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Crystal structure of 4,4′-(ethane-1,2-diyl)bis(2,6-dibromoaniline)

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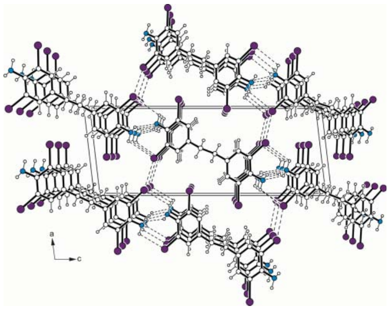
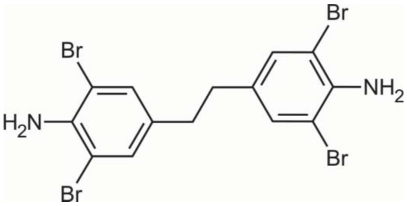


In the title compound, $C_{14}H_{12}Br_4N_2$, the molecule lies across an inversion center and hence the benzene rings are strictly coplanar. In the crystal, molecules are linked by N—H⋯N and weak N—H⋯Br hydrogen bonds, forming a two-dimensional network parallel to (101). In addition, type II Br⋯Br interactions [3.625 (4) Å] complete a three-dimensional supramolecular network.

1. Chemical context

Spacer-type compounds are vital for the generation of a variety of framework structures including metal organic (MOF) (MacGillivray, 2010), hydrogen-bonded (HBN) (Elemans *et al.*, 2009) or covalent organic (COF) (El-Kaden *et al.*, 2007) network species. The title compound is an intermediate substance of a corresponding synthesis of a corresponding spacer molecule. Moreover, tecton-like molecules having terminally attached interacting sites are interesting building blocks in the field of organic crystal engineering (Tiekink *et al.*, 2010), in particular involving potentially competitive groups, in itself forming hydrogen bonds (Braga & Crepioni, 2004) or halogen contacts (Awwadi *et al.*, 2006; Metrangolo & Resnati, 2008) by preference in the crystal state. Such a test case is given with the oligobromoamino-containing title compound.



2. Structural commentary

The title molecule lies across an inversion center and hence the benzene rings are strictly coplanar (Fig. 1). The confor-

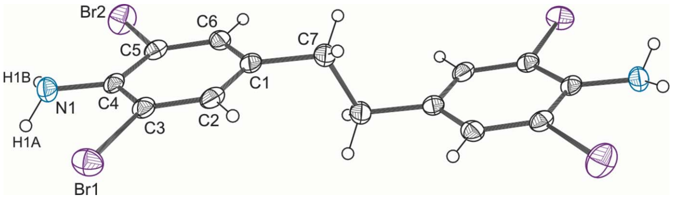


Figure 1
The molecular structure of the title compound with displacement ellipsoids for non-H atoms drawn at the 50% probability level. Unlabeled atoms are related by the symmetry operator $(-x + 1, -y + 2, -z)$.

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N1—H1A⋯N1^{i}	0.88 (2)	2.45 (3)	3.206 (4)	145 (2)
N1—H1B⋯Br1^{i}	0.88 (2)	3.03 (3)	3.521 (4)	117 (2)

Symmetry code: (i) $-x+\frac{1}{2}, y-\frac{1}{2}, -z+\frac{1}{2}$.

mation of the molecular backbone agrees well with those found in the structure of 1,2-biphenylethane (Harada & Ogawa, 2001) and a great number of its ring-substituted derivatives (Kahr *et al.*, 1995; Moorthy *et al.*, 2005). The Csp^3—Csp^3 and Csp^3—Csp^2 bond lengths of 1.535 (6) and 1.514 (4) Å are in the normal range.

3. Supramolecular features

The amino group hydrogen atoms take part in molecular association (Table 1) by forming conventional N—H⋯N hydrogen bonds (Jeffrey, 1997, see Table 1) and weak N—H⋯Br contacts (Desiraju & Steiner, 1999) resulting in the formation of a layer structure parallel to (101) (Fig. 2). Interlayer association is accomplished by type II, Br⋯Br contacts [3.625 (4) Å, θ_1 = 109.7 (2), θ_2 = 150.7 (2)°] (Awwadi *et al.*, 2006; Metrangolo & Resnati, 2008).

4. Synthesis and crystallization

In an imitation of a described procedure (Berger *et al.*, 1998) preparation of the title compound was achieved by a bromination reaction of a solution of 4,4′-diaminobiphenyl (10.0 g, 47.14 mmol) in glacial acetic acid (760 ml) using bromine (30.3 g, 0.19 mol, dissolved in 40 ml glacial acetic acid). After having stirred for 2 h at room temperature, water was added to the mixture. The raw product which precipitated was collected, washed with water and treated with boiling glacial acetic acid to yield 19.6 g (79%) of a greenish powder. Slow crystallization from toluene gave colourless needles of the title compound suitable for X-ray structural analysis. M.p. >593 K. IR (KBr) 3329, 3190, 3033, 2940, 2915, 2851, 1617, 1581, 1542, 1486, 1060, 892, 871. MS (EI) m/z: found – 527.5; calculated for $C_{14}H_{12}N_2Br_4$ – 527.87. Elemental analysis: found – C 31.53, H 2.34, N 5.59; calculated for $C_{14}H_{12}N_2Br_4$ – C 31.85, H 2.29, N 5.31. 4,4′-Diaminobibenzyl was purchased (Sigma–Aldrich). The melting point was measured on a hot-stage microscope (Rapido Dresden). IR and mass (EI–MS) spectra were performed using Nicolet 510 FTIR and Finnigan Mat 8200 instruments, respectively.

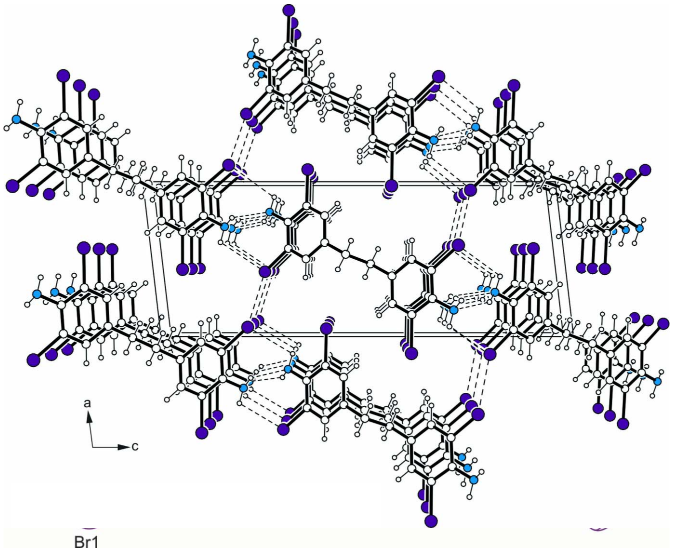


Figure 2
Part of the crystal structure viewed along the b axis. N atoms are displayed as blue and Br atoms as violet circles. Hydrogen bonds and Br⋯Br contacts are shown as dashed lines.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{12}Br_4N_2$
M_r	527.86
Crystal system, space group	Monoclinic, $P2_1/n$
Temperature (K)	153
a, b, c (Å)	8.1219 (4), 4.4962 (2), 21.5327 (9)
β (°)	96.706 (3)
V (Å^3)	780.95 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	10.30
Crystal size (mm)	0.30 × 0.20 × 0.08
Data collection	
Diffractometer	Bruker APEXII CCD area detector
Absorption correction	Multi-scan (*SADABS*; Bruker, 2007)
$T_{\min}$, $T_{\max}$	0.148, 0.493
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	6211, 1356, 1213
$R_{\rm int}$	0.034
(sin $\theta/\lambda)_{\max}$ (Å^{-1})	0.597
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.023, 0.057, 1.05
No. of reflections	1356
No. of parameters	99
No. of restraints	2
H-atom treatment	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å^{-3})	0.52, −0.29

Computer programs: *APEX2* and *SAINT* (Bruker, 2007), *SHELXS97*, *SHELXL97* and *SHELXTL* (Sheldrick, 2008), *ORTEP-3 for Windows* (Farrugia, 2012).

5. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. C-bound H atoms were positioned geometrically (C—H = 0.93 Å for aromatic and C—H 0.97 Å for methylene H) and refined using a riding model with $U_{\rm iso}$(H) = 1.2 $U_{\rm eq}$(C). The amino H atoms were located in a Fourier map and the N—H distances restrained to 0.89 (1) Å.

Acknowledgements

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supporting information

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Crystal structure of 4,4′-(ethane-1,2-diyl)bis(2,6-dibromoaniline)

Ines Hauptvogel, Wilhelm Seichter and Edwin Weber

Computing details

Data collection: *APEX2* (Bruker, 2007); cell refinement: *SAINT* (Bruker, 2007); data reduction: *SAINT* (Bruker, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

4,4′-(Ethane-1,2-diyl)bis(2,6-dibromoaniline)

Crystal data

$C_{14}H_{12}Br_4N_2$
$M_r = 527.86$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 8.1219$ (4) Å
$b = 4.4962$ (2) Å
$c = 21.5327$ (9) Å
$\beta = 96.706$ (3)°
$V = 780.95$ (6) Å^3
$Z = 2$
$F(000) = 500$
$D_x = 2.245$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3117 reflections
$\theta = 2.6$–$26.4°$
$\mu = 10.30$ mm^{-1}
$T = 153$ K
Needle, colourless
0.30 × 0.20 × 0.08 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (SADABS; Bruker, 2007)
$T_{min} = 0.148$, $T_{max} = 0.493$
6211 measured reflections
1356 independent reflections
1213 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 25.1°$, $\theta_{min} = 2.6°$
$h = -9 \rightarrow 9$
$k = -5 \rightarrow 4$
$l = -25 \rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.023$
$wR(F^2) = 0.057$
$S = 1.05$
1356 reflections
99 parameters
2 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0287P)^2 + 0.4643P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.52$ e Å^{-3}
$\Delta\rho_{min} = -0.29$ e Å^{-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. The distances of N—H bonds were restrained to a target value of 0.89(0.01) Å.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	$U_{\rm iso}$*/$U_{\rm eq}$
Br1	0.57978 (4)	0.36821 (8)	0.225361 (14)	0.03020 (13)
Br2	−0.06304 (4)	0.52607 (9)	0.094219 (15)	0.03690 (14)
N1	0.2009 (3)	0.2907 (7)	0.19806 (11)	0.0243 (6)
H1A	0.260 (3)	0.140 (5)	0.2143 (13)	0.020 (9)*
H1B	0.102 (2)	0.223 (8)	0.1841 (14)	0.033 (9)*
C1	0.3975 (4)	0.8813 (7)	0.07282 (13)	0.0216 (7)
C2	0.4981 (3)	0.7477 (7)	0.12150 (13)	0.0221 (7)
H2	0.6107	0.7920	0.1274	0.026*
C3	0.4334 (3)	0.5501 (7)	0.16131 (13)	0.0203 (7)
C4	0.2654 (3)	0.4736 (7)	0.15549 (12)	0.0190 (7)
C5	0.1679 (3)	0.6141 (7)	0.10623 (13)	0.0210 (7)
C6	0.2309 (4)	0.8108 (7)	0.06593 (13)	0.0222 (7)
H6	0.1604	0.8969	0.0338	0.027*
C7	0.4705 (4)	1.0862 (8)	0.02740 (14)	0.0279 (7)
H7A	0.5633	1.1936	0.0493	0.034*
H7B	0.3875	1.2306	0.0113	0.034*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.02849 (19)	0.0311 (3)	0.02914 (19)	0.00445 (14)	−0.00444 (13)	−0.00097 (14)
Br2	0.02079 (19)	0.0507 (3)	0.0385 (2)	−0.00335 (15)	0.00032 (14)	0.00005 (17)
N1	0.0284 (14)	0.0220 (17)	0.0237 (13)	−0.0027 (12)	0.0073 (11)	0.0028 (13)
C1	0.0308 (16)	0.0158 (18)	0.0196 (14)	0.0001 (13)	0.0095 (12)	−0.0052 (13)
C2	0.0205 (14)	0.0208 (18)	0.0264 (15)	−0.0016 (13)	0.0089 (12)	−0.0068 (15)
C3	0.0232 (15)	0.0212 (19)	0.0171 (13)	0.0019 (13)	0.0044 (12)	−0.0044 (13)
C4	0.0234 (15)	0.0183 (18)	0.0165 (13)	−0.0006 (13)	0.0070 (12)	−0.0056 (13)
C5	0.0198 (14)	0.0220 (19)	0.0218 (14)	0.0003 (12)	0.0051 (11)	−0.0061 (14)
C6	0.0311 (16)	0.0189 (19)	0.0172 (13)	0.0041 (13)	0.0050 (12)	−0.0015 (13)
C7	0.0422 (19)	0.0171 (19)	0.0273 (16)	−0.0008 (15)	0.0159 (14)	−0.0017 (14)

Geometric parameters (Å, º)

Br1—C3	1.898 (3)	C2—H2	0.9300
Br2—C5	1.905 (3)	C3—C4	1.398 (4)

N1—C4	1.380 (4)	C4—C5	1.398 (4)
N1—H1A	0.877 (10)	C5—C6	1.378 (4)
N1—H1B	0.879 (10)	C6—H6	0.9300
C1—C6	1.381 (4)	C7—C7^{i}	1.535 (6)
C1—C2	1.388 (4)	C7—H7A	0.9700
C1—C7	1.514 (4)	C7—H7B	0.9700
C2—C3	1.381 (4)		

C4—N1—H1A	119.6 (19)	C3—C4—C5	114.7 (3)
C4—N1—H1B	113 (2)	C6—C5—C4	123.3 (3)
H1A—N1—H1B	108 (3)	C6—C5—Br2	118.6 (2)
C6—C1—C2	117.7 (3)	C4—C5—Br2	118.1 (2)
C6—C1—C7	121.5 (3)	C5—C6—C1	120.7 (3)
C2—C1—C7	120.7 (3)	C5—C6—H6	119.7
C3—C2—C1	120.9 (3)	C1—C6—H6	119.7
C3—C2—H2	119.5	C1—C7—C7^{i}	111.7 (4)
C1—C2—H2	119.5	C1—C7—H7A	109.3
C2—C3—C4	122.8 (3)	C7^{i}—C7—H7A	109.3
C2—C3—Br1	118.5 (2)	C1—C7—H7B	109.3
C4—C3—Br1	118.8 (2)	C7^{i}—C7—H7B	109.3
N1—C4—C3	122.0 (3)	H7A—C7—H7B	107.9
N1—C4—C5	123.2 (3)		

C6—C1—C2—C3	0.4 (4)	C3—C4—C5—C6	0.5 (4)
C7—C1—C2—C3	−177.0 (3)	N1—C4—C5—Br2	−4.4 (4)
C1—C2—C3—C4	−0.2 (5)	C3—C4—C5—Br2	−179.9 (2)
C1—C2—C3—Br1	178.3 (2)	C4—C5—C6—C1	−0.4 (5)
C2—C3—C4—N1	−175.7 (3)	Br2—C5—C6—C1	180.0 (2)
Br1—C3—C4—N1	5.8 (4)	C2—C1—C6—C5	−0.1 (4)
C2—C3—C4—C5	−0.2 (4)	C7—C1—C6—C5	177.3 (3)
Br1—C3—C4—C5	−178.7 (2)	C6—C1—C7—C7^{i}	−89.9 (4)
N1—C4—C5—C6	176.0 (3)	C2—C1—C7—C7^{i}	87.4 (4)

Symmetry code: (i) −*x*+1, −*y*+2, −*z*.

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*A*···N1^{ii}	0.88 (2)	2.45 (3)	3.206 (4)	145 (2)
N1—H1*B*···Br1^{ii}	0.88 (2)	3.03 (3)	3.521 (4)	117 (2)

Symmetry code: (ii) −*x*+1/2, *y*−1/2, −*z*+1/2.