

4-Bromo-*N*-phenylbenzamidoxime

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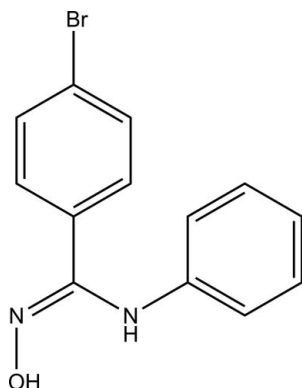
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Key indicators: single-crystal X-ray study; $T = 200$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.037; wR factor = 0.090; data-to-parameter ratio = 15.2.

The title compound, $\text{C}_{13}\text{H}_{11}\text{BrN}_2\text{O}$, a hydroxyamidine derivative (an amidoxime), was obtained by addition of the corresponding imidoyl chloride to hydroxylamine. The benzene and phenyl rings are twisted from the mean plane of the hydroxyamidine group by 34.4 (1) and 59.2 (1)°, respectively. In the crystal structure, intermolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonds link pairs of molecules, forming centrosymmetric dimers.

Related literature

For the synthesis, properties and applications of *N*-substituted hydroxyamidines/amidoximes see: Krajete *et al.* (2004), Srivastava *et al.* (1997); Dondoni *et al.* (1975, 1977); Dürüst *et al.* (2000, 2008); Exner *et al.* (1974); Briggs *et al.* (1976); Deb *et al.* (1991). For a description of the Cambridge Structural Database, see: Allen *et al.* (1987).



Experimental

Crystal data

$\text{C}_{13}\text{H}_{11}\text{BrN}_2\text{O}$
 $M_r = 291.15$
 Monoclinic, $P2_1/n$
 $a = 6.1752$ (1) Å

$b = 15.2628$ (3) Å
 $c = 13.1312$ (2) Å
 $\beta = 103.415$ (1)°
 $V = 1203.86$ (4) Å³

$Z = 4$
 Cu $K\alpha$ radiation
 $\mu = 4.53$ mm⁻¹

$T = 200$ K
 $0.18 \times 0.15 \times 0.09$ mm

Data collection

Bruker APEXII diffractometer
 Absorption correction: multi-scan
 (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.532$, $T_{\max} = 0.665$

15615 measured reflections
 2356 independent reflections
 2273 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.090$
 $S = 1.11$
 2356 reflections

155 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.39$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.68$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O1}-\text{H1}\cdots\text{N1}^i$	0.84	1.99	2.733 (2)	147

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

Data collection: APEX2 (Bruker, 2009); cell refinement: SAINT (Bruker, 2009); data reduction: SAINT; 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: UDMX (Maris, 2004).

The authors are grateful to the Natural Sciences and Engineering Research Council of Canada and the University of Montreal for financial assistance and to the Canadian Post-Doctoral Research Fellowship Program (PDRF).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2914).

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supplementary materials

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4-Bromo-*N*-phenylbenzamidoxime

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Comment

Although extensively studied for their biological activity (antituberculars, hypotensives), their pharmacological properties (bactericidal, fungicidal, local anaesthetics) (Srivastava, 1997) and also as precursors in the synthesis of cyclic compounds (Dürüst, 2000 and 2008), *N*-substituted hydroxyamidines/amidoximes have been less investigated concerning their role in coordination and supramolecular chemistry. They act as bidentate ligands to form 5-membered chelate rings with metal ions, forming stable metal complexes. The good electronic delocalization presented by their structures, and the interesting design possibilities, suggest that *N*-substituted hydroxyamidines/amidoximes and their complexes could be successfully incorporated into supramolecular assemblies based on coordination chemistry and hydrogen bonding. Herein we report the synthesis and crystal structure of a new amidoxime derivative.

The molecular structure of the title compound is shown in Fig. 1. The amidoxime group is present in its neutral form, $N=C=N-OH$ and the bond lengths and angles are within normal ranges (Allen, 1987). The mean planes of the benzene and phenyl rings are tilted with respect to each other by $64.63(9)^\circ$ and, the amidoxime group forms dihedral angles with the benzene and the phenyl rings of $34.4(1)$ and $59.2(1)^\circ$, respectively. This value is less than that reported for the bulky substituted *N*-aryl compound (Krajete, 2004) due to the lesser influence of steric crowding in the title compound.

As illustrated in Fig. 2, the hydrogen bond is of crucial importance to the self-assembly. Molecules are paired by two hydrogen bonds involving the *N*-hydroxyl group rather than the amidoxime moieties. In the crystal structure, the *N*-hydroxyl groups participate in hydrogen bonding of the $O-H\cdots N$ type in which two molecules are joined *via* $O-H\cdots N$ hydrogen bonds to form a dimer across an inversion center (Table 1).

Experimental

The title compound was synthesized according to the procedure of Krajete *et al.* (2004). 4-Bromo-*N*-phenylbenzamide (1.5 g, 5.43 mmol) and an excess of thionyl chloride (15 ml) were refluxed for 2 h under nitrogen atmosphere, yielding the corresponding imidoyl chloride as a pale yellow solid. This compound was dissolved in dry dichloromethane and added drop-wise to a mixture of hydroxylamine hydrochloride (0.4 g, 5.97 mmol) in anhydrous ethanol and triethylamine (3.8 ml, 27.1 mmol) in dry dichloromethane at 195K. The reaction mixture was brought to room temperature and then was heated at reflux for 16 h. The resulting yellow solution was washed with distilled water and the organic materials were subsequently extracted with diethyl ether, dried over anhydrous Na_2SO_4 and filtered. X-ray quality crystals were obtained from a solution of the title compound in aqueous EtOH by slow evaporation at room temperature.

1H NMR (DMSO- d_6 , 300 MHz, δ , p.p.m.): 10.66 (s, 1H), 8.34 (s, 1H), 7.52(d, $J = 8.4$ Hz, 2H), 7.30, (d, $J = 8.4$ Hz, 2H), 7.08 (t, $J = 7.8, 7.8$ Hz, 2H), 6.80 (t, $J = 7.3, 7.3$ Hz, 1H), 6.65 (d, $J = 7.8$ Hz, 2H).

Refinement

The H atoms were generated geometrically (C—H 0.95, N—H 0.88, O—H 0.84 Å) and were included in the refinement in the riding model approximation; their temperature factors were set to 1.5 and 1.2 times for oxygen atom and for those of the equivalent isotropic temperature factors of the parent site, respectively.

Figures

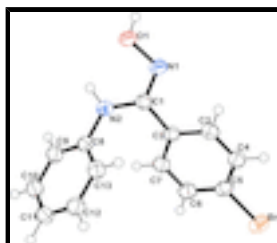


Fig. 1. The molecular structure of the title compound (50% probability displacement ellipsoids).

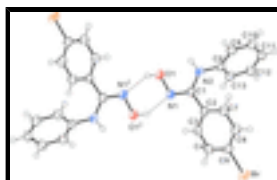


Fig. 2. A pair of molecules linked through intermolecular N—H...O bonds [Symmetry code: (i) $1 - x, 1 - y, 2 - z$]. Hydrogen bonds are shown as dashed lines.

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Crystal data

$C_{13}H_{11}BrN_2O$

$M_r = 291.15$

Monoclinic, $P2_1/n$

Hall symbol: $-P 2_1n$

$a = 6.1752$ (1) Å

$b = 15.2628$ (3) Å

$c = 13.1312$ (2) Å

$\beta = 103.415$ (1)°

$V = 1203.86$ (4) Å³

$Z = 4$

$F_{000} = 584$

$D_x = 1.606$ Mg m⁻³

Cu $K\alpha$ radiation, $\lambda = 1.54178$ Å

Cell parameters from 11676 reflections

$\theta = 2.9$ – 71.9 °

$\mu = 4.53$ mm⁻¹

$T = 200$ K

Block, yellow

$0.18 \times 0.15 \times 0.09$ mm

Data collection

Bruker APEXII
diffractometer

Radiation source: Rotating Anode

Monochromator: Montel 200 optics

Detector resolution: 5.5 pixels mm⁻¹

$T = 200$ K

ω scans

2356 independent reflections

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

$R_{int} = 0.033$

$\theta_{max} = 72.5$ °

$\theta_{min} = 4.5$ °

$h = -7 \rightarrow 7$

Absorption correction: multi-scan
(SADABS; Sheldrick, 1996) $k = -18 \rightarrow 18$
 $T_{\min} = 0.532$, $T_{\max} = 0.665$ $l = -15 \rightarrow 16$
15615 measured reflections

Refinement

Refinement on F^2 Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0601P)^2 + 0.3484P]$
 $R[F^2 > 2\sigma(F^2)] = 0.037$ where $P = (F_o^2 + 2F_c^2)/3$
 $wR(F^2) = 0.090$ $(\Delta/\sigma)_{\max} = 0.001$
 $S = 1.11$ $\Delta\rho_{\max} = 0.39 \text{ e } \text{\AA}^{-3}$
2356 reflections $\Delta\rho_{\min} = -0.68 \text{ e } \text{\AA}^{-3}$
155 parameters Extinction correction: SHELXL97 (Sheldrick, 2008),
 $F_c^* = kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Primary atom site location: structure-invariant direct methods Extinction coefficient: 0.0212 (8)
Secondary atom site location: difference Fourier map

Special details

Experimental. X-ray crystallographic data for **(I)** were collected from a single-crystal sample, which was mounted on a loop fiber. Data were collected using a Bruker Platform diffractometer, equipped with a Bruker *SMART* 4 K Charged-Coupled Device (CCD) Area Detector using the program *APEX2* and a Nonius FR591 rotating anode equipped with a Montel 200 optics. The crystal-to-detector distance was 5.0 cm, and the data collection was carried out in 512 x 512 pixel mode. The initial unit-cell parameters were determined by a least-squares fit of the angular setting of strong reflections, collected by a 10.0 degree scan in 33 frames over four different parts of the reciprocal space (133 frames total). One complete sphere of data was collected, to better than 0.80Å resolution.

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br	1.22913 (4)	0.643427 (14)	0.618702 (18)	0.04819 (16)
O1	0.4208 (2)	0.40817 (9)	0.94989 (11)	0.0393 (3)
H1	0.3752	0.4375	0.9949	0.059*
N1	0.5789 (3)	0.45874 (10)	0.91086 (12)	0.0340 (3)
N2	0.4624 (3)	0.36287 (11)	0.77216 (14)	0.0410 (4)
H2	0.3431	0.3517	0.7958	0.049*

supplementary materials

C1	0.5957 (3)	0.42884 (11)	0.82101 (14)	0.0313 (4)
C2	0.7549 (3)	0.47517 (11)	0.77017 (13)	0.0299 (4)
C3	0.9510 (3)	0.50983 (12)	0.83173 (14)	0.0346 (4)
H3	0.9873	0.4994	0.9051	0.041*
C4	1.0932 (3)	0.55912 (13)	0.78747 (15)	0.0368 (4)
H4	1.2261	0.5828	0.8299	0.044*
C5	1.0391 (3)	0.57343 (12)	0.68075 (15)	0.0353 (4)
C6	0.8484 (4)	0.53857 (14)	0.61731 (15)	0.0408 (4)
H6	0.8153	0.5479	0.5438	0.049*
C7	0.7060 (3)	0.48970 (13)	0.66248 (15)	0.0381 (4)
H7	0.5738	0.4659	0.6196	0.046*
C8	0.4934 (3)	0.31015 (12)	0.68770 (14)	0.0337 (4)
C9	0.3113 (3)	0.29434 (13)	0.60544 (16)	0.0386 (4)
H9	0.1703	0.3189	0.6062	0.046*
C10	0.3362 (4)	0.24228 (13)	0.52181 (16)	0.0417 (4)
H10	0.2117	0.2309	0.4656	0.050*
C11	0.5407 (4)	0.20724 (13)	0.52029 (16)	0.0414 (4)
H11	0.5577	0.1726	0.4626	0.050*
C12	0.7220 (3)	0.22247 (14)	0.60292 (17)	0.0418 (5)
H12	0.8629	0.1980	0.6017	0.050*
C13	0.6989 (3)	0.27319 (13)	0.68740 (15)	0.0384 (4)
H13	0.8226	0.2826	0.7446	0.046*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br	0.0483 (2)	0.0459 (2)	0.0568 (2)	-0.00414 (8)	0.02515 (13)	0.00910 (8)
O1	0.0486 (8)	0.0365 (7)	0.0400 (7)	-0.0037 (6)	0.0248 (6)	-0.0008 (5)
N1	0.0401 (8)	0.0326 (8)	0.0336 (7)	0.0003 (6)	0.0173 (6)	0.0020 (6)
N2	0.0419 (9)	0.0438 (9)	0.0439 (10)	-0.0102 (7)	0.0235 (8)	-0.0114 (7)
C1	0.0353 (8)	0.0289 (8)	0.0315 (8)	0.0025 (7)	0.0113 (7)	-0.0001 (6)
C2	0.0346 (8)	0.0272 (8)	0.0300 (8)	0.0029 (6)	0.0118 (7)	0.0004 (6)
C3	0.0399 (9)	0.0362 (9)	0.0280 (8)	0.0020 (7)	0.0088 (7)	0.0005 (7)
C4	0.0353 (9)	0.0370 (9)	0.0380 (9)	-0.0008 (7)	0.0086 (7)	-0.0007 (7)
C5	0.0383 (9)	0.0304 (8)	0.0409 (10)	0.0017 (7)	0.0170 (7)	0.0038 (7)
C6	0.0492 (11)	0.0437 (10)	0.0298 (9)	-0.0029 (9)	0.0101 (8)	0.0063 (8)
C7	0.0422 (10)	0.0403 (10)	0.0306 (9)	-0.0052 (8)	0.0061 (7)	0.0018 (7)
C8	0.0394 (9)	0.0307 (8)	0.0344 (9)	-0.0060 (7)	0.0156 (7)	-0.0028 (7)
C9	0.0377 (9)	0.0352 (9)	0.0439 (10)	-0.0029 (7)	0.0113 (8)	-0.0017 (8)
C10	0.0479 (11)	0.0383 (10)	0.0373 (10)	-0.0075 (8)	0.0065 (8)	-0.0035 (8)
C11	0.0565 (12)	0.0332 (9)	0.0389 (10)	-0.0079 (8)	0.0199 (9)	-0.0072 (7)
C12	0.0410 (10)	0.0356 (10)	0.0534 (11)	-0.0016 (7)	0.0203 (9)	-0.0058 (8)
C13	0.0374 (9)	0.0372 (9)	0.0409 (10)	-0.0031 (7)	0.0099 (8)	-0.0046 (8)

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

Br—C5	1.9040 (18)	C6—C7	1.387 (3)
O1—N1	1.430 (2)	C6—H6	0.9500
O1—H1	0.8400	C7—H7	0.9500

N1—C1	1.292 (2)	C8—C9	1.388 (3)
N2—C1	1.363 (2)	C8—C13	1.390 (3)
N2—C8	1.419 (2)	C9—C10	1.393 (3)
N2—H2	0.8800	C9—H9	0.9500
C1—C2	1.489 (2)	C10—C11	1.376 (3)
C2—C7	1.394 (2)	C10—H10	0.9500
C2—C3	1.394 (3)	C11—C12	1.386 (3)
C3—C4	1.383 (3)	C11—H11	0.9500
C3—H3	0.9500	C12—C13	1.387 (3)
C4—C5	1.381 (3)	C12—H12	0.9500
C4—H4	0.9500	C13—H13	0.9500
C5—C6	1.382 (3)		
N1—O1—H1	109.5	C7—C6—H6	120.5
C1—N1—O1	110.06 (15)	C6—C7—C2	120.66 (17)
C1—N2—C8	127.65 (17)	C6—C7—H7	119.7
C1—N2—H2	116.2	C2—C7—H7	119.7
C8—N2—H2	116.2	C9—C8—C13	120.19 (17)
N1—C1—N2	121.56 (17)	C9—C8—N2	118.38 (18)
N1—C1—C2	116.31 (16)	C13—C8—N2	121.42 (17)
N2—C1—C2	121.95 (16)	C8—C9—C10	119.66 (19)
C7—C2—C3	118.85 (16)	C8—C9—H9	120.2
C7—C2—C1	121.35 (16)	C10—C9—H9	120.2
C3—C2—C1	119.67 (15)	C11—C10—C9	120.21 (19)
C4—C3—C2	120.89 (17)	C11—C10—H10	119.9
C4—C3—H3	119.6	C9—C10—H10	119.9
C2—C3—H3	119.6	C10—C11—C12	120.06 (18)
C5—C4—C3	119.02 (17)	C10—C11—H11	120.0
C5—C4—H4	120.5	C12—C11—H11	120.0
C3—C4—H4	120.5	C11—C12—C13	120.36 (19)
C4—C5—C6	121.51 (17)	C11—C12—H12	119.8
C4—C5—Br	119.69 (15)	C13—C12—H12	119.8
C6—C5—Br	118.80 (14)	C12—C13—C8	119.50 (18)
C5—C6—C7	119.05 (17)	C12—C13—H13	120.3
C5—C6—H6	120.5	C8—C13—H13	120.3
O1—N1—C1—N2	4.8 (2)	Br—C5—C6—C7	-178.10 (16)
O1—N1—C1—C2	179.94 (14)	C5—C6—C7—C2	-0.5 (3)
C8—N2—C1—N1	-164.13 (19)	C3—C2—C7—C6	-0.7 (3)
C8—N2—C1—C2	21.0 (3)	C1—C2—C7—C6	175.18 (18)
N1—C1—C2—C7	-141.09 (18)	C1—N2—C8—C9	-135.4 (2)
N2—C1—C2—C7	34.0 (3)	C1—N2—C8—C13	46.0 (3)
N1—C1—C2—C3	34.7 (2)	C13—C8—C9—C10	-0.9 (3)
N2—C1—C2—C3	-150.13 (18)	N2—C8—C9—C10	-179.53 (17)
C7—C2—C3—C4	1.1 (3)	C8—C9—C10—C11	-0.5 (3)
C1—C2—C3—C4	-174.82 (16)	C9—C10—C11—C12	1.1 (3)
C2—C3—C4—C5	-0.3 (3)	C10—C11—C12—C13	-0.2 (3)
C3—C4—C5—C6	-1.0 (3)	C11—C12—C13—C8	-1.3 (3)
C3—C4—C5—Br	178.52 (14)	C9—C8—C13—C12	1.8 (3)
C4—C5—C6—C7	1.4 (3)	N2—C8—C13—C12	-179.64 (18)

supplementary materials

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1 \cdots N1 ⁱ	0.84	1.99	2.733 (2)	147

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

Fig. 1

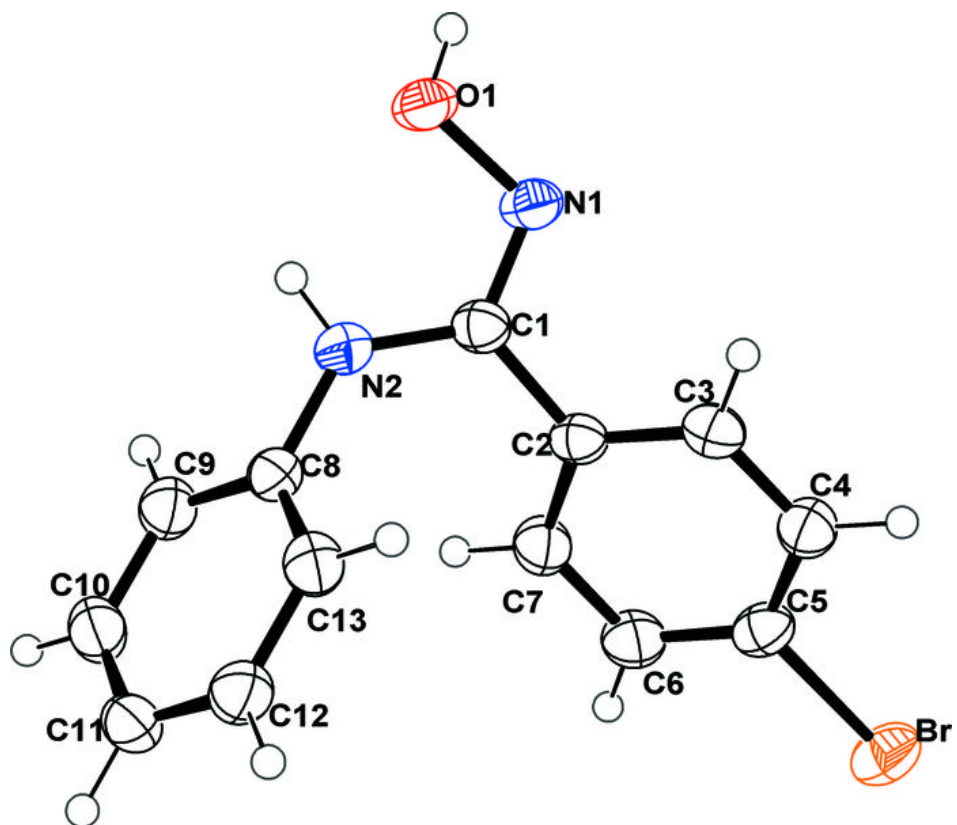


Fig. 2

