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# (*E*)-4-[(4-Amino-5-bromopyridin-3-yl)-iminomethyl]phenol

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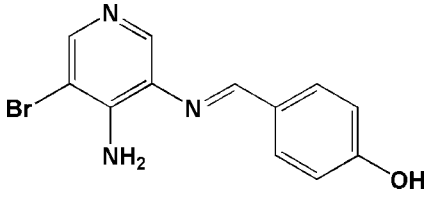
Key indicators: single-crystal X-ray study; $T$ = 113 K; mean $\sigma$(C–C) = 0.004 Å; $R$ factor = 0.041; $wR$ factor = 0.100; data-to-parameter ratio = 16.8.

In the molecule of the title compound, $C_{12}H_{10}BrN_3O$, the pyridine and benzene rings are oriented at a dihedral angle of 34.93 (3)°. Intramolecular N—H···N and N—H···Br hydrogen bonds result in the formation of two non-planar five-membered rings. In the crystal structure, intermolecular O—H···N and N—H···O hydrogen bonds link the molecules to form a three-dimensional network.

## Related literature

For general background, see: Liu *et al.* (2002).




## Experimental

### Crystal data

$C_{12}H_{10}BrN_3O$
$M_r$ = 292.14
Monoclinic, $P2_1/n$
$a$ = 4.9607 (10) Å
$b$ = 15.586 (3) Å
$c$ = 14.906 (3) Å
$\beta$ = 95.65 (3)°
$V$ = 1146.9 (4) Å$^3$
$Z$ = 4
Mo $K\alpha$ radiation
$\mu$ = 3.57 mm$^{-1}$
$T$ = 113 (2) K
0.10 × 0.08 × 0.06 mm

### Data collection

Rigaku Saturn diffractometer
Absorption correction: multi-scan (Blessing, 1995)
$T_{min}$ = 0.717, $T_{max}$ = 0.814
14191 measured reflections
2739 independent reflections
2123 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.053

### Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
$S$ = 1.02
2739 reflections
163 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.53 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.59 e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O1—H1···N1$^{i}$ | 0.82 | 1.88 | 2.688 (3) | 167 |
| N3—H3$A$···Br1 | 0.877 (18) | 2.72 (3) | 3.125 (4) | 110.0 (19) |
| N3—H3$A$···O1$^{ii}$ | 0.877 (18) | 2.54 (2) | 2.967 (5) | 111.0 (19) |
| N3—H3$B$···N2 | 0.889 (16) | 2.28 (3) | 2.700 (5) | 109 (2) |

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

Data collection: *CrystalClear* (Rigaku/MSC, 2005); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2003).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2438).

## References

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Rigaku/MSC (2005). *CrystalClear*. Rigaku/MSC, The Woodlands, Texas, USA.
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# supporting information

*Acta Cryst.* (2008). E**64**, o1053 [doi:10.1107/S160053680800812X]

## (*E*)-4-[(4-Amino-5-bromopyridin-3-yl)iminomethyl]phenol

**Mingjian Cai, Mingjie Zhang and Yongliang Hu**

### S1. Comment

Schiff bases, as substrates, are important organic intermediates. Their recent applications in asymmetric catalytic hydrogenation, asymmetric chemical reduction and oxidation and asymmetric alkylidation of carbon atom, as well as reactions with Lawessen regent are very active (Liu *et al.*, 2002). We have recently synthesized the novel title compound, (I), and report herein its crystal structure.

In the molecule of the title compound, (I), (Fig. 1) the bond lengths and angles are within normal ranges. Rings A (N1/C1–C5) and B (C7–C12) are, of course, planar and the dihedral angle between them is A/B = 34.93 (3)°. The intramolecular N—H···N and N—H···Br hydrogen bonds (Table 1) result in the formation of two non-planar five-membered rings; C (N2/C4/C5/N3/H3B) and D (Br1/C1/C5/N3/H3A).

In the crystal structure, intermolecular O—H···N and N—H···O hydrogen bonds (Table 1) link the molecules to form a three-dimensional network (Fig. 2), in which they may be effective in the stabilization of the structure.

### S2. Experimental

5-bromopyridine-3,4-diamine (1.88 g, 10 mmol) was added to a solution of 4-hydroxybenzaldehyde (1.22 g, 10 mmol)in MeOH (50 ml). The solution was refluxed for 10 h, and then dried over magnesium sulfate, filtered and the volatiles were removed under reduced pressure. The crude product was further purified and recystallized from MeOH affording yellow crystals of (I) (yield; 70%).

### S3. Refinement

H atoms (for $NH_2$) were located in a difference synthesis and refined isotropically [N—H = 0.876 (10) and 0.889 (10) Å; $U_{iso}$(H) = 0.028 (8) and 0.027 (8) Å$^2$]. The remaining H atoms were positioned geometrically, with O—H = 0.82 Å (for OH) and C—H = 0.93 Å for aromatic H, respectively, and constrained to ride on their parent atoms with $U_{iso}$(H) = x$U_{eq}$(C,O), where x = 1.5 for OH H and x = 1.2 for aromatic H atoms.

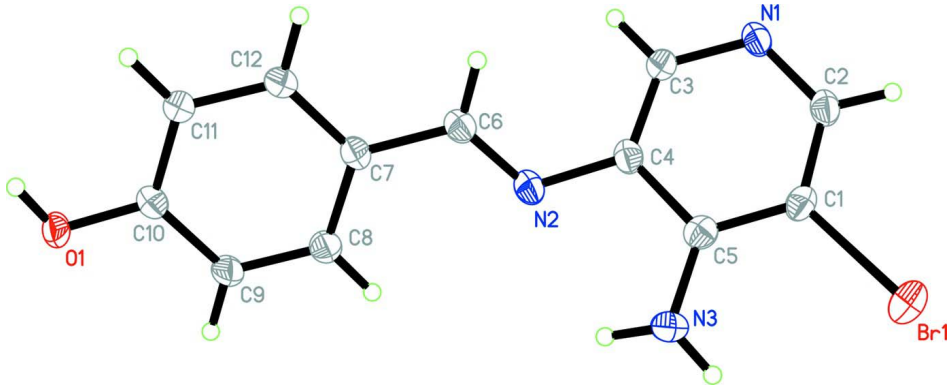


**Figure 1**

The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 35% probability level.

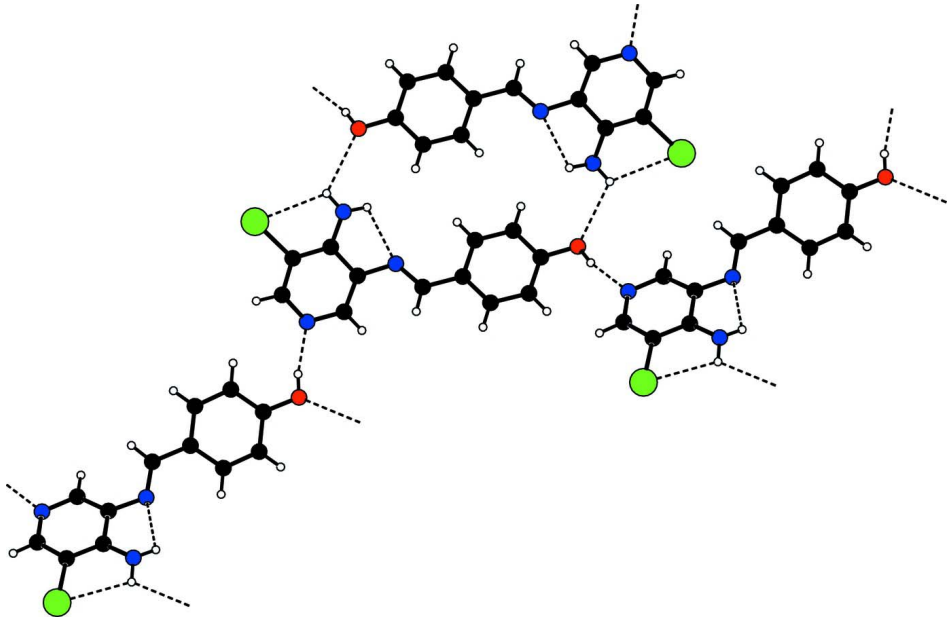

**Figure 2**

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

### (*E*)-4-[(4-amino-5-bromopyridin-3-yl)iminomethyl]phenol

*Crystal data*

$C_{12}H_{10}BrN_3O$
$M_r = 292.14$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 4.9607\ (10)$ Å
$b = 15.586\ (3)$ Å
$c = 14.906\ (3)$ Å
$\beta = 95.65\ (3)°$
$V = 1146.9\ (4)$ Å$^3$
$Z = 4$

$F(000) = 584$
$D_x = 1.692$ Mg m$^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3259 reflections
$\theta = 1.9–27.8°$
$\mu = 3.57$ mm$^{-1}$
$T = 113$ K
Plate, yellow
0.10 × 0.08 × 0.06 mm

*Data collection*

Rigaku Saturn diffractometer
Radiation source: rotating anode
Confocal monochromator
$\omega$ scans
Absorption correction: multi-scan (Blessing, 1995)
$T_{min}$ = 0.717, $T_{max}$ = 0.814
14191 measured reflections
2739 independent reflections
2123 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.053
$\theta_{max}$ = 27.9°, $\theta_{min}$ = 2.6°
$h$ = −6→6
$k$ = −20→20
$l$ = −19→19

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.040
$wR(F^2)$ = 0.100
$S$ = 1.02
2739 reflections
163 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0558P)^2 + 0.0115P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.53 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.59 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 $F^2 > 2\text{sigma}(F^2)$ 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 | 0.22060 (6) | 0.579793 (19) | 0.40491 (2) | 0.03830 (14) |
| O1 | 1.2134 (4) | 0.29970 (11) | −0.18529 (12) | 0.0258 (4) |
| H1 | 1.2791 | 0.2515 | −0.1871 | 0.039* |
| N1 | −0.0149 (4) | 0.34708 (13) | 0.29398 (14) | 0.0207 (5) |
| N2 | 0.4754 (4) | 0.40060 (14) | 0.12855 (15) | 0.0214 (5) |
| N3 | 0.5400 (5) | 0.53733 (15) | 0.23987 (17) | 0.0263 (5) |
| C1 | 0.1953 (5) | 0.48149 (16) | 0.32940 (17) | 0.0213 (5) |
| C2 | 0.0159 (5) | 0.41727 (16) | 0.34483 (18) | 0.0220 (6) |
| H2 | −0.0886 | 0.4231 | 0.3930 | 0.026* |
| C3 | 0.1392 (5) | 0.34101 (15) | 0.22483 (17) | 0.0197 (5) |
| H3 | 0.1206 | 0.2921 | 0.1890 | 0.024* |
| C4 | 0.3231 (5) | 0.40235 (16) | 0.20351 (17) | 0.0199 (5) |
| C5 | 0.3553 (5) | 0.47740 (16) | 0.25818 (17) | 0.0202 (5) |
| C6 | 0.5619 (5) | 0.32877 (16) | 0.10100 (17) | 0.0209 (5) |
| H6 | 0.5200 | 0.2789 | 0.1310 | 0.025* |

| | | | | |
|---|---|---|---|---|
| C7 | 0.7226 (5) | 0.32179 (16) | 0.02482 (17) | 0.0192 (5) |
| C8 | 0.7946 (5) | 0.39343 (16) | −0.02422 (18) | 0.0224 (6) |
| H8 | 0.7318 | 0.4474 | −0.0098 | 0.027* |
| C9 | 0.9575 (5) | 0.38505 (16) | −0.09363 (18) | 0.0232 (6) |
| H9 | 1.0021 | 0.4333 | −0.1257 | 0.028* |
| C10 | 1.0566 (5) | 0.30420 (16) | −0.11623 (17) | 0.0202 (5) |
| C11 | 0.9849 (5) | 0.23290 (16) | −0.06839 (17) | 0.0208 (5) |
| H11 | 1.0475 | 0.1789 | −0.0829 | 0.025* |
| C12 | 0.8202 (5) | 0.24182 (16) | 0.00099 (17) | 0.0213 (6) |
| H12 | 0.7736 | 0.1933 | 0.0324 | 0.026* |
| H3A | 0.508 (6) | 0.5891 (10) | 0.2593 (19) | 0.028 (8)* |
| H3B | 0.590 (5) | 0.5330 (19) | 0.1844 (9) | 0.027 (8)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| Br1 | 0.0515 (2) | 0.02764 (19) | 0.0375 (2) | −0.00060 (13) | 0.01289 (16) | −0.01098 (13) |
| O1 | 0.0335 (11) | 0.0214 (9) | 0.0253 (10) | 0.0049 (8) | 0.0168 (8) | 0.0036 (8) |
| N1 | 0.0210 (11) | 0.0234 (11) | 0.0186 (11) | 0.0013 (9) | 0.0061 (9) | 0.0025 (9) |
| N2 | 0.0192 (11) | 0.0245 (11) | 0.0212 (12) | 0.0001 (9) | 0.0060 (9) | 0.0012 (9) |
| N3 | 0.0292 (13) | 0.0188 (12) | 0.0321 (14) | −0.0044 (10) | 0.0090 (11) | −0.0002 (10) |
| C1 | 0.0241 (13) | 0.0191 (12) | 0.0207 (13) | 0.0038 (10) | 0.0024 (11) | −0.0032 (10) |
| C2 | 0.0235 (14) | 0.0238 (13) | 0.0195 (13) | 0.0042 (11) | 0.0067 (11) | 0.0009 (11) |
| C3 | 0.0220 (13) | 0.0181 (12) | 0.0194 (13) | 0.0009 (10) | 0.0038 (10) | −0.0005 (10) |
| C4 | 0.0211 (13) | 0.0219 (12) | 0.0171 (13) | 0.0029 (10) | 0.0040 (10) | 0.0014 (10) |
| C5 | 0.0205 (13) | 0.0185 (12) | 0.0211 (13) | 0.0032 (10) | 0.0003 (10) | 0.0015 (10) |
| C6 | 0.0187 (13) | 0.0227 (13) | 0.0216 (13) | −0.0001 (10) | 0.0042 (10) | 0.0021 (11) |
| C7 | 0.0181 (12) | 0.0229 (13) | 0.0168 (13) | −0.0019 (10) | 0.0030 (10) | 0.0001 (10) |
| C8 | 0.0235 (13) | 0.0191 (12) | 0.0253 (14) | 0.0027 (11) | 0.0063 (11) | 0.0031 (11) |
| C9 | 0.0269 (14) | 0.0180 (12) | 0.0259 (14) | 0.0019 (11) | 0.0093 (11) | 0.0058 (11) |
| C10 | 0.0196 (13) | 0.0223 (12) | 0.0193 (13) | −0.0008 (10) | 0.0039 (10) | 0.0022 (10) |
| C11 | 0.0222 (13) | 0.0186 (12) | 0.0222 (13) | −0.0003 (10) | 0.0054 (11) | −0.0001 (10) |
| C12 | 0.0228 (13) | 0.0187 (12) | 0.0229 (14) | −0.0013 (10) | 0.0059 (11) | 0.0025 (10) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| Br1—C1 | 1.898 (2) | C3—H3 | 0.9300 |
| O1—C10 | 1.352 (3) | C4—C5 | 1.426 (3) |
| O1—H1 | 0.8200 | C6—C7 | 1.455 (3) |
| N1—C2 | 1.331 (3) | C6—H6 | 0.9300 |
| N1—C3 | 1.346 (3) | C7—C12 | 1.396 (3) |
| N2—C6 | 1.281 (3) | C7—C8 | 1.400 (3) |
| N2—C4 | 1.409 (3) | C8—C9 | 1.380 (4) |
| N3—C5 | 1.355 (3) | C8—H8 | 0.9300 |
| N3—H3A | 0.876 (10) | C9—C10 | 1.406 (3) |
| N3—H3B | 0.889 (10) | C9—H9 | 0.9300 |
| C1—C2 | 1.374 (4) | C10—C11 | 1.386 (3) |
| C1—C5 | 1.388 (4) | C11—C12 | 1.387 (3) |

| | | | |
|---|---|---|---|
| C2—H2 | 0.9300 | C11—H11 | 0.9300 |
| C3—C4 | 1.380 (3) | C12—H12 | 0.9300 |
| | | | |
| C10—O1—H1 | 109.5 | N2—C6—C7 | 122.8 (2) |
| C2—N1—C3 | 116.9 (2) | N2—C6—H6 | 118.6 |
| C6—N2—C4 | 119.6 (2) | C7—C6—H6 | 118.6 |
| C5—N3—H3A | 115 (2) | C12—C7—C8 | 117.8 (2) |
| C5—N3—H3B | 113.1 (19) | C12—C7—C6 | 119.7 (2) |
| H3A—N3—H3B | 117 (3) | C8—C7—C6 | 122.4 (2) |
| C2—C1—C5 | 121.5 (2) | C9—C8—C7 | 120.9 (2) |
| C2—C1—Br1 | 119.7 (2) | C9—C8—H8 | 119.5 |
| C5—C1—Br1 | 118.76 (19) | C7—C8—H8 | 119.5 |
| N1—C2—C1 | 122.9 (2) | C8—C9—C10 | 120.6 (2) |
| N1—C2—H2 | 118.5 | C8—C9—H9 | 119.7 |
| C1—C2—H2 | 118.5 | C10—C9—H9 | 119.7 |
| N1—C3—C4 | 124.5 (2) | O1—C10—C11 | 123.1 (2) |
| N1—C3—H3 | 117.8 | O1—C10—C9 | 118.0 (2) |
| C4—C3—H3 | 117.8 | C11—C10—C9 | 118.8 (2) |
| C3—C4—N2 | 126.0 (2) | C10—C11—C12 | 120.2 (2) |
| C3—C4—C5 | 118.4 (2) | C10—C11—H11 | 119.9 |
| N2—C4—C5 | 115.5 (2) | C12—C11—H11 | 119.9 |
| N3—C5—C1 | 124.8 (2) | C11—C12—C7 | 121.6 (2) |
| N3—C5—C4 | 119.4 (2) | C11—C12—H12 | 119.2 |
| C1—C5—C4 | 115.8 (2) | C7—C12—H12 | 119.2 |
| | | | |
| C3—N1—C2—C1 | −0.2 (4) | N2—C4—C5—C1 | 176.8 (2) |
| C5—C1—C2—N1 | 0.7 (4) | C4—N2—C6—C7 | −179.3 (2) |
| Br1—C1—C2—N1 | 179.2 (2) | N2—C6—C7—C12 | 177.2 (2) |
| C2—N1—C3—C4 | −0.4 (4) | N2—C6—C7—C8 | −0.1 (4) |
| N1—C3—C4—N2 | −175.8 (2) | C12—C7—C8—C9 | −0.2 (4) |
| N1—C3—C4—C5 | 0.4 (4) | C6—C7—C8—C9 | 177.1 (2) |
| C6—N2—C4—C3 | −35.7 (4) | C7—C8—C9—C10 | −0.5 (4) |
| C6—N2—C4—C5 | 148.0 (2) | C8—C9—C10—O1 | 179.5 (2) |
| C2—C1—C5—N3 | −178.7 (2) | C8—C9—C10—C11 | 0.8 (4) |
| Br1—C1—C5—N3 | 2.9 (3) | O1—C10—C11—C12 | −179.1 (2) |
| C2—C1—C5—C4 | −0.7 (4) | C9—C10—C11—C12 | −0.6 (4) |
| Br1—C1—C5—C4 | −179.13 (17) | C10—C11—C12—C7 | −0.1 (4) |
| C3—C4—C5—N3 | 178.2 (2) | C8—C7—C12—C11 | 0.5 (4) |
| N2—C4—C5—N3 | −5.1 (3) | C6—C7—C12—C11 | −176.9 (2) |
| C3—C4—C5—C1 | 0.2 (3) | | |

*Hydrogen-bond geometry (Å, º)*

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| O1—H1···N1$^{i}$ | 0.82 | 1.88 | 2.688 (3) | 167 |
| N3—H3*A*···Br1 | 0.88 (2) | 2.72 (3) | 3.125 (4) | 110 (2) |

| | | | | |
|---|---|---|---|---|
| N3—H3*A*···O1$^{ii}$ | 0.88 (2) | 2.54 (2) | 2.967 (5) | 111 (2) |
| N3—H3*B*···N2 | 0.89 (2) | 2.28 (3) | 2.700 (5) | 109 (2) |

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