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## Redetermination of 1,2-bis(2-bromobenzylidene)hydrazine

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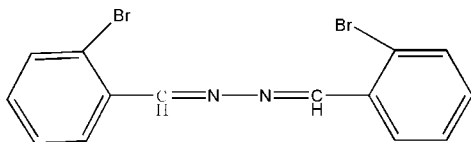
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Key indicators: single-crystal X-ray study;  $T = 298$  K; mean  $\sigma(\text{C}-\text{C}) = 0.007$  Å;  $R$  factor = 0.051;  $wR$  factor = 0.130; data-to-parameter ratio = 13.8.

The title compound, a Schiff base,  $\text{C}_{14}\text{H}_{10}\text{Br}_2\text{N}_2$ , has crystallographically imposed inversion symmetry. The molecule is planar, the largest deviation from the plane being 0.055 (4) Å for the Br atom. Weak intramolecular hydrogen bonding (C—H $\cdots$ Br) stabilizes the planar conformation. The structure has been reported previously [Marignan, Galigné & Falgueirettes (1972). *Acta Cryst. B* **28**, 93–97], but the quality of the refinement has been greatly improved.

### Related literature

The crystal structure of the title compound was previously reported by Marignan *et al.* (1972). For related literature, see: Alemi & Shaabani (2000); Alizadeh *et al.* (1999); Allen (2002); Johnson *et al.* (1996); Kim & Shin (1999); Wang & Zheng (2007).



### Experimental

#### Crystal data

$\text{C}_{14}\text{H}_{10}\text{Br}_2\text{N}_2$

$M_r = 366.06$

Monoclinic,  $P2_1/c$

$a = 6.8715$  (8) Å

$b = 4.0423$  (5) Å

$c = 23.602$  (3) Å

$\beta = 91.058$  (2)°

$V = 655.48$  (14) Å<sup>3</sup>

$Z = 2$

Mo  $K\alpha$  radiation

$\mu = 6.17$  mm<sup>-1</sup>

$T = 298$  (2) K

0.26 × 0.22 × 0.16 mm

#### Data collection

Bruker APEXII area-detector

diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2004)

$T_{\min} = 0.218$ ,  $T_{\max} = 0.377$

3700 measured reflections

1131 independent reflections

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

$R_{\text{int}} = 0.136$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.130$

$S = 1.04$

1131 reflections

82 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 1.33$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.82$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C7-H7\cdots Br1$	0.93	2.79	3.203 (4)	108

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2004); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-III* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2272).

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**supplementary materials**

*Acta Cryst.* (2007). E63, o4732 [ doi:10.1107/S1600536807057911 ]

## Redetermination of 1,2-bis(2-bromobenzylidene)hydrazine

M.-H. Yang and Y.-H. Zheng

### Comment

Schiff base ligands have significant importance in chemistry, especially in the development of Schiff base complexes, (Johnson *et al.*, 1996; Alizadeh *et al.*, 1999; Wang & Zheng, 2007). Schiff bases that have solvent-dependent UV/vis spectra (solvatochromicity) can be suitable NLO (nonlinear optically active) materials (Alemi & Shaabani, 2000). They are also useful in the asymmetric oxidation of methyl phenyl sulfide and give good enantioselectivity (Kim & Shin, 1999). The structure of the title compound (I), has been reported previously (Marignan *et al.*, 1972), but the results of this new study are of higher precision.

The molecular structure of the title compound has crystallographically imposed inversion symmetry located in the middle of the N—N bond (Fig. 1). The molecule is planar with the largest deviation from the mean plane being 0.055 (4) Å at Br1.

There is one intramolecular hydrogen bond (C7—H7···Br1) (Table 1). The C7—N1 are 1.272 (5) Å, indicative of a C=N double bond. The other C—N, C—Br, and C—C distances show no remarkable features (Allen, 2002). It is interesting to note that neighboring molecules are separated by relatively short Br···Br contact with 3.7702 (7) Å. These Br···Br interactions may help to stabilize the packing.

### Experimental

Under nitrogen, a mixture of 2-bromobenzaldehyde (3.7 g, 20 mmol), Na<sub>2</sub>SO<sub>4</sub> (3.0 g) and hydrazine (30% in water, 10 mmol) in absolute ethanol (20 ml) was refluxed for about 12 h to yield a yellow precipitate. The product was collected by vacuum filtration and washed with ethanol. The crude solid was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (100 ml) and washed with water (2\*10 ml) and brine (10 ml). After dried over Na<sub>2</sub>SO<sub>4</sub>, the solvent was removed under vacuum, and yellow solid was isolated in yield 92% (3.1 g). Colourless single crystals of the compound suitable for X-ray analysis were grown from CH<sub>2</sub>Cl<sub>2</sub> and absolute ethanol (4:1) by slow evaporation of the solvent at room temperature over a period of about two weeks.

### Refinement

All H atoms were placed in calculated positions and treated as riding on their parent atoms with C—H = 0.93 Å and  $U_{iso}(H) = 1.2U_{eq}(C)$ .

The maximum residual peak is located on the C1—Br1 bond, 1.04 Å from Br1.

## Figures

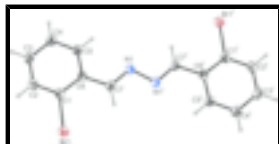


Fig. 1. Molecular view of (I) showing the atom-numbering scheme. Displacement ellipsoids are represented at the 30% probability level. H atoms are shown as small spheres of arbitrary radii. [Symmetry code (i):  $-x + 1, -y + 1, -z + 1$ ]

## 1,2-bis(2-bromobenzylidene)hydrazine

### Crystal data

$C_{14}H_{10}Br_2N_2$

$M_r = 366.06$

Monoclinic,  $P2_1/c$

Hall symbol:  $-P\ 2ybc$

$a = 6.8715$  (8) Å

$b = 4.0423$  (5) Å

$c = 23.602$  (3) Å

$\beta = 91.058$  (2)°

$V = 655.48$  (14) Å<sup>3</sup>

$Z = 2$

$F_{000} = 356$

$D_x = 1.855$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71073$  Å

Cell parameters from 1131 reflections

$\theta = 3.0$ – $25.1$ °

$\mu = 6.17$  mm<sup>-1</sup>

$T = 298$  (2) K

Block, colourless

$0.26 \times 0.22 \times 0.16$  mm

### Data collection

Bruker APEXII area-detector diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 298$ (2) K

$\varphi$  and  $\omega$  scans

Absorption correction: multi-scan (SADABS; Bruker, 2004)

$T_{\min} = 0.218$ ,  $T_{\max} = 0.377$

3700 measured reflections

1131 independent reflections

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

$R_{\text{int}} = 0.136$

$\theta_{\max} = 25.1$ °

$\theta_{\min} = 3.0$ °

$h = -8 \rightarrow 7$

$k = -4 \rightarrow 4$

$l = -28 \rightarrow 28$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.051$

$wR(F^2) = 0.130$

$S = 1.04$

1131 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.33$  e Å<sup>-3</sup>

82 parameters

$$\Delta\rho_{\min} = -0.82 \text{ e } \text{\AA}^{-3}$$

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 ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	0.8273 (7)	0.4656 (10)	0.65065 (17)	0.0358 (9)
C2	0.9996 (8)	0.3733 (11)	0.67720 (19)	0.0428 (11)
H2	1.0185	0.4150	0.7157	0.051*
C3	1.1421 (7)	0.2214 (12)	0.6474 (2)	0.0480 (12)
H3	1.2571	0.1573	0.6657	0.058*
C4	1.1158 (8)	0.1618 (12)	0.5895 (2)	0.0477 (12)
H4	1.2120	0.0562	0.5690	0.057*
C5	0.9434 (7)	0.2629 (13)	0.56299 (19)	0.0410 (10)
H5	0.9275	0.2287	0.5242	0.049*
C6	0.7955 (7)	0.4119 (11)	0.59219 (17)	0.0345 (9)
C7	0.6189 (6)	0.5142 (11)	0.56233 (17)	0.0407 (10)
H7	0.5262	0.6384	0.5811	0.049*
Br1	0.63312 (7)	0.66624 (12)	0.695542 (17)	0.0464 (3)
N1	0.5899 (6)	0.4354 (12)	0.51072 (16)	0.0471 (10)

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
C1	0.041 (2)	0.031 (2)	0.0346 (19)	−0.0041 (19)	−0.0059 (18)	0.0023 (17)
C2	0.046 (3)	0.044 (2)	0.038 (2)	−0.004 (2)	−0.010 (2)	0.0021 (18)
C3	0.036 (3)	0.052 (3)	0.055 (3)	0.005 (2)	−0.013 (2)	0.003 (2)
C4	0.038 (3)	0.054 (3)	0.052 (3)	0.007 (2)	0.002 (2)	0.000 (2)
C5	0.032 (2)	0.052 (2)	0.039 (2)	0.003 (2)	−0.0008 (19)	−0.001 (2)
C6	0.032 (2)	0.037 (2)	0.034 (2)	−0.0035 (18)	−0.0010 (18)	0.0004 (16)
C7	0.032 (2)	0.050 (3)	0.040 (2)	0.009 (2)	−0.0043 (18)	0.000 (2)
Br1	0.0442 (4)	0.0549 (4)	0.0400 (4)	0.00242 (19)	0.0035 (2)	−0.00488 (18)
N1	0.038 (2)	0.067 (2)	0.0362 (19)	0.013 (2)	−0.0067 (16)	−0.0035 (19)

## supplementary materials

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### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

C1—C2	1.381 (7)	C4—H4	0.9300
C1—C6	1.410 (5)	C5—C6	1.378 (7)
C1—Br1	1.901 (5)	C5—H5	0.9300
C2—C3	1.362 (8)	C6—C7	1.452 (6)
C2—H2	0.9300	C7—N1	1.271 (5)
C3—C4	1.396 (7)	C7—H7	0.9300
C3—H3	0.9300	N1—N1 <sup>i</sup>	1.425 (8)
C4—C5	1.391 (7)		
C2—C1—C6	121.3 (4)	C3—C4—H4	120.6
C2—C1—Br1	117.9 (3)	C6—C5—C4	122.3 (4)
C6—C1—Br1	120.9 (3)	C6—C5—H5	118.9
C3—C2—C1	120.4 (4)	C4—C5—H5	118.9
C3—C2—H2	119.8	C5—C6—C1	117.0 (4)
C1—C2—H2	119.8	C5—C6—C7	120.0 (4)
C2—C3—C4	120.1 (5)	C1—C6—C7	123.0 (4)
C2—C3—H3	119.9	N1—C7—C6	120.6 (4)
C4—C3—H3	119.9	N1—C7—H7	119.7
C5—C4—C3	118.9 (5)	C6—C7—H7	119.7
C5—C4—H4	120.6	C7—N1—N1 <sup>i</sup>	111.6 (5)

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

### Hydrogen-bond geometry ( $\text{\AA}$ , $^\circ$ )

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C7—H7 $\cdots$ Br1	0.93	2.79	3.203 (4)	108

Fig. 1

