

FORMATION OF 2D SHEETS THROUGH H...H INTERACTION IN THE CRYSTAL PACKING OF 1,2-BIS(3-BROMOBENZYLIDENE)HYDRAZINE

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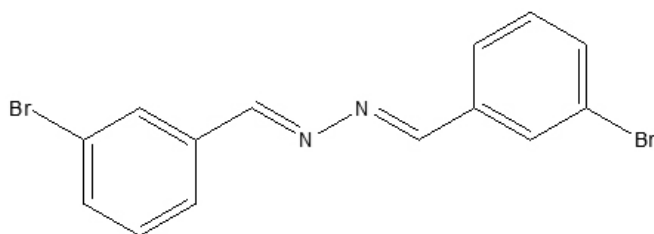
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ABSTRACT

The title compound was prepared by condensation of 3-bromobenzaldehyde and hydrazine hydrate in absolute ethyl alcohol and in the presence of sulfuric acid. The title Schiff base compound, $C_{14}H_{10}Br_2N_2$, crystallizes with one half-molecule in the asymmetric unit in $P2_1/c$ monoclinic space group. The mid-point of the N-N bond (1.412(13) Å) lies on an inversion center. The molecular skeleton is approximately planar. In the crystal packing of this complex, neighboring molecules are linked to each other by H...H intermolecular interactions to form 2D sheets.

INTRODUCTION

Schiff bases have received more attention in recent years due to various promising applications such as antimicrobial,^{1,2} antifungal,³ antitumor reagents.⁴ Moreover, Schiff bases are used as substrates in the preparation of number of industrial and biologically active compounds via ring closure, cycloaddition and replacement reactions. Schiff bases have also been employed as ligands for complexation of metal ions.⁵ Also, a wide numbers of papers have focused on the metal complexes of Schiff bases in the field of coordination, biological and material chemistry.⁶⁻⁸ These compounds also suitable for NLO (nonlinear optically active) materials.⁹ In this regard, crystal structure of eight monohalogenated symmetrical bis(x-halobenzylidene)hydrazine have been reported. In *ortho*-position, chloro,¹⁰ bromo¹¹ and iodo¹² substituents have been studied previously. From *meta*-position derivatives, only iodinated complex has been reported,¹³ while crystal structure of all four *para*-halogenated are determined crystallographically.¹⁴⁻¹⁷ From these series, herein, we report the synthesis and crystal structure of bis(3-bromobenzylidene)hydrazine, **1**, Scheme 1, for the first time.



Scheme 1. Molecular structure of bis(3-bromobenzylidene)hydrazine, **1**.

EXPERIMENTAL

Materials and Physical Methods

3-bromobenzaldehyde, hydrazine hydrate and other materials were purchased from Merck and used as received. Elemental analysis was performed using a Heraeus CHN-O Rapid analyzer. Melting point was obtained by a Kofler Heizbank Rechart type 7841 melting point apparatus.

Synthesis

A mixture of 3-bromobenzaldehyde (7.4 g, 0.04 mol) and hydrazine hydrate (1.0 ml, 0.02 mol) in 25 ml of absolute ethyl alcohol containing 2 drops of 4 M sulfuric acid was refluxed for about 5 h. On cooling, yellow precipitate formed that was filtered off. Suitable crystals for X-ray diffraction measurement were obtained by slow evaporation from ethyl alcohol over one week (yield 065.0%). Analysis for $C_{14}H_{10}F_2N_2$: Found (calculated): C 68.65 (68.85), H 4.18 (4.13), N 11.35% (11.47%).

Crystal structure determination

The X-ray diffraction measurement was made on a Bruker APEX II CCD (Karlsruhe, Germany) area detector diffractometer at 120 K and with Mo-K α radiation, graphite monochromator, $\lambda = 0.71073$ Å. The structure of **1** was solved by SHELX-97 and absorption correction was done using the SADABS programs.¹⁸ Data collection, cell refinement, and data reduction was done by APEX II,¹⁸ SAINT, SHELXTL,¹⁹ PLATON,²⁰ and MERCURY²¹ softwares.

RESULTS AND DISCUSSION

The molecular structure of the compounds **1** was determined by X-ray crystallographic analysis. The crystallographic data and refinement parameters are listed in Table 1. The ORTEP diagram of molecular structure and packing are shown in Figures 1 and 2.

Table 1. Crystallographic and structure refinement data for **1**.

Formula	$C_{14}H_{10}Br_2N_2$
Formula weight	366.04
Temperature /K	120(2)
Wavelength λ /Å	0.71073
Crystal system	Monoclinic
Space Group	$P2_1/c$
a /Å	3.8867(5)
b /Å	14.8312(14)
c /Å	11.2322(15)
α /°	90
β /°	91.716(10)
γ /°	90
Volume/Å ³	647.18(13)
Z	2
Density (calc.) /g cm ⁻³	1.878
θ ranges for data collection	2.75-27.00
$F(000)$	356
Absorption coefficient mm ⁻¹	6.244
Index ranges	$-4 \leq h \leq 4$ $-17 \leq k \leq 18$ $-14 \leq l \leq 14$
Unique data (R_{int})	1395, (0.0912)
Completeness to theta	99.4
Parameters, restraints	82,0
Final R_1 , wR_2 (Obs. data)	0.0423, 0.1011
Final R_1 , wR_2 (All data)	0.0498, 0.1102
Goodness of fit on F^2 (S)	1.061
Largest diff peak and hole/e.Å ⁻³	0.512, -0.500

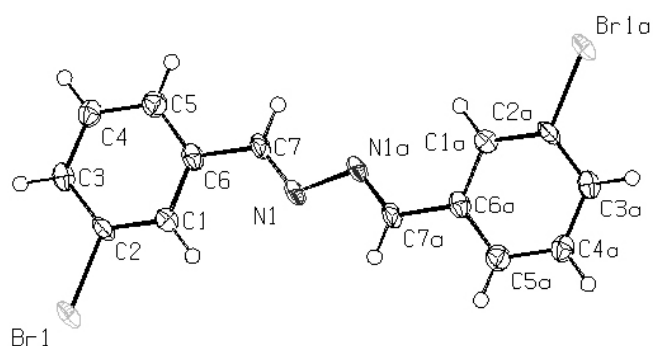


Figure 1. The labeled diagram of **1**. Thermal ellipsoids are at 30% probability level. Symmetry code: (a) $-x+1, -y+1, -z$.

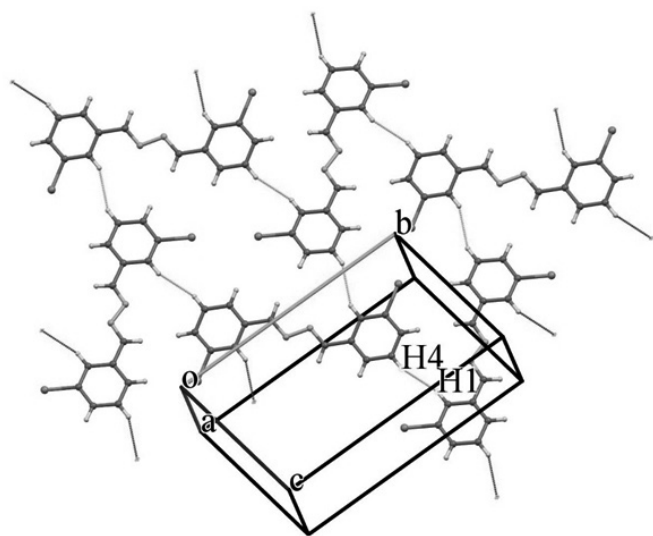


Figure 2. A side view representation of **1**, showing the presence of CH...HC interactions, in generation of 2D sheets.

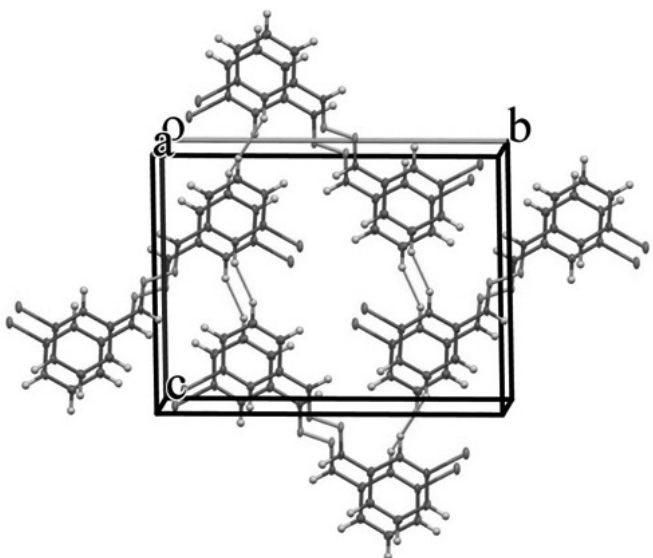


Figure 3. A representation of part of **1**, in *a*-direction, showing the formation of overall supramolecular structure from the linkage of neighbouring molecules, through head-to-tail $\pi \dots \pi$ interactions.

As it is clear from Figure 1, in the solid state, the molecule of **1** possesses a crystallographically imposed center of symmetry at the mid-point of the N—N bond. So, the asymmetric unit of the compound is composed of one half of the molecule. The C=N—N=C linkage is planar. The N—N bond [1.412(13) Å], Table 2, is slightly longer than in related azine compounds.²²⁻²⁴ The C=N—N angle [110.3(8)°], Table 2, is significantly smaller than the ideal sp^2 value of 120°, as a consequence of repulsion between the nitrogen lone pairs and the adjacent C=N bond. The imino group in this compound is nearly coplanar with the two benzene rings (C5—C6—C7—N1: 172.2(9)°, Table 2, with similar torsion angles in comparison with compounds *ortho*-BrC₆H₄(CH=N—N=HC)C₆H₄Br-*ortho*¹¹ and *para*-BrC₆H₄(CH=N—N=HC)C₆H₄Br-*para*.¹⁶ The two benzene rings are also in *trans* configuration with respect to C7—N1 and C7A—N1A bonds relative to N1—N1A. In the crystal packing of this complex, neighboring molecules are linked to each other by H...H intermolecular interactions to form 2D sheets, Figure 2, Table 3. The H...H distance between adjacent molecules is 2.412 Å. In the packing of this complex, the overall supramolecular structure results from the head-to-tail $\pi \dots \pi$ interactions between adjacent phenyl rings from neighbouring 2D sheets with ring centroid-to-centroid distances of 3.887(8) Å, Figure 3.

Table 2. Bond distances (Å) and bond angles (°) for **1**.

C2—Br1	1.897(8)	C6—C7—Br1	122.0(8)
C6—C7	1.480(11)	C7—N1—N1 ⁱ	110.3(8)
C7—N1	1.272(11)	C5—C6—C7—N1	172.2(9)
N1—N1 ⁱ	1.412(13)	C6—C7—N1—N1 ⁱ	-180.0(8)
C1—C2—Br1	119.5(6)	C7—N1—N1 ⁱ —C7 ⁱ	-180.0(8)
C3—C2—Br1	118.5(6)		

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

Table 3. Geometrical parameters of H...H interaction in compound **1**.

D—H... H'—D'	d (D...H)	D (H'— D')	d (H... H')	d (D... D')	<(DH H')	<(DH H')	Symmetry Code
C1— H1... H4—C4	0.93	0.93	2.412	4.10 (1)	147	148	-1+x, 3/2-y, -1/2+z

SUPPORTING INFORMATION

CCDC-1418738 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge at <http://www.ccdc.cam.ac.uk/const/retrieving.html> or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk.

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