

3-(2-Bromo-4,5-dimethoxyphenyl)-propionitrile

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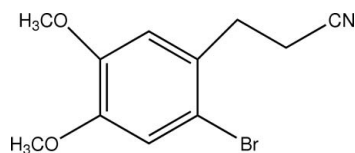
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.012$ Å; R factor = 0.053; wR factor = 0.114; data-to-parameter ratio = 8.2.

In the molecule of the title compound, $\text{C}_{11}\text{H}_{12}\text{BrNO}_2$, a weak intramolecular $\text{C}-\text{H}\cdots\text{Br}$ hydrogen bond results in the formation of a five-membered ring, which adopts an envelope conformation with the H atom displaced by 0.486 Å from the plane of the other ring atoms. In the crystal structure, intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds link the molecules.

Related literature

For related literature, see: Kametani *et al.* (1973); Paull & Cheng (1972); Lerestif *et al.* (2005).



Experimental

Crystal data

$\text{C}_{11}\text{H}_{12}\text{BrNO}_2$

$M_r = 270.13$

Tetragonal, $P4_2bc$

$a = 17.552$ (3) Å

$c = 7.4870$ (15) Å

$V = 2306.5$ (7) Å³

$Z = 8$

Mo $K\alpha$ radiation

$\mu = 3.54$ mm⁻¹

$T = 294$ (2) K

$0.30 \times 0.10 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer

Absorption correction: ψ scan (North *et al.*, 1968)

$T_{\min} = 0.416$, $T_{\max} = 0.718$

4281 measured reflections

1128 independent reflections

657 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.047$

3 standard reflections

frequency: 120 min

intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.113$

$S = 0.99$

1128 reflections

137 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.36$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

Absolute structure: Flack (1983),

with no Friedel pairs

Flack parameter: 0.00 (3)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C2}-\text{H2A}\cdots\text{O1}^1$	0.97	2.32	3.193 (10)	150
$\text{C3}-\text{H3B}\cdots\text{Br}$	0.97	2.76	3.195 (9)	108

Symmetry code: (i) $-x + \frac{3}{2}, y + \frac{1}{2}, z$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); software used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2461).

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supplementary materials

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3-(2-Bromo-4,5-dimethoxyphenyl)propionitrile

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Comment

2-Bromo-4,5-dimethoxyhydrocinnamonitrile is the precursor of 1-cyano-4,5-dimethoxybenzocyclobutene, which is a key intermediate of ivabradine (Lerestif *et al.*, 2005), xylopinine (Kametani *et al.*, 1973) and 4-substituted 3a,4,5,9b-tetrahydrobenz[e]isoindolea (Paull & Cheng, 1972). As part of our studies in this area, we report herein the synthesis and crystal structure of the title compound, (I).

In the molecule of (I), (Fig. 1), ring A (C4-C9) is, of course, planar. Br, O1, O2, C3 and C10 atoms lie in the ring plane. A weak intramolecular C-H \cdots Br [C3-H3B = 0.97, H3B \cdots Br = 2.76, C3 \cdots Br = 3.195 (9) Å and C3-H3B \cdots Br = 108°] hydrogen bond results in the formation of a five-membered ring B (C3-C5/Br/H3B), which adopts envelope conformation with hydrogen atom displaced by -0.486 (3) Å from the plane of the other ring atoms.

In the crystal structure, intermolecular C-H \cdots O [C2-H2A = 0.97, H2A \cdots O1 = 2.32, C2 \cdots O1 = 3.193 (8) Å and C2-H2A \cdots O1 = 150°] hydrogen bonds link the molecules (Fig. 2), in which they may be effective in the stabilization of the structure.

Experimental

For the preparation of the title compound, beta-(2-bromo-4,5-dimethoxyphenyl)-alpha-cyanopropionic acid (16 mmol) was dissolved in dimethylacetamide (10 ml), the mixture was heated at 443 K and evolution of the calculated amount of CO₂ ceased after 30 min. The mixture was poured into water and set aside overnight. Crystals were separated, collected and washed with water and hexane. Crystals of (I) suitable for X-ray analysis were obtained by slow evaporation of a methanol solution.

Refinement

H atoms were positioned geometrically, with C-H = 0.93, 0.97 and 0.96 Å for aromatic, methylene and methyl H, respectively, and constrained to ride on their parent atoms with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C})$, where $x = 1.5$ for methyl H, and $x = 1.2$ for all other H atoms.

Figures

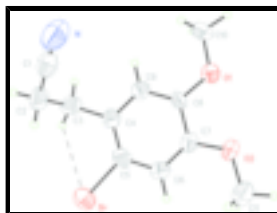


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen bond is shown as dashed line.

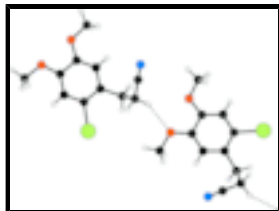


Fig. 2. A partial packing diagram of (I). Hydrogen bonds are shown as dashed lines.

3-(2-Bromo-4,5-dimethoxyphenyl)propionitrile

Crystal data

$C_{11}H_{12}BrNO_2$	$Z = 8$
$M_r = 270.13$	$F_{000} = 1088$
Tetragonal, $P4_2bc$	$D_x = 1.556 \text{ Mg m}^{-3}$
Hall symbol: P 4c -2ab	Mo $K\alpha$ radiation
$a = 17.552(3) \text{ \AA}$	$\lambda = 0.71073 \text{ \AA}$
$b = 17.552(3) \text{ \AA}$	Cell parameters from 25 reflections
$c = 7.4870(15) \text{ \AA}$	$\theta = 10\text{--}13^\circ$
$\alpha = 90^\circ$	$\mu = 3.54 \text{ mm}^{-1}$
$\beta = 90^\circ$	$T = 294(2) \text{ K}$
$\gamma = 90^\circ$	Block, colorless
$V = 2306.5(7) \text{ \AA}^3$	$0.30 \times 0.10 \times 0.10 \text{ mm}$

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{\text{int}} = 0.047$
Radiation source: fine-focus sealed tube	$\theta_{\text{max}} = 25.2^\circ$
Monochromator: graphite	$\theta_{\text{min}} = 1.6^\circ$
$T = 294(2) \text{ K}$	$h = -21 \rightarrow 21$
$\omega/2\theta$ scans	$k = -21 \rightarrow 0$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$l = 0 \rightarrow 8$
$T_{\text{min}} = 0.416$, $T_{\text{max}} = 0.718$	3 standard reflections
4281 measured reflections	every 120 min
1128 independent reflections	intensity decay: none
657 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	H-atom parameters constrained
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.052$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.113$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.99$	$\Delta\rho_{\text{max}} = 0.36 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

1128 reflections Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 137 parameters Extinction coefficient: 0.0026 (5)
 Primary atom site location: structure-invariant direct Absolute structure: Flack (1983), with no Friedel
 methods pairs
 Secondary atom site location: difference Fourier map Flack parameter: 0.00 (3)
 Hydrogen site location: inferred from neighbouring
 sites

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	x	y	z	U_{iso}^*/U_{eq}
Br	0.95483 (5)	0.91044 (5)	0.9098 (3)	0.0796 (5)
N	0.6404 (5)	0.9114 (5)	0.6468 (17)	0.083 (4)
O1	0.7337 (3)	0.6500 (3)	0.8860 (13)	0.051 (2)
O2	0.8737 (4)	0.6253 (3)	0.8147 (10)	0.055 (2)
C1	0.6900 (6)	0.9379 (5)	0.7195 (18)	0.057 (3)
C2	0.7527 (6)	0.9707 (5)	0.8211 (15)	0.060 (4)
H2A	0.7383	1.0216	0.8585	0.073*
H2B	0.7965	0.9754	0.7429	0.073*
C3	0.7763 (5)	0.9255 (5)	0.9855 (13)	0.050 (3)
H3A	0.7329	0.9212	1.0649	0.060*
H3B	0.8158	0.9535	1.0482	0.060*
C4	0.8058 (4)	0.8459 (4)	0.9433 (19)	0.040 (3)
C5	0.8811 (4)	0.8304 (4)	0.906 (2)	0.043 (2)
C6	0.9068 (5)	0.7583 (5)	0.8663 (14)	0.053 (5)
H6A	0.9585	0.7501	0.8462	0.064*
C7	0.8568 (5)	0.6988 (4)	0.8560 (11)	0.034 (3)
C8	0.7797 (4)	0.7129 (4)	0.899 (2)	0.038 (2)
C9	0.7556 (4)	0.7846 (4)	0.939 (2)	0.040 (3)
H9A	0.7043	0.7929	0.9639	0.047*
C10	0.6556 (4)	0.6598 (4)	0.932 (3)	0.056 (3)
H10A	0.6297	0.6117	0.9225	0.084*
H10B	0.6326	0.6957	0.8516	0.084*
H10C	0.6519	0.6784	1.0520	0.084*
C11	0.9502 (5)	0.6090 (5)	0.758 (2)	0.077 (4)
H11A	0.9549	0.5556	0.7324	0.116*

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H11B	0.9852	0.6228	0.8507	0.116*
H11C	0.9615	0.6378	0.6519	0.116*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0517 (6)	0.0477 (6)	0.1394 (12)	-0.0149 (4)	-0.0013 (13)	-0.0086 (14)
N	0.084 (7)	0.070 (6)	0.095 (10)	0.022 (5)	-0.025 (8)	-0.018 (7)
O1	0.039 (3)	0.036 (3)	0.078 (7)	-0.003 (2)	0.006 (5)	-0.015 (5)
O2	0.044 (4)	0.031 (4)	0.090 (6)	0.010 (3)	0.009 (4)	0.000 (4)
C1	0.067 (8)	0.041 (6)	0.062 (10)	0.013 (6)	0.002 (7)	-0.009 (6)
C2	0.064 (7)	0.032 (6)	0.085 (10)	0.008 (5)	-0.007 (7)	-0.010 (6)
C3	0.042 (6)	0.055 (6)	0.052 (9)	0.002 (5)	0.009 (5)	-0.012 (6)
C4	0.041 (5)	0.035 (4)	0.045 (8)	-0.001 (3)	-0.002 (7)	-0.006 (7)
C5	0.042 (5)	0.038 (5)	0.047 (7)	-0.011 (4)	-0.006 (9)	-0.007 (9)
C6	0.033 (4)	0.042 (5)	0.085 (14)	0.001 (4)	0.003 (6)	-0.003 (6)
C7	0.041 (5)	0.031 (4)	0.030 (8)	0.005 (4)	-0.008 (4)	-0.002 (4)
C8	0.039 (4)	0.026 (4)	0.048 (7)	-0.007 (3)	0.013 (8)	-0.001 (7)
C9	0.037 (4)	0.038 (4)	0.044 (7)	0.001 (4)	-0.005 (7)	0.002 (7)
C10	0.036 (5)	0.053 (5)	0.079 (8)	-0.013 (4)	0.001 (9)	0.008 (10)
C11	0.054 (6)	0.049 (6)	0.128 (13)	0.009 (5)	0.000 (8)	-0.013 (8)

Geometric parameters (\AA , $^\circ$)

Br—C5	1.911 (7)	C4—C9	1.391 (10)
N—C1	1.128 (13)	C5—C6	1.376 (11)
O1—C8	1.371 (9)	C6—C7	1.367 (11)
O1—C10	1.422 (9)	C6—H6A	0.9300
O2—C7	1.358 (9)	C7—C8	1.414 (10)
O2—C11	1.438 (10)	C8—C9	1.360 (10)
C1—C2	1.456 (14)	C9—H9A	0.9300
C2—C3	1.521 (13)	C10—H10A	0.9600
C2—H2A	0.9700	C10—H10B	0.9600
C2—H2B	0.9700	C10—H10C	0.9600
C3—C4	1.524 (11)	C11—H11A	0.9600
C3—H3A	0.9700	C11—H11B	0.9600
C3—H3B	0.9700	C11—H11C	0.9600
C4—C5	1.376 (11)		
C8—O1—C10	116.9 (6)	C5—C6—H6A	119.9
C7—O2—C11	117.4 (7)	O2—C7—C6	126.7 (8)
N—C1—C2	177.3 (14)	O2—C7—C8	115.3 (7)
C1—C2—C3	115.0 (9)	C6—C7—C8	117.9 (8)
C1—C2—H2A	108.5	C9—C8—O1	125.3 (7)
C3—C2—H2A	108.5	C9—C8—C7	120.7 (7)
C1—C2—H2B	108.5	O1—C8—C7	113.9 (7)
C3—C2—H2B	108.5	C8—C9—C4	121.5 (8)
H2A—C2—H2B	107.5	C8—C9—H9A	119.2
C2—C3—C4	113.7 (8)	C4—C9—H9A	119.2

C2—C3—H3A	108.8	O1—C10—H10A	109.5
C4—C3—H3A	108.8	O1—C10—H10B	109.5
C2—C3—H3B	108.8	H10A—C10—H10B	109.5
C4—C3—H3B	108.8	O1—C10—H10C	109.5
H3A—C3—H3B	107.7	H10A—C10—H10C	109.5
C5—C4—C9	116.8 (7)	H10B—C10—H10C	109.5
C5—C4—C3	123.3 (7)	O2—C11—H11A	109.5
C9—C4—C3	119.9 (8)	O2—C11—H11B	109.5
C4—C5—C6	122.7 (7)	H11A—C11—H11B	109.5
C4—C5—Br	120.1 (6)	O2—C11—H11C	109.5
C6—C5—Br	117.1 (6)	H11A—C11—H11C	109.5
C7—C6—C5	120.2 (8)	H11B—C11—H11C	109.5
C7—C6—H6A	119.9		
C1—C2—C3—C4	62.4 (12)	C5—C6—C7—C8	-4.2 (18)
C2—C3—C4—C5	88.6 (16)	C10—O1—C8—C9	-6(3)
C2—C3—C4—C9	-90.8 (16)	C10—O1—C8—C7	178.6 (13)
C9—C4—C5—C6	0(2)	O2—C7—C8—C9	-178.5 (13)
C3—C4—C5—C6	-179.2 (13)	C6—C7—C8—C9	4(2)
C9—C4—C5—Br	-179.7 (11)	O2—C7—C8—O1	-2.4 (17)
C3—C4—C5—Br	1(2)	C6—C7—C8—O1	-179.8 (11)
C4—C5—C6—C7	2(2)	O1—C8—C9—C4	-177.5 (13)
Br—C5—C6—C7	-177.9 (9)	C7—C8—C9—C4	-2(3)
C11—O2—C7—C6	-7.0 (15)	C5—C4—C9—C8	0(3)
C11—O2—C7—C8	175.9 (12)	C3—C4—C9—C8	179.1 (13)
C5—C6—C7—O2	178.7 (11)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C2—H2A...O1 ⁱ	0.97	2.32	3.193 (10)	150
C3—H3B...Br	0.97	2.76	3.195 (9)	108

Symmetry codes: (i) $-x+3/2, y+1/2, z$.

Fig. 1

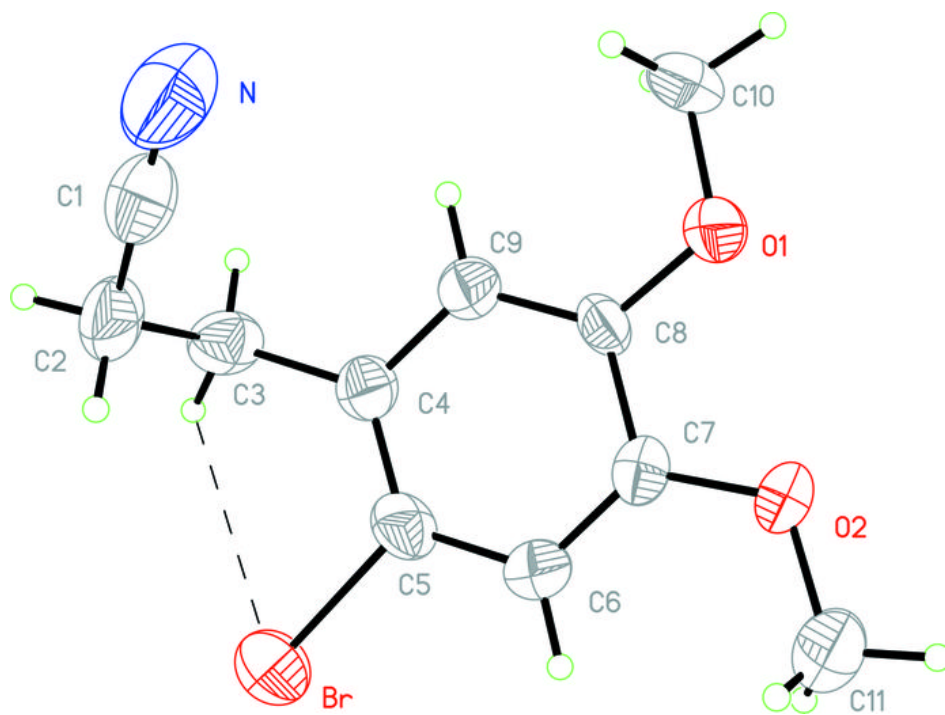


Fig. 2

