Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

5-Bromophthalazine hemihydrate

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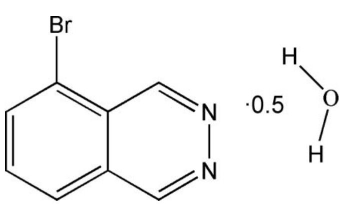
Received 25 May 2012; accepted 3 July 2012

Key indicators: single-crystal X-ray study; *T* = 113 K; mean σ(C–C) = 0.004 Å; *R* factor = 0.029; *wR* factor = 0.074; data-to-parameter ratio = 16.7.

The title compound, $C_8H_5BrN_2 \cdot 0.5H_2O$, is a phthalazine derivative synthesized from 3-bromobenzene-1,2-dicarbaldehyde and hydrazine. The molecule is essentially planar, the deviation from the mean plane of the phthalazine ring being 0.015 (3) Å. The O atom of the solvent water molecule is situated on a twofold rotation axis. In the crystal, O—H···N hydrogen bonds and short N···Br [2.980 (3) Å] contacts lead to the formation of a two-dimensional network parallel to (101).

Related literature

For general background on applications of phthalazines, see: Caira *et al.* (2011); Musa *et al.* (2012).



Experimental

Crystal data

$C_8H_5BrN_2 \cdot 0.5H_2O$
M_r = 218.06
Orthorhombic, *Fdd*2
a = 13.5000 (18) Å
b = 29.964 (5) Å
c = 7.5565 (5) Å
V = 3056.7 (7) Å^3
Z = 16
Mo *Kα* radiation
μ = 5.31 mm^{-1}
T = 113 K
0.30 × 0.22 × 0.18 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
T_{min} = 0.299, T_{max} = 0.448
7799 measured reflections
1819 independent reflections
1781 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.074
S = 1.06
1819 reflections
109 parameters
2 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Absolute structure: Flack (1983), 839 Friedel pairs
Flack parameter: −0.002 (10)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···N1	0.82 (2)	2.07 (3)	2.887 (3)	175 (5)

Data collection: *CrystalClear* (Rigaku/MSC, 2002); 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: *DIAMOND* (Crystal Impact, 2009); software used to prepare material for publication: *CrystalStructure* (Rigaku/MSC, 2006).

The authors thank Professor Wang, Department of Chemistry, Nankai University, for providing experimental facilities.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IM2382).

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supporting information

Acta Cryst. (2012). E**68**, o2421 [https://doi.org/10.1107/S1600536812030358]

5-Bromophthalazine hemihydrate

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S1. Comment

Phthalazine derivatives have played an important role in the development of corrosion science as they can inhibit the corrosion of mild steel (Musa *et al.*, 2012). Moreover, they are of particular interest owing to their biological activity and optical properties (Caira, *et al.*, 2011).

In this paper, the title new phthalazine derivative derived from the condensation of 3-bromo-benzene-1,2-dicarboxaldehyde with hydrazine is reported. The molecular structure of the title compound (Fig.1) is essentially planar with a deviation from the mean plane of the phthalazine ring of 0.0115 (3) Å. All bond lengths have normal values.The oxygen atom of the solvent water molecule is situated on a twofold rotation axis. In the crystal, O—H···N hydrogen bonds and short N···Br contacts lead to the formation of a two dimensional network structure (Fig.2).

S2. Experimental

A solution of 0.1 mol of 3-bromo-benzene-1,2-dicarboxaldehyde is dissolved in 100 ml of ethanol and added dropwise with constant stirring, under a blanket of nitrogen, to an ice-cooled solution of 0.3 mol of hydrazine hydrate in 100 ml of ethanol. The light yellowish reaction mixture is kept with constant stirring for an additional three hours. Ethanol and excess hydrazine are removed under reduced pressure. The remaining yellowish solid may be purified by recrystallization from diethyl ether to yield the yellowish title compound (yield 48%). Finally, the title compound was dissolved in a small amount of methanol and the solution was kept for 10 days at ambient temperature to give rise to white flake crystals due to slow evaporation of the solvent.

S3. Refinement

The H atom of the solvent water was located in a difference fourier map and refined as a riding atom with U_{iso}(H) = 1.2U_{eq}(O). Remaining H atoms were positioned geometrically with C—H = 0.93–0.98 Å and constrained to ride on their parent atoms with U_{iso}(H) = 1.2U_{eq}(C).

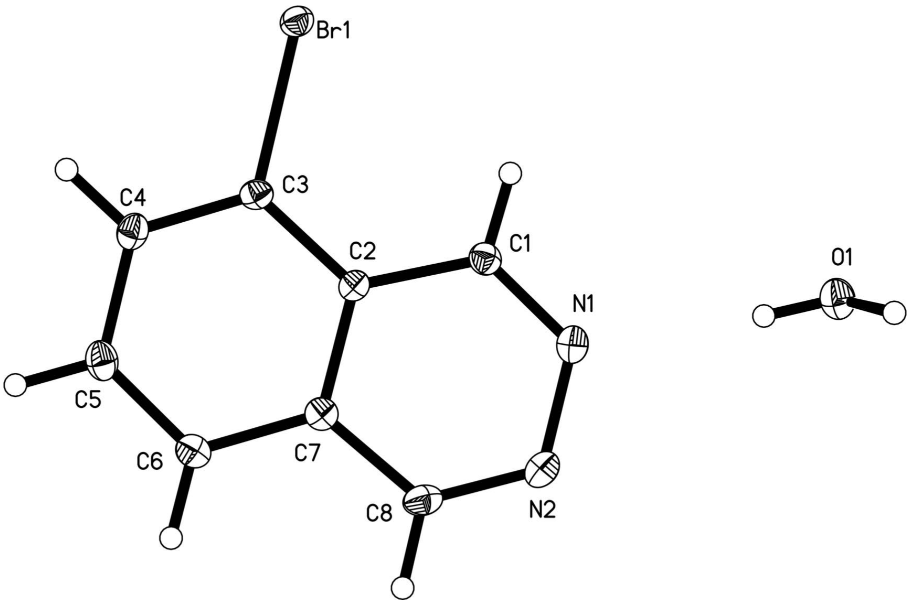

Figure 1

Molecular structure of the title compound showing 30% probability displacement ellipsoids.

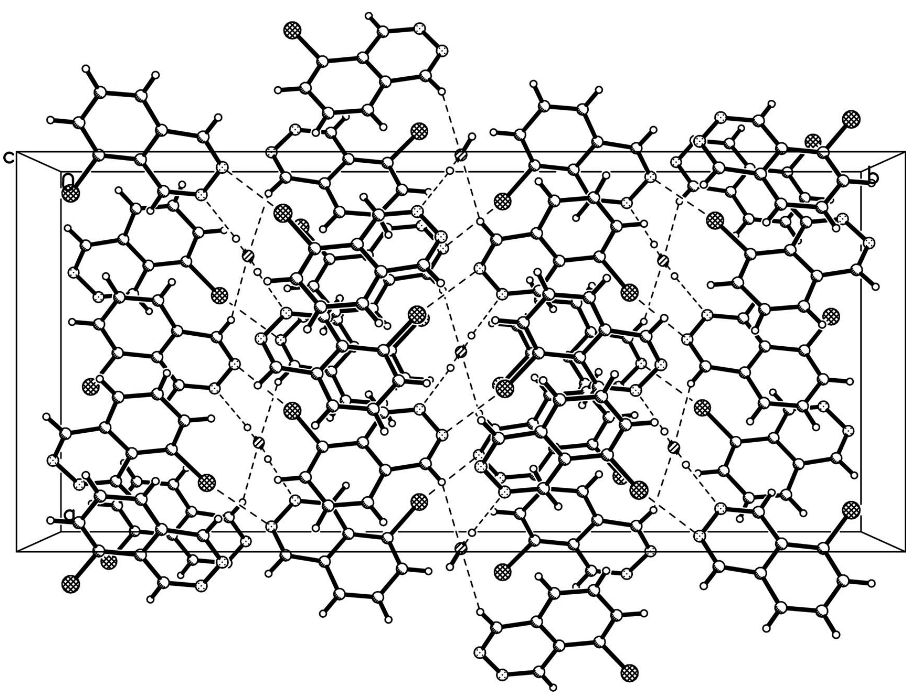

Figure 2

Molecular packing of the title compound with hydrogen bonds and N···Br contacts shown as dashed lines.

5-Bromophthalazine hemihydrate

Crystal data

$C_8H_5BrN_2{\cdot}0.5H_2O$
M_r = 218.06

Orthorhombic, *Fdd*2
Hall symbol: F 2 -2d

a = 13.5000 (18) Å
b = 29.964 (5) Å
c = 7.5565 (5) Å
V = 3056.7 (7) Å^3
Z = 16
F(000) = 1712
D_x = 1.895 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 2874 reflections
θ = 1.4–28.0°
μ = 5.31 mm^{-1}
T = 113 K
Prism, colorless
0.30 × 0.22 × 0.18 mm

Data collection

Rigaku Saturn724 CCD diffractometer
Radiation source: rotating anode
Multilayer monochromator
Detector resolution: 14.22 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku/MSC, 2002)
T_{min} = 0.299, T_{max} = 0.448
7799 measured reflections
1819 independent reflections
1781 reflections with $I > 2\sigma(I)$
R_{int} = 0.064
θ_{max} = 27.8°, θ_{min} = 2.7°
h = −17→17
k = −37→39
l = −9→9

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.074
S = 1.06
1819 reflections
109 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
$w = 1/[\sigma^2(F_o^2) + (0.0496P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.74 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Absolute structure: Flack (1983), **839 Friedel pairs**
Absolute structure parameter: −0.002 (10)

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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
Br1	0.655288 (19)	0.300585 (8)	0.53761 (6)	0.02108 (10)
N1	0.65121 (19)	0.45112 (8)	0.5432 (5)	0.0234 (5)
N2	0.71705 (19)	0.47790 (9)	0.6304 (4)	0.0256 (6)
C1	0.6599 (2)	0.40781 (10)	0.5487 (6)	0.0204 (6)
H1	0.6127	0.3904	0.4862	0.024*
C2	0.7360 (2)	0.38513 (10)	0.6426 (4)	0.0176 (5)
C3	0.7467 (2)	0.33818 (10)	0.6536 (4)	0.0184 (6)

C4	0.8227 (2)	0.32011 (10)	0.7484 (4)	0.0220 (6)
H4	0.8286	0.2886	0.7578	0.026*
C5	0.8923 (2)	0.34786 (12)	0.8323 (4)	0.0245 (7)
H5	0.9461	0.3348	0.8946	0.029*
C6	0.8843 (2)	0.39313 (11)	0.8259 (4)	0.0228 (7)
H6	0.9313	0.4115	0.8846	0.027*
C7	0.8049 (2)	0.41233 (10)	0.7306 (4)	0.0189 (6)
C8	0.7888 (2)	0.45888 (11)	0.7189 (5)	0.0255 (7)
H8	0.8337	0.4778	0.7801	0.031*
O1	0.5000	0.5000	0.3550 (5)	0.0295 (8)
H1A	0.543 (2)	0.4874 (15)	0.413 (5)	0.045 (14)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02422 (15)	0.01764 (14)	0.02139 (15)	−0.00117 (9)	−0.00086 (12)	−0.00143 (13)
N1	0.0232 (12)	0.0237 (12)	0.0231 (13)	0.0039 (8)	0.0011 (11)	0.0018 (14)
N2	0.0291 (14)	0.0195 (12)	0.0281 (15)	0.0028 (10)	0.0021 (12)	−0.0008 (12)
C1	0.0179 (12)	0.0221 (13)	0.0211 (15)	0.0007 (10)	0.0008 (12)	−0.0016 (16)
C2	0.0202 (14)	0.0169 (13)	0.0157 (14)	0.0005 (11)	0.0021 (11)	−0.0001 (12)
C3	0.0226 (13)	0.0184 (14)	0.0141 (12)	−0.0010 (10)	0.0015 (11)	−0.0028 (11)
C4	0.0273 (14)	0.0201 (14)	0.0185 (15)	0.0043 (12)	0.0017 (12)	0.0000 (12)
C5	0.0232 (15)	0.0290 (16)	0.0214 (17)	0.0063 (13)	0.0003 (11)	0.0005 (12)
C6	0.0212 (14)	0.0255 (14)	0.0215 (18)	−0.0005 (12)	−0.0004 (11)	−0.0018 (12)
C7	0.0193 (13)	0.0220 (14)	0.0154 (13)	0.0011 (11)	0.0036 (10)	−0.0018 (11)
C8	0.0265 (16)	0.0216 (14)	0.0284 (16)	−0.0023 (11)	0.0020 (13)	−0.0067 (13)
O1	0.0263 (18)	0.0323 (18)	0.0298 (18)	0.0044 (14)	0.000	0.000

Geometric parameters (Å, º)

Br1—C3	1.887 (3)	C4—C5	1.406 (5)
N1—C1	1.304 (4)	C4—H4	0.9500
N1—N2	1.367 (4)	C5—C6	1.362 (5)
N2—C8	1.308 (4)	C5—H5	0.9500
C1—C2	1.421 (4)	C6—C7	1.413 (4)
C1—H1	0.9500	C6—H6	0.9500
C2—C7	1.405 (4)	C7—C8	1.414 (4)
C2—C3	1.417 (4)	C8—H8	0.9500
C3—C4	1.363 (4)	O1—H1A	0.82 (2)
C1—N1—N2	120.7 (3)	C5—C4—H4	119.8
C8—N2—N1	118.2 (3)	C6—C5—C4	121.3 (3)
N1—C1—C2	123.9 (3)	C6—C5—H5	119.3
N1—C1—H1	118.1	C4—C5—H5	119.3
C2—C1—H1	118.1	C5—C6—C7	118.9 (3)
C7—C2—C3	118.7 (3)	C5—C6—H6	120.5
C7—C2—C1	115.9 (3)	C7—C6—H6	120.5
C3—C2—C1	125.3 (3)	C2—C7—C6	120.5 (3)

C4—C3—C2	120.2 (3)	C2—C7—C8	116.2 (3)
C4—C3—Br1	119.9 (2)	C6—C7—C8	123.3 (3)
C2—C3—Br1	119.9 (2)	N2—C8—C7	125.1 (3)
C3—C4—C5	120.3 (3)	N2—C8—H8	117.4
C3—C4—H4	119.8	C7—C8—H8	117.4

C1—N1—N2—C8	0.1 (5)	C4—C5—C6—C7	−1.0 (5)
N2—N1—C1—C2	0.0 (6)	C3—C2—C7—C6	1.0 (4)
N1—C1—C2—C7	−0.9 (5)	C1—C2—C7—C6	−179.1 (3)
N1—C1—C2—C3	178.9 (4)	C3—C2—C7—C8	−178.3 (3)
C7—C2—C3—C4	0.1 (4)	C1—C2—C7—C8	1.6 (4)
C1—C2—C3—C4	−179.8 (3)	C5—C6—C7—C2	−0.6 (4)
C7—C2—C3—Br1	179.8 (2)	C5—C6—C7—C8	178.7 (3)
C1—C2—C3—Br1	0.0 (4)	N1—N2—C8—C7	0.7 (5)
C2—C3—C4—C5	−1.6 (5)	C2—C7—C8—N2	−1.6 (5)
Br1—C3—C4—C5	178.7 (2)	C6—C7—C8—N2	179.1 (3)
C3—C4—C5—C6	2.0 (5)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*A*···N1	0.82 (2)	2.07 (3)	2.887 (3)	175 (5)