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# 5-Bromo-*N*-(3,4-dimethoxybenzyl)-pyridin-2-amine

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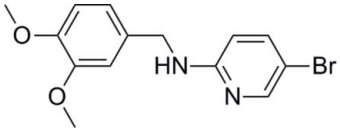
Key indicators: single-crystal X-ray study; $T$ = 130 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.027; $wR$ factor = 0.060; data-to-parameter ratio = 13.7.

The title compound, $C_{14}H_{15}BrN_2O_2$, an intermediate in drug discovery, was synthesized by the reaction of 5-bromopyridin-2-amine and 3,4-dimethoxybenzaldehyde. In the crystal, molecules are linked *via* pairs ofN—H···N hydrogen bonds, leading to the formation of inversion dimers. A short contact occurs between the aryl H atom (*ortho* position from N) and the centroid of the benzene ring.

## Related literature

For the anti-tumor activity of related compounds, see: Kovala-Demertzi *et al.* (2007). For the anti-ulcer activity of related compounds, see: Cho *et al.* (2001). For the anti-viral activity of related compounds, see: Mavel *et al.* (2002). For the anti-microbial activity of related compounds, see: Yeong *et al.* (2004).




## Experimental

### Crystal data

$C_{14}H_{15}BrN_2O_2$
$M_r$ = 323.18
Monoclinic, $P2_1/c$
$a$ = 6.3202 (2) Å
$b$ = 13.7940 (4) Å
$c$ = 15.8582 (6) Å
$\beta$ = 100.961 (4)°
$V$ = 1357.31 (8) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 3.03 mm$^{-1}$
$T$ = 130 K
0.42 × 0.30 × 0.15 mm

### Data collection

Agilent Xcalibur Eos diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{min}$ = 0.509, $T_{max}$ = 1.000
8188 measured reflections
2384 independent reflections
2055 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.030

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.027
$wR(F^2)$ = 0.060
$S$ = 1.03
2384 reflections
174 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.47 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.49 e Å$^{-3}$

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

*Cg* is the centroid of the C7–C12 ring.

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| N2—H2···N1$^{i}$ | 0.88 | 2.31 | 3.090 (3) | 149 |
| C2—H2$A$···$Cg^{i}$ | 0.95 | 2.50 | 3.397 (3) | 158 |

Symmetry code: (i) $-x+1, -y+2, -z$.

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

The authors thank Mr Zhi-Hua Mao of Sichuan University for the X-ray data collection.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2346).

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# supplementary materials

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## 5-Bromo-*N*-(3,4-dimethoxybenzyl)pyridin-2-amine

**Jie Li, Lin-Yan Lu, Wang-Xing Shen and Jian-You Shi**

### Comment

The pyridine skeleton is a great importance to chemistry as well as biology which are well known for their versatile pharmacological activities such as anti-tumor (Kovala-Demertzi *et al.*, 2007), anti-ulcer (Cho *et al.*, 2001), anti-viral (Mavel *et al.*, 2002) and antimicrobial (Yeong *et al.*, 2004). The title compound is one of these compounds. The crystal packing is stabilized by a pair of strong intermolecular N2–H2···N1$^{i}$ classical hydrogen bonds conecting two moleculars to form a centrosymmtric dimer. The H2A atom from pyridine moiety has short contact (2.50Å) with Cg$^{i}$ of phenyl ring (C7-C12). Symmetry code: (i) 1-*x*, 2-*y*, -*z*.

### Experimental

A methanol solution of 5-bromopyridin-2-amine (1.73 g, 0.01 mol), 3,4-dimethoxybenzaldehyde (1.66 g, 0.01 mol) with sodium cyanoborohydride (0.69 g, 0.011 mol) was heated to reflux for 3 h. The mixture was poured into cold water and then filtered to get this compound. Single crystals were obtained from the powder in ethanol after 5 days.

### Refinement

H atoms were positioned geometrically (C–H = 0.95-0.99Å and N–H = 0.88Å) and refined using a riding model, with $U_{iso}$(H) = 1.5$U_{eq}$(C) for methyl groups and $U_{iso}$(H) = 1.2$U_{eq}$(C, N) for others.

### Computing details

Data collection: *CrysAlis PRO* (Agilent, 2011); cell refinement: *CrysAlis PRO* (Agilent, 2011); data reduction: *CrysAlis PRO* (Agilent, 2011); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2* (Dolomanov *et al.*, 2009).

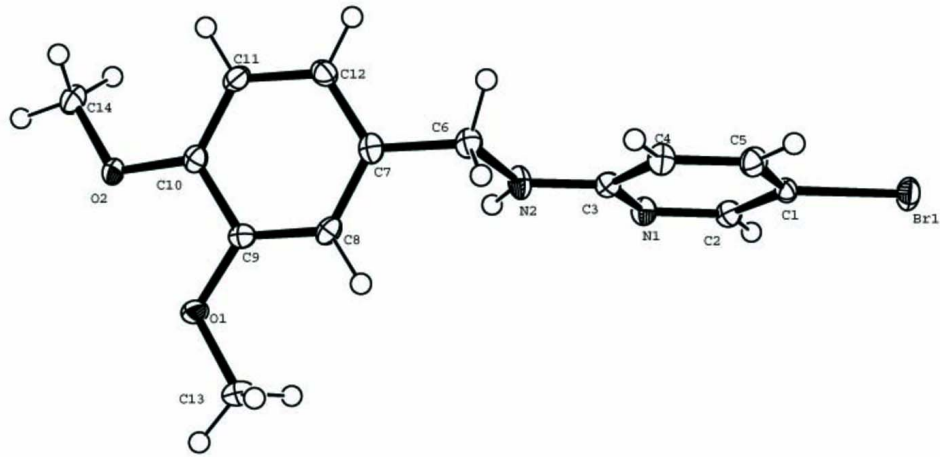


**Figure 1**

The molecular structure of title compound with the atom numbering scheme. Displacement ellipsoids are drawn at 50% probability level. H atoms are presented as a small spheres of arbitrary radius.

**5-Bromo-*N*-(3,4-dimethoxybenzyl)pyridin-2-amine**

*Crystal data*

$C_{14}H_{15}BrN_2O_2$
$M_r = 323.18$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 6.3202$ (2) Å
$b = 13.7940$ (4) Å
$c = 15.8582$ (6) Å
$\beta = 100.961$ (4)°
$V = 1357.31$ (8) Å$^3$
$Z = 4$
$F(000) = 656$
$D_x = 1.582$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.7107$ Å
Cell parameters from 3191 reflections
$\theta = 3.0$–$29.3°$
$\mu = 3.03$ mm$^{-1}$
$T = 130$ K
Block, colourless
0.42 × 0.30 × 0.15 mm

*Data collection*

Agilent Xcalibur Eos diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.0874 pixels mm$^{-1}$
$\omega$–scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2011)
$T_{min} = 0.509$, $T_{max} = 1.000$
8188 measured reflections
2384 independent reflections
2055 reflections with $I > 2\sigma(I)$
$R_{int} = 0.030$
$\theta_{max} = 25.0°$, $\theta_{min} = 3.0°$
$h = -7 \rightarrow 7$
$k = -15 \rightarrow 16$
$l = -18 \rightarrow 15$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.060$
$S = 1.03$
2384 reflections
174 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
$w = 1/[\sigma^2(F_o^2) + (0.0214P)^2 + 1.0069P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.47$ e Å$^{-3}$
$\Delta\rho_{min} = -0.49$ e Å$^{-3}$

*Special details*

**Experimental**. Absorption correction: *CrysAlis Pro* (Agilent Technologies, 2011) Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm.

**Geometry**. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å²)*

| | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| Br1 | 0.29705 (4) | 0.620125 (18) | 0.137802 (17) | 0.02180 (10) |
| O1 | 0.8391 (3) | 1.38453 (12) | 0.14221 (11) | 0.0181 (4) |
| O2 | 1.1319 (3) | 1.40582 (12) | 0.05188 (11) | 0.0185 (4) |
| N1 | 0.4443 (3) | 0.89466 (14) | 0.06525 (13) | 0.0164 (5) |
| N2 | 0.7225 (3) | 1.00200 (15) | 0.10747 (13) | 0.0178 (5) |
| H2 | 0.6482 | 1.0443 | 0.0722 | 0.021* |
| C1 | 0.4393 (4) | 0.74052 (17) | 0.13319 (15) | 0.0148 (5) |
| C2 | 0.3514 (4) | 0.80926 (17) | 0.07365 (16) | 0.0165 (5) |
| H2A | 0.2181 | 0.7951 | 0.0368 | 0.020* |
| C3 | 0.6333 (4) | 0.91502 (18) | 0.11831 (15) | 0.0147 (5) |
| C4 | 0.7300 (4) | 0.84807 (18) | 0.18126 (16) | 0.0177 (5) |
| H4 | 0.8617 | 0.8637 | 0.2186 | 0.021* |
| C5 | 0.6323 (4) | 0.76009 (18) | 0.18814 (16) | 0.0182 (6) |
| H5 | 0.6958 | 0.7138 | 0.2297 | 0.022* |
| C6 | 0.9380 (4) | 1.02800 (18) | 0.15245 (16) | 0.0176 (6) |
| H6A | 1.0436 | 0.9803 | 0.1387 | 0.021* |
| H6B | 0.9432 | 1.0263 | 0.2152 | 0.021* |
| C7 | 0.9971 (4) | 1.12777 (17) | 0.12650 (15) | 0.0154 (5) |
| C8 | 0.8867 (4) | 1.20894 (18) | 0.14866 (15) | 0.0153 (5) |
| H8 | 0.7767 | 1.2007 | 0.1814 | 0.018* |
| C9 | 0.9355 (4) | 1.30058 (17) | 0.12366 (15) | 0.0144 (5) |
| C10 | 1.0981 (4) | 1.31318 (18) | 0.07442 (15) | 0.0148 (5) |
| C11 | 1.2084 (4) | 1.23269 (18) | 0.05377 (16) | 0.0175 (6) |
| H11 | 1.3198 | 1.2404 | 0.0217 | 0.021* |
| C12 | 1.1576 (4) | 1.14027 (18) | 0.07967 (16) | 0.0175 (6) |
| H12 | 1.2342 | 1.0856 | 0.0649 | 0.021* |
| C13 | 0.6735 (4) | 1.37654 (19) | 0.19176 (17) | 0.0209 (6) |
| H13A | 0.5605 | 1.3329 | 0.1627 | 0.031* |
| H13B | 0.6116 | 1.4407 | 0.1979 | 0.031* |
| H13C | 0.7347 | 1.3506 | 0.2487 | 0.031* |
| C14 | 1.2631 (4) | 1.41893 (19) | −0.01160 (17) | 0.0214 (6) |
| H14A | 1.2102 | 1.3772 | −0.0611 | 0.032* |
| H14B | 1.4126 | 1.4018 | 0.0130 | 0.032* |
| H14C | 1.2564 | 1.4868 | −0.0301 | 0.032* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.02543 (15) | 0.01635 (15) | 0.02437 (16) | −0.00657 (11) | 0.00660 (11) | 0.00055 (11) |
| O1 | 0.0203 (9) | 0.0166 (9) | 0.0204 (10) | 0.0020 (7) | 0.0109 (8) | 0.0025 (8) |
| O2 | 0.0218 (9) | 0.0140 (9) | 0.0227 (10) | −0.0044 (7) | 0.0116 (8) | −0.0004 (7) |
| N1 | 0.0156 (10) | 0.0169 (11) | 0.0153 (11) | −0.0021 (9) | −0.0002 (9) | 0.0000 (9) |
| N2 | 0.0173 (10) | 0.0137 (11) | 0.0193 (12) | −0.0020 (9) | −0.0044 (9) | 0.0042 (9) |
| C1 | 0.0196 (12) | 0.0115 (13) | 0.0146 (13) | −0.0018 (10) | 0.0067 (11) | −0.0018 (10) |
| C2 | 0.0154 (12) | 0.0180 (13) | 0.0155 (14) | −0.0032 (10) | 0.0017 (11) | −0.0036 (11) |
| C3 | 0.0146 (12) | 0.0162 (13) | 0.0131 (13) | −0.0010 (10) | 0.0024 (10) | −0.0010 (10) |
| C4 | 0.0163 (12) | 0.0185 (13) | 0.0161 (14) | −0.0007 (10) | −0.0021 (11) | 0.0030 (11) |
| C5 | 0.0194 (13) | 0.0185 (14) | 0.0167 (14) | 0.0007 (11) | 0.0037 (11) | 0.0045 (11) |
| C6 | 0.0136 (12) | 0.0178 (14) | 0.0194 (14) | −0.0014 (10) | −0.0014 (11) | 0.0006 (11) |
| C7 | 0.0145 (12) | 0.0159 (13) | 0.0135 (13) | −0.0030 (10) | −0.0034 (10) | −0.0010 (10) |
| C8 | 0.0136 (12) | 0.0197 (14) | 0.0124 (13) | −0.0030 (10) | 0.0019 (10) | 0.0018 (10) |
| C9 | 0.0121 (12) | 0.0176 (13) | 0.0129 (13) | 0.0002 (10) | 0.0008 (10) | −0.0018 (11) |
| C10 | 0.0138 (12) | 0.0168 (13) | 0.0129 (13) | −0.0033 (10) | 0.0000 (10) | −0.0018 (10) |
| C11 | 0.0145 (12) | 0.0213 (14) | 0.0180 (14) | −0.0034 (11) | 0.0061 (11) | −0.0018 (11) |
| C12 | 0.0157 (12) | 0.0150 (14) | 0.0212 (14) | 0.0003 (10) | 0.0018 (11) | −0.0039 (11) |
| C13 | 0.0179 (12) | 0.0259 (15) | 0.0206 (14) | 0.0019 (11) | 0.0076 (11) | −0.0013 (12) |
| C14 | 0.0215 (13) | 0.0210 (14) | 0.0236 (15) | −0.0048 (11) | 0.0095 (12) | 0.0014 (12) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C1 | 1.897 (2) | C6—H6B | 0.9900 |
| O1—C9 | 1.366 (3) | C6—C7 | 1.504 (3) |
| O1—C13 | 1.427 (3) | C7—C8 | 1.399 (3) |
| O2—C10 | 1.355 (3) | C7—C12 | 1.377 (3) |
| O2—C14 | 1.432 (3) | C8—H8 | 0.9500 |
| N1—C2 | 1.334 (3) | C8—C9 | 1.377 (3) |
| N1—C3 | 1.353 (3) | C9—C10 | 1.414 (3) |
| N2—H2 | 0.8800 | C10—C11 | 1.383 (3) |
| N2—C3 | 1.350 (3) | C11—H11 | 0.9500 |
| N2—C6 | 1.457 (3) | C11—C12 | 1.395 (3) |
| C1—C2 | 1.378 (3) | C12—H12 | 0.9500 |
| C1—C5 | 1.384 (3) | C13—H13A | 0.9800 |
| C2—H2A | 0.9500 | C13—H13B | 0.9800 |
| C3—C4 | 1.411 (3) | C13—H13C | 0.9800 |
| C4—H4 | 0.9500 | C14—H14A | 0.9800 |
| C4—C5 | 1.375 (3) | C14—H14B | 0.9800 |
| C5—H5 | 0.9500 | C14—H14C | 0.9800 |
| C6—H6A | 0.9900 | | |
| | | | |
| C9—O1—C13 | 117.18 (18) | C12—C7—C8 | 119.3 (2) |
| C10—O2—C14 | 116.51 (18) | C7—C8—H8 | 119.6 |
| C2—N1—C3 | 118.3 (2) | C9—C8—C7 | 120.8 (2) |
| C3—N2—H2 | 119.0 | C9—C8—H8 | 119.6 |
| C3—N2—C6 | 122.0 (2) | O1—C9—C8 | 125.6 (2) |
| C6—N2—H2 | 119.0 | O1—C9—C10 | 114.5 (2) |

| | | | |
|---|---|---|---|
| C2—C1—Br1 | 119.77 (18) | C8—C9—C10 | 119.8 (2) |
| C2—C1—C5 | 119.3 (2) | O2—C10—C9 | 115.4 (2) |
| C5—C1—Br1 | 120.93 (18) | O2—C10—C11 | 125.6 (2) |
| N1—C2—C1 | 123.2 (2) | C11—C10—C9 | 118.9 (2) |
| N1—C2—H2A | 118.4 | C10—C11—H11 | 119.7 |
| C1—C2—H2A | 118.4 | C10—C11—C12 | 120.6 (2) |
| N1—C3—C4 | 121.1 (2) | C12—C11—H11 | 119.7 |
| N2—C3—N1 | 116.5 (2) | C7—C12—C11 | 120.5 (2) |
| N2—C3—C4 | 122.4 (2) | C7—C12—H12 | 119.8 |
| C3—C4—H4 | 120.2 | C11—C12—H12 | 119.8 |
| C5—C4—C3 | 119.5 (2) | O1—C13—H13A | 109.5 |
| C5—C4—H4 | 120.2 | O1—C13—H13B | 109.5 |
| C1—C5—H5 | 120.7 | O1—C13—H13C | 109.5 |
| C4—C5—C1 | 118.5 (2) | H13A—C13—H13B | 109.5 |
| C4—C5—H5 | 120.7 | H13A—C13—H13C | 109.5 |
| N2—C6—H6A | 109.6 | H13B—C13—H13C | 109.5 |
| N2—C6—H6B | 109.6 | O2—C14—H14A | 109.5 |
| N2—C6—C7 | 110.42 (19) | O2—C14—H14B | 109.5 |
| H6A—C6—H6B | 108.1 | O2—C14—H14C | 109.5 |
| C7—C6—H6A | 109.6 | H14A—C14—H14B | 109.5 |
| C7—C6—H6B | 109.6 | H14A—C14—H14C | 109.5 |
| C8—C7—C6 | 120.1 (2) | H14B—C14—H14C | 109.5 |
| C12—C7—C6 | 120.6 (2) | | |

*Hydrogen-bond geometry (Å, º)*

Cg is the centroid of the C7–C12 ring.

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N2—H2···N1$^{i}$ | 0.88 | 2.31 | 3.090 (3) | 149 |
| C2—H2*A*···*Cg*$^{i}$ | 0.95 | 2.50 | 3.397 (3) | 158 |

Symmetry code: (i) −*x*+1, −*y*+2, −*z*.