

4-Bromo-N-(3,4-methylenedioxybenzyl)-aniline

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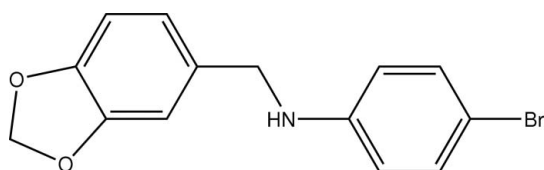
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Key indicators: single-crystal X-ray study; $T = 298$ K; mean $\sigma(\text{C}-\text{C}) = 0.008$ Å; R factor = 0.045; wR factor = 0.106; data-to-parameter ratio = 13.1.

In the title compound, $\text{C}_{14}\text{H}_{12}\text{BrNO}_2$, the molecules are linked by one $\text{C}-\text{H}\cdots\text{Br}$ hydrogen bond, so forming a $C(13)$ chain running parallel to the [010] direction, and these chains are linked by further $\text{C}-\text{H}\cdots\pi$ and $\text{C}-\text{H}\cdots\text{Br}$ hydrogen bonds, resulting in a three-dimensional network structure.

Related literature

For related literature, see: Allen *et al.* (1987); Bernstein *et al.* (1995); Koşar *et al.* (2004); Silversides *et al.* (2006); Yang *et al.* (2007).



Experimental

Crystal data

$\text{C}_{14}\text{H}_{12}\text{BrNO}_2$	$V = 1246.7(2) \text{ \AA}^3$
$M_r = 306.16$	$Z = 4$
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
$a = 14.6264(13) \text{ \AA}$	$\mu = 3.29 \text{ mm}^{-1}$
$b = 14.2650(12) \text{ \AA}$	$T = 298(2) \text{ K}$
$c = 5.9752(8) \text{ \AA}$	$0.55 \times 0.48 \times 0.41 \text{ mm}$

Data collection

Siemens SMART 1000 CCD area-detector diffractometer	4925 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	2133 independent reflections
$T_{\min} = 0.265$, $T_{\max} = 0.346$	1641 reflections with $I > 2\sigma(I)$
(expected range = 0.199–0.260)	$R_{\text{int}} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.045$	H-atom parameters constrained
$wR(F^2) = 0.106$	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
$S = 1.06$	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
2133 reflections	Absolute structure: Flack (1983),
163 parameters	917 Freidel pairs
1 restraint	Flack parameter: $-0.028(18)$

Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the $C2-C7$ and $C9-C14$ rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C8-H8a\cdots Br1^i$	0.97	3.02	3.813(9)	140
$C8-H8b\cdots Br1^{ii}$	0.97	3.08	3.958(6)	151
$C11-H11\cdots Br1^{iii}$	0.93	3.09	3.944(6)	154
$C6-H6\cdots Cg1^{iv}$	0.93	2.83	3.53(2)	133
$C13-H13\cdots Cg2^v$	0.93	2.81	3.62(2)	147

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+\frac{3}{2}, y-1, z-\frac{1}{2}$; (iii) $-x+\frac{3}{2}, y, z-\frac{1}{2}$; (iv) $-x+1, -y+1, z-\frac{1}{2}$; (v) $-x+1, -y+2, z+\frac{1}{2}$.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997a); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997a); molecular graphics: SHELXTL (Sheldrick, 1997b); software used to prepare material for publication: SHELXTL.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: AT2430).

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supplementary materials

Acta Cryst. (2007). E63, o4404 [doi:10.1107/S1600536807051744]

4-Bromo-N-(3,4-methylenedioxybenzyl)aniline

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Comment

We have reported recently the crystal structure of an aniline derivative (Yang *et al.*, 2007). As part of our study of the aniline derivatives, we report here the crystal structures of (I) (Fig.1).

The title compound (I), crystallizes in the orthorhombic space group $Pca2_1$ with $Z = 4$. In (I), the dihedral angle between the two benzene rings are $59.8 (1)^\circ$. Geometric parameters of (I) are normal (Allen *et al.*, 1987) and selected geometric parameters are listed in the Table 1. The aniline N1—C9 bonds length is $1.391 (7) \text{ \AA}$, this value is near with the aniline C—N bonds of the analogs reported (C—N = 1.396 \AA , Silversides *et al.*, C—N = $1.396 (5) \text{ \AA}$, Yyang *et al.* 2007), but slightly shorter than the aniline C—N bonds of the analog reported (C—N = 1.414 \AA , Koşar *et al.*, 2004), this is probably due to the weakly inductive negative effect of the bromine atom on the aryl residue.

In the crystal structure of (I), the molecules are linked by one C—H \cdots Br hydrogen bond into a simple C(13) chain (Bernstein *et al.*, 1995) running parallel to the [010] direction. The atom C8 in the molecule at (x, y, z) acts as a hydrogen-bond donor, *via* H8a, to the atom Br1 in the molecule at $(x, -1 + y, z)$. These chains are linked by further C—H \cdots π and C—H \cdots Br hydrogen bonds, resulting in a three-dimensional network structure (Table 2 and Fig. 2).

Experimental

The mixture containing piperonaldehyde (1.5 g, 10 mmol) and 4-bromoaniline (1.72 g, 10 mmol) was refluxed for about 6 h in ethanol, then borohydride sodium (1.52 g, 40 mmol) was added and refluxed continually for about 2 h, then acetone (20 ml) and water (40 ml) were added in turn, and the reaction mixture was cooled and the products were filtered off, washed with ethanol and dried. Colourless crystals of (I) suitable for X-ray structure analysis were obtained by recrystallizing the crude product from ethanol (m.p. 370–372 K).

Refinement

All H atoms were located in difference Fourier maps. H atoms bonded to C and N atoms were treated as riding atoms, with C—H distances of 0.93 \AA (aryl), 0.97 \AA (methylene), N—H distances of 0.86 \AA (amino), and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C}, \text{N})$ (aryl, methylene, amino).

Figures

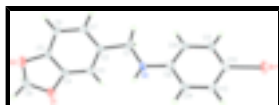


Fig. 1. A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.



Fig. 2. A view of part of the crystal structure of (I), showing the formation of a C(13) chain. For clarity, the H atoms not involved in the motif have been omitted. Dashed lines indicate hydrogen bonds. [Symmetry codes: (*) $x, -1 + y, z$; (#) $x, 1 + y, z$].

4-Bromo-*N*-(3,4-methylenedioxybenzyl)aniline

Crystal data

$C_{14}H_{12}BrNO_2$	$D_x = 1.631 \text{ Mg m}^{-3}$
$M_r = 306.16$	Melting point: 370 K
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation
Hall symbol: P 2c -2ac	$\lambda = 0.71073 \text{ \AA}$
$a = 14.6264 (13) \text{ \AA}$	Cell parameters from 1828 reflections
$b = 14.2650 (12) \text{ \AA}$	$\theta = 2.8\text{--}25.8^\circ$
$c = 5.9752 (8) \text{ \AA}$	$\mu = 3.29 \text{ mm}^{-1}$
$V = 1246.7 (2) \text{ \AA}^3$	$T = 298 (2) \text{ K}$
$Z = 4$	Block, yellow
$F_{000} = 616$	$0.55 \times 0.48 \times 0.41 \text{ mm}$

Data collection

Siemens SMART 1000 CCD area-detector diffractometer	2133 independent reflections
Radiation source: fine-focus sealed tube	1641 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.050$
$T = 298(2) \text{ K}$	$\theta_{\text{max}} = 25.0^\circ$
φ and ω scans	$\theta_{\text{min}} = 2.0^\circ$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -11 \rightarrow 17$
$T_{\text{min}} = 0.265, T_{\text{max}} = 0.346$	$k = -15 \rightarrow 16$
4925 measured reflections	$l = -7 \rightarrow 7$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.045$	$w = 1/[\sigma^2(F_o^2) + (0.0507P)^2]$
$wR(F^2) = 0.106$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{\text{max}} = 0.001$
2133 reflections	$\Delta\rho_{\text{max}} = 0.35 \text{ e \AA}^{-3}$
163 parameters	$\Delta\rho_{\text{min}} = -0.47 \text{ e \AA}^{-3}$
1 restraint	Extinction correction: none
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack (1983), 917 Freidel pairs
Secondary atom site location: difference Fourier map	Flack parameter: $-0.028 (18)$

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 $F^2 > 2\sigma(F^2)$ 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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.6106 (3)	0.7514 (4)	0.8425 (10)	0.0380 (12)
H1	0.5825	0.7105	0.9227	0.046*
O1	0.6680 (3)	0.3832 (3)	0.8088 (8)	0.0518 (12)
O2	0.6013 (3)	0.3398 (3)	0.4741 (9)	0.0499 (12)
Br1	0.62189 (4)	1.15367 (4)	1.17625 (16)	0.0473 (2)
C1	0.6536 (4)	0.7235 (4)	0.6345 (13)	0.0416 (17)
H1a	0.7190	0.7340	0.6446	0.050*
H1b	0.6301	0.7617	0.5132	0.050*
C2	0.6358 (4)	0.6212 (4)	0.5839 (10)	0.0328 (14)
C3	0.6636 (3)	0.5539 (4)	0.7388 (9)	0.0334 (15)
H3	0.6907	0.5704	0.8741	0.040*
C4	0.6491 (3)	0.4622 (4)	0.6815 (15)	0.0334 (11)
C5	0.6106 (4)	0.4358 (4)	0.4820 (11)	0.0328 (14)
C6	0.5841 (4)	0.5002 (4)	0.3254 (11)	0.0365 (15)
H6	0.5588	0.4826	0.1889	0.044*
C7	0.5974 (4)	0.5944 (4)	0.3832 (10)	0.0361 (14)
H7	0.5797	0.6406	0.2823	0.043*
C8	0.6530 (4)	0.3075 (4)	0.6599 (17)	0.0570 (18)
H8a	0.6201	0.2578	0.7360	0.068*
H8b	0.7111	0.2826	0.6090	0.068*
C9	0.6144 (3)	0.8443 (4)	0.9130 (11)	0.0318 (13)
C14	0.5678 (4)	0.8713 (4)	1.1078 (9)	0.0368 (16)
H14	0.5339	0.8269	1.1860	0.044*
C13	0.5708 (3)	0.9618 (3)	1.1860 (13)	0.0348 (12)
H13	0.5391	0.9786	1.3147	0.042*
C12	0.6215 (4)	1.0273 (4)	1.0709 (10)	0.0335 (14)
C11	0.6678 (4)	1.0037 (4)	0.8828 (11)	0.0363 (15)
H11	0.7012	1.0492	0.8069	0.044*
C10	0.6662 (4)	0.9125 (4)	0.8017 (11)	0.0375 (14)
H10	0.6992	0.8967	0.6742	0.045*

supplementary materials

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.054 (3)	0.016 (2)	0.045 (3)	-0.007 (2)	0.007 (2)	0.000 (2)
O1	0.075 (3)	0.028 (2)	0.052 (3)	0.004 (2)	-0.019 (2)	0.005 (2)
O2	0.067 (3)	0.025 (3)	0.058 (3)	-0.001 (2)	-0.009 (2)	-0.007 (2)
Br1	0.0532 (3)	0.0253 (3)	0.0635 (4)	-0.0009 (3)	0.0084 (5)	-0.0109 (4)
C1	0.060 (3)	0.026 (3)	0.039 (5)	-0.008 (3)	0.010 (3)	-0.002 (3)
C2	0.037 (3)	0.026 (3)	0.036 (4)	0.003 (3)	0.006 (2)	-0.001 (3)
C3	0.037 (3)	0.035 (4)	0.028 (4)	-0.001 (3)	-0.004 (2)	-0.003 (3)
C4	0.038 (2)	0.029 (3)	0.034 (3)	0.000 (2)	-0.004 (4)	0.004 (4)
C5	0.039 (3)	0.022 (3)	0.038 (4)	0.001 (3)	0.002 (3)	-0.004 (3)
C6	0.044 (3)	0.036 (4)	0.030 (4)	-0.001 (3)	-0.009 (3)	-0.005 (3)
C7	0.048 (3)	0.028 (3)	0.033 (4)	0.004 (3)	-0.005 (3)	0.007 (3)
C8	0.078 (4)	0.028 (3)	0.065 (5)	0.005 (3)	-0.016 (5)	0.002 (5)
C9	0.030 (3)	0.025 (3)	0.040 (4)	0.002 (3)	-0.002 (2)	0.001 (3)
C14	0.037 (3)	0.033 (3)	0.040 (4)	-0.005 (3)	0.010 (2)	0.004 (3)
C13	0.037 (2)	0.032 (3)	0.035 (3)	0.001 (2)	0.002 (4)	-0.011 (4)
C12	0.030 (3)	0.024 (3)	0.047 (4)	0.000 (3)	-0.002 (3)	-0.003 (3)
C11	0.037 (3)	0.022 (3)	0.050 (4)	-0.005 (2)	0.013 (3)	-0.001 (3)
C10	0.041 (3)	0.029 (4)	0.042 (4)	0.001 (3)	0.009 (3)	-0.002 (3)

Geometric parameters (\AA , $^\circ$)

N1—C9	1.391 (7)	C5—C6	1.368 (8)
N1—C1	1.450 (9)	C6—C7	1.400 (7)
N1—H1	0.8600	C6—H6	0.9300
O1—C4	1.387 (8)	C7—H7	0.9300
O1—C8	1.417 (9)	C8—H8a	0.9700
O2—C5	1.377 (6)	C8—H8b	0.9700
O2—C8	1.420 (10)	C9—C10	1.401 (8)
Br1—C12	1.910 (6)	C9—C14	1.404 (8)
C1—C2	1.512 (8)	C14—C13	1.373 (7)
C1—H1a	0.9700	C14—H14	0.9300
C1—H1b	0.9700	C13—C12	1.377 (8)
C2—C7	1.379 (8)	C13—H13	0.9300
C2—C3	1.395 (7)	C12—C11	1.355 (8)
C3—C4	1.368 (7)	C11—C10	1.389 (7)
C3—H3	0.9300	C11—H11	0.9300
C4—C5	1.372 (10)	C10—H10	0.9300
C9—N1—C1	120.3 (5)	C2—C7—H7	118.7
C9—N1—H1	119.9	C6—C7—H7	118.7
C1—N1—H1	119.9	O1—C8—O2	109.0 (5)
C4—O1—C8	104.1 (6)	O1—C8—H8a	109.9
C5—O2—C8	104.1 (5)	O2—C8—H8a	109.9
N1—C1—C2	111.2 (5)	O1—C8—H8b	109.9
N1—C1—H1a	109.4	O2—C8—H8b	109.9

C2—C1—H1a	109.4	H8a—C8—H8b	108.3
N1—C1—H1b	109.4	N1—C9—C10	122.6 (6)
C2—C1—H1b	109.4	N1—C9—C14	119.6 (5)
H1a—C1—H1b	108.0	C10—C9—C14	117.7 (5)
C7—C2—C3	120.3 (6)	C13—C14—C9	121.7 (5)
C7—C2—C1	120.8 (6)	C13—C14—H14	119.2
C3—C2—C1	118.8 (6)	C9—C14—H14	119.2
C4—C3—C2	116.5 (6)	C14—C13—C12	119.0 (6)
C4—C3—H3	121.7	C14—C13—H13	120.5
C2—C3—H3	121.7	C12—C13—H13	120.5
C3—C4—C5	123.0 (6)	C11—C12—C13	121.0 (5)
C3—C4—O1	127.4 (7)	C11—C12—Br1	120.4 (4)
C5—C4—O1	109.6 (5)	C13—C12—Br1	118.5 (4)
C6—C5—C4	121.8 (5)	C12—C11—C10	120.9 (6)
C6—C5—O2	128.1 (6)	C12—C11—H11	119.6
C4—C5—O2	110.1 (5)	C10—C11—H11	119.6
C5—C6—C7	115.9 (6)	C11—C10—C9	119.7 (6)
C5—C6—H6	122.1	C11—C10—H10	120.2
C7—C6—H6	122.1	C9—C10—H10	120.2
C2—C7—C6	122.5 (6)		
C9—N1—C1—C2	-176.4 (5)	C1—C2—C7—C6	176.7 (5)
N1—C1—C2—C7	125.0 (6)	C5—C6—C7—C2	0.8 (8)
N1—C1—C2—C3	-58.5 (7)	C4—O1—C8—O2	-16.7 (7)
C7—C2—C3—C4	-1.1 (8)	C5—O2—C8—O1	17.4 (7)
C1—C2—C3—C4	-177.6 (5)	C1—N1—C9—C10	-6.2 (8)
C2—C3—C4—C5	0.9 (8)	C1—N1—C9—C14	176.2 (6)
C2—C3—C4—O1	-177.9 (5)	N1—C9—C14—C13	178.9 (5)
C8—O1—C4—C3	-171.6 (6)	C10—C9—C14—C13	1.2 (8)
C8—O1—C4—C5	9.5 (6)	C9—C14—C13—C12	-0.5 (8)
C3—C4—C5—C6	0.2 (9)	C14—C13—C12—C11	0.2 (9)
O1—C4—C5—C6	179.2 (5)	C14—C13—C12—Br1	178.0 (4)
C3—C4—C5—O2	-177.8 (5)	O2 ⁱ —Br1—C12—C11	-165.5 (5)
O1—C4—C5—O2	1.3 (7)	O2 ⁱ —Br1—C12—C13	16.6 (10)
C8—O2—C5—C6	170.9 (6)	C13—C12—C11—C10	-0.6 (9)
C8—O2—C5—C4	-11.4 (7)	Br1—C12—C11—C10	-178.4 (4)
C4—C5—C6—C7	-1.0 (9)	C12—C11—C10—C9	1.3 (9)
O2—C5—C6—C7	176.5 (5)	N1—C9—C10—C11	-179.2 (5)
C3—C2—C7—C6	0.3 (9)	C14—C9—C10—C11	-1.6 (8)

Symmetry codes: (i) $x, y+1, z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
C8—H8a \cdots Br1 ⁱⁱ	0.97	3.02	3.813 (9)	140
C8—H8b \cdots Br1 ⁱⁱⁱ	0.97	3.08	3.958 (6)	151
C11—H11 \cdots Br1 ^{iv}	0.93	3.09	3.944 (6)	154
C6—H6 \cdots Cg1 ^v	0.93	2.83	3.53 (2)	133

supplementary materials

C13—H13 \cdots Cg2^{vi}

0.93

2.81

3.62 (2)

147

Symmetry codes: (ii) $x, y-1, z$; (iii) $-x+3/2, y-1, z-1/2$; (iv) $-x+3/2, y, z-1/2$; (v) $-x+1, -y+1, z-1/2$; (vi) $-x+1, -y+2, z+1/2$.

Fig. 1

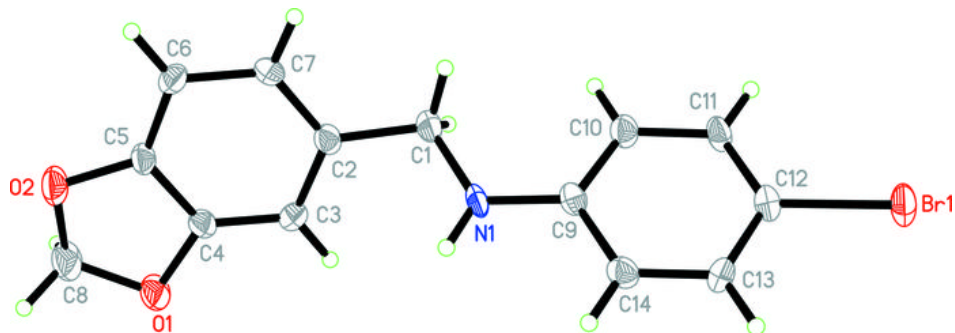


Fig. 2

