

Keywords: crystal structure; 4,4'-(ethane-1,2-diyl)bis(2,6-dibromoaniline); framework structures

CCDC reference: 1038844

Supporting information: this article has supporting information at journals.iucr.org/e

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

Ines Hauptvogel, Wilhelm Seichter and Edwin Weber*

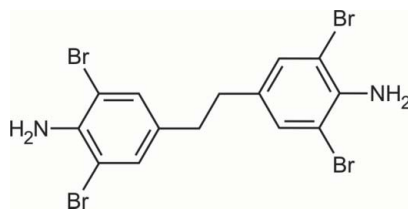
Institut für Organische Chemie, TU Bergakademie Freiberg, Leipziger Strasse 29, D-09596 Freiberg/Sachsen, Germany.

*Correspondence e-mail: Edwin.Weber@chemie.tu-freiberg.de

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 $N-H\cdots N$ and weak $N-H\cdots Br$ hydrogen bonds, forming a two-dimensional network parallel to (101). In addition, type II $Br\cdots Br$ 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-

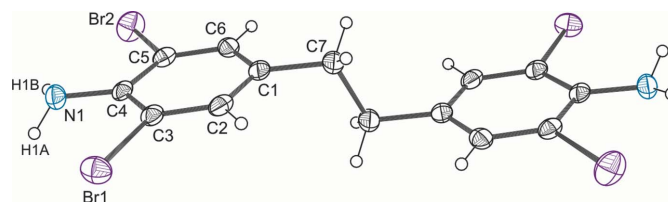


Figure 1

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 $(-x + 1, -y + 2, -z)$.

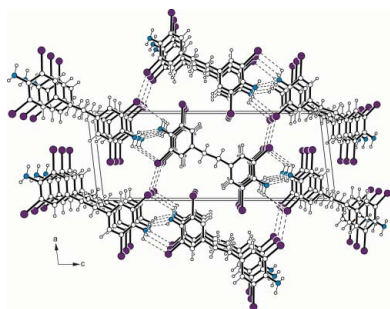


Table 1
Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$N1-H1A\cdots N1^i$	0.88 (2)	2.45 (3)	3.206 (4)	145 (2)
$N1-H1B\cdots Br1^i$	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 $N-H\cdots N$ hydrogen bonds (Jeffrey, 1997, see Table 1) and weak $N-H\cdots Br$ contacts (Desiraju & Steiner, 1999) resulting in the formation of a layer structure parallel to (101) (Fig. 2). Interlayer association is accomplished by type II, $Br\cdots Br$ contacts [3.625 (4) Å, $\theta_1 = 109.7$ (2), $\theta_2 = 150.7$ (2)^o] (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

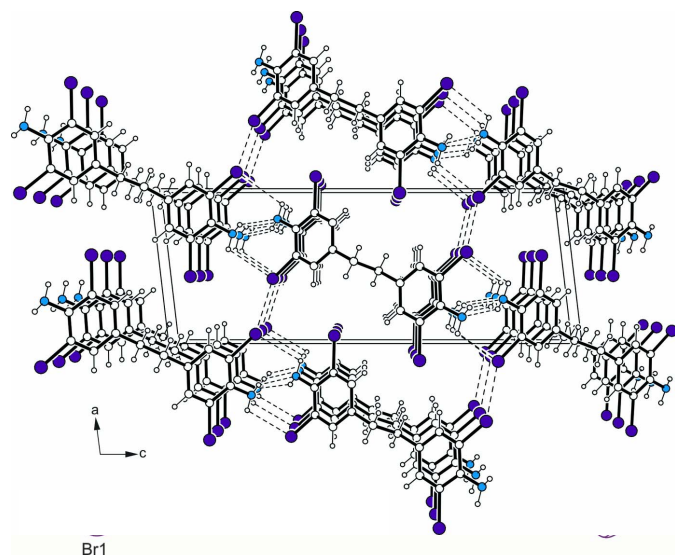


Figure 2
Part of the crystal structure viewed along the b axis. N atoms are displayed as blue and Br atoms as violet circles. Hydrogen bonds and $Br\cdots Br$ contacts are shown as dashed lines.

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_{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).

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'-Diaminobiphenyl 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.

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 $U_{iso}(H) = 1.2 U_{eq}(C)$. The amino H atoms were located in a Fourier map and the $N-H$ distances restrained to 0.89 (1) Å.

Acknowledgements

We gratefully acknowledge financial support by the Deutsche Forschungsgemeinschaft within the priority program 'Porous Metal-Organic Frameworks' (DFG-Project SPP 1362).

References

- Awwadi, F. F., Willett, R. D., Peterson, K. A. & Twamley, B. (2006). *Chem. Eur. J.* **12**, 8952–8960.
- Berger, R., Beckmann, R. & Reichelt, H. (1998). Ger. Offen. DE 19643769 A1 19980430.
- Braga, D. & Crepioni, F. (2004). In *Encyclopedia of Supramolecular Chemistry*, pp. 357–363. Boca Raton: CRC Press.
- Bruker (2007). APEX 2, SAINT and SADABS. Bruker AXS Inc., Madison, Wisconsin, USA.
- Desiraju, G. R. & Steiner, T. (1999). *The Weak Hydrogen Bond in Structural Chemistry and Biology*, ch. 2. Oxford University Press.
- Elemans, J. A. A. W., Lei, S. & De Feyter, S. (2009). *Angew. Chem. Int. Ed.* **48**, 7298–7332.
- El-Kaderi, H. M., Hunt, J. R., Mendoza-Cortés, J. L., Côté, A. P., Taylor, R. E., O'Keefe, M. & Yaghi, O. M. (2007). *Science*, **316**, 268–272.
- Farrugia, L. J. (2012). *J. Appl. Cryst.* **45**, 849–854.
- Harada, J. & Ogawa, K. (2001). *Struct. Chem.* **12**, 243–250.
- Jeffrey, G. A. (1997). In *An Introduction to Hydrogen Bonding*. Oxford University Press.
- Kahr, B., Mitchell, C. A., Chance, J. M., Clark, R. V., Gantzel, P., Baldrige, K. K. & Siegel, J. S. (1995). *J. Am. Chem. Soc.* **117**, 4479–4482.
- MacGillivray, L. R. (2010). Editor. *Metal–Organic Frameworks*. Hoboken: Wiley.
- Metrangolo, P. & Resnati, G. (2008). In *Halogen Bonding – Structure and Bonding*, Vol. 126. Berlin-Heidelberg: Springer.
- Moorthy, J. N., Natarajan, R. & Venugopalan, R. (2005). *J. Mol. Struct.* **741**, 107–114.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tiekink, E. R. T., Vittal, J. J. & Zaworotko, M. J. (2010). Editors. *Organic Crystal Engineering*. Chichester: Wiley.

supporting information

Acta Cryst. (2015). E71, 97-99 [doi:10.1107/S2056989014027182]

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) Å³

$Z = 2$

$F(000) = 500$

$D_x = 2.245$ 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

$0.30 \times 0.20 \times 0.08$ 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 $I > 2\sigma(I)$

$R_{\text{int}} = 0.034$

$\theta_{\max} = 25.1$ °, $\theta_{\min} = 2.6$ °

$h = -9 \rightarrow 9$

$k = -5 \rightarrow 4$

$l = -25 \rightarrow 25$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
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 (\AA^2)

	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 (\AA , °)

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 (\AA , $^\circ$)

<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>
N1—H1A \cdots N1 ⁱⁱ	0.88 (2)	2.45 (3)	3.206 (4)	145 (2)
N1—H1B \cdots Br1 ⁱⁱ	0.88 (2)	3.03 (3)	3.521 (4)	117 (2)

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