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

Peter Kirsop, John M. D. Storey and William T. A. Harrison*

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, Scotland

Correspondence e-mail:
w.harrison@abdn.ac.uk

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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.

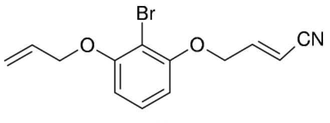
Key indicators

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.

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 Csp^2—Csp 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

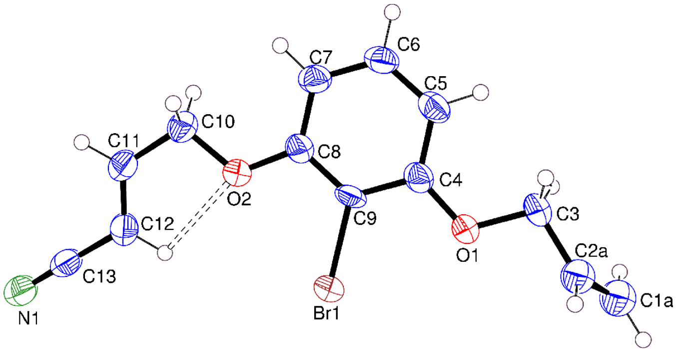


Figure 1
View of (I) (50% displacement ellipsoids for the non-H atoms). Only the major disorder component for C1 and C2 is shown and H atoms are drawn as small spheres of arbitrary radius. The possible intramolecular C—H···O interaction is indicated by a dashed line.

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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 π—π 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: δ_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: δ_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: δ_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. ν_{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
β = 97.570 (4)°
V = 1249.09 (14) Å^3
Z = 4

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

Data collection

Nonius KappaCCD diffractometer
φ and ω 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
θ_{max} = 27.6°
h = −5 → 5
k = −24 → 24
l = −19 → 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}

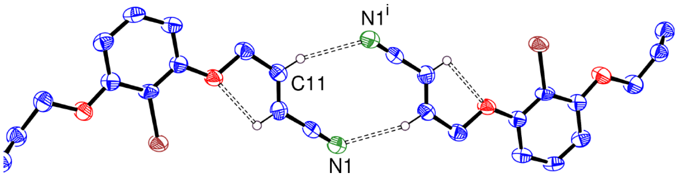

Figure 2
A dimeric association of two molecules of (I) *via* two C—H⋯N interactions (dashed lines). The symmetry code is as in Table 2. All H atoms except for H11 and H12 have been omitted for clarity.

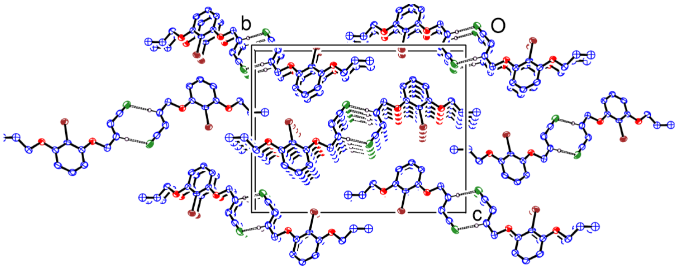

Figure 3
Unit-cell packing in (I), viewed down [100] (50% displacement ellipsoids). All H atoms except for H11 have been omitted for clarity.

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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supporting information

Acta Cryst. (2004). E**60**, o1636–o1638 [https://doi.org/10.1107/S1600536804020677]

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V = 1249.09 (14) Å^3
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D_x = 1.564 Mg m^{-3}
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Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
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$h = -5 \rightarrow 5$
$k = -24 \rightarrow 24$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.133
S = 1.02
2871 reflections
153 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
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}

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. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$	Occ. (<1)
C1A	−0.584 (2)	0.5535 (5)	−0.1148 (5)	0.053 (3)*	0.710 (19)
H1A	−0.4538	0.5683	−0.1570	0.064*	0.710 (19)
H2A	−0.6442	0.5855	−0.0721	0.064*	0.710 (19)
C2A	−0.685 (2)	0.4863 (5)	−0.1156 (5)	0.045 (2)*	0.710 (19)
H3A	−0.8158	0.4715	−0.0734	0.055*	0.710 (19)
C1B	−0.761 (7)	0.5324 (13)	−0.1075 (13)	0.067 (7)*	0.290 (19)
H1B	−0.9639	0.5157	−0.1257	0.081*	0.290 (19)
H2B	−0.7298	0.5738	−0.0729	0.081*	0.290 (19)
C2B	−0.548 (6)	0.5020 (10)	−0.1278 (12)	0.049 (6)*	0.290 (19)
H3B	−0.3460	0.5192	−0.1092	0.059*	0.290 (19)
C3	−0.5902 (12)	0.4356 (2)	−0.1833 (3)	0.0513 (13)	
H4	−0.7735	0.4117	−0.2152	0.062*	
H5	−0.4821	0.4602	−0.2280	0.062*	
C4	−0.3122 (10)	0.3282 (2)	−0.1780 (3)	0.0383 (10)	
C5	−0.4243 (10)	0.3126 (2)	−0.2675 (3)	0.0414 (11)	
H6	−0.5650	0.3431	−0.3017	0.050*	
C6	−0.3282 (10)	0.2524 (2)	−0.3053 (3)	0.0423 (11)	
H7	−0.4067	0.2419	−0.3658	0.051*	
C7	−0.1232 (11)	0.2070 (2)	−0.2589 (3)	0.0406 (10)	
H8	−0.0598	0.1661	−0.2869	0.049*	
C8	−0.0092 (10)	0.2221 (2)	−0.1696 (3)	0.0372 (10)	
C9	−0.1043 (10)	0.2819 (2)	−0.1303 (2)	0.0375 (10)	
C10	0.2921 (10)	0.1178 (2)	−0.1518 (3)	0.0414 (10)	
H9	0.3864	0.1264	−0.2072	0.050*	
H10	0.1121	0.0866	−0.1667	0.050*	
C11	0.5206 (10)	0.0852 (2)	−0.0825 (3)	0.0410 (10)	
H11	0.5965	0.0402	−0.0946	0.049*	
C12	0.6251 (10)	0.1146 (2)	−0.0052 (3)	0.0433 (11)	
H12	0.5542	0.1598	0.0077	0.052*	
C13	0.8433 (11)	0.0801 (2)	0.0602 (3)	0.0434 (11)	
N1	1.0142 (10)	0.0530 (2)	0.1137 (3)	0.0545 (11)	
O1	−0.3859 (8)	0.38583 (15)	−0.13333 (19)	0.0496 (8)	
O2	0.1970 (7)	0.18162 (14)	−0.11670 (18)	0.0417 (7)	
Br1	0.04780 (12)	0.30109 (2)	−0.00932 (3)	0.0501 (2)	

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C3	0.075 (3)	0.040 (3)	0.036 (2)	0.016 (2)	−0.004 (2)	0.0093 (19)
C4	0.049 (3)	0.032 (2)	0.033 (2)	−0.0029 (19)	0.0029 (19)	0.0066 (17)

C5	0.049 (3)	0.043 (3)	0.031 (2)	−0.002 (2)	0.0003 (19)	0.0092 (18)
C6	0.055 (3)	0.040 (3)	0.029 (2)	−0.010 (2)	−0.003 (2)	−0.0010 (18)
C7	0.054 (3)	0.035 (2)	0.033 (2)	−0.008 (2)	0.003 (2)	−0.0021 (18)
C8	0.046 (3)	0.033 (2)	0.032 (2)	0.0000 (19)	0.0025 (19)	0.0042 (17)
C9	0.054 (3)	0.040 (2)	0.0168 (18)	−0.002 (2)	−0.0008 (18)	0.0022 (16)
C10	0.051 (3)	0.031 (2)	0.043 (3)	−0.003 (2)	0.006 (2)	−0.0024 (19)
C11	0.046 (3)	0.032 (2)	0.045 (3)	0.0010 (19)	0.006 (2)	−0.0039 (19)
C12	0.046 (3)	0.036 (2)	0.046 (3)	0.005 (2)	0.002 (2)	0.002 (2)
C13	0.049 (3)	0.040 (3)	0.041 (2)	0.005 (2)	0.007 (2)	−0.011 (2)
N1	0.063 (3)	0.049 (2)	0.048 (2)	0.011 (2)	−0.006 (2)	−0.0121 (19)
O1	0.076 (2)	0.0384 (18)	0.0312 (15)	0.0182 (16)	−0.0038 (15)	0.0020 (13)
O2	0.0562 (19)	0.0360 (17)	0.0310 (15)	0.0068 (14)	−0.0014 (14)	−0.0021 (12)
Br1	0.0721 (4)	0.0451 (3)	0.0293 (3)	0.0144 (2)	−0.0078 (2)	−0.00387 (19)

Geometric parameters (Å, º)

C1A—C2A	1.362 (17)	C5—H6	0.9500
C1A—H1A	0.9500	C6—C7	1.372 (6)
C1A—H2A	0.9500	C6—H7	0.9500
C2A—C3	1.506 (9)	C7—C8	1.399 (6)
C2A—H3A	0.9500	C7—H8	0.9500
C1B—C2B	1.17 (4)	C8—O2	1.364 (5)
C1B—H1B	0.9500	C8—C9	1.380 (6)
C1B—H2B	0.9500	C9—Br1	1.888 (4)
C2B—C3	1.521 (19)	C10—O2	1.417 (5)
C2B—H3B	0.9500	C10—C11	1.483 (6)
C3—O1	1.448 (5)	C10—H9	0.9900
C3—H4	0.9900	C10—H10	0.9900
C3—H5	0.9900	C11—C12	1.318 (6)
C4—O1	1.354 (5)	C11—H11	0.9500
C4—C9	1.399 (6)	C12—C13	1.437 (6)
C4—C5	1.403 (6)	C12—H12	0.9500
C5—C6	1.377 (6)	C13—N1	1.148 (5)
C2A—C1A—H1A	120.0	C7—C6—C5	122.5 (4)
C2A—C1A—H2A	120.0	C7—C6—H7	118.8
H1A—C1A—H2A	120.0	C5—C6—H7	118.8
C1A—C2A—C3	120.0 (9)	C6—C7—C8	118.8 (4)
C1A—C2A—H3A	120.0	C6—C7—H8	120.6
C3—C2A—H3A	120.0	C8—C7—H8	120.6
C2B—C1B—H1B	120.0	O2—C8—C9	116.0 (3)
C2B—C1B—H2B	120.0	O2—C8—C7	124.4 (4)
H1B—C1B—H2B	120.0	C9—C8—C7	119.6 (4)
C1B—C2B—C3	121 (3)	C8—C9—C4	121.4 (4)
C1B—C2B—H3B	119.4	C8—C9—Br1	119.1 (3)
C3—C2B—H3B	119.4	C4—C9—Br1	119.5 (3)
O1—C3—C2A	106.4 (4)	O2—C10—C11	107.9 (3)
O1—C3—C2B	104.4 (8)	O2—C10—H9	110.1

C2A—C3—C2B	27.3 (8)	C11—C10—H9	110.1
O1—C3—H4	110.4	O2—C10—H10	110.1
C2A—C3—H4	110.4	C11—C10—H10	110.1
C2B—C3—H4	133.2	H9—C10—H10	108.4
O1—C3—H5	110.4	C12—C11—C10	124.1 (4)
C2A—C3—H5	110.4	C12—C11—H11	117.9
C2B—C3—H5	86.5	C10—C11—H11	117.9
H4—C3—H5	108.6	C11—C12—C13	121.8 (4)
O1—C4—C9	116.5 (4)	C11—C12—H12	119.1
O1—C4—C5	125.1 (4)	C13—C12—H12	119.1
C9—C4—C5	118.4 (4)	N1—C13—C12	178.6 (5)
C6—C5—C4	119.3 (4)	C4—O1—C3	116.9 (3)
C6—C5—H6	120.4	C8—O2—C10	118.7 (3)
C4—C5—H6	120.4		

C1A—C2A—C3—O1	111.3 (7)	O1—C4—C9—C8	−179.0 (4)
C1A—C2A—C3—C2B	21.8 (16)	C5—C4—C9—C8	0.1 (7)
C1B—C2B—C3—O1	−129.0 (19)	O1—C4—C9—Br1	1.5 (6)
C1B—C2B—C3—C2A	−30.9 (18)	C5—C4—C9—Br1	−179.4 (3)
O1—C4—C5—C6	179.3 (4)	O2—C10—C11—C12	−4.0 (6)
C9—C4—C5—C6	0.3 (7)	C10—C11—C12—C13	179.0 (4)
C4—C5—C6—C7	−0.6 (7)	C9—C4—O1—C3	177.4 (4)
C5—C6—C7—C8	0.5 (7)	C5—C4—O1—C3	−1.7 (7)
C6—C7—C8—O2	−179.4 (4)	C2A—C3—O1—C4	169.1 (6)
C6—C7—C8—C9	−0.1 (7)	C2B—C3—O1—C4	−162.7 (11)
O2—C8—C9—C4	179.1 (4)	C9—C8—O2—C10	177.0 (4)
C7—C8—C9—C4	−0.3 (7)	C7—C8—O2—C10	−3.6 (6)
O2—C8—C9—Br1	−1.3 (5)	C11—C10—O2—C8	178.5 (4)
C7—C8—C9—Br1	179.3 (3)		

Hydrogen-bond geometry (Å, º)

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) −*x*+2, −*y*, −*z*.