

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

N-(3-Bromo-2-methylphenyl)-2-oxo-1,2-dihydropyridine-3-carboxamide

Yun-Hua Xu^a and Sihui Long^{b*}

^aSchool of Science, Beijing Jiaotong University, Beijing 100044, People's Republic of China, and ^bCollege of Pharmacy, Ohio State University, Columbus, OH 43210, USA

Correspondence e-mail: longsihui@yahoo.com

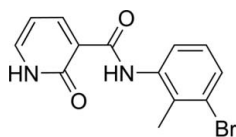
Received 7 March 2012; accepted 15 March 2012

Key indicators: single-crystal X-ray study; $T = 90$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.031; wR factor = 0.072; data-to-parameter ratio = 16.1.

The title compound, $\text{C}_{13}\text{H}_{11}\text{BrN}_2\text{O}_2$, consists of two six-membered rings linked by an amide group and adopts a near planar conformation. The dihedral angle between the two rings is 8.38 (11)°. In the crystal structure, there are intra- and intermolecular $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds, the latter forming inversion dimers.

Related literature

For a related structure, see: Long *et al.* (2006). For background and details of synthesis, see: Ting *et al.* (1990).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{11}\text{BrN}_2\text{O}_2$

$M_r = 307.15$

Triclinic, $P\bar{1}$

$a = 7.164$ (1) Å

$b = 7.715$ (1) Å

$c = 10.446$ (2) Å

$\alpha = 88.23$ (1)°

$\beta = 89.18$ (1)°

$\gamma = 89.68$ (1)°

$V = 577.01$ (16) Å³

$Z = 2$

Mo $K\alpha$ radiation

$\mu = 3.56$ mm⁻¹
 $T = 90$ K

$0.30 \times 0.10 \times 0.04$ mm

Data collection

Nonius KappaCCD diffractometer

Absorption correction: multi-scan

(SCALEPACK; Otwinowski &

Minor, 1997)

$T_{\min} = 0.415$, $T_{\max} = 0.871$

5027 measured reflections

2637 independent reflections

2273 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$

$wR(F^2) = 0.072$

$S = 1.07$

2637 reflections

164 parameters

H-atom parameters constrained

$\Delta\rho_{\max} = 0.94$ e Å⁻³

$\Delta\rho_{\min} = -0.61$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O2}$	0.88	1.90	2.660 (3)	144
$\text{N2}-\text{H2A}\cdots\text{O2}^i$	0.88	1.91	2.785 (3)	171

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

Data collection: COLLECT (Nonius, 2002); cell refinement: DENZO-SMN (Otwinowski & Minor, 1997); data reduction: DENZO-SMN; 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: SHELXL97.

SL thanks Drs Tonglei Li and Sean Parkin for support and laboratory facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: FF2058).

References

- Long, S., Siegler, M. & Li, T. (2006). *Acta Cryst.* **E62**, o4278–o4279.
 Nonius (2002). COLLECT. Nonius BV, Delft, The Netherlands.
 Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography, Part A*, edited by C. W. Carter Jr & R. M. Sweet, pp. 307–326. New York: Academic Press.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Ting, P. C., Kaminski, J. J., Sherlock, M. H., Tom, W. C., Lee, J. F., Bryant, R. W., Watnick, A. S. & McPhail, A. T. (1990). *J. Med. Chem.* **33**, 2697–2706.

supplementary materials

Acta Cryst. (2012). E68, o1134 [doi:10.1107/S1600536812011294]

N*-(3-Bromo-2-methylphenyl)-2-oxo-1,2-dihydropyridine-3-carboxamide*Yun-Hua Xu and Sihui Long****Comment**

The title compound (I) was obtained as a by-product during an effort to make 2-(2-methyl-3-bromoanilino)nicotinic acid by reacting 2-chloronicotinic acid with 3-bromo-2-methylaniline through a modified procedure from Ting *et al.* (1990). Similar to the case of *N*-(3-chloro-2-methylphenyl)-1,2-dihydro-2-oxo-3-pyridinecarboxamide (Long *et al.*, 2006), the crystal structure analysis revealed it is the keto-amine (or lactam) tautomer, rather than the hydroxy-pyridine tautomer (II) (Fig. 1, Table 1). The two aromatic rings of the molecule are linked by an amide group. Due to the extended π -conjugation system throughout the whole molecule *via* the amide bridge, the molecule takes a near planar conformation. The dihedral angle between the two aromatic rings is 8.38 (11)°.

Centrosymmetric dimers are formed through intra- and intermolecular N—H \cdots O hydrogen bonds (Table 2). Essentially, the title compound is isostructural with *N*-(3-chloro-2-methylphenyl)-1,2-dihydro-2-oxo-3-pyridinecarboxamide, since the only difference is bromine in the title compound and chlorine in the counterpart.

Experimental

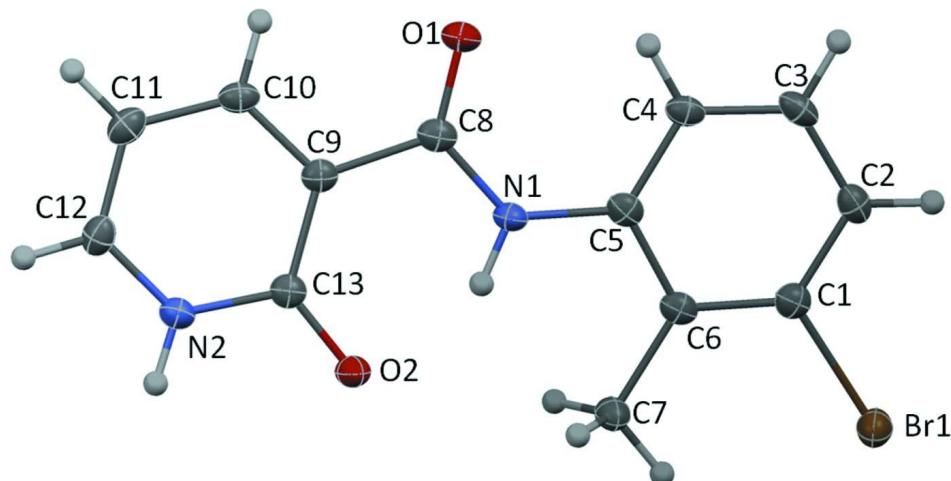
2-Chloronicotinic acid (1.9 g, 12.1 mmol), 3-bromo-2-methyl-aniline (2.5 g, 13.4 mmol), and pyridine (1.0 ml, 12 mmol) were added to a round-bottom flask, followed by introduction of *p*-toluenesulfonic acid (0.3 g, 1.8 mmol) in 10 ml of water. The resulted solution was refluxed overnight. Colorless solid precipitated out after the mixture was cooled down to room temperature, and it was characterized by NMR to be the title compound (I). Crystals were grown from MeOH solution by slow evaporation.

Refinement

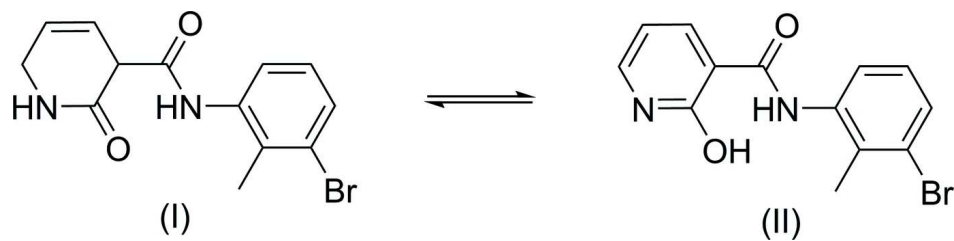
H atoms were located in difference Fourier maps and subsequently placed in idealized positions with constrained C—H distances of 0.95 (C_{Ar}—H), 0.98 (C_{Me}—H) and 0.88 Å (N—H). $U_{\text{iso}}(\text{H})$ values were set to $1.2U_{\text{eq}}(\text{C}, \text{N})$ or $1.5U_{\text{eq}}(\text{C})$ for methyl group.

Computing details

Data collection: *COLLECT* (Nonius, 2002); cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN* (Otwinowski & Minor, 1997); 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: *SHELXL97* (Sheldrick, 2008).


Figure 1

The molecular structure of (I), with displacement ellipsoids drawn at the 50% probability level (arbitrary spheres for the H atoms).


Figure 2

Tautomerism of the title compound.

N-(3-Bromo-2-methylphenyl)-2-oxo-1,2-dihydropyridine-3-carboxamide

Crystal data

$C_{13}H_{11}BrN_2O_2$

$M_r = 307.15$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.164$ (1) Å

$b = 7.715$ (1) Å

$c = 10.446$ (2) Å

$\alpha = 88.23$ (1)°

$\beta = 89.18$ (1)°

$\gamma = 89.68$ (1)°

$V = 577.01$ (16) Å³

$Z = 2$

$F(000) = 308$

$D_x = 1.768$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 2552 reflections

$\theta = 1.0$ – 27.5 °

$\mu = 3.56$ mm⁻¹

$T = 90$ K

Thick plate, colourless

$0.30 \times 0.10 \times 0.04$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

Detector resolution: 18 pixels mm⁻¹

ω scans at fixed $\chi = 55$ °

Absorption correction: multi-scan

(*SCALEPACK*; Otwinowski & Minor, 1997)

$T_{\min} = 0.415$, $T_{\max} = 0.871$

5027 measured reflections

2637 independent reflections

2273 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.032$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.0^\circ$
 $h = -9 \rightarrow 9$

$k = -10 \rightarrow 10$
 $l = -13 \rightarrow 13$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.072$
 $S = 1.07$
 2637 reflections
 164 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
 $w = 1/[\sigma^2(F_o^2) + (0.0231P)^2 + 0.5699P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.94 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.61 \text{ e } \text{\AA}^{-3}$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.1649 (3)	0.2509 (3)	0.8354 (2)	0.0184 (5)
C2	0.1129 (3)	0.0867 (3)	0.7987 (3)	0.0194 (5)
H2	0.0843	-0.0021	0.8608	0.023*
C3	0.1039 (3)	0.0564 (3)	0.6692 (3)	0.0201 (5)
H3	0.0677	-0.0547	0.6421	0.024*
C4	0.1469 (3)	0.1848 (3)	0.5786 (2)	0.0179 (5)
H4	0.1410	0.1614	0.4900	0.021*
C5	0.1990 (3)	0.3492 (3)	0.6174 (2)	0.0170 (5)
C6	0.2097 (3)	0.3859 (3)	0.7489 (2)	0.0160 (5)
C7	0.2664 (4)	0.5641 (3)	0.7890 (2)	0.0193 (5)
H7A	0.2662	0.5674	0.8827	0.029*
H7B	0.1780	0.6505	0.7548	0.029*
H7C	0.3920	0.5900	0.7555	0.029*
C8	0.2416 (3)	0.4880 (3)	0.3990 (2)	0.0176 (5)
C9	0.3033 (3)	0.6573 (3)	0.3379 (2)	0.0161 (5)
C10	0.2884 (3)	0.6775 (3)	0.2073 (2)	0.0189 (5)
H10	0.2405	0.5845	0.1603	0.023*
C11	0.3414 (4)	0.8303 (3)	0.1408 (2)	0.0213 (6)
H11	0.3299	0.8417	0.0505	0.026*
C12	0.4098 (4)	0.9616 (4)	0.2098 (2)	0.0199 (5)
H12	0.4471	1.0668	0.1674	0.024*
C13	0.3763 (3)	0.7979 (3)	0.4092 (2)	0.0160 (5)
N1	0.2464 (3)	0.4838 (3)	0.52988 (19)	0.0163 (4)
H1	0.2850	0.5797	0.5642	0.020*

N2	0.4252 (3)	0.9437 (3)	0.3384 (2)	0.0174 (4)
H2A	0.4699	1.0318	0.3796	0.021*
O1	0.1914 (3)	0.3676 (2)	0.33371 (17)	0.0226 (4)
O2	0.3985 (2)	0.7976 (2)	0.52859 (16)	0.0190 (4)
Br1	0.17131 (4)	0.28503 (3)	1.01565 (2)	0.02315 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0152 (13)	0.0185 (13)	0.0217 (13)	0.0025 (10)	-0.0020 (10)	-0.0010 (10)
C2	0.0146 (13)	0.0158 (12)	0.0275 (13)	0.0003 (10)	-0.0007 (10)	0.0019 (10)
C3	0.0145 (13)	0.0144 (12)	0.0316 (14)	-0.0011 (10)	-0.0022 (11)	-0.0040 (11)
C4	0.0142 (12)	0.0184 (12)	0.0214 (13)	-0.0003 (10)	-0.0024 (10)	-0.0048 (10)
C5	0.0103 (12)	0.0172 (12)	0.0234 (13)	0.0008 (9)	-0.0019 (10)	-0.0012 (10)
C6	0.0099 (12)	0.0162 (12)	0.0220 (12)	0.0017 (9)	-0.0008 (10)	-0.0035 (10)
C7	0.0238 (14)	0.0165 (12)	0.0178 (12)	-0.0005 (10)	0.0017 (10)	-0.0026 (10)
C8	0.0120 (12)	0.0189 (12)	0.0223 (13)	0.0025 (10)	-0.0013 (10)	-0.0046 (10)
C9	0.0113 (12)	0.0186 (12)	0.0185 (12)	0.0018 (9)	-0.0005 (9)	-0.0021 (10)
C10	0.0149 (13)	0.0224 (13)	0.0198 (12)	0.0006 (10)	-0.0025 (10)	-0.0055 (10)
C11	0.0186 (13)	0.0275 (14)	0.0177 (12)	0.0031 (11)	-0.0024 (10)	-0.0001 (11)
C12	0.0159 (13)	0.0248 (14)	0.0187 (12)	0.0001 (10)	0.0004 (10)	0.0037 (10)
C13	0.0120 (12)	0.0174 (12)	0.0186 (12)	0.0026 (9)	0.0008 (9)	-0.0025 (10)
N1	0.0179 (11)	0.0150 (10)	0.0163 (10)	-0.0017 (8)	-0.0014 (8)	-0.0038 (8)
N2	0.0165 (11)	0.0171 (10)	0.0187 (10)	-0.0014 (8)	-0.0011 (8)	-0.0024 (8)
O1	0.0279 (10)	0.0191 (9)	0.0212 (9)	-0.0042 (8)	-0.0045 (8)	-0.0050 (7)
O2	0.0217 (9)	0.0193 (9)	0.0163 (9)	-0.0035 (7)	-0.0004 (7)	-0.0026 (7)
Br1	0.02871 (16)	0.02031 (14)	0.02034 (14)	0.00082 (10)	0.00016 (10)	0.00063 (10)

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

C1—C2	1.389 (4)	C8—O1	1.228 (3)
C1—C6	1.394 (4)	C8—N1	1.368 (3)
C1—Br1	1.911 (3)	C8—C9	1.502 (3)
C2—C3	1.382 (4)	C9—C10	1.375 (3)
C2—H2	0.9500	C9—C13	1.439 (3)
C3—C4	1.382 (4)	C10—C11	1.401 (4)
C3—H3	0.9500	C10—H10	0.9500
C4—C5	1.398 (3)	C11—C12	1.359 (4)
C4—H4	0.9500	C11—H11	0.9500
C5—N1	1.403 (3)	C12—N2	1.353 (3)
C5—C6	1.414 (3)	C12—H12	0.9500
C6—C7	1.509 (3)	C13—O2	1.259 (3)
C7—H7A	0.9800	C13—N2	1.371 (3)
C7—H7B	0.9800	N1—H1	0.8800
C7—H7C	0.9800	N2—H2A	0.8800
C2—C1—C6	123.6 (2)	O1—C8—N1	124.9 (2)
C2—C1—Br1	115.94 (19)	O1—C8—C9	121.1 (2)
C6—C1—Br1	120.48 (19)	N1—C8—C9	114.0 (2)
C3—C2—C1	118.1 (2)	C10—C9—C13	118.9 (2)

C3—C2—H2	121.0	C10—C9—C8	117.7 (2)
C1—C2—H2	121.0	C13—C9—C8	123.4 (2)
C4—C3—C2	121.1 (2)	C9—C10—C11	122.3 (2)
C4—C3—H3	119.4	C9—C10—H10	118.8
C2—C3—H3	119.4	C11—C10—H10	118.8
C3—C4—C5	119.9 (2)	C12—C11—C10	117.9 (2)
C3—C4—H4	120.0	C12—C11—H11	121.1
C5—C4—H4	120.0	C10—C11—H11	121.1
C4—C5—N1	122.4 (2)	N2—C12—C11	120.5 (2)
C4—C5—C6	120.8 (2)	N2—C12—H12	119.8
N1—C5—C6	116.7 (2)	C11—C12—H12	119.8
C1—C6—C5	116.5 (2)	O2—C13—N2	118.3 (2)
C1—C6—C7	123.5 (2)	O2—C13—C9	125.9 (2)
C5—C6—C7	120.1 (2)	N2—C13—C9	115.8 (2)
C6—C7—H7A	109.5	C8—N1—C5	129.5 (2)
C6—C7—H7B	109.5	C8—N1—H1	115.2
H7A—C7—H7B	109.5	C5—N1—H1	115.2
C6—C7—H7C	109.5	C12—N2—C13	124.7 (2)
H7A—C7—H7C	109.5	C12—N2—H2A	117.7
H7B—C7—H7C	109.5	C13—N2—H2A	117.7
C6—C1—C2—C3	-0.5 (4)	N1—C8—C9—C13	5.0 (3)
Br1—C1—C2—C3	179.22 (18)	C13—C9—C10—C11	-0.1 (4)
C1—C2—C3—C4	0.5 (4)	C8—C9—C10—C11	179.8 (2)
C2—C3—C4—C5	-0.5 (4)	C9—C10—C11—C12	0.1 (4)
C3—C4—C5—N1	179.1 (2)	C10—C11—C12—N2	-0.1 (4)
C3—C4—C5—C6	0.4 (4)	C10—C9—C13—O2	-179.7 (2)
C2—C1—C6—C5	0.4 (4)	C8—C9—C13—O2	0.4 (4)
Br1—C1—C6—C5	-179.30 (17)	C10—C9—C13—N2	0.2 (3)
C2—C1—C6—C7	-179.9 (2)	C8—C9—C13—N2	-179.7 (2)
Br1—C1—C6—C7	0.4 (3)	O1—C8—N1—C5	0.3 (4)
C4—C5—C6—C1	-0.4 (3)	C9—C8—N1—C5	179.9 (2)
N1—C5—C6—C1	-179.1 (2)	C4—C5—N1—C8	4.3 (4)
C4—C5—C6—C7	179.9 (2)	C6—C5—N1—C8	-177.0 (2)
N1—C5—C6—C7	1.1 (3)	C11—C12—N2—C13	0.2 (4)
O1—C8—C9—C10	4.8 (4)	O2—C13—N2—C12	179.7 (2)
N1—C8—C9—C10	-174.9 (2)	C9—C13—N2—C12	-0.2 (3)
O1—C8—C9—C13	-175.3 (2)		

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2	0.88	1.90	2.660 (3)	144
N2—H2A \cdots O2 ⁱ	0.88	1.91	2.785 (3)	171

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