

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

***N,N*-Bis(2-bromoethyl)aniline**

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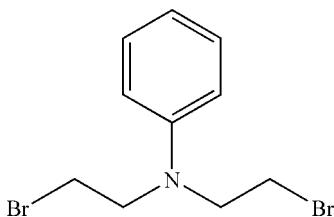
Received 3 November 2007; accepted 6 November 2007

Key indicators: single-crystal X-ray study; $T = 297$ K; mean $\sigma(\text{C}-\text{C}) = 0.007$ Å; R factor = 0.037; wR factor = 0.088; data-to-parameter ratio = 19.5.

The molecule of the title compound, $\text{C}_{10}\text{H}_{13}\text{Br}_2\text{N}$, has a twofold rotation axis along the $\text{N}-\text{C}_{\text{phenyl}}$ bond. The compound shows a slightly distorted trigonal planar geometry around the N atom. The structural study shows the presence of intermolecular $\text{C}-\text{H}\cdots\text{Br}$ interactions, resulting in a three-dimensional supramolecular architecture.

Related literature

For related literature, see: Bricks *et al.* (2005); Chapman & Triggle (1963); Ross (1949); Hartley *et al.* (2000); Palmer *et al.* (1990); Panthananickal *et al.* (1978).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{13}\text{Br}_2\text{N}$
 $M_r = 307.03$
 Orthorhombic, $Fdd2$
 $a = 13.682$ (12) Å
 $b = 13.926$ (12) Å
 $c = 12.215$ (10) Å

$V = 2327$ (3) Å³
 $Z = 8$
 Mo $K\alpha$ radiation
 $\mu = 6.92$ mm⁻¹
 $T = 297$ (2) K
 $0.27 \times 0.23 \times 0.09$ mm

Data collection

Bruker SMART APEX
 diffractometer
 Absorption correction: multi-scan
 (*SADABS*; Bruker, 2000)
 $T_{\min} = 0.155$, $T_{\max} = 0.534$

4145 measured reflections
 1191 independent reflections
 893 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.047$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.088$
 $S = 0.99$
 1191 reflections
 61 parameters
 1 restraint

H-atom parameters constrained
 $\Delta\rho_{\max} = 0.61$ e Å⁻³
 $\Delta\rho_{\min} = -0.41$ e Å⁻³
 Absolute structure: Flack (1983),
 564 Friedel pairs
 Flack parameter: 0.05 (3)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C5}-\text{H5B}\cdots\text{Br1}^i$	0.97	3.05	3.933 (6)	153

Symmetry code: (i) $-x + \frac{3}{4}, y + \frac{1}{4}, z - \frac{1}{4}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 2000); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Bruker, 2001); program(s) used to refine structure: *SHELXTL*; molecular graphics: *DIAMOND* (Brandenburg & Putz, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2007).

Financial support from CNCSIS 2/397/2007 is gratefully acknowledged. The authors also thank the National Center for X-Ray Diffraction, Cluj-Napoca, for help with the structure determination.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CF2168).

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supporting information

Acta Cryst. (2008). E64, o86 [https://doi.org/10.1107/S1600536807056279]

***N,N*-Bis(2-bromoethyl)aniline**

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S1. Comment

N,N-Bis(2-halogenoalkyl)anilines are widely prepared compounds due to their potential pharmacological activity (Ross, 1949; Chapman & Triggle, 1963; Panthananickal *et al.*, 1978; Palmer *et al.*, 1990). The most common preparation method uses the corresponding alcohol, which upon reaction with a halogenating agent gives the desired aniline derivative (Ross, 1949; Chapman & Triggle, 1963). Some derivatives show anti-adrenaline and anti-noradrenalin activities and have also been investigated as anticancer drugs (Palmer *et al.*, 1990). The great variety of obtainable derivatives upon changing the alkyl or the aryl group bonded to the nitrogen atom has made this type of compounds applicable as starting materials in the synthesis of macrocycles (Bricks *et al.*, 2005; Hartley *et al.*, 2000). The title compound was prepared according to a general method described in the literature starting from *N,N*-bis(2-hydroxyethyl)-aniline, which was treated with PBr₃ (Ross, 1949).

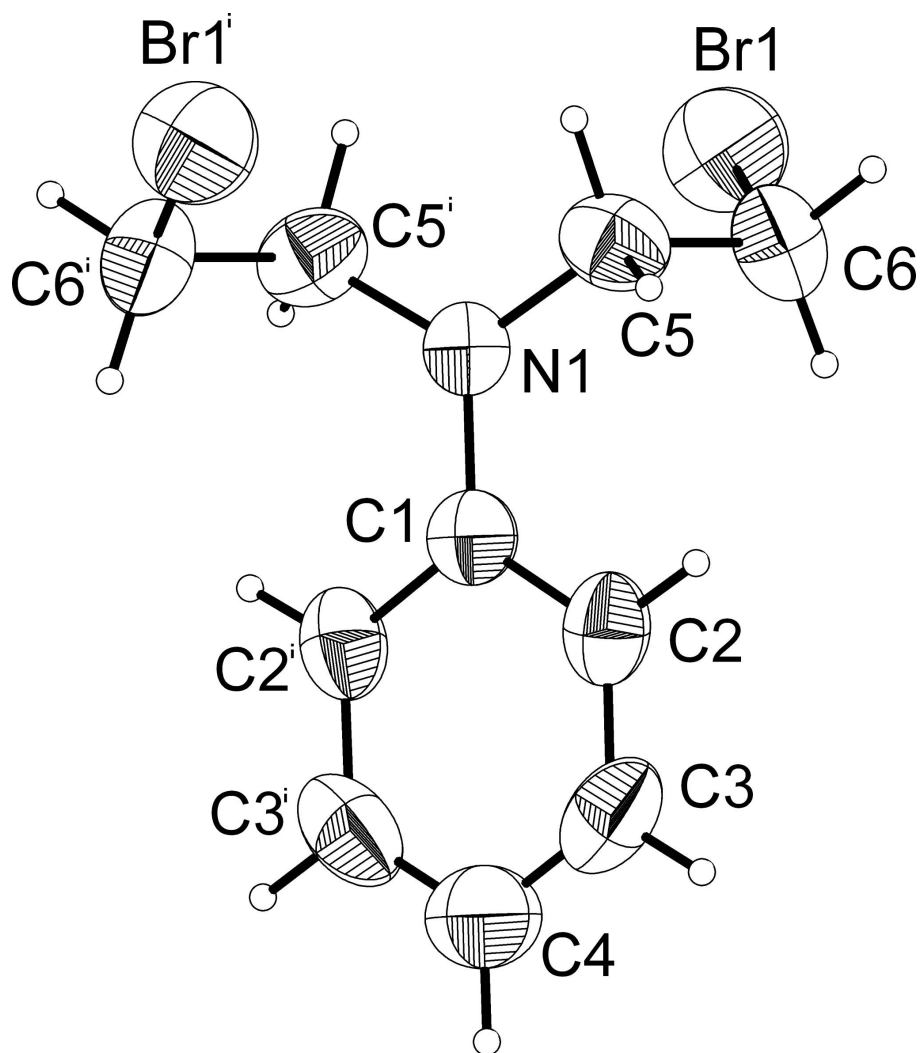
The isolated *N,N*-bis(2-bromoethyl)aniline crystallizes from benzene. The molecule has a twofold rotation axis through the *N*—C_{phenyl} bond (Fig. 1). The bond angles around the N1 atom [C1—N1—C5 = 120.7 (3)° and C5—N1—C5ⁱ 118.6 (6)°; symmetry code: (i) 0.5 - *x*, 0.5 - *y*, *z*] are consistent with a trigonal planar geometry and thus an *sp*² nature can be considered due to conjugation with the phenyl ring. The structural analysis shows the presence of intermolecular C—H⋯Br interactions in the crystal structure. One molecule of *N,N*-bis(2-bromoethyl)aniline forms interactions with four neighboring molecules [H5⋯Br1ⁱⁱ = 3.05 Å; symmetry code: (ii) -*x* + 3/4, *y* + 1/4, *z* - 1/4] (Fig. 2). These interactions result in a three-dimensional supramolecular architecture (Fig. 3).

S2. Experimental

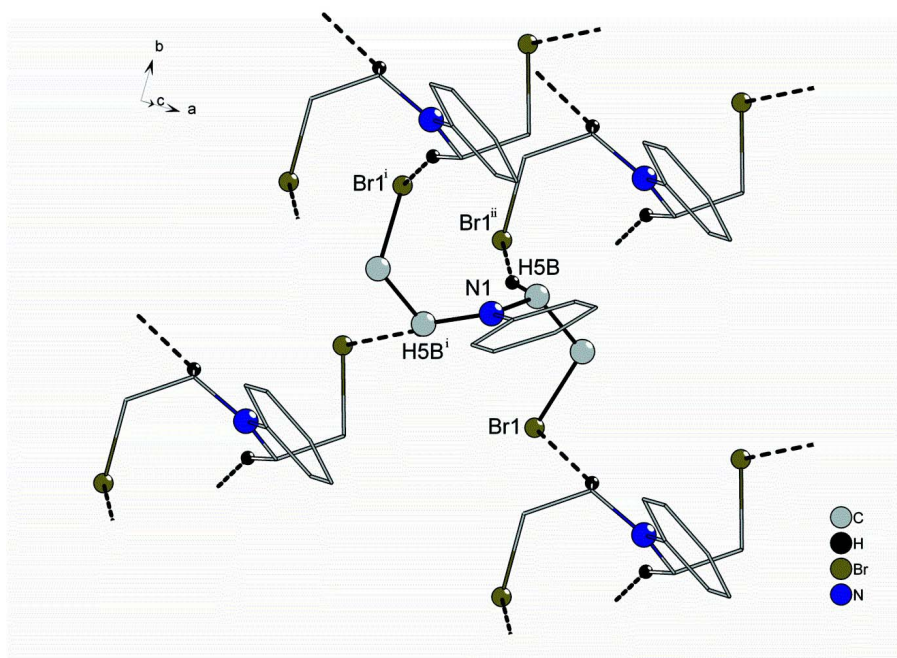
Colourless crystals of *N,N*-bis(2-bromoethyl)aniline, prepared according to the literature (Ross, 1949), were obtained from benzene. The compound was also characterized by ¹H, ¹³C and two-dimensional NMR spectroscopy in CDCl₃ solution. NMR data: ¹H NMR (300 MHz): δ 3.47 (t, 4H, CH₂Br, ³J_{HH} = 7.4 Hz), 3.79 (t, 4H, CH₂N, ³J_{HH} = 7.4 Hz), 6.75 (d, 2H, H_o, ³J_{HH} = 8.3 Hz), 6.84 (t, 1H, H_p, ³J_{HH} = 7.3 Hz), 7.30 (m, 2H, H_m, ³J_{HH} = 7.5 Hz); ¹³C NMR (75.5 MHz): δ 27.95 (s, CH₂Br), 53.47 (s, CH₂N), 112.35 (s, C_o), 118.43 (s, C_p), 129.80 (s, C_m), 145.14 (s, C_i).

S3. Refinement

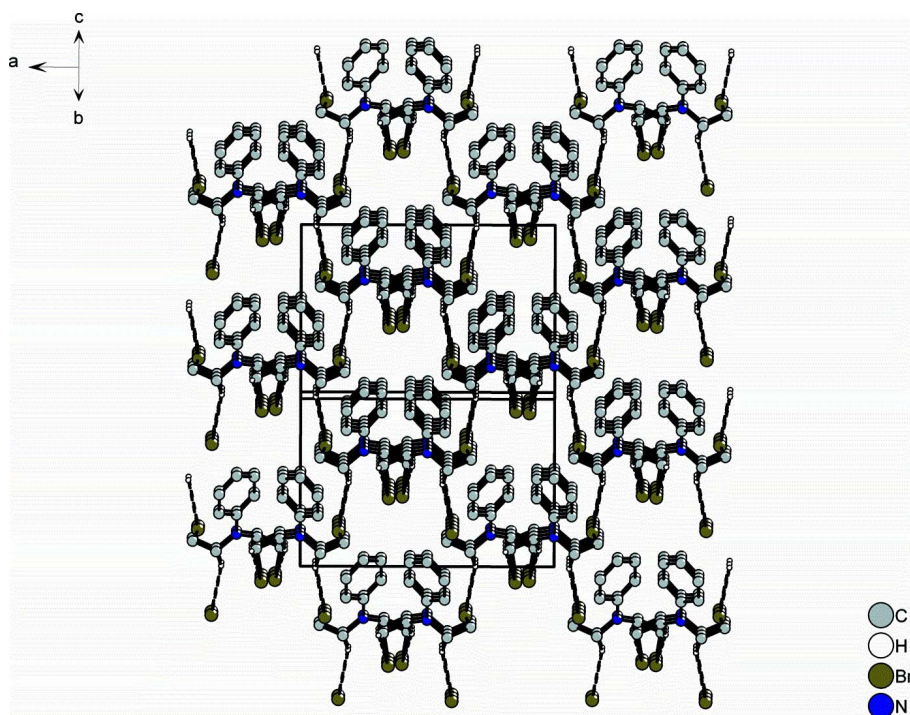
All hydrogen atoms were placed in calculated positions using a riding model, with C—H = 0.93 or 0.97 Å and with *U*_{iso}(H) = 1.2*U*_{eq}(C).

**Figure 1**

The molecular structure, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have arbitrary radii. Symmetry code: (i) 0.5 - x, 0.5 - y, z.

**Figure 2**

Hydrogen-bonded framework (dashed lines) in the title compound. Symmetry codes: (i) $0.5 - x, 0.5 - y, z$; (ii) $-x + 3/4, y + 1/4, z - 1/4$.

**Figure 3**

The crystal packing of the title compound, with hydrogen bonds shown as dashed lines.

N,N-Bis(2-bromoethyl)aniline*Crystal data* $C_{10}H_{13}Br_2N$ $M_r = 307.03$ Orthorhombic, *Fdd2*Hall symbol: *F* 2 -2d $a = 13.682$ (12) Å $b = 13.926$ (12) Å $c = 12.215$ (10) Å $V = 2327$ (3) Å³ $Z = 8$ $F(000) = 1200$ $D_x = 1.752$ Mg m⁻³Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 1908 reflections

 $\theta = 2.7$ – 24.3° $\mu = 6.92$ mm⁻¹ $T = 297$ K

Block, colourless

 $0.27 \times 0.23 \times 0.09$ mm*Data collection*

Bruker SMART APEX

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

 φ and ω scans

Absorption correction: multi-scan

(SADABS; Bruker, 2000)

 $T_{\min} = 0.155$, $T_{\max} = 0.534$

4145 measured reflections

1191 independent reflections

893 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.047$ $\theta_{\max} = 26.4^\circ$, $\theta_{\min} = 2.7^\circ$ $h = -17 \rightarrow 17$ $k = -17 \rightarrow 17$ $l = -15 \rightarrow 15$ *Refinement*Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.037$ $wR(F^2) = 0.088$ $S = 0.99$

1191 reflections

61 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier

map

Hydrogen site location: inferred from

neighbouring sites

H-atom parameters constrained

 $w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.61$ e Å⁻³ $\Delta\rho_{\min} = -0.41$ e Å⁻³

Absolute structure: Flack (1983), 564 Friedel

pairs

Absolute structure parameter: 0.05 (3)

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 (Å²)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C6	0.4227 (4)	0.2321 (4)	0.3885 (5)	0.0665 (14)
H6A	0.4458	0.2250	0.4632	0.080*
H6B	0.4729	0.2653	0.3472	0.080*

C5	0.3302 (4)	0.2919 (4)	0.3884 (4)	0.0595 (14)
H5A	0.3448	0.3544	0.4193	0.071*
H5B	0.3097	0.3016	0.3132	0.071*
Br1	0.40184 (5)	0.10577 (5)	0.32538 (10)	0.0854 (3)
C1	0.2500	0.2500	0.5638 (6)	0.0453 (14)
N1	0.2500	0.2500	0.4487 (4)	0.0521 (13)
C2	0.3190 (3)	0.3010 (4)	0.6240 (4)	0.0569 (13)
H2	0.3669	0.3356	0.5871	0.068*
C3	0.3183 (5)	0.3014 (4)	0.7376 (5)	0.0687 (16)
H3	0.3649	0.3371	0.7753	0.082*
C4	0.2500	0.2500	0.7949 (7)	0.074 (2)
H4	0.2500	0.2500	0.8710	0.089*

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

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C6	0.053 (3)	0.067 (3)	0.079 (4)	−0.001 (2)	0.012 (3)	−0.004 (3)
C5	0.071 (3)	0.052 (3)	0.056 (3)	0.007 (3)	0.008 (3)	0.008 (2)
Br1	0.0888 (4)	0.0783 (4)	0.0891 (4)	0.0256 (3)	0.0001 (4)	−0.0161 (4)
C1	0.047 (3)	0.036 (3)	0.053 (4)	0.012 (3)	0.000	0.000
N1	0.044 (3)	0.062 (3)	0.051 (3)	0.000 (3)	0.000	0.000
C2	0.045 (3)	0.051 (3)	0.075 (3)	−0.004 (2)	−0.004 (2)	−0.007 (3)
C3	0.061 (3)	0.069 (4)	0.076 (4)	0.015 (3)	−0.025 (3)	−0.014 (3)
C4	0.078 (6)	0.083 (6)	0.062 (5)	0.019 (5)	0.000	0.000

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

C6—C5	1.515 (7)	C1—C2	1.391 (6)
C6—Br1	1.942 (6)	C1—N1	1.406 (9)
C6—H6A	0.970	C2—C3	1.388 (8)
C6—H6B	0.970	C2—H2	0.930
C5—N1	1.445 (6)	C3—C4	1.370 (8)
C5—H5A	0.970	C3—H3	0.930
C5—H5B	0.970	C4—H4	0.930
C5—C6—Br1	112.0 (4)	C2—C1—N1	121.9 (3)
C5—C6—H6A	109.2	C1—N1—C5	120.7 (3)
Br1—C6—H6A	109.2	C1—N1—C5 ⁱ	120.7 (3)
C5—C6—H6B	109.2	C5—N1—C5 ⁱ	118.6 (6)
Br1—C6—H6B	109.2	C3—C2—C1	121.7 (5)
H6A—C6—H6B	107.9	C3—C2—H2	119.1
N1—C5—C6	114.3 (4)	C1—C2—H2	119.1
N1—C5—H5A	108.7	C4—C3—C2	120.9 (6)
C6—C5—H5A	108.7	C4—C3—H3	119.6
N1—C5—H5B	108.7	C2—C3—H3	119.6
C6—C5—H5B	108.7	C3—C4—C3 ⁱ	118.6 (8)
H5A—C5—H5B	107.6	C3—C4—H4	120.7
C2 ⁱ —C1—C2	116.2 (7)	C3 ⁱ —C4—H4	120.7

C2 ⁱ —C1—N1	121.9 (3)		
Br1—C6—C5—N1	59.5 (6)	C6—C5—N1—C5 ⁱ	−105.7 (5)
C2 ⁱ —C1—N1—C5	−171.0 (3)	C2 ⁱ —C1—C2—C3	−0.5 (4)
C2—C1—N1—C5	9.0 (3)	N1—C1—C2—C3	179.5 (4)
C2 ⁱ —C1—N1—C5 ⁱ	8.9 (3)	C1—C2—C3—C4	1.1 (7)
C2—C1—N1—C5 ⁱ	−171.1 (3)	C2—C3—C4—C3 ⁱ	−0.5 (4)
C6—C5—N1—C1	74.3 (5)		

Symmetry code: (i) $-x+1/2, -y+1/2, z$.

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>
C5—H5B $\cdots$ Br1 ⁱⁱ	0.97	3.05	3.933 (6)	153

Symmetry code: (ii) $-x+3/4, y+1/4, z-1/4$.