organic compounds

6-Chloro-N'-(3,5-dibromo-2-hydroxy-benzylidene)nicotinohydrazide

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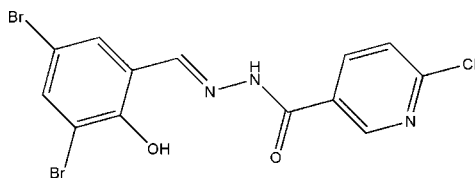
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In the title compound, $C_{13}H_8Br_2ClN_3O_2$, the dihedral angle between the pyridine and benzene rings is 2.7 (4)°; an intramolecular O—H···N hydrogen bond contributes to the conformation of the molecule. In the crystal structure, intermolecular N—H···O hydrogen bonds link molecules into chains along the b-axis direction, while C—H···O and C—H···Cl interactions form head-to-tail chains in the ac plane.

Related literature

For the biological properties of Schiff base compounds, see: Brückner et al. (2000); Harrop et al. (2003); Ren et al. (2002). For related structures, see: Diao (2007); Diao et al. (2007); Li et al. (2007).

Experimental

Crystal data

$C_{13}H_8Br_2ClN_3O_2$	γ = 98.93 (3)°
M_r = 433.49	V = 716.1 (3) Å^3
Triclinic, $P\bar{1}$	Z = 2
a = 4.940 (1) Å	Mo $K\alpha$ radiation
b = 8.0750 (16) Å	μ = 5.85 mm^{-1}
c = 18.598 (4) Å	T = 298 (2) K
α = 101.98 (3)°	0.32 × 0.27 × 0.26 mm
β = 90.88 (3)°	

Data collection

Bruker SMART CCD area-detector diffractometer	6137 measured reflections
Absorption correction: multi-scan (SADABS; Bruker, 2000)	3160 independent reflections
T_{min} = 0.256, T_{max} = 0.311 (expected range = 0.179–0.218)	2003 reflections with $I > 2\sigma(I)$
	R_{int} = 0.037

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2)$ = 0.103	
S = 0.95	
3160 reflections	$\Delta\rho_{max}$ = 0.74 e Å^{-3}
194 parameters	$\Delta\rho_{min}$ = −0.48 e Å^{-3}
1 restraint	

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2···O2^i	0.896 (10)	2.050 (17)	2.929 (5)	166 (5)
O1—H1···N1	0.82	1.85	2.565 (5)	146
C6—H6···Cl1^{ii}	0.93	2.77	3.662 (5)	161
C11—H11···O1^{iii}	0.93	2.38	3.160 (5)	142

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

Data collection: SMART (Bruker, 2000); cell refinement: SAINT (Bruker, 2000); data reduction: SAINT; program(s) used to solve structure: SHELXTL (Bruker, 2000); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL; software used to prepare material for publication: SHELXTL.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SJ2413).

References

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Bruker (2000). SMART (Version 5.625), SAINT (Version 6.01), SHELXTL (Version 6.10) and SADABS (Version 2.03). Bruker AXS Inc., Madison, Wisconsin, USA.
Diao, Y.-P. (2007). Acta Cryst. E63, m1453–m1454.
Diao, Y.-P., Shu, X.-H., Zhang, B.-J., Zhen, Y.-H. & Kang, T.-G. (2007). Acta Cryst. E63, m1816.
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supplementary materials

6-Chloro-*N'*-(3,5-dibromo-2-hydroxybenzylidene)nicotinohydrazide

S.-S. Huang, Q. Zhou and Y.-P. Diao

Comment

Schiff base compounds have received much attention in recent years. Some of the complexes have been found to have pharmacological and antitumor properties (Brückner *et al.*, 2000; Harrop *et al.*, 2003; Ren *et al.*, 2002). As part of our research programme on the structure of Schiff base compounds (Diao *et al.*, 2007; Diao, 2007; Li *et al.*, 2007) we report here the structure of the title compound.

In the title compound, $C_{13}H_8Br_2ClN_3O_2$, (I), Fig. 1, the dihedral angle between the pyridine ring and the benzene ring is 2.7 (4) ° and an intramolecular O1—H1···N1 hydrogen bond contributes to the conformation of the molecule. In the crystal structure, intermolecular N2—H2···O2 hydrogen bonds link molecules into chains down b while C11–H11···O1, and C6–H6···Cl1 interactions form head-to-tail chains in the *ac* plane·(Table 1 and Fig. 2).

Experimental

3,5-Dibromosalicylaldehyde (1.0 mmol, 280.0 mg) and 6-chloronicotinic acid hydrazide (1.0 mmol, 171.3 mg) were dissolved in a methanol (70 ml). The mixture was stirred at reflux for 1 h and cooled to room temperature. After keeping the solution in air for three days, yellow block-like crystals were formed.

Refinement

The crystals obtained were small and weakly diffracting so that the extent of diffraction observed is poor. H2 was located from a difference Fourier map and refined isotropically, with the N–H distance restrained to 0.90 (1) Å. Other H atoms were placed in calculated positions and constrained to ride on their parent atoms, with C–H distances of 0.93 Å, O–H distance of 0.82 Å, and with $U_{iso}(H) = 1.2U_{eq}(C)$ and $1.5U_{eq}(O)$.
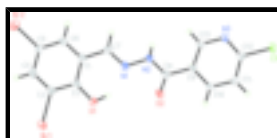
Figures

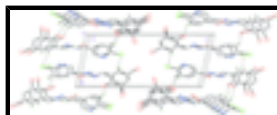Fig. 1. The structure of (I) with displacement parameters drawn at the 30% probability level.

Fig. 2. Crystal packing of (I) viewed along the *b* axis.

6-Chloro-N'-(3,5-dibromo-2-hydroxybenzylidene)nicotinohydrazide

Crystal data

$C_{13}H_8Br_2ClN_3O_2$	$Z = 2$
$M_r = 433.49$	$F_{000} = 420$
Triclinic, $P\bar{1}$	$D_x = 2.011$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$a = 4.940$ (1) Å	Cell parameters from 1135 reflections
$b = 8.0750$ (16) Å	$\theta = 2.4$–24.3º
$c = 18.598$ (4) Å	$\mu = 5.85$ mm^{-1}
$\alpha = 101.98$ (3)º	$T = 298$ (2) K
$\beta = 90.88$ (3)º	Block, yellow
$\gamma = 98.93$ (3)º	$0.32 \times 0.27 \times 0.26$ mm
$V = 716.1$ (3) Å^3	

Data collection

Bruker SMART CCD area-detector diffractometer	3160 independent reflections
Radiation source: fine-focus sealed tube	2003 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.037$
$T = 298(2)$ K	$\theta_{max} = 27.5º$
ω scans	$\theta_{min} = 1.1º$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -6 \rightarrow 6$
$T_{min} = 0.256$, $T_{max} = 0.311$	$k = -10 \rightarrow 10$
6137 measured reflections	$l = -24 \rightarrow 23$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.103$	$w = 1/[\sigma^2(F_o^2) + (0.0406P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.95$	$(\Delta/\sigma)_{max} = {<}0.001$
3160 reflections	$\Delta\rho_{max} = 0.74$ e Å^{-3}
194 parameters	$\Delta\rho_{min} = -0.48$ e Å^{-3}
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	

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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Br1	0.64704 (10)	1.12018 (6)	0.38390 (3)	0.04623 (18)
Br2	−0.23098 (12)	0.65585 (7)	0.45596 (3)	0.0650 (2)
Cl1	−0.2558 (3)	0.61628 (17)	−0.30227 (7)	0.0535 (4)
O1	0.4050 (6)	0.9711 (4)	0.23082 (17)	0.0463 (8)
H1	0.3335	0.9344	0.1893	0.069*
O2	0.3840 (6)	0.7890 (5)	0.02625 (18)	0.0554 (10)
N1	0.0455 (7)	0.7899 (5)	0.1333 (2)	0.0392 (9)
N2	−0.0540 (7)	0.7455 (5)	0.0606 (2)	0.0374 (9)
N3	−0.2934 (7)	0.5806 (5)	−0.1668 (2)	0.0389 (9)
C1	0.0041 (9)	0.7871 (5)	0.2593 (2)	0.0370 (11)
C2	0.2486 (8)	0.9024 (5)	0.2799 (2)	0.0336 (10)
C3	0.3328 (8)	0.9506 (5)	0.3537 (3)	0.0366 (11)
C4	0.1922 (9)	0.8769 (5)	0.4061 (2)	0.0387 (11)
H4	0.2538	0.9074	0.4553	0.046*
C5	−0.0410 (9)	0.7572 (6)	0.3839 (2)	0.0390 (11)
C6	−0.1377 (9)	0.7133 (5)	0.3116 (3)	0.0391 (11)
H6	−0.2976	0.6344	0.2978	0.047*
C7	−0.0995 (9)	0.7370 (6)	0.1826 (3)	0.0394 (11)
H7	−0.2690	0.6675	0.1699	0.047*
C8	0.1354 (9)	0.7578 (6)	0.0096 (3)	0.0380 (11)
C9	0.0327 (8)	0.7262 (5)	−0.0682 (2)	0.0332 (10)
C10	0.1878 (9)	0.8054 (6)	−0.1171 (3)	0.0435 (12)
H10	0.3502	0.8798	−0.1006	0.052*
C11	0.1000 (10)	0.7732 (6)	−0.1896 (3)	0.0453 (12)
H11	0.1985	0.8260	−0.2232	0.054*
C12	−0.1389 (9)	0.6601 (6)	−0.2108 (2)	0.0369 (11)
C13	−0.2042 (9)	0.6156 (6)	−0.0962 (2)	0.0381 (11)
H13	−0.3088	0.5618	−0.0639	0.046*
H2	−0.234 (3)	0.750 (7)	0.056 (3)	0.080*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0403 (3)	0.0556 (3)	0.0381 (3)	−0.0031 (2)	−0.0101 (2)	0.0083 (2)
Br2	0.0754 (4)	0.0764 (4)	0.0414 (4)	−0.0097 (3)	0.0074 (3)	0.0246 (3)
Cl1	0.0615 (8)	0.0617 (8)	0.0335 (7)	−0.0032 (6)	−0.0119 (6)	0.0126 (6)
O1	0.0376 (19)	0.065 (2)	0.0302 (19)	−0.0083 (16)	−0.0008 (15)	0.0104 (18)
O2	0.0275 (19)	0.099 (3)	0.036 (2)	0.0031 (18)	−0.0058 (15)	0.0132 (19)
N1	0.033 (2)	0.056 (2)	0.028 (2)	0.0031 (18)	−0.0041 (17)	0.0094 (19)
N2	0.027 (2)	0.055 (2)	0.028 (2)	0.0040 (18)	−0.0028 (18)	0.0063 (19)
N3	0.039 (2)	0.044 (2)	0.030 (2)	−0.0025 (18)	−0.0045 (18)	0.0060 (18)
C1	0.036 (3)	0.044 (3)	0.031 (3)	0.004 (2)	0.000 (2)	0.009 (2)
C2	0.027 (2)	0.041 (3)	0.032 (3)	0.0000 (19)	0.001 (2)	0.010 (2)
C3	0.028 (2)	0.043 (3)	0.037 (3)	0.002 (2)	−0.004 (2)	0.009 (2)
C4	0.041 (3)	0.046 (3)	0.030 (3)	0.009 (2)	−0.001 (2)	0.009 (2)
C5	0.044 (3)	0.045 (3)	0.029 (3)	0.007 (2)	0.008 (2)	0.008 (2)
C6	0.038 (3)	0.037 (3)	0.039 (3)	−0.002 (2)	0.002 (2)	0.006 (2)
C7	0.033 (3)	0.046 (3)	0.035 (3)	0.002 (2)	−0.003 (2)	0.002 (2)
C8	0.035 (3)	0.044 (3)	0.034 (3)	0.003 (2)	−0.002 (2)	0.007 (2)
C9	0.029 (2)	0.042 (3)	0.028 (3)	0.006 (2)	−0.001 (2)	0.008 (2)
C10	0.033 (3)	0.057 (3)	0.036 (3)	−0.008 (2)	−0.004 (2)	0.011 (2)
C11	0.044 (3)	0.055 (3)	0.037 (3)	−0.002 (2)	0.006 (2)	0.017 (2)
C12	0.039 (3)	0.041 (3)	0.032 (3)	0.009 (2)	0.000 (2)	0.009 (2)
C13	0.038 (3)	0.045 (3)	0.028 (3)	−0.003 (2)	0.001 (2)	0.008 (2)

Geometric parameters (Å, °)

Br1—C3	1.896 (4)	C2—C3	1.386 (6)
Br2—C5	1.898 (4)	C3—C4	1.386 (6)
Cl1—C12	1.734 (4)	C4—C5	1.381 (6)
O1—C2	1.355 (5)	C4—H4	0.9300
O1—H1	0.8200	C5—C6	1.375 (6)
O2—C8	1.236 (5)	C6—H6	0.9300
N1—C7	1.275 (5)	C7—H7	0.9300
N1—N2	1.386 (5)	C8—C9	1.482 (6)
N2—C8	1.350 (6)	C9—C13	1.380 (6)
N2—H2	0.896 (10)	C9—C10	1.391 (6)
N3—C12	1.323 (5)	C10—C11	1.369 (6)
N3—C13	1.337 (5)	C10—H10	0.9300
C1—C6	1.387 (6)	C11—C12	1.372 (6)
C1—C2	1.400 (6)	C11—H11	0.9300
C1—C7	1.461 (6)	C13—H13	0.9300
C2—O1—H1	109.5	C1—C6—H6	120.1
C7—N1—N2	119.4 (4)	N1—C7—C1	119.1 (4)
C8—N2—N1	115.8 (4)	N1—C7—H7	120.4
C8—N2—H2	128 (4)	C1—C7—H7	120.4
N1—N2—H2	112 (4)	O2—C8—N2	121.9 (4)

C12—N3—C13	115.9 (4)	O2—C8—C9	121.1 (4)
C6—C1—C2	119.9 (4)	N2—C8—C9	117.0 (4)
C6—C1—C7	119.0 (4)	C13—C9—C10	117.3 (4)
C2—C1—C7	121.0 (4)	C13—C9—C8	123.7 (4)
O1—C2—C3	118.4 (4)	C10—C9—C8	118.9 (4)
O1—C2—C1	122.8 (4)	C11—C10—C9	119.6 (4)
C3—C2—C1	118.8 (4)	C11—C10—H10	120.2
C4—C3—C2	121.3 (4)	C9—C10—H10	120.2
C4—C3—Br1	119.2 (3)	C10—C11—C12	117.6 (4)
C2—C3—Br1	119.5 (3)	C10—C11—H11	121.2
C5—C4—C3	118.7 (4)	C12—C11—H11	121.2
C5—C4—H4	120.7	N3—C12—C11	125.3 (4)
C3—C4—H4	120.7	N3—C12—Cl1	115.9 (3)
C6—C5—C4	121.3 (4)	C11—C12—Cl1	118.8 (4)
C6—C5—Br2	120.3 (3)	N3—C13—C9	124.3 (4)
C4—C5—Br2	118.4 (4)	N3—C13—H13	117.8
C5—C6—C1	119.8 (4)	C9—C13—H13	117.8
C5—C6—H6	120.1		

Hydrogen-bond geometry (Å, °)

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N2—H2⋯O2[i]	0.896 (10)	2.050 (17)	2.929 (5)	166 (5)
O1—H1⋯N1	0.82	1.85	2.565 (5)	146
C6—H6⋯Cl1[ii]	0.93	2.77	3.662 (5)	161
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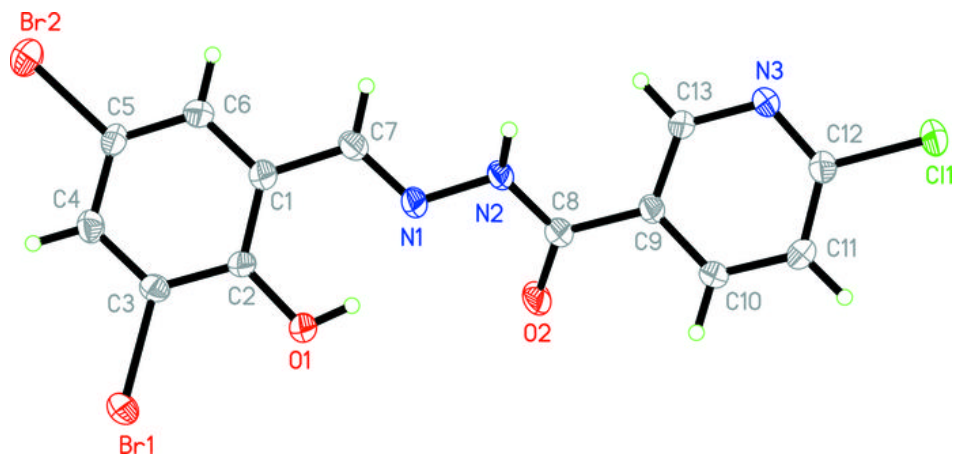Symmetry codes: (i) $x-1, y, z$; (ii) $-x-1, -y+1, -z$; (iii) $-x+1, -y+2, -z$.

Fig. 1

Fig. 2