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

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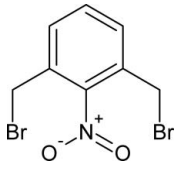
Key indicators: single-crystal X-ray study; T = 185 K; mean σ(C–C) = 0.005 Å; R factor = 0.037; wR factor = 0.083; data-to-parameter ratio = 19.1.

In the title compound, $C_8H_7Br_2NO_2$, an intermediate for the synthesis of macrocycles, the NO_2 group makes a dihedral angle of 65.07 (19)° 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

$C_8H_7Br_2NO_2$
M_r = 308.97
Monoclinic, $P2_1/n$
a = 7.7837 (13) Å
b = 7.7573 (13) Å
c = 15.938 (3) Å
β = 90.933 (3)°
V = 962.2 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 8.39 mm^{-1}
T = 185 K
0.20 × 0.20 × 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_{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^{-3}
$\Delta\rho_{min}$ = −1.31 e Å^{-3}

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; 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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1,3-Bis(bromomethyl)-2-nitrobenzene

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S1. 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)° 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)° and 80.99(0.28)°, respectively). The molecules therefore closely approximate *C*2 point group symmetry in the crystal.

S2. Experimental

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

S3. 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 Fo—Fc: Highest peak 1.35 at 0.7472 0.2174 0.6981 [0.78 A from BR2] Deepest hole -1.31 at 0.7372 0.0534 0.6462 [0.75 A from BR2]

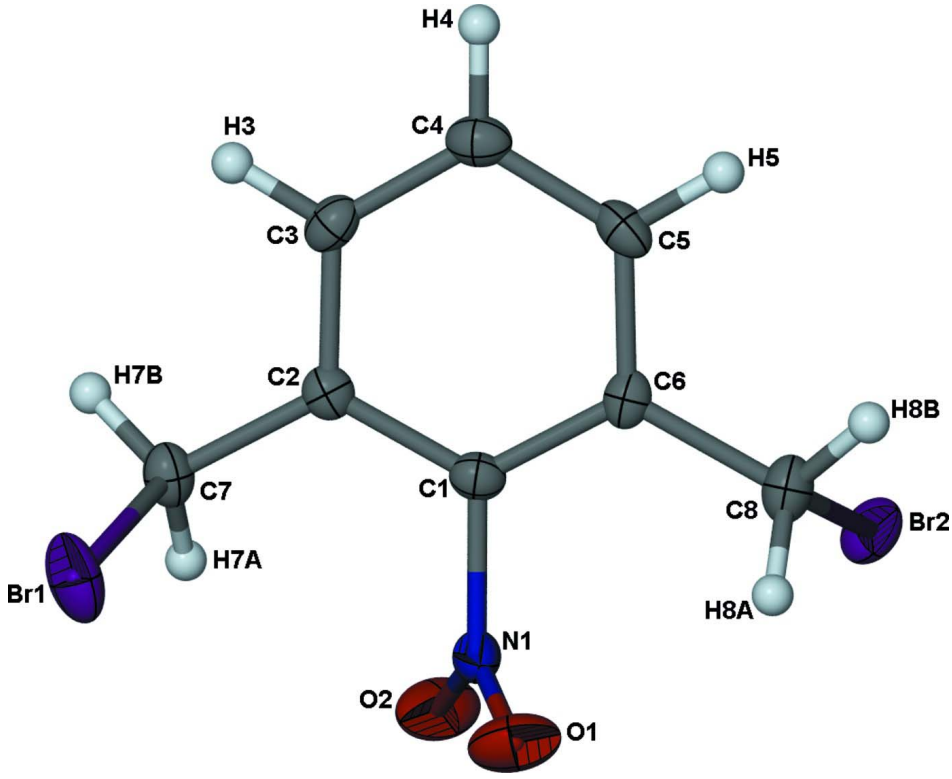

Figure 1

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

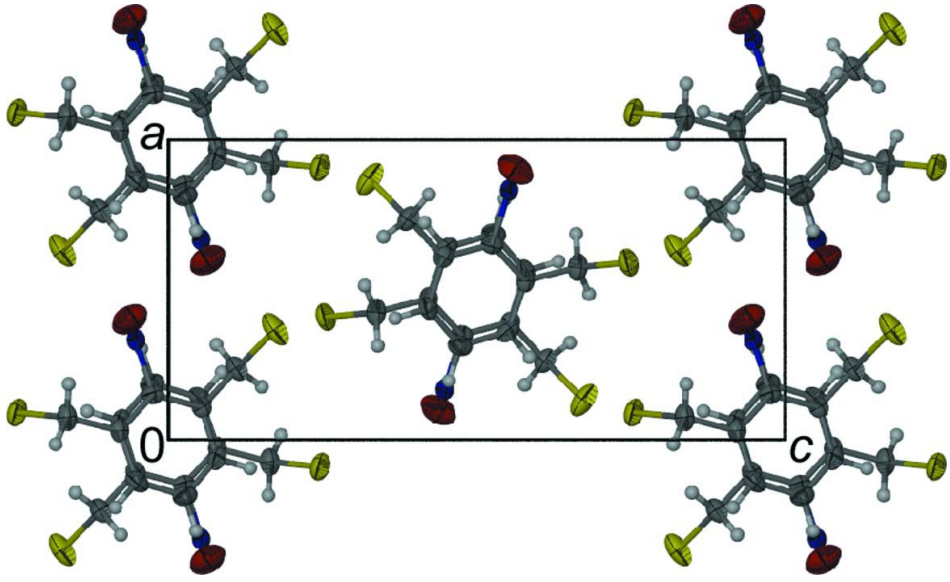

Figure 2

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

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Crystal data

$C_8H_7Br_2NO_2$
$M_r = 308.97$
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^3
$Z = 4$
$F(000) = 592$
$D_x = 2.133$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1024 reflections
$\theta = 2.6$–$28.0°$
$\mu = 8.39$ mm^{-1}
$T = 185$ K
Needles, colorless
0.20 × 0.20 × 0.08 mm

Data collection

Bruker SMART 1K diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
ω 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 $I > 2\sigma(I)$
$R_{int} = 0.041$
$\theta_{max} = 28.0°$, $\theta_{min} = 2.6°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 10$
$l = -21 \rightarrow 20$

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^{-3}
$\Delta\rho_{min} = -1.31$ e Å^{-3}

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 (Å^2)

	x	y	z	U_{iso}*/U_{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 (Å²)

	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)

Geometric parameters (Å, º)

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)