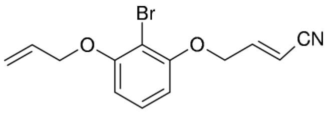
## Comment

The title compound, 4-(3-allyloxy-2-bromophenoxy)but-2-enenitrile, (I) (Fig. 1), arose during our studies to determine the philicity of aryl radicals by competetive cyclization (Kirsop *et al.*, 2004*a*,*b*,*c*).



(I)

Compound (I) possesses normal geometrical parameters (Table 1). The C12—C13 bond was flagged (Spek, 2003) as being longer than expected for a C$sp^2$—C$sp$ bond, but similar equivalent C—C bond lengths have been seen in other cyanoethenyl groupings [*e.g.* Ishii *et al.* (2000); bond length = 1.424 (6) Å]. The *exo* C1—C2 vinyl group in (I) is disordered over two positions, with refined relative occupancies of 0.710 (19):0.210 (19) for the isotropically refined major (C1*a*—C2*a*) and minor (C1*b*—C2*b*) components, respectively. The C4–C9 phenyl ring and its attached non-H atoms (O1, O2 and Br1) is statistically flat [r.m.s. deviation from the best least-squares plane = 0.011 Å, maximum deviation = 0.018 (3) Å for O2]. A *PLATON* (Spek, 2003) analysis of (I) indicated that the backbone of the nitrile side chain may be stabilized by an

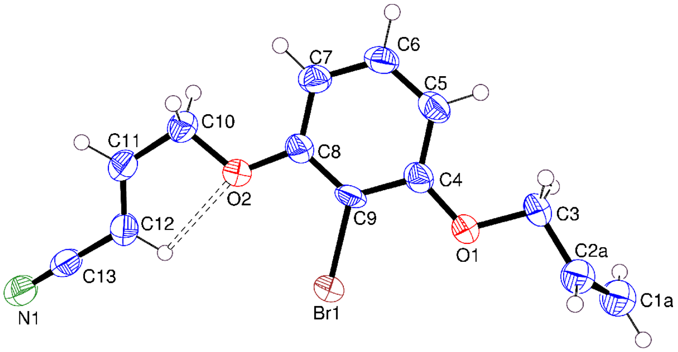


**Figure 1**
View of (I) (50% displacement ellipsoids for the non-H atoms). Only the major disorder component for C1 and C2 is shown and H atoms are drawn as small spheres of arbitrary radius. The possible intramolecular C—H···O interaction is indicated by a dashed line.

intramolecular C—H···O interaction (Fig. 1 and Table 2), thereby helping to establish an essentially planar arrangement of atoms O2, C10, C11 and C12 (Table 1). Dimers of (I) associate together by way of a pair of inversion-symmetry-generated C—H···N interactions (Table 2 and Fig. 2), resulting in centrosymmetric $R_2^2(10)$ loops (Bernstein *et al.*, 1995). There are no significant $\pi$—$\pi$ interactions in the unit cell of (I); the unit-cell packing is shown in Fig. 3.

## Experimental

Crotonitrile (2.00 g, 0.03 mol), *N*-bromosuccinamide (6.3 g, 0.04 mol) and azoisobutyronitrile (0.49 g, 0.003 mol) were added to dry acetone (100 ml). The mixture was stirred at reflux under a nitrogen atmosphere for 4 h. After cooling, the solvent was removed at reduced pressure to give a quantity of dark-brown oil. Distillation under reduced pressure yielded bromocrotonitrile as a pale-brown oil (b.p. 345–347 K at 7 mm Hg) (3.5 g, 80%). $^1$H NMR: $\delta_H$ ($CDCl_3$) 4.1 (2H, *d*, *J* = 7.0 Hz), 5.5 (1H, *d*, *J* = 12.5 Hz), 6.7 (1H, *m*).

3-Allyloxy-2-bromophenol (2.00 g, 0.009 mol) (Kirsop *et al.*, 2004*c*), bromocrotonitrile (1.58 g, 0.011 mol) and potassium carbonate (8.00 g, 0.058 mol) were added to dry acetone (100 ml). 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 pale-yellow oil (1.81 g, 68%). Thin-layer chromatography (4:1 hexane–ethyl acetate) showed 4-(3-allyloxy-2-bromophenoxy)but-2-enenitrile, (I), as a sharp spot at $R_F$ = 0.38. The crude product was purified by flash column chromatography to give (I) as a white powder (1.42 g, 54%). A sample of this powder was recrystalized from hot hexane–ethyl acetate (20:1) to give white needles (m.p. 349–351 K). $^1$H NMR: $\delta_H$ ($CDCl_3$) 4.58 (2H, *m*, $CH_2$), 4.68 (2H, *m*, $CH_2$), 5.27 (1H, *d*, *J* = 10.6 Hz, CH), 5.45 (1H, *d*, *J* = 17.1 Hz, CH), 5.97 (1H, *m*, CH), 6.03 (1H, *m*, CH), 6.45 (1H, *d*, *J* = 8.5 Hz, Ar-H), 6.59 (1H, *d*, *J* = 8.5 Hz, Ar-H), 6.81 (1H, *dt*, *J* = 16.0 and 3.5 Hz, CH), 7.16 (1H, *t*, *J* = 8.5 Hz, Ar-H). $^{13}$C NMR: $\delta_C$ 67.1, 69.8, 101.0, 102.4, 105.9, 107.2, 116.9, 117.8, 128.3, 132.4, 147.8, 155.2, 156.5. $\nu_{max}$ (KBr)/cm$^{-1}$ 2226, 1588, 1471, 1258, 1120, 1052, 759.

### *Crystal data*

$C_{13}H_{12}BrNO_2$
$M_r$ = 294.15
Monoclinic, $P2_1/c$
$a$ = 4.3681 (3) Å
$b$ = 19.1969 (12) Å
$c$ = 15.0270 (9) Å
$\beta$ = 97.570 (4)°
$V$ = 1249.09 (14) Å$^3$
$Z$ = 4

$D_x$ = 1.564 Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 2721 reflections
$\theta$ = 2.9–27.5°
$\mu$ = 3.28 mm$^{-1}$
$T$ = 120 (2) K
Needle, colourless
0.40 × 0.03 × 0.02 mm

### *Data collection*

Nonius KappaCCD diffractometer
$\varphi$ and $\omega$ scans
Absorption correction: multi-scan (SORTAV; Blessing, 1995)
$T_{min}$ = 0.354, $T_{max}$ = 0.937
17155 measured reflections
2871 independent reflections

1930 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.089
$\theta_{max}$ = 27.6°
$h = -5 \rightarrow 5$
$k = -24 \rightarrow 24$
$l = -19 \rightarrow 19$

### *Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.133
$S$ = 1.02
2871 reflections
153 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 1.5353P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.46 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.58 e Å$^{-3}$

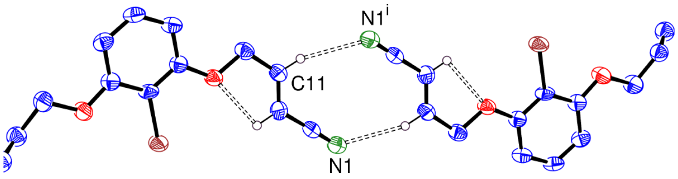


**Figure 2**
A dimeric association of two molecules of (I) *via* two C—H···N interactions (dashed lines). The symmetry code is as in Table 2. All H atoms except for H11 and H12 have been omitted for clarity.

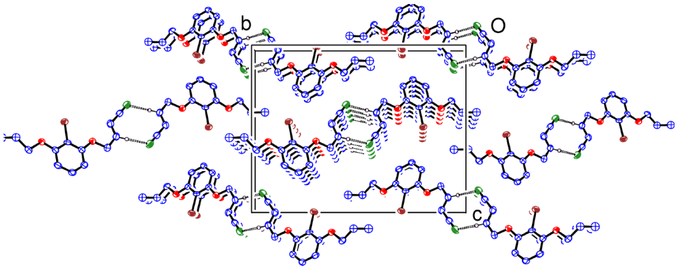


**Figure 3**
Unit-cell packing in (I), viewed down [100] (50% displacement ellipsoids). All H atoms except for H11 have been omitted for clarity.

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

| | | | |
|---|---|---|---|
| C9—Br1 | 1.888 (4) | C12—C13 | 1.437 (6) |
| C11—C12 | 1.318 (6) | C13—N1 | 1.148 (5) |
| | | | |
| C1*a*—C2*a*—C3—O1 | 111.3 (7) | C10—C11—C12—C13 | 179.0 (4) |
| O2—C10—C11—C12 | −4.0 (6) | | |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| C12—H12···O2 | 0.95 | 2.31 | 2.671 (5) | 102 |
| C11—H11···N1$^i$ | 0.95 | 2.51 | 3.410 (6) | 158 |

Symmetry code: (i) $2-x, -y, -z$.

All the H atoms were placed in idealized locations and refined by riding on their carrier atoms (C—H = 0.95–0.99 Å). For all H atoms, the constraint $U_{iso}(H) = 1.2U_{eq}$(parent atom) was applied.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK* and *SORTAV* (Blessing, 1995); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*3 (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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