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(*E*)-2,4-Dibromo-6-(hydrazinylidenemethyl)phenol

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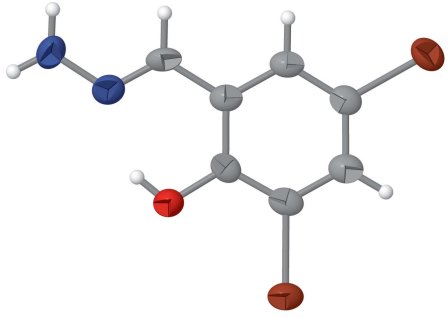
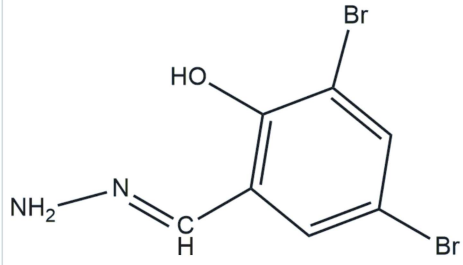
The title compound, $C_7H_6Br_2N_2O$, was obtained from a condensation reaction of 3,5-dibromo-2-hydroxybenzaldehyde and hydrazine hydrate. The molecule is approximately planar, the largest deviation from the mean plane through all of the non-H atoms being 0.053 (1) Å. The molecular conformation is stabilized by an intramolecular O—H···N hydrogen bond, generating an *S*(6) ring motif. In the crystal, intermolecular N—H···Br and N—H···O hydrogen bonds link the molecules, forming chains parallel to the *b* axis. Molecules are further linked by π–π stacking interactions, with centroid–centroid distances of 3.925 (3)–3.926 (3) Å, forming a three-dimensional network.

3D view



Chemical scheme



Structure description

Hydrazine-based Schiff bases are of great interest due to their ability to behave as non-innocent ligands (Arion *et al.*, 1997; Knof *et al.*, 1993; Mukhopadhyay & Pal, 2009). These compounds also play an important role in the development of photomolecular devices, as probes for biological macromolecules and in organic synthesis (Boyer *et al.*, 2010; Samojlowicz *et al.*, 2009; Nagaraju *et al.*, 2012). The crystal structures of related compounds, such as 2-(hydrazonomethyl)phenol (Shang *et al.*, 2009), 2-ethoxy-4-{[(2-nitrophenyl)hydrazono]methyl}phenol (Yin *et al.*, 2009) and 2-ethoxy-4-[2-(3-nitrophenyl)hydrazonomethyl]phenol (Chen *et al.*, 2009), have been reported. As part of our studies of the coordination chemistry of Schiff bases (Gupta *et al.*, 2015), we have synthesized the title compound and determined its crystal structure.

The molecular structure of the title complex is shown in Fig. 1. The whole molecule is almost planar, with the largest deviation from the mean plane through all of the non-H atoms in the molecule being 0.053 (1) Å for atom Br2*A*. The molecular conformation is stabilized by an intramolecular O1*A*—H1*A*···N1*A* hydrogen bond (Table 1), generating

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

D—H···A	D—H	H···A	D···A	D—H···A
O1A—H1A···N1A	0.82	1.85	2.579 (7)	147
N2A—H2AB···Br1A^{i}	0.86	2.94	3.774 (6)	163
N2A—H2AB···O1A^{i}	0.86	2.47	3.088 (8)	129

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

an S(6) ring motif (Bernstein *et al.*, 1995). This also contributes to the planarity of the molecule.

Intermolecular N2A—H2AB···Br1A and N2A—H2AB···O1A hydrogen bonds link the molecules, forming a chain parallel to the b axis (Fig. 2 and Table 1). Molecules in the crystal structure are also linked by intermolecular π–π stacking interactions [$Cg1\cdots Cg1(x, y-1, z) = 3.926$ (3) Å and $Cg1\cdots Cg1(x, y+1, z) = 3.925$ (3) Å; $Cg1$ is the centroid of the C1A–C6A ring] (Fig. 3). These contacts combine with the classical hydrogen bonds to generate a three-dimensional network.

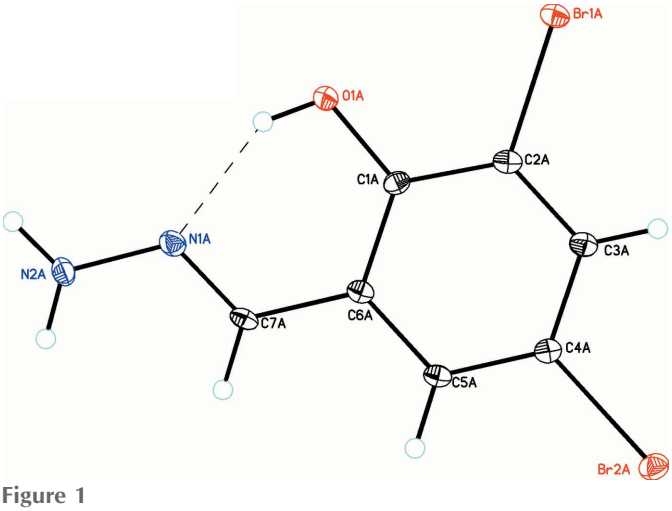


Figure 1
The molecular structure of the title compound, showing 50% probability displacement ellipsoids. The intramolecular O—H···N hydrogen bond forming an S(6) ring motif is shown as a dashed line.

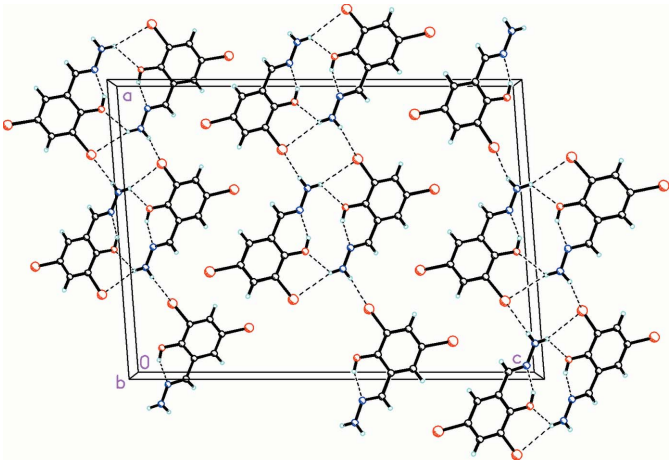


Figure 2
The crystal packing of the title compound, viewed along the b axis. Dashed lines indicate intermolecular N—H···Br and N—H···O hydrogen bonds.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_7H_6Br_2N_2O$
M_r	293.96
Crystal system, space group	Monoclinic, *I*2/*a*
Temperature (K)	295
a, b, c (Å)	18.020 (2), 3.9253 (4), 24.933 (2)
β (°)	94.259 (8)
V (Å^3)	1758.7 (3)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	9.17
Crystal size (mm)	0.5 × 0.2 × 0.1
Data collection	
Diffractometer	Rigaku XtaLAB Mini II CCD
Absorption correction	Multi-scan (*CrysAlis PRO*; Rigaku, 2017)
T_{min}, T_{max}	0.230, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	10326, 1613, 1282
R_{int}	0.070
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.603
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.104, 1.14
No. of reflections	1613
No. of parameters	113
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.56, −0.57

Computer programs: *CrysAlis PRO* (Rigaku, 2017), *SHELXT* (Sheldrick, 2015*a*), *SHELXL2017* (Sheldrick, 2015*b*) and *SHELXTL* (Sheldrick, 2008).

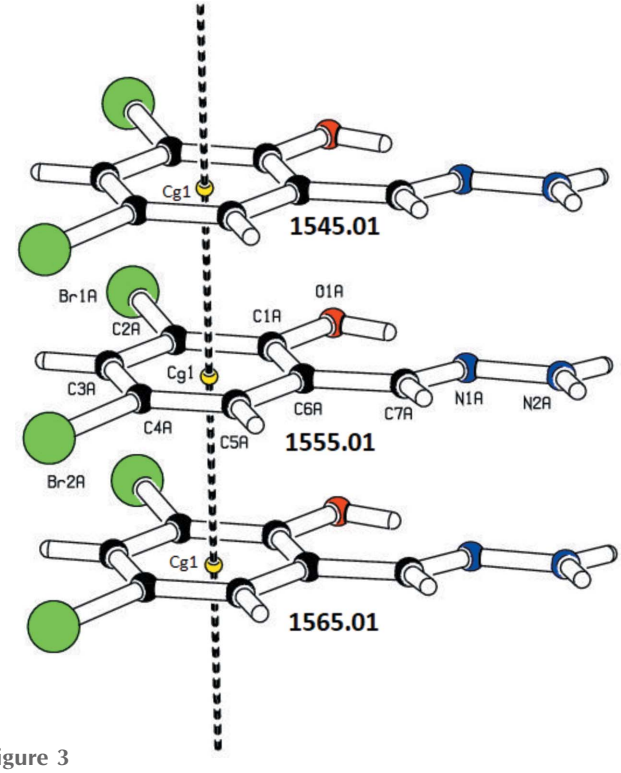


Figure 3
π–π contacts for the title compound (symmetry codes: 1545.01 = $x, y-1, z$; 1565.01 = $x, y+1, z$).

Synthesis and crystallization

A hot ethanolic solution of hydrazine hydrate (0.25 g, 0.005 mol) was added dropwise to a hot stirred solution of 3,5-dibromo-2-hydroxybenzaldehyde (1.22 g, 0.005 mol) in ethanol (Fig. 4). The resulting solution was heated under reflux for 3 h. The solution was allowed to cool to ambient temperature. Slow evaporation of the solvent resulted in yellow plate-like crystals of the title compound suitable for X-ray analysis after 8 d (yield: 1.05 g, 80%; m.p. 436–438 K). Analysis calculated for $C_7H_6Br_2N_2O$: C 28.60, H 2.05, N 9.53%; found: C 28.36, H 2.02, N 9.63%.

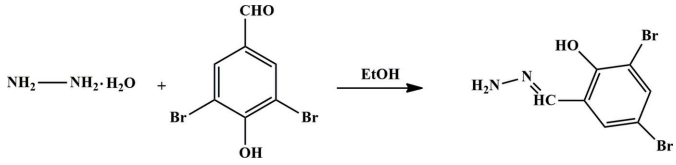


Figure 4
A reaction scheme showing the synthesis of the title compound.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x171386 [https://doi.org/10.1107/S2414314617013864]

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(*E*)-2,4-Dibromo-6-(hydrazinylidenemethyl)phenol

Crystal data

$C_7H_6Br_2N_2O$
M_r = 293.96
Monoclinic, *I*2/*a*
a = 18.020 (2) Å
b = 3.9253 (4) Å
c = 24.933 (2) Å
β = 94.259 (8)°
V = 1758.7 (3) Å^3
Z = 8
F(000) = 1120
D_x = 2.220 Mg m^{-3}
Mo *K*α radiation, λ = 0.71073 Å
Cell parameters from 5125 reflections
θ = 2.2–30.0°
μ = 9.17 mm^{-1}
T = 295 K
Plate, yellow
0.5 × 0.2 × 0.1 mm

Data collection

Rigaku XtaLAB Mini II CCD diffractometer
Radiation source: fine-focus sealed X-ray tube
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Rigaku, 2017)
T_{min} = 0.230, T_{max} = 1.000
10326 measured reflections
1613 independent reflections
1282 reflections with $I > 2\sigma(I)$
R_{int} = 0.070
θ_{max} = 25.4°, θ_{min} = 3.3°
h = −21→21
k = −4→4
l = −30→30

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.104
S = 1.14
1613 reflections
113 parameters
0 restraints
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0459P)^2 + 6.910P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.56 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Br1A	0.23412 (4)	0.47804 (16)	0.09034 (2)	0.0453 (2)
Br2A	0.13772 (4)	−0.13520 (18)	0.27766 (2)	0.0517 (3)
O1A	0.0732 (3)	0.3890 (12)	0.05254 (16)	0.0461 (11)
H1A	0.029080	0.366058	0.042689	0.035 (18)*
N1A	−0.0627 (3)	0.1941 (14)	0.05791 (19)	0.0446 (13)
N2A	−0.1345 (3)	0.1576 (17)	0.0353 (2)	0.0541 (15)
H2AA	−0.166666	0.045254	0.051968	0.19 (6)*
H2AB	−0.147083	0.247164	0.004444	0.08 (3)*
C1A	0.0862 (3)	0.2597 (15)	0.1025 (2)	0.0365 (14)
C2A	0.1570 (4)	0.2827 (15)	0.1280 (2)	0.0385 (15)
C3A	0.1729 (4)	0.1632 (15)	0.1793 (2)	0.0410 (15)
H3AA	0.220759	0.181028	0.195826	0.049*
C4A	0.1169 (4)	0.0170 (14)	0.2059 (2)	0.0383 (14)
C5A	0.0458 (4)	−0.0200 (14)	0.1816 (2)	0.0380 (14)
H5AA	0.009054	−0.125981	0.199841	0.046*
C6A	0.0296 (3)	0.1025 (14)	0.1294 (2)	0.0356 (14)
C7A	−0.0458 (4)	0.0585 (15)	0.1036 (2)	0.0396 (14)
H7AA	−0.080992	−0.067710	0.120485	0.047*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1A	0.0412 (4)	0.0464 (4)	0.0497 (4)	−0.0024 (3)	0.0143 (3)	0.0030 (3)
Br2A	0.0606 (5)	0.0497 (4)	0.0448 (4)	−0.0013 (4)	0.0041 (3)	0.0120 (3)
O1A	0.037 (3)	0.063 (3)	0.039 (2)	−0.006 (2)	0.005 (2)	0.005 (2)
N1A	0.039 (4)	0.056 (3)	0.040 (3)	−0.002 (3)	0.009 (2)	−0.005 (3)
N2A	0.031 (3)	0.087 (4)	0.044 (3)	0.003 (3)	0.001 (3)	0.001 (3)
C1A	0.045 (4)	0.035 (3)	0.030 (3)	0.003 (3)	0.008 (3)	−0.002 (2)
C2A	0.046 (4)	0.030 (3)	0.041 (3)	0.002 (3)	0.015 (3)	−0.002 (3)
C3A	0.045 (4)	0.035 (3)	0.045 (3)	−0.002 (3)	0.011 (3)	−0.003 (3)
C4A	0.045 (4)	0.032 (3)	0.038 (3)	0.002 (3)	0.008 (3)	−0.001 (3)
C5A	0.041 (4)	0.032 (3)	0.043 (3)	−0.003 (3)	0.013 (3)	−0.001 (3)
C6A	0.038 (4)	0.031 (3)	0.039 (3)	−0.002 (3)	0.011 (3)	−0.005 (2)
C7A	0.034 (4)	0.042 (3)	0.045 (3)	−0.005 (3)	0.018 (3)	−0.004 (3)

Geometric parameters (Å, º)

Br1A—C2A	1.896 (6)	C1A—C6A	1.405 (8)
Br2A—C4A	1.897 (6)	C2A—C3A	1.374 (8)
O1A—C1A	1.350 (6)	C3A—C4A	1.373 (8)
O1A—H1A	0.8200	C3A—H3AA	0.9300
N1A—C7A	1.273 (8)	C4A—C5A	1.383 (9)
N1A—N2A	1.380 (7)	C5A—C6A	1.398 (8)
N2A—H2AA	0.8600	C5A—H5AA	0.9300
N2A—H2AB	0.8600	C6A—C7A	1.470 (9)

C1A—C2A	1.384 (8)	C7A—H7AA	0.9300
C1A—O1A—H1A	109.5	C4A—C3A—H3AA	120.6
C7A—N1A—N2A	118.5 (5)	C3A—C4A—C5A	121.5 (6)
N1A—N2A—H2AA	120.0	C3A—C4A—Br2A	119.0 (5)
N1A—N2A—H2AB	120.0	C5A—C4A—Br2A	119.5 (4)
H2AA—N2A—H2AB	120.0	C4A—C5A—C6A	119.7 (5)
O1A—C1A—C2A	119.3 (5)	C4A—C5A—H5AA	120.1
O1A—C1A—C6A	121.5 (5)	C6A—C5A—H5AA	120.1
C2A—C1A—C6A	119.2 (5)	C5A—C6A—C1A	119.0 (6)
C3A—C2A—C1A	121.8 (5)	C5A—C6A—C7A	119.4 (5)
C3A—C2A—Br1A	119.3 (5)	C1A—C6A—C7A	121.6 (5)
C1A—C2A—Br1A	118.9 (4)	N1A—C7A—C6A	119.6 (5)
C2A—C3A—C4A	118.8 (6)	N1A—C7A—H7AA	120.2
C2A—C3A—H3AA	120.6	C6A—C7A—H7AA	120.2
O1A—C1A—C2A—C3A	178.3 (5)	C4A—C5A—C6A—C1A	0.4 (8)
C6A—C1A—C2A—C3A	−1.6 (9)	C4A—C5A—C6A—C7A	179.3 (5)
O1A—C1A—C2A—Br1A	−2.7 (7)	O1A—C1A—C6A—C5A	−178.6 (5)
C6A—C1A—C2A—Br1A	177.4 (4)	C2A—C1A—C6A—C5A	1.3 (8)
C1A—C2A—C3A—C4A	0.1 (9)	O1A—C1A—C6A—C7A	2.6 (9)
Br1A—C2A—C3A—C4A	−178.9 (4)	C2A—C1A—C6A—C7A	−177.5 (5)
C2A—C3A—C4A—C5A	1.7 (9)	N2A—N1A—C7A—C6A	−178.1 (5)
C2A—C3A—C4A—Br2A	−178.0 (4)	C5A—C6A—C7A—N1A	174.2 (6)
C3A—C4A—C5A—C6A	−2.0 (9)	C1A—C6A—C7A—N1A	−7.0 (9)
Br2A—C4A—C5A—C6A	177.8 (4)		

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*A*—H1*A*···N1*A*	0.82	1.85	2.579 (7)	147
N2*A*—H2*AB*···Br1*A*^{i}	0.86	2.94	3.774 (6)	163
N2*A*—H2*AB*···O1*A*^{i}	0.86	2.47	3.088 (8)	129

Symmetry code: (i) −*x*, −*y*+1, −*z*.