

## 1,3-Bis(bromomethyl)-2-nitrobenzene

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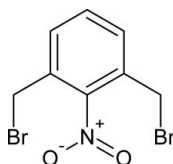
Received 4 February 2010; accepted 24 February 2010

Key indicators: single-crystal X-ray study;  $T = 185$  K; mean  $\sigma(\text{C}-\text{C}) = 0.005$  Å;  $R$  factor = 0.037;  $wR$  factor = 0.083; data-to-parameter ratio = 19.1.

In the title compound,  $\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2$ , an intermediate for the synthesis of macrocycles, the  $\text{NO}_2$  group makes a dihedral angle of  $65.07$  ( $19^\circ$ ) with the arene ring, and the bromomethyl substituents adopt a *trans* conformation about the ring such that the molecule closely approximates  $C_2$  symmetry.

### Related literature

For related structures, see: Li *et al.* (2006); Qin *et al.* (2005). For related compounds, see: Raatikainen *et al.* (2008); Mough *et al.* (2004). For the synthesis, see: Boeckmann & Vögtle (1981).



### Experimental

#### Crystal data

$\text{C}_8\text{H}_7\text{Br}_2\text{NO}_2$   
 $M_r = 308.97$   
 Monoclinic,  $P2_1/n$

$a = 7.7837$  (13) Å  
 $b = 7.7573$  (13) Å  
 $c = 15.938$  (3) Å

$\beta = 90.933$  (3) $^\circ$   
 $V = 962.2$  (3) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation

$\mu = 8.39$  mm<sup>-1</sup>  
 $T = 185$  K  
 $0.20 \times 0.20 \times 0.08$  mm

#### Data collection

Bruker SMART 1K diffractometer  
 Absorption correction: multi-scan  
 (*SADABS*; Bruker, 2001)  
 $T_{\min} = 0.285$ ,  $T_{\max} = 0.553$

8228 measured reflections  
 2259 independent reflections  
 1812 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.041$

#### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.037$   
 $wR(F^2) = 0.083$   
 $S = 1.06$   
 2259 reflections

118 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 1.35$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -1.31$  e Å<sup>-3</sup>

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997), *PLATON* (Spek, 2009) and *X-SEED* (Barbour, 2001); software used to prepare material for publication: *WinGX* (Farrugia, 1999) and *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2729).

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**supplementary materials**

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## 1,3-Bis(bromomethyl)-2-nitrobenzene

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### Comment

Derivatives of 1,3-bis(bromomethyl)benzene have been widely used to synthesize macrocycles via  $S_N2$  reactions. For recent examples, see Raatikainen *et al.*, 2008 and Mough *et al.*, 2004.

The crystal structure of the title compound is in comparison with the already reported 1,3-bis(bromomethyl)benzene (II) (Li *et al.*, 2006) and 2,3-bis(bromomethyl)-1-methoxy-4-nitrobenzene (III) (Qin *et al.*, 2005). The nitro group of I is oriented at a dihedral angle of  $65.07(0.19)^\circ$  to the arene ring. The bromomethyl groups (C7/Br1 and C8/Br2) are oriented anti to each other and exhibit almost identical dihedral angles with respect to arene ring carbons atoms ( $80.34(0.27)^\circ$  and  $80.99(0.28)^\circ$ , respectively). The molecules therefore closely approximate  $C_2$  point group symmetry in the crystal.

### Experimental

The title compound was prepared following the method reported by Boeckmann and Vögtle *et al.*, 1981.

### Refinement

The aromatic and methylene H-atoms were positioned geometrically and refined using a riding model with  $d(C-H) = 0.95$  Å,  $U_{iso} = 1.2U_{eq}$  (C) for aromatic  $0.99$  Å,  $U_{iso} = 1.2U_{eq}$  (C) for methylene

Electron density synthesis with coefficients  $F_o - F_c$ : Highest peak 1.35 at 0.7472 0.2174 0.6981 [ 0.78 Å from BR2 ]  
Deepest hole -1.31 at 0.7372 0.0534 0.6462 [ 0.75 Å from BR2 ]

### Figures

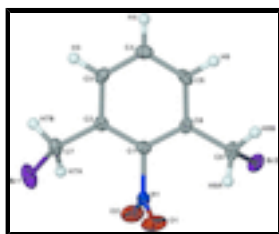


Fig. 1. The labelled thermal ellipsoid plot of (I) at the 50% probability level.

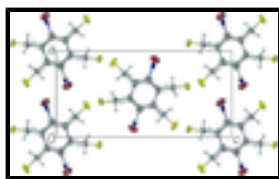


Fig. 2. The unit cell packing diagram of (I) as viewed down the *b* axis.

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### Crystal data

C<sub>8</sub>H<sub>7</sub>Br<sub>2</sub>NO<sub>2</sub>

$M_r = 308.97$

Monoclinic,  $P2_1/n$

Hall symbol: -P 2yn

$a = 7.7837$  (13) Å

$b = 7.7573$  (13) Å

$c = 15.938$  (3) Å

$\beta = 90.933$  (3)°

$V = 962.2$  (3) Å<sup>3</sup>

$Z = 4$

$F(000) = 592$

$D_x = 2.133$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

Cell parameters from 1024 reflections

$\theta = 2.6$ – $28.0^\circ$

$\mu = 8.39$  mm<sup>-1</sup>

$T = 185$  K

Needles, colorless

$0.20 \times 0.20 \times 0.08$  mm

### Data collection

Bruker SMART 1K  
diffractometer

Radiation source: fine-focus sealed tube  
graphite

$\omega$  scan

Absorption correction: multi-scan  
(SADABS; Bruker, 2001)

$T_{\min} = 0.285$ ,  $T_{\max} = 0.553$

8228 measured reflections

2259 independent reflections

1812 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.041$

$\theta_{\max} = 28.0^\circ$ ,  $\theta_{\min} = 2.6^\circ$

$h = -10 \rightarrow 10$

$k = -10 \rightarrow 10$

$l = -21 \rightarrow 20$

### Refinement

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.037$

$wR(F^2) = 0.083$

$S = 1.06$

2259 reflections

118 parameters

0 restraints

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

$w = 1/[\sigma^2(F_o^2) + (0.0289P)^2 + 1.9462P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$

$\Delta\rho_{\max} = 1.35$  e Å<sup>-3</sup>

$\Delta\rho_{\min} = -1.31$  e Å<sup>-3</sup>

### Special details

**Geometry.** All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds

in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 ( $\text{\AA}^2$ )*

|     | $x$         | $y$         | $z$          | $U_{\text{iso}}^*/U_{\text{eq}}$ |
|-----|-------------|-------------|--------------|----------------------------------|
| Br1 | 0.20766 (5) | 0.59088 (5) | 0.74548 (2)  | 0.03326 (13)                     |
| Br2 | 0.26732 (6) | 0.86865 (6) | 0.32665 (3)  | 0.04186 (15)                     |
| C1  | 0.2474 (4)  | 0.6504 (4)  | 0.5246 (2)   | 0.0211 (7)                       |
| N1  | 0.2391 (4)  | 0.8324 (4)  | 0.55227 (19) | 0.0245 (7)                       |
| C2  | 0.1776 (4)  | 0.6087 (4)  | 0.4461 (2)   | 0.0203 (7)                       |
| C3  | 0.1891 (5)  | 0.4378 (5)  | 0.4212 (2)   | 0.0238 (8)                       |
| H3  | 0.1450      | 0.4051      | 0.3676       | 0.029*                           |
| O1  | 0.3753 (4)  | 0.9089 (4)  | 0.5617 (2)   | 0.0434 (8)                       |
| C6  | 0.3228 (4)  | 0.5301 (5)  | 0.5786 (2)   | 0.0205 (7)                       |
| C5  | 0.3295 (5)  | 0.3604 (5)  | 0.5504 (2)   | 0.0249 (8)                       |
| H5  | 0.3807      | 0.2750      | 0.5855       | 0.030*                           |
| C7  | 0.3935 (5)  | 0.5748 (5)  | 0.6637 (2)   | 0.0281 (8)                       |
| H7A | 0.4550      | 0.6864      | 0.6610       | 0.034*                           |
| H7B | 0.4768      | 0.4854      | 0.6820       | 0.034*                           |
| O2  | 0.0993 (4)  | 0.8953 (4)  | 0.5634 (2)   | 0.0426 (8)                       |
| C4  | 0.2638 (5)  | 0.3131 (5)  | 0.4729 (2)   | 0.0260 (8)                       |
| H4  | 0.2695      | 0.1965      | 0.4550       | 0.031*                           |
| C8  | 0.0943 (5)  | 0.7371 (5)  | 0.3889 (2)   | 0.0259 (8)                       |
| H8A | 0.0239      | 0.8174      | 0.4222       | 0.031*                           |
| H8B | 0.0170      | 0.6766      | 0.3487       | 0.031*                           |

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

|     | $U^{11}$    | $U^{22}$    | $U^{33}$    | $U^{12}$      | $U^{13}$     | $U^{23}$      |
|-----|-------------|-------------|-------------|---------------|--------------|---------------|
| Br1 | 0.0391 (2)  | 0.0396 (2)  | 0.0212 (2)  | -0.00245 (18) | 0.00494 (16) | -0.00610 (16) |
| Br2 | 0.0346 (2)  | 0.0541 (3)  | 0.0370 (3)  | -0.0017 (2)   | 0.00213 (18) | 0.0232 (2)    |
| C1  | 0.0198 (17) | 0.0187 (17) | 0.0247 (18) | -0.0006 (14)  | 0.0027 (14)  | -0.0005 (14)  |
| N1  | 0.0324 (18) | 0.0223 (16) | 0.0188 (15) | 0.0027 (13)   | -0.0022 (13) | 0.0000 (12)   |
| C2  | 0.0161 (16) | 0.0231 (18) | 0.0218 (18) | -0.0003 (14)  | 0.0033 (14)  | 0.0018 (14)   |
| C3  | 0.0227 (18) | 0.030 (2)   | 0.0190 (18) | -0.0043 (15)  | 0.0030 (15)  | -0.0041 (15)  |
| O1  | 0.0381 (17) | 0.0343 (16) | 0.058 (2)   | -0.0126 (14)  | 0.0095 (15)  | -0.0141 (15)  |
| C6  | 0.0153 (16) | 0.0287 (18) | 0.0175 (17) | -0.0005 (14)  | 0.0020 (14)  | 0.0005 (14)   |
| C5  | 0.0254 (19) | 0.0218 (17) | 0.028 (2)   | 0.0038 (15)   | 0.0060 (16)  | 0.0076 (15)   |
| C7  | 0.0247 (19) | 0.038 (2)   | 0.0215 (19) | 0.0002 (16)   | -0.0013 (15) | 0.0014 (16)   |
| O2  | 0.0310 (16) | 0.0359 (16) | 0.061 (2)   | 0.0146 (13)   | -0.0064 (15) | -0.0158 (15)  |
| C4  | 0.0258 (19) | 0.0215 (18) | 0.031 (2)   | -0.0022 (15)  | 0.0074 (16)  | -0.0021 (15)  |
| C8  | 0.0228 (19) | 0.031 (2)   | 0.0236 (19) | -0.0007 (16)  | 0.0001 (15)  | 0.0058 (15)   |

## supplementary materials

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### Geometric parameters (Å, °)

|             |            |              |            |
|-------------|------------|--------------|------------|
| Br1—C7      | 1.967 (4)  | C3—H3        | 0.9500     |
| Br2—C8      | 1.971 (4)  | C6—C5        | 1.392 (5)  |
| C1—C6       | 1.392 (5)  | C6—C7        | 1.497 (5)  |
| C1—C2       | 1.395 (5)  | C5—C4        | 1.379 (5)  |
| C1—N1       | 1.480 (5)  | C5—H5        | 0.9500     |
| N1—O2       | 1.209 (4)  | C7—H7A       | 0.9900     |
| N1—O1       | 1.222 (4)  | C7—H7B       | 0.9900     |
| C2—C3       | 1.387 (5)  | C4—H4        | 0.9500     |
| C2—C8       | 1.491 (5)  | C8—H8A       | 0.9900     |
| C3—C4       | 1.392 (5)  | C8—H8B       | 0.9900     |
| C6—C1—C2    | 123.6 (3)  | C6—C5—H5     | 119.2      |
| C6—C1—N1    | 118.4 (3)  | C6—C7—Br1    | 110.6 (2)  |
| C2—C1—N1    | 118.0 (3)  | C6—C7—H7A    | 109.5      |
| O2—N1—O1    | 124.5 (3)  | Br1—C7—H7A   | 109.5      |
| O2—N1—C1    | 118.2 (3)  | C6—C7—H7B    | 109.5      |
| O1—N1—C1    | 117.3 (3)  | Br1—C7—H7B   | 109.5      |
| C3—C2—C1    | 116.9 (3)  | H7A—C7—H7B   | 108.1      |
| C3—C2—C8    | 119.6 (3)  | C5—C4—C3     | 119.4 (3)  |
| C1—C2—C8    | 123.5 (3)  | C5—C4—H4     | 120.3      |
| C2—C3—C4    | 121.6 (3)  | C3—C4—H4     | 120.3      |
| C2—C3—H3    | 119.2      | C2—C8—Br2    | 111.1 (2)  |
| C4—C3—H3    | 119.2      | C2—C8—H8A    | 109.4      |
| C1—C6—C5    | 116.9 (3)  | Br2—C8—H8A   | 109.4      |
| C1—C6—C7    | 123.3 (3)  | C2—C8—H8B    | 109.4      |
| C5—C6—C7    | 119.7 (3)  | Br2—C8—H8B   | 109.4      |
| C4—C5—C6    | 121.7 (3)  | H8A—C8—H8B   | 108.0      |
| C4—C5—H5    | 119.2      |              |            |
| C6—C1—N1—O2 | -115.0 (4) | N1—C1—C6—C5  | -179.6 (3) |
| C2—C1—N1—O2 | 64.5 (5)   | C2—C1—C6—C7  | -178.4 (3) |
| C6—C1—N1—O1 | 65.5 (5)   | N1—C1—C6—C7  | 1.0 (5)    |
| C2—C1—N1—O1 | -115.1 (4) | C1—C6—C5—C4  | -0.3 (5)   |
| C6—C1—C2—C3 | -1.5 (5)   | C7—C6—C5—C4  | 179.1 (3)  |
| N1—C1—C2—C3 | 179.1 (3)  | C1—C6—C7—Br1 | 80.1 (4)   |
| C6—C1—C2—C8 | 179.0 (3)  | C5—C6—C7—Br1 | -99.3 (3)  |
| N1—C1—C2—C8 | -0.4 (5)   | C6—C5—C4—C3  | 0.2 (5)    |
| C1—C2—C3—C4 | 1.2 (5)    | C2—C3—C4—C5  | -0.6 (5)   |
| C8—C2—C3—C4 | -179.2 (3) | C3—C2—C8—Br2 | -98.9 (3)  |
| C2—C1—C6—C5 | 1.0 (5)    | C1—C2—C8—Br2 | 80.6 (4)   |

Fig. 1

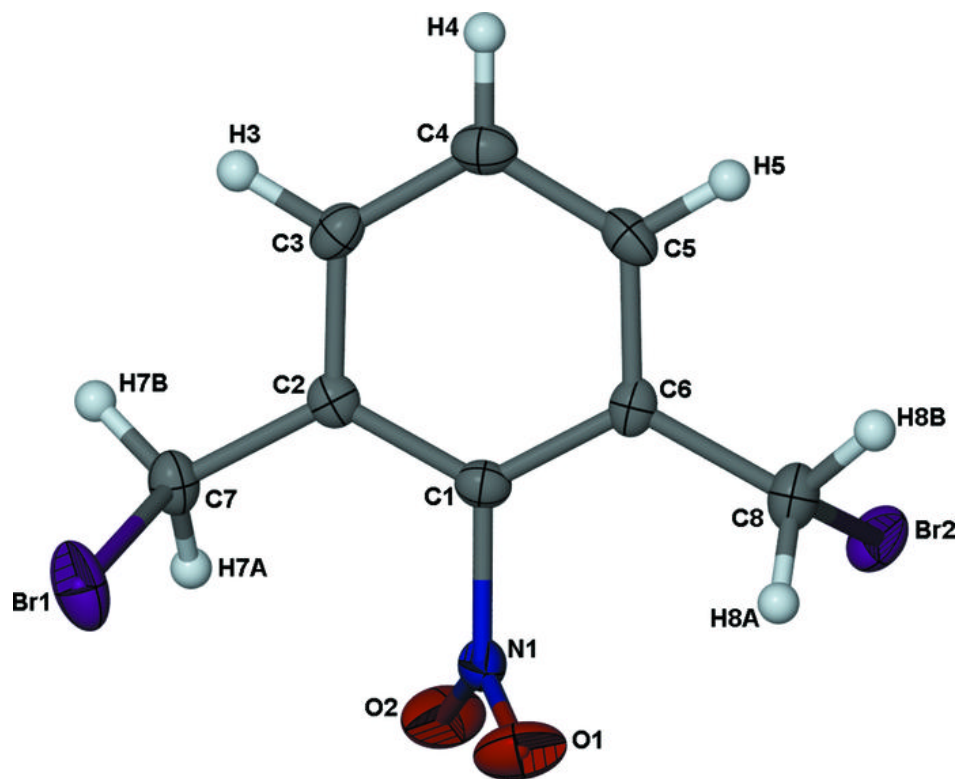


Fig. 2

