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1,4-Bis(2-nitrobenzyl)piperazine

Hugh I. Crundwell,* Rhiannon I. Grimmett, Guy Crundwell and Barry L. Westcott

Department of Chemistry & Biochemistry, Central Connecticut State University, 1619 Stanley Street, New Britain, CT 06053, USA. *Correspondence e-mail: crundwellg@ccsu.edu

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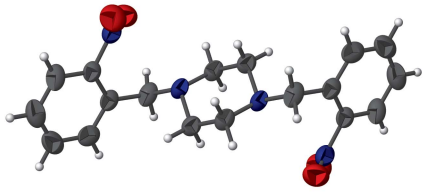
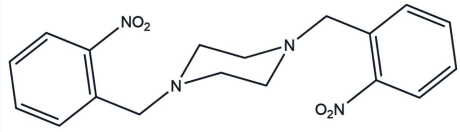
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{18}H_{20}N_4O_4$, was synthesized *via* the base-assisted reaction of piperazine and 2-nitrobenyl bromide in toluene: the complete molecule is generated by a crystallographic inversion centre in the solid state.

3D view



Chemical scheme



Structure description

The title compound, $C_{18}H_{20}N_4O_4$, has been previously studied by Schlager *et al.* (1996) and Cameron & Fréchet (1991). In the solid state, the complete molecule is generated by a crystallographic inversion center and the exocyclic N—C bonds have equatorial orientations (bond-angle sum for N1 = 332.4°). The nitro group makes a torsion angle of 45.36 (6)° with its attached C4–C9 phenyl ring. All bond lengths and angles fall within expected values. The molecular structure is shown in Fig. 1 and a view of the unit-cell packing along [100] is shown in Fig. 2. No directional intermolecular interactions beyond normal van der Waals contacts could be identified in the extended structure.

Synthesis and crystallization

1,4-Bis(2-nitrobenzyl)piperazine was made according to the published method of Schlager *et al.* (1996). In an Erlenmeyer flask placed in an 60°C oil bath, 40 mmol (3.45 g) of 1,4-diazacyclohexane was added to 100 ml of toluene with stirring. To that solution, 80 mmol (17.3 g) of 2-nitrobenzyl bromide was added. Once dissolved, 90 mmol of powdered KOH (4.98 g) were slowly added with stirring. The mixture was allowed to stir overnight in the oil bath. Upon removal from the oil bath and subsequent cooling, large block-like yellow crystals of the title compound formed. The title compound melts at 409 K. ^{1}H NMR data (Schlager *et al.*, 1996) and FTIR data (Cameron & Fréchet, 1991) are in agreement with published values.

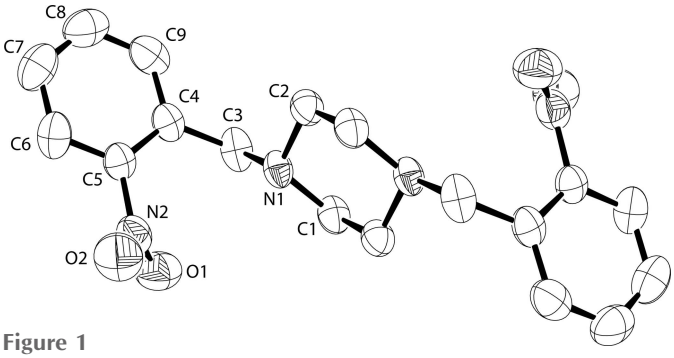


Figure 1
The molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level. Unlabelled atoms are generated by the symmetry operation $(1 - x, -y, -z)$ and H atoms are omitted for clarity.

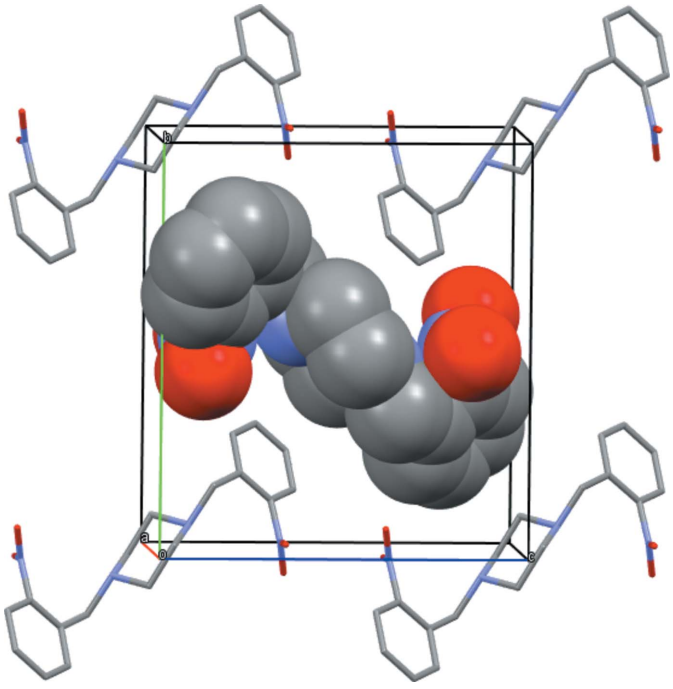


Figure 2
A view approximately along [100] of the unit-cell packing.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. Reflections affected by the beam stop were omitted from the refinement.

Table 1
Experimental details.

Crystal data	
Chemical formula	$C_{18}H_{20}N_4O_4$
M_r	356.38
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	6.0338 (3), 12.9814 (6), 11.4890 (5)
β (°)	91.185 (4)
V (Å^3)	899.71 (7)
Z	2
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.41 × 0.40 × 0.22
Data collection	
Diffractometer	Oxford Diffraction Xcalibur, Sapphire3
Absorption correction	Multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min}, T_{max}	0.801, 1.000
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	22354, 3335, 2339
R_{int}	0.029
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.779
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.056, 0.153, 1.03
No. of reflections	3335
No. of parameters	118
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.19, −0.21

Computer programs: *CrysAlis CCD* and *CrysAlis RED* (Oxford Diffraction, 2009), *SHELXS2014* (Sheldrick, 2008), *SHELXL2014* (Sheldrick, 2015), *ORTEP-3 for Windows* (Farrugia, 2012) and *OLEX2* (Bourhis *et al.*, 2015).

Acknowledgements

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full crystallographic data

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Crystal data

$C_{18}H_{20}N_4O_4$
M_r = 356.38
Monoclinic, $P2_1/c$
a = 6.0338 (3) Å
b = 12.9814 (6) Å
c = 11.4890 (5) Å
β = 91.185 (4)°
V = 899.71 (7) Å^3
Z = 2
$F(000)$ = 376.1911
D_x = 1.315 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 5355 reflections
θ = 4.8–31.0°
μ = 0.10 mm^{-1}
T = 293 K
Block, yellow
0.41 × 0.40 × 0.22 mm

Data collection

Oxford Diffraction Xcalibur, Sapphire3 diffractometer
Radiation source: Enhance (Mo) X-ray Source
Graphite monochromator
Detector resolution: 16.1790 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (CrysAlis PRO; Oxford Diffraction, 2009)
T_{min} = 0.801, T_{max} = 1.000
22354 measured reflections
3335 independent reflections
2339 reflections with $I > 2\sigma(I)$
R_{int} = 0.029
θ_{max} = 33.6°, θ_{min} = 4.7°
h = −9→9
k = −19→19
l = −17→17

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.153
S = 1.03
3335 reflections
118 parameters
0 restraints
Primary atom site location: iterative
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0652P)^2 + 0.1367P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.19 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 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 $F^2 > 2\text{sigma}(F^2)$ 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.
H atoms were included in calculated positions with C–H = 0.93–0.97 Å and were included in the refinement in the riding motion approximation with $U_{iso} = 1.2U_{eq}$(carrier).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.40223 (19)	0.01928 (9)	0.36223 (11)	0.0757 (3)
O2	0.7134 (2)	−0.06112 (8)	0.37260 (12)	0.0810 (4)
N1	0.50057 (15)	0.06204 (8)	0.10262 (8)	0.0423 (2)
N2	0.6030 (2)	0.01681 (8)	0.35741 (9)	0.0543 (3)
C1	0.29557 (18)	0.01964 (11)	0.05348 (10)	0.0479 (3)
H1A	0.2284	0.0690	0.0000	0.058*
H1B	0.1921	0.0067	0.1153	0.058*
C2	0.65771 (19)	0.07935 (10)	0.01003 (10)	0.0478 (3)
H2A	0.7949	0.1067	0.0430	0.057*
H2B	0.5975	0.1297	−0.0444	0.057*
C3	0.4604 (2)	0.15692 (11)	0.16799 (11)	0.0538 (3)
H3A	0.3272	0.1492	0.2130	0.065*
H3B	0.4378	0.2137	0.1142	0.065*
C4	0.6537 (2)	0.18024 (9)	0.24814 (10)	0.0460 (3)
C5	0.7236 (2)	0.11288 (9)	0.33597 (10)	0.0444 (3)
C6	0.9076 (2)	0.13108 (11)	0.40618 (12)	0.0582 (3)
H6	0.9492	0.0840	0.4636	0.070*
C7	1.0285 (3)	0.21903 (12)	0.39046 (15)	0.0669 (4)
H7	1.1513	0.2326	0.4382	0.080*
C8	0.9686 (3)	0.28655 (12)	0.30476 (15)	0.0688 (4)
H8	1.0525	0.3457	0.2934	0.083*
C9	0.7835 (3)	0.26779 (10)	0.23431 (12)	0.0609 (4)
H9	0.7452	0.3149	0.1764	0.073*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0701 (7)	0.0770 (8)	0.0805 (8)	−0.0093 (6)	0.0174 (6)	0.0004 (6)
O2	0.1077 (9)	0.0464 (6)	0.0885 (8)	0.0106 (6)	−0.0089 (7)	0.0041 (5)
N1	0.0397 (4)	0.0547 (6)	0.0325 (4)	0.0097 (4)	0.0008 (3)	−0.0032 (4)
N2	0.0721 (7)	0.0484 (6)	0.0422 (5)	0.0029 (5)	0.0009 (5)	−0.0028 (4)
C1	0.0367 (5)	0.0678 (8)	0.0394 (5)	0.0076 (5)	0.0042 (4)	−0.0029 (5)
C2	0.0422 (5)	0.0606 (7)	0.0407 (5)	0.0005 (5)	0.0026 (4)	−0.0008 (5)
C3	0.0590 (7)	0.0590 (7)	0.0433 (6)	0.0228 (6)	−0.0049 (5)	−0.0061 (5)
C4	0.0560 (6)	0.0437 (6)	0.0384 (5)	0.0127 (5)	0.0029 (5)	−0.0056 (4)
C5	0.0520 (6)	0.0414 (5)	0.0400 (5)	0.0076 (5)	0.0005 (4)	−0.0061 (4)
C6	0.0649 (8)	0.0552 (7)	0.0540 (7)	0.0142 (6)	−0.0142 (6)	−0.0113 (6)
C7	0.0583 (8)	0.0660 (9)	0.0761 (10)	0.0030 (7)	−0.0061 (7)	−0.0261 (8)
C8	0.0742 (9)	0.0568 (8)	0.0764 (10)	−0.0126 (7)	0.0212 (8)	−0.0227 (7)

C9	0.0864 (10)	0.0461 (7)	0.0507 (7)	0.0066 (7)	0.0140 (7)	−0.0015 (5)

Geometric parameters (Å, º)

O1—N2	1.2143 (15)	C3—H3B	0.9700
O2—N2	1.2218 (15)	C3—C4	1.5015 (17)
N1—C1	1.4570 (15)	C4—C5	1.3941 (16)
N1—C2	1.4570 (14)	C4—C9	1.3912 (19)
N1—C3	1.4653 (15)	C5—C6	1.3792 (17)
N2—C5	1.4673 (16)	C6—H6	0.9300
C1—H1A	0.9700	C6—C7	1.369 (2)
C1—H1B	0.9700	C7—H7	0.9300
C1—C2^{i}	1.5072 (18)	C7—C8	1.361 (2)
C2—C1^{i}	1.5072 (18)	C8—H8	0.9300
C2—H2A	0.9700	C8—C9	1.388 (2)
C2—H2B	0.9700	C9—H9	0.9300
C3—H3A	0.9700		
C1—N1—C2	109.60 (9)	H3A—C3—H3B	108.1
C1—N1—C3	111.61 (9)	C4—C3—H3A	109.6
C2—N1—C3	111.20 (10)	C4—C3—H3B	109.6
O1—N2—O2	123.83 (13)	C5—C4—C3	122.48 (12)
O1—N2—C5	118.94 (11)	C9—C4—C3	121.77 (12)
O2—N2—C5	117.19 (12)	C9—C4—C5	115.62 (12)
N1—C1—H1A	109.6	C4—C5—N2	120.72 (11)
N1—C1—H1B	109.6	C6—C5—N2	116.33 (11)
N1—C1—C2^{i}	110.12 (9)	C6—C5—C4	122.95 (12)
H1A—C1—H1B	108.2	C5—C6—H6	120.3
C2^{i}—C1—H1A	109.6	C7—C6—C5	119.36 (14)
C2^{i}—C1—H1B	109.6	C7—C6—H6	120.3
N1—C2—C1^{i}	110.67 (10)	C6—C7—H7	120.0
N1—C2—H2A	109.5	C8—C7—C6	119.91 (14)
N1—C2—H2B	109.5	C8—C7—H7	120.0
C1^{i}—C2—H2A	109.5	C7—C8—H8	119.8
C1^{i}—C2—H2B	109.5	C7—C8—C9	120.48 (14)
H2A—C2—H2B	108.1	C9—C8—H8	119.8
N1—C3—H3A	109.6	C4—C9—H9	119.2
N1—C3—H3B	109.6	C8—C9—C4	121.67 (14)
N1—C3—C4	110.45 (9)	C8—C9—H9	119.2

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