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

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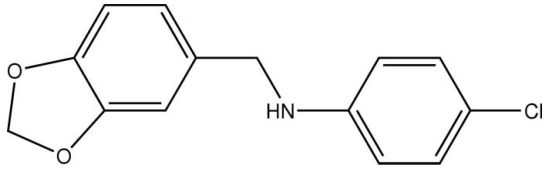
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.007 Å; R factor = 0.056; wR factor = 0.130; data-to-parameter ratio = 12.3.

Molecules of the title compound, $C_{14}H_{12}ClNO_2$, are linked by one C—H···Cl hydrogen bond, forming a $C(13)$ chain running parallel to the [010] direction; these chains are linked by further C—H···π and C—H···Cl 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

$C_{14}H_{12}ClNO_2$
M_r = 261.70
Orthorhombic, $Pca2_1$
a = 14.4986 (13) Å
b = 13.9962 (14) Å
c = 5.9375 (8) Å
V = 1204.9 (2) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.31 mm^{-1}
T = 298 (2) K
0.24 × 0.11 × 0.07 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.930, T_{max} = 0.979
4750 measured reflections
2001 independent reflections
1217 reflections with $I > 2\sigma(I)$
R_{int} = 0.079

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.056
$wR(F^2)$ = 0.130
S = 0.91
2001 reflections
163 parameters
1 restraint
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.30 e Å^{-3}
$\Delta\rho_{min}$ = −0.21 e Å^{-3}
Absolute structure: Flack (1983), 848 Freidel pairs
Flack parameter: −0.02 (13)

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

*Cg*1 and *Cg*2 are the centroids of the C2–C7 and C9–C14 rings, respectively.

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8A···Cl1^{i}	0.97	2.96	3.741 (7)	139
C11—H11···Cl1^{ii}	0.93	2.95	3.819 (5)	155
C8—H8B···Cl1^{iii}	0.97	3.00	3.874 (5)	151
C6—H6···$Cg1^{iv}$	0.93	2.80	3.50 (2)	133
C13—H13···$Cg2^{v}$	0.93	2.70	3.51 (2)	146

Symmetry codes: (i) $x, y-1, z$; (ii) $-x+\frac{1}{2}, y, z-\frac{1}{2}$; (iii) $-x+\frac{1}{2}, y-1, z-\frac{1}{2}$; (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, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); 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: AT2429).

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supplementary materials

Acta Cryst. (2007). E**63**, o4403 [**doi:10.1107/S1600536807051732**]

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

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Comment

We have reported recently the crystyl structure of an aniline derives (Yang *et al.*, 2007). As part of our study of the aniline derives, 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 60.1 (1)°. 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 1.387 (6) Å, slightly shorter than the aniline C—N bonds of the analogs reported (C—N = 1.396 Å, Silversides *et al.*, 2006; C—N = 1.414 Å, Koşar *et al.*, 2004; C—N = 1.396 (5) Å, Yang *et al.,* 2007), this is probably due to the inductive negative effect of the halogen atom on the aryl residue.

In the crystal structure of (I), the molecules are linked by one C—H···Cl 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 Cl1 in the molecule at $(x, -1 + y, z)$. These chains are linked by further C—H···π and C—H···Cl 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-chloroaniline (1.27 g, 10 mmol) was refluxed for about 6 h in ethanol, then borohydride sodium(1.52 g, 40 mmol) was added and refluxed continuely 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) suitatble for X-ray structure analysis were obtained by recrystallizing the crude product from ethanol.(m.p.362–363 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 0.93Å (aryl), 0.97Å (methylene), N—H distances of 0.86Å (amino), and with $U_{iso}(H) = 1.2U_{eq}(C,N)$ (aryl, methylene, amino).

Figures

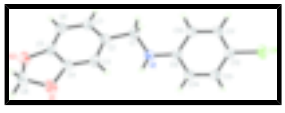

Fig. 1. A molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level.

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

Crystal data

$C_{14}H_{12}ClNO_2$	$D_x = 1.443$ Mg m^{-3}
$M_r = 261.70$	Melting point: 362 K
Orthorhombic, $Pca2_1$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: P 2c -2ac	Cell parameters from 904 reflections
$a = 14.4986$ (13) Å	$\theta = 2.8$–$25.2°$
$b = 13.9962$ (14) Å	$\mu = 0.31$ mm^{-1}
$c = 5.9375$ (8) Å	$T = 298$ (2) K
$V = 1204.9$ (2) Å^3	Needle, colourless
$Z = 4$	0.24 × 0.11 × 0.07 mm
$F_{000} = 544$	

Data collection

Bruker SMART CCD area-detector diffractometer	2001 independent reflections
Radiation source: fine-focus sealed tube	1217 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.079$
$T = 298$(2) K	$\theta_{max} = 25.0°$
φ and ω scans	$\theta_{min} = 1.5°$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$h = -17\rightarrow12$
$T_{min} = 0.930$, $T_{max} = 0.979$	$k = -16\rightarrow15$
4750 measured reflections	$l = -7\rightarrow6$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H-atom parameters constrained
$R[F^2 > 2\sigma(F^2)] = 0.056$	$w = 1/[\sigma^2(F_o^2) + (0.0563P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.130$	$(\Delta/\sigma)_{max} < 0.001$
$S = 0.91$	$\Delta\rho_{max} = 0.30$ e Å^{-3}
2001 reflections	$\Delta\rho_{min} = -0.21$ e Å^{-3}
163 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 848 Freidel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: −0.02 (13)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.37654 (9)	1.15071 (8)	1.1159 (3)	0.0662 (5)
N1	0.3911 (3)	0.7548 (3)	0.7777 (7)	0.0531 (10)
H1	0.4207	0.7130	0.8556	0.064*
O1	0.3321 (3)	0.3804 (2)	0.7531 (7)	0.0641 (10)
O2	0.3978 (2)	0.3355 (2)	0.4179 (7)	0.0639 (11)
C1	0.3476 (3)	0.7259 (3)	0.5713 (10)	0.0566 (14)
H1a	0.3718	0.7640	0.4482	0.068*
H1b	0.2818	0.7378	0.5815	0.068*
C2	0.3637 (3)	0.6218 (3)	0.5221 (9)	0.0474 (12)
C3	0.3375 (3)	0.5532 (3)	0.6795 (8)	0.0494 (14)
H3	0.3122	0.5707	0.8174	0.059*
C4	0.3501 (3)	0.4608 (3)	0.6250 (10)	0.0448 (11)
C5	0.3891 (3)	0.4328 (3)	0.4238 (10)	0.0476 (12)
C6	0.4156 (3)	0.4980 (3)	0.2673 (10)	0.0517 (13)
H6	0.4412	0.4796	0.1303	0.062*
C7	0.4028 (3)	0.5935 (3)	0.3221 (9)	0.0508 (13)
H7	0.4212	0.6400	0.2197	0.061*
C8	0.3467 (4)	0.3028 (4)	0.6030 (13)	0.0714 (16)
H8a	0.3799	0.2520	0.6792	0.086*
H8b	0.2879	0.2776	0.5526	0.086*
C9	0.3864 (3)	0.8482 (3)	0.8544 (9)	0.0451 (12)
C10	0.3341 (3)	0.9186 (3)	0.7439 (9)	0.0509 (13)
H10	0.3014	0.9032	0.6141	0.061*
C11	0.3314 (3)	1.0091 (3)	0.8266 (10)	0.0507 (13)
H11	0.2961	1.0547	0.7522	0.061*
C12	0.3785 (3)	1.0349 (3)	1.0138 (8)	0.0476 (13)
C13	0.4303 (3)	0.9661 (3)	1.1291 (10)	0.0476 (12)
H13	0.4620	0.9818	1.2601	0.057*
C14	0.4333 (3)	0.8749 (3)	1.0443 (8)	0.0478 (13)
H14	0.4686	0.8294	1.1190	0.057*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0658 (8)	0.0487 (7)	0.0839 (11)	0.0012 (6)	−0.0075 (9)	−0.0143 (8)
N1	0.066 (3)	0.038 (2)	0.056 (3)	0.0058 (19)	−0.009 (2)	0.001 (2)
O1	0.078 (3)	0.050 (2)	0.064 (2)	−0.003 (2)	0.016 (2)	0.010 (2)
O2	0.070 (3)	0.048 (2)	0.074 (3)	−0.0013 (16)	0.005 (2)	−0.006 (2)
C1	0.073 (3)	0.046 (3)	0.051 (4)	−0.002 (2)	−0.006 (3)	−0.003 (3)
C2	0.046 (3)	0.047 (3)	0.049 (3)	0.000 (2)	−0.006 (2)	−0.002 (3)
C3	0.051 (3)	0.045 (3)	0.052 (4)	0.004 (2)	0.004 (2)	−0.006 (2)
C4	0.042 (3)	0.048 (3)	0.045 (3)	−0.0022 (19)	0.003 (3)	−0.002 (3)
C5	0.043 (3)	0.038 (3)	0.062 (4)	−0.003 (2)	−0.006 (3)	−0.011 (3)
C6	0.052 (3)	0.059 (3)	0.045 (3)	−0.001 (2)	0.011 (2)	−0.005 (3)
C7	0.058 (3)	0.048 (3)	0.047 (3)	−0.007 (2)	0.005 (2)	0.001 (3)
C8	0.080 (4)	0.046 (3)	0.088 (5)	−0.006 (2)	0.013 (4)	0.000 (4)
C9	0.045 (3)	0.045 (3)	0.045 (3)	−0.004 (2)	−0.001 (2)	0.000 (2)
C10	0.053 (3)	0.046 (3)	0.054 (3)	0.003 (2)	−0.012 (2)	−0.005 (3)
C11	0.046 (3)	0.041 (3)	0.065 (4)	0.005 (2)	−0.009 (3)	0.002 (3)
C12	0.035 (3)	0.046 (3)	0.061 (4)	−0.005 (2)	0.000 (2)	−0.008 (3)
C13	0.047 (3)	0.052 (3)	0.043 (3)	−0.004 (2)	−0.004 (3)	−0.002 (3)
C14	0.050 (3)	0.044 (3)	0.049 (3)	0.001 (2)	−0.005 (2)	0.003 (2)

Geometric parameters (Å, °)

N1—C9	1.387 (6)	C5—C6	1.358 (7)
N1—C1	1.436 (6)	C6—C7	1.388 (6)
N1—H1	0.8600	C6—H6	0.9300
O1—C4	1.383 (6)	C7—H7	0.9300
O1—C8	1.420 (7)	C8—H8a	0.9700
O2—C5	1.368 (5)	C8—H8b	0.9700
O2—C8	1.402 (7)	C9—C14	1.368 (7)
Cl1—C12	1.730 (4)	C9—C10	1.406 (6)
C1—C2	1.504 (6)	C10—C11	1.359 (6)
C1—H1a	0.9700	C10—H10	0.9300
C1—H1b	0.9700	C11—C12	1.354 (7)
C2—C7	1.374 (7)	C11—H11	0.9300
C2—C3	1.393 (6)	C12—C13	1.400 (6)
C3—C4	1.346 (6)	C13—C14	1.373 (6)
C3—H3	0.9300	C13—H13	0.9300
C4—C5	1.379 (8)	C14—H14	0.9300
C9—N1—C1	121.7 (4)	C2—C7—H7	118.8
C9—N1—H1	119.2	C6—C7—H7	118.8
C1—N1—H1	119.2	O2—C8—O1	108.7 (4)
C4—O1—C8	104.5 (4)	O2—C8—H8a	110.0
C5—O2—C8	104.8 (4)	O1—C8—H8a	110.0
N1—C1—C2	111.7 (4)	O2—C8—H8b	110.0
N1—C1—H1a	109.3	O1—C8—H8b	110.0

C2—C1—H1b	109.3	H8a—C8—H8b	108.3
N1—C1—H1b	109.3	C14—C9—N1	120.3 (5)
C2—C1—H1b	109.3	C14—C9—C10	117.5 (5)
H1a—C1—H1b	107.9	N1—C9—C10	122.2 (5)
C7—C2—C3	119.6 (4)	C11—C10—C9	120.0 (5)
C7—C2—C1	120.7 (5)	C11—C10—H10	120.0
C3—C2—C1	119.7 (5)	C9—C10—H10	120.0
C4—C3—C2	117.7 (4)	C12—C11—C10	122.1 (5)
C4—C3—H3	121.2	C12—C11—H11	118.9
C2—C3—H3	121.2	C10—C11—H11	118.9
C3—C4—C5	122.5 (5)	C11—C12—C13	119.2 (4)
C3—C4—O1	128.7 (5)	C11—C12—Cl1	122.0 (4)
C5—C4—O1	108.8 (4)	C13—C12—Cl1	118.8 (4)
C6—C5—O2	128.7 (5)	C14—C13—C12	118.5 (4)
C6—C5—C4	121.2 (5)	C14—C13—H13	120.7
O2—C5—C4	110.1 (5)	C12—C13—H13	120.7
C5—C6—C7	116.7 (5)	C9—C14—C13	122.7 (5)
C5—C6—H6	121.7	C9—C14—H14	118.6
C7—C6—H6	121.7	C13—C14—H14	118.6
C2—C7—C6	122.4 (5)		
C9—N1—C1—C2	179.0 (4)	C1—C2—C7—C6	−177.6 (4)
N1—C1—C2—C7	−124.2 (5)	C5—C6—C7—C2	−1.2 (7)
N1—C1—C2—C3	56.8 (6)	C5—O2—C8—O1	−17.6 (6)
C7—C2—C3—C4	−1.4 (7)	C4—O1—C8—O2	17.3 (5)
C1—C2—C3—C4	177.6 (4)	C1—N1—C9—C14	−175.9 (5)
C2—C3—C4—C5	1.3 (7)	C1—N1—C9—C10	4.4 (7)
C2—C3—C4—O1	178.1 (4)	C14—C9—C10—C11	−0.1 (7)
C8—O1—C4—C3	172.6 (5)	N1—C9—C10—C11	179.6 (5)
C8—O1—C4—C5	−10.3 (5)	C9—C10—C11—C12	0.5 (8)
C8—O2—C5—C6	−171.0 (5)	C10—C11—C12—C13	−1.3 (8)
C8—O2—C5—C4	11.1 (5)	C10—C11—C12—Cl1	178.9 (4)
C3—C4—C5—C6	−1.2 (8)	O2^{i}—Cl1—C12—C11	167.7 (5)
O1—C4—C5—C6	−178.5 (4)	O2^{i}—Cl1—C12—C13	−12.2 (10)
C3—C4—C5—O2	176.9 (4)	C11—C12—C13—C14	1.6 (7)
O1—C4—C5—O2	−0.4 (5)	Cl1—C12—C13—C14	−178.5 (3)
O2—C5—C6—C7	−176.7 (4)	N1—C9—C14—C13	−179.3 (4)
C4—C5—C6—C7	1.0 (7)	C10—C9—C14—C13	0.5 (7)
C3—C2—C7—C6	1.4 (7)	C12—C13—C14—C9	−1.2 (7)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8a···Cl1^{ii}	0.97	2.96	3.741 (7)	139
C11—H11···Cl1^{iii}	0.93	2.95	3.819 (5)	155
C8—H8b···Cl1^{iv}	0.97	3.00	3.874 (5)	151
C6—H6···Cg1^{v}	0.93	2.80	3.50 (2)	133

C13—H13···Cg2^{vi}	0.93	2.70	3.51 (2)	146

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

Fig. 1

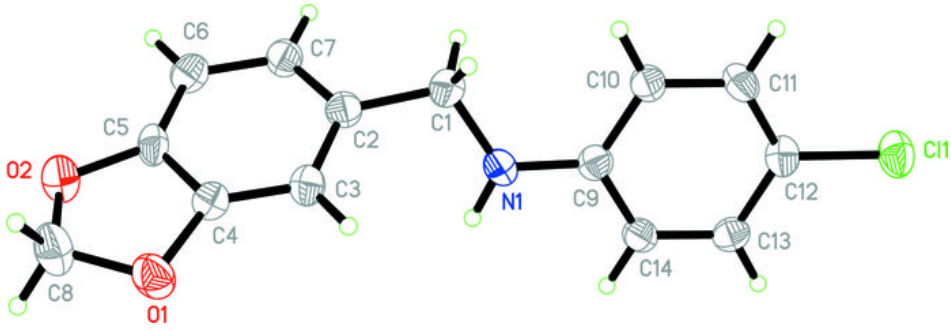

Fig. 2