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2,4-Dibromo-6-[(4-methylpiperazin-1-yl)iminomethyl]phenol

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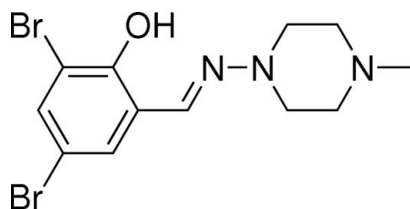
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Key indicators: single-crystal X-ray study; $T = 294$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.045; wR factor = 0.134; data-to-parameter ratio = 15.1.

The title compound, $\text{C}_{12}\text{H}_{15}\text{Br}_2\text{N}_3\text{O}$, is a hydrazone in which 3,5-dibromo-2-hydroxybenzaldehyde has reacted with 1-amino-4-methylpiperazine to form a product containing a $\text{C}=\text{N}$ double bond. The piperazine ring adopts a chair conformation. The dihedral angle between the benzene ring and the $\text{C}=\text{N}-\text{N}$ plane is 6.0 (5)°. Intramolecular $\text{O}-\text{H}\cdots\text{N}$ hydrogen bonding generates an $S(6)$ ring motif, while short intermolecular $\text{Br}\cdots\text{Br}$ and $\text{Br}\cdots\text{N}$ contacts [3.5846 (10) and 3.379 (4) Å, respectively] link the molecules to form a three-dimensional network.

Related literature

For related structures, see: Özek *et al.*, (2007); Guo (2007); Xu & Liu (2006). For normal ranges of molecular bond lengths, see: Allen *et al.* (1987). For related literature, see: Brown (1976).



Experimental

Crystal data

$\text{C}_{12}\text{H}_{15}\text{Br}_2\text{N}_3\text{O}$
 $M_r = 377.09$
 Monoclinic, $P2_1/c$
 $a = 9.5733$ (13) Å
 $b = 9.5493$ (13) Å
 $c = 16.039$ (2) Å
 $\beta = 105.236$ (2)°

$V = 1414.8$ (3) Å³
 $Z = 4$
 Mo $K\alpha$ radiation
 $\mu = 5.72$ mm⁻¹
 $T = 294$ (2) K
 $0.28 \times 0.22 \times 0.10$ mm

Data collection

Bruker SMART CCD area-detector diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{\min} = 0.243$, $T_{\max} = 0.565$

6952 measured reflections
 2493 independent reflections
 1846 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.033$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$
 $wR(F^2) = 0.134$
 $S = 1.04$
 2493 reflections

165 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.93$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.66$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{N1}$	0.82	1.91	2.624 (6)	144

Data collection: *SMART* (Bruker 1997); cell refinement: *SAINTE* (Bruker 1997); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2017).

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supplementary materials

Acta Cryst. (2007). E63, o4641 [doi:10.1107/S1600536807055705]

2,4-Dibromo-6-[(4-methylpiperazin-1-yl)iminomethyl]phenol

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Comment

Salicylaldehyde, piperazine and their derivatives are important in diverse fields of chemistry and biochemistry. Thus, the chemists are prompted to generate the derivatives by introducing different substituents into the existing skeleton of the molecule (Özek *et al.*, 2007; Guo, 2007; Xu & Liu, 2006). Here, we report the structure of the title compound, (I), Fig. 1, a new hydrazone, which was prepared by reaction of 3,5-dibromo-2-hydroxybenzaldehyde with 1-amino-4-methylpiperazine.

In the structure of the title compound, the aromatic substituent and methylpiperazine group lie *trans* to the C=N double bond. The C7=N1 double bond is effectively coplanar with the benzene ring [N1—C7—C6—C1 = 1.5 (7)°]. The piperazine ring has a chair conformation. The bond distances and angles are normal, within experimental error (Allen *et al.*, 1987).

Atom H1 is involved in a strong intramolecular O1—H1···N1 hydrogen bond (Brown, 1976). The molecules are loosely aggregated into a three-dimensional framework *via* some short intermolecular Br1···Br2ⁱ and Br2···N3ⁱⁱ contacts ($d[\text{Br1}\cdots\text{Br2}] = 3.5846(10) \text{ \AA}$, $d[\text{Br2}\cdots\text{N3}] = 3.379(4) \text{ \AA}$; symmetry codes: (i) $1 - x, -1/2 + y, -1/2 - z$; (ii) $-1 + x, 1/2 - y, -1/2 + z$). A packing diagram for (I) is shown in Fig. 2.

Experimental

The title compound, (I), was prepared by reaction of 3,5-dibromo-2-hydroxybenzaldehyde (1.4 g, 5 mmol) with 1-amino-4-methylpiperazine (0.7 g 6 mmol) in 20 ml of 95% ethanol. The mixture was stirred and heated in air at reflux temperature for 30 min, after which 10 ml distilled water was added, the resulting product was separated by filtration (1.6 g, yield 84.2%). The pure product (0.5 g) was heated and dissolved in 20 ml of 95% ethanol. Single crystals were obtained from this solution by slow evaporation over a period of 3 days at room temperature.

Refinement

The OH H-atom was located from a difference Fourier map, however, during refinement the O—H distance was fixed at 0.82 Å and U_{iso} set to $1.5U_{\text{eq}}(\text{O})$. The other H atoms were included in calculated positions and treated as riding atoms, with C—H = 0.93–0.97 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ [$1.5U_{\text{eq}}(\text{C})$ for methyl].

Figures

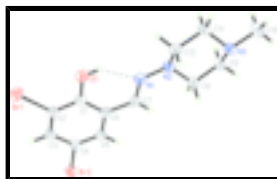


Fig. 1. A view of the molecular structure of (I), showing the atom-numbering scheme and the O1—H1···N1 hydrogen bond (dashed line); displacement ellipsoids are drawn at the 30% probability level.

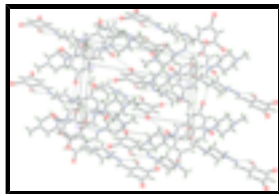


Fig. 2. Crystal packing diagram of (I) viewed down the *a* axis, showing the hydrogen bonds and short intermolecular contacts as dashed lines.

2,4-Dibromo-6-[(4-methylpiperazin-1-yl)iminomethyl]phenol

Crystal data

$C_{12}H_{15}Br_2N_3O$	$F_{000} = 744$
$M_r = 377.09$	$D_x = 1.770 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: -P 2ybc	$\lambda = 0.71073 \text{ \AA}$
$a = 9.5733 (13) \text{ \AA}$	Cell parameters from 2492 reflections
$b = 9.5493 (13) \text{ \AA}$	$\theta = 2.5\text{--}26.0^\circ$
$c = 16.039 (2) \text{ \AA}$	$\mu = 5.72 \text{ mm}^{-1}$
$\beta = 105.236 (2)^\circ$	$T = 294 (2) \text{ K}$
$V = 1414.8 (3) \text{ \AA}^3$	Block, colourless
$Z = 4$	$0.28 \times 0.22 \times 0.10 \text{ mm}$

Data collection

Bruker SMART CCD area-detector diffractometer	2493 independent reflections
Radiation source: fine-focus sealed tube	1846 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.033$
$T = 294(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.2^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 10$
$T_{\text{min}} = 0.243$, $T_{\text{max}} = 0.565$	$k = -11 \rightarrow 11$
6952 measured reflections	$l = -19 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.134$	$w = 1/[\sigma^2(F_o^2) + (0.0698P)^2 + 2.1718P]$
$S = 1.04$	where $P = (F_o^2 + 2F_c^2)/3$
2493 reflections	$(\Delta/\sigma)_{\text{max}} = 0.002$
165 parameters	$\Delta\rho_{\text{max}} = 0.93 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.66 \text{ e \AA}^{-3}$

Primary atom site location: structure-invariant direct methods Extinction correction: none

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 $F^2 > 2\sigma(F^2)$ 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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7537 (4)	0.0040 (4)	-0.0332 (3)	0.0509 (10)
H1	0.7714	-0.0277	0.0159	0.076*
Br1	0.65266 (7)	0.08480 (6)	-0.22008 (4)	0.0576 (2)
Br2	0.27011 (6)	0.42615 (6)	-0.09443 (4)	0.0539 (2)
C1	0.6499 (5)	0.1018 (5)	-0.0435 (4)	0.0402 (13)
C2	0.5886 (5)	0.1544 (5)	-0.1266 (3)	0.0389 (12)
C3	0.4798 (5)	0.2531 (5)	-0.1417 (3)	0.0400 (12)
H3	0.4410	0.2880	-0.1971	0.048*
C4	0.4290 (5)	0.2996 (5)	-0.0733 (3)	0.0395 (12)
C5	0.4873 (5)	0.2501 (5)	0.0091 (3)	0.0398 (12)
H5	0.4524	0.2828	0.0544	0.048*
C6	0.5984 (5)	0.1511 (5)	0.0251 (3)	0.0386 (12)
C7	0.6533 (5)	0.0983 (5)	0.1133 (4)	0.0416 (13)
H7	0.6151	0.1319	0.1571	0.050*
C8	0.7700 (6)	0.0154 (6)	0.2849 (4)	0.0484 (14)
H8A	0.6673	0.0360	0.2723	0.058*
H8B	0.8225	0.1033	0.2961	0.058*
C9	0.8139 (6)	-0.0777 (6)	0.3645 (4)	0.0507 (15)
H9A	0.7987	-0.0280	0.4142	0.061*
H9B	0.7540	-0.1611	0.3557	0.061*
C10	1.0082 (7)	-0.2029 (7)	0.4601 (4)	0.0661 (18)
H10A	1.1110	-0.2176	0.4750	0.099*
H10B	0.9595	-0.2917	0.4502	0.099*
H10C	0.9822	-0.1553	0.5066	0.099*
C11	0.9862 (6)	-0.1933 (6)	0.3076 (4)	0.0512 (14)
H11A	0.9251	-0.2759	0.2978	0.061*
H11B	1.0862	-0.2237	0.3196	0.061*
C12	0.9499 (6)	-0.1026 (6)	0.2270 (4)	0.0471 (14)
H12A	1.0157	-0.0235	0.2347	0.056*
H12B	0.9605	-0.1566	0.1778	0.056*
N1	0.7538 (4)	0.0059 (5)	0.1303 (3)	0.0427 (11)

supplementary materials

N2	0.8007 (4)	-0.0527 (4)	0.2115 (3)	0.0409 (10)
N3	0.9649 (4)	-0.1172 (5)	0.3810 (3)	0.0441 (11)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.046 (2)	0.053 (2)	0.055 (3)	0.0105 (18)	0.014 (2)	-0.0020 (19)
Br1	0.0601 (4)	0.0621 (4)	0.0590 (4)	-0.0025 (3)	0.0307 (3)	-0.0079 (3)
Br2	0.0549 (4)	0.0579 (4)	0.0504 (4)	0.0162 (3)	0.0164 (3)	0.0064 (3)
C1	0.028 (2)	0.035 (3)	0.057 (4)	-0.007 (2)	0.010 (2)	-0.003 (2)
C2	0.038 (3)	0.040 (3)	0.040 (3)	-0.011 (2)	0.014 (2)	-0.008 (2)
C3	0.035 (3)	0.040 (3)	0.044 (3)	-0.004 (2)	0.008 (2)	0.004 (2)
C4	0.035 (3)	0.039 (3)	0.043 (3)	0.000 (2)	0.009 (2)	0.000 (2)
C5	0.036 (3)	0.043 (3)	0.041 (3)	-0.003 (2)	0.010 (2)	-0.005 (2)
C6	0.033 (3)	0.040 (3)	0.040 (3)	-0.009 (2)	0.006 (2)	-0.006 (2)
C7	0.032 (3)	0.048 (3)	0.044 (3)	-0.003 (2)	0.008 (2)	-0.008 (2)
C8	0.035 (3)	0.062 (4)	0.049 (3)	0.015 (2)	0.011 (3)	0.008 (3)
C9	0.035 (3)	0.065 (4)	0.054 (4)	0.007 (3)	0.014 (3)	0.010 (3)
C10	0.054 (4)	0.081 (5)	0.060 (4)	0.013 (3)	0.009 (3)	0.018 (3)
C11	0.043 (3)	0.047 (3)	0.062 (4)	0.010 (2)	0.010 (3)	0.006 (3)
C12	0.037 (3)	0.049 (3)	0.055 (4)	0.012 (2)	0.011 (3)	-0.001 (3)
N1	0.031 (2)	0.045 (3)	0.049 (3)	-0.0034 (19)	0.004 (2)	0.000 (2)
N2	0.031 (2)	0.043 (2)	0.047 (3)	0.0023 (18)	0.006 (2)	0.002 (2)
N3	0.037 (2)	0.044 (2)	0.048 (3)	0.0064 (19)	0.006 (2)	0.006 (2)

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

O1—C1	1.342 (6)	C8—H8A	0.9700
O1—H1	0.8200	C8—H8B	0.9700
Br1—C2	1.884 (5)	C9—N3	1.450 (7)
Br2—C4	1.902 (5)	C9—H9A	0.9700
C1—C6	1.400 (8)	C9—H9B	0.9700
C1—C2	1.401 (7)	C10—N3	1.475 (7)
C2—C3	1.378 (7)	C10—H10A	0.9600
C3—C4	1.384 (7)	C10—H10B	0.9600
C3—H3	0.9300	C10—H10C	0.9600
C4—C5	1.376 (7)	C11—N3	1.443 (7)
C5—C6	1.396 (7)	C11—C12	1.518 (8)
C5—H5	0.9300	C11—H11A	0.9700
C6—C7	1.463 (7)	C11—H11B	0.9700
C7—N1	1.281 (6)	C12—N2	1.464 (6)
C7—H7	0.9300	C12—H12A	0.9700
C8—N2	1.441 (7)	C12—H12B	0.9700
C8—C9	1.522 (8)	N1—N2	1.380 (6)
C1—O1—H1	109.5	C8—C9—H9A	109.6
O1—C1—C6	122.7 (5)	N3—C9—H9B	109.6
O1—C1—C2	118.5 (5)	C8—C9—H9B	109.6
C6—C1—C2	118.8 (5)	H9A—C9—H9B	108.1

C3—C2—C1	121.3 (5)	N3—C10—H10A	109.5
C3—C2—Br1	119.4 (4)	N3—C10—H10B	109.5
C1—C2—Br1	119.2 (4)	H10A—C10—H10B	109.5
C2—C3—C4	119.2 (5)	N3—C10—H10C	109.5
C2—C3—H3	120.4	H10A—C10—H10C	109.5
C4—C3—H3	120.4	H10B—C10—H10C	109.5
C5—C4—C3	120.8 (5)	N3—C11—C12	111.0 (4)
C5—C4—Br2	119.5 (4)	N3—C11—H11A	109.4
C3—C4—Br2	119.6 (4)	C12—C11—H11A	109.4
C4—C5—C6	120.5 (5)	N3—C11—H11B	109.4
C4—C5—H5	119.8	C12—C11—H11B	109.4
C6—C5—H5	119.8	H11A—C11—H11B	108.0
C5—C6—C1	119.4 (5)	N2—C12—C11	108.9 (5)
C5—C6—C7	118.3 (5)	N2—C12—H12A	109.9
C1—C6—C7	122.2 (5)	C11—C12—H12A	109.9
N1—C7—C6	120.2 (5)	N2—C12—H12B	109.9
N1—C7—H7	119.9	C11—C12—H12B	109.9
C6—C7—H7	119.9	H12A—C12—H12B	108.3
N2—C8—C9	110.5 (5)	C7—N1—N2	121.4 (5)
N2—C8—H8A	109.5	N1—N2—C8	120.1 (4)
C9—C8—H8A	109.5	N1—N2—C12	110.7 (4)
N2—C8—H8B	109.5	C8—N2—C12	114.1 (4)
C9—C8—H8B	109.5	C11—N3—C9	109.3 (4)
H8A—C8—H8B	108.1	C11—N3—C10	110.8 (4)
N3—C9—C8	110.3 (5)	C9—N3—C10	110.0 (5)
N3—C9—H9A	109.6		
O1—C1—C2—C3	178.8 (4)	C5—C6—C7—N1	179.0 (5)
C6—C1—C2—C3	0.1 (7)	C1—C6—C7—N1	1.5 (7)
O1—C1—C2—Br1	0.6 (6)	N2—C8—C9—N3	55.4 (6)
C6—C1—C2—Br1	-178.1 (3)	N3—C11—C12—N2	-56.9 (6)
C1—C2—C3—C4	-0.9 (7)	C6—C7—N1—N2	-175.5 (4)
Br1—C2—C3—C4	177.3 (4)	C7—N1—N2—C8	-18.3 (7)
C2—C3—C4—C5	1.0 (7)	C7—N1—N2—C12	-154.6 (5)
C2—C3—C4—Br2	-175.8 (4)	C9—C8—N2—N1	172.3 (4)
C3—C4—C5—C6	-0.4 (7)	C9—C8—N2—C12	-52.8 (6)
Br2—C4—C5—C6	176.4 (4)	C11—C12—N2—N1	-167.9 (4)
C4—C5—C6—C1	-0.4 (7)	C11—C12—N2—C8	53.0 (6)
C4—C5—C6—C7	-177.9 (4)	C12—C11—N3—C9	61.8 (6)
O1—C1—C6—C5	-178.2 (4)	C12—C11—N3—C10	-176.8 (5)
C2—C1—C6—C5	0.5 (7)	C8—C9—N3—C11	-60.3 (6)
O1—C1—C6—C7	-0.7 (7)	C8—C9—N3—C10	177.9 (5)
C2—C1—C6—C7	178.0 (4)		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1—H1 \cdots N1	0.82	1.91	2.624 (6)	144

Fig. 1

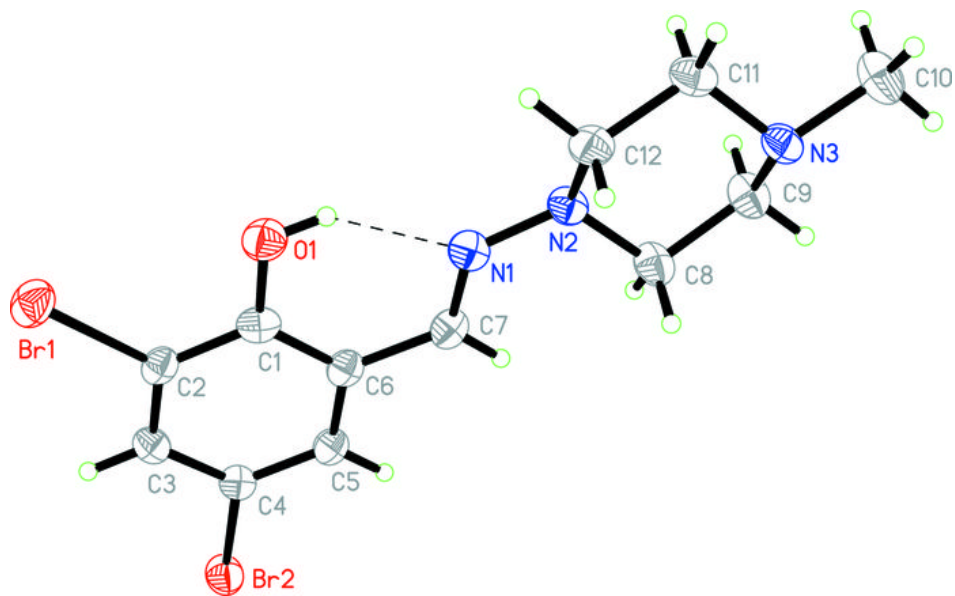


Fig. 2

