organic compounds

N,N-Bis(2-bromoethyl)aniline

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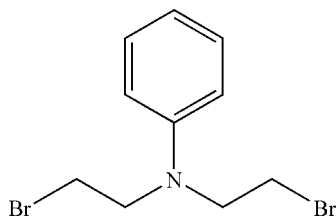
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The molecule of the title compound, $C_{10}H_{13}Br_2N$, has a twofold rotation axis along the $N-C_{phenyl}$ bond. The compound shows a slightly distorted trigonal planar geometry around the N atom. The structural study shows the presence of intermolecular $C-H\cdots Br$ 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

$C_{10}H_{13}Br_2N$
$M_r = 307.03$
Orthorhombic, $Fdd2$
$a = 13.682\ (12)$ Å
$b = 13.926\ (12)$ Å
$c = 12.215\ (10)$ Å

$V = 2327\ (3)$ Å^3
$Z = 8$
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 $I > 2\sigma(I)$
$R_{int} = 0.047$

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, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C5—H5B···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).

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

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supplementary materials

N,N-Bis(2-bromoethyl)aniline

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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 PBr_3 (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—C5[i] 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 sructural 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···Br1[ii] = 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).

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, ^{13}C and two-dimensional NMR spectroscopy in $CDCl_3$ solution. NMR data: ^1H NMR (300 MHz): δ 3.47 (t, 4H, CH_2Br, $^3J_{HH}$ = 7.4 Hz), 3.79 (t, 4H, CH_2N, $^3J_{HH}$ = 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); ^{13}C NMR (75.5 MHz): δ 27.95 (s, CH_2Br), 53.47 (s, CH_2N), 112.35 (s, C_o), 118.43 (s, C_p), 129.80 (s, C_m), 145.14 (s, C_i).

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) = $1.2U_{eq}$(C).
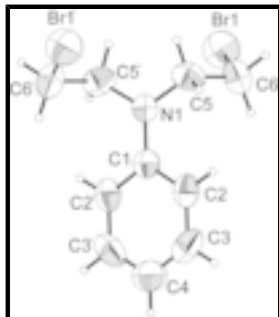
supplementary materials

Figures

Fig. 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) $0.5 - x, 0.5 - y, z$.
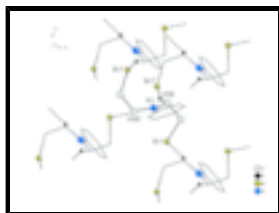

Fig. 2. : Hydrogen-bonded framework (dashed lines) in the title compound. Symmetry codes: (i) $0.5 - x, 0.5 - y, z$; (ii) $-x + 3/4, y + 1/4, z - 1/4$.
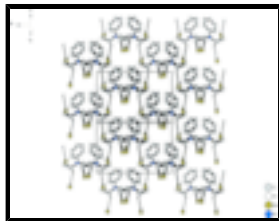

Fig. 3. : The crystal packing of the title compound, with hydrogen bonds shown as dashed lines.

N,N-Bis(2-bromoethyl)aniline

Crystal data

$C_{10}H_{13}Br_2N$	$F_{000} = 1200$
$M_r = 307.03$	$D_x = 1.752$ Mg m^{-3}
Orthorhombic, *Fdd*2	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: F 2 -2d	Cell parameters from 1908 reflections
$a = 13.682$ (12) Å	θ = 2.7–24.3º
$b = 13.926$ (12) Å	μ = 6.92 mm^{-1}
$c = 12.215$ (10) Å	$T = 297$ (2) K
$V = 2327$ (3) Å^3	Block, colourless
$Z = 8$	0.27 × 0.23 × 0.09 mm

Data collection

Bruker SMART APEX diffractometer	1191 independent reflections
Radiation source: fine-focus sealed tube	893 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.047$
$T = 297(2)$ K	$\theta_{max} = 26.4º$

φ and ω scans	$\theta_{min} = 2.7°$
Absorption correction: multi-scan (SADABS; Bruker, 2000)	$h = -17 \rightarrow 17$
$T_{min} = 0.155$, $T_{max} = 0.534$	$k = -17 \rightarrow 17$
4145 measured reflections	$l = -15 \rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.037$	$w = 1/[\sigma^2(F_o^2) + (0.0396P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.088$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.99$	$\Delta\rho_{max} = 0.61$ e Å^{-3}
1191 reflections	$\Delta\rho_{min} = -0.41$ e Å^{-3}
61 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 564 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.05 (3)
Secondary atom site location: difference Fourier map	

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 > 2sigma(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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
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 (Å^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 (Å, °)

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 codes: (i) −x+1/2, −y+1/2, z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
C5—H5B···Br1[ii]	0.97	3.05	3.933 (6)	153

Symmetry codes: (ii) −*x*+3/4, *y*+1/4, *z*−1/4.

Fig. 1

Fig. 2

Fig. 3