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4-[Bis(2-chloroethyl)amino]benzaldehyde

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Keywords: crystal structure; aniline; benzaldehyde; C—H···O and C—H···Cl hydrogen bonding; C—H···π interactions; framework.

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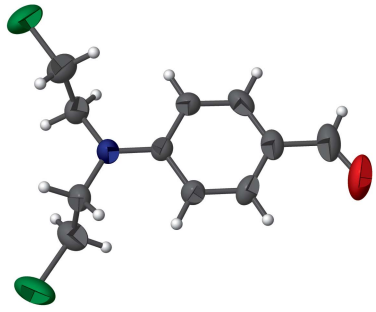
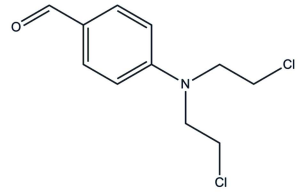
Structural data: full structural data are available from iucrdata.iucr.org

In the title compound, $C_{11}H_{13}Cl_2NO$, the chloroethyl amino groups are twisted with respect to the amino group, with N—C—C—Cl torsion angles of −177.4 (4) and 179.2 (3)°. The carbonyl group lies in the plane of the benzene ring to which it is attached; torsion angles C_{ar}—C_{ar}—C=O are 0.1 (8) and −178.2 (5)°. In the crystal, C—H···Cl and C—H···O hydrogen bonds link the molecules, forming sheets parallel to (20$\bar{1}$). The sheets are linked by C—H···π interactions, forming a three-dimensional framework.

3D view



Chemical scheme



Structure description

An heterocyclic skeleton containing an N atom is the basis of many essential pharmaceuticals and of many physiologically active natural products. Molecules containing heterocyclic substructures continue to be attractive targets for synthesis since they often exhibit diverse and important biological properties. For example, pyridine is used in the pharmaceutical industry as a raw material for various drugs, vitamins and fungicides, and as a solvent (Shinkai *et al.*, 2000; Jansen *et al.*, 2001; Amr *et al.*, 2006) while 2-amino-3-cyanopyridines have been identified as IKK-inhibitors (Murata *et al.*, 2003).

In the title compound (Fig. 1), torsion angle N1—C8—C9—Cl1 = −177.4 (4)°, indicates a (−)antiperiplanar conformation and torsion angle N1—C10—C11—Cl2 = 179.2 (3)°, indicates a (+)antiperiplanar conformation of the chloroethyl amino groups. Atom N1 deviates by −0.029 (3) Å from the benzene ring plane, while the carbonyl group (considering the plane C3/C7/O1) is inclined to the benzene ring by 1.7 (7)°.

In the crystal, C—H···Cl and C—H···O hydrogen bonds link the molecules, forming sheets parallel to (20$\bar{1}$) (Fig. 2 and Table 1). The sheets are linked by C—H···π interactions, forming a three-dimensional framework (Fig. 3 and Table 1).

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

Cg is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···Cl1^{i}	0.93	2.81	3.715 (5)	164
C8—H8*A*···O1^{ii}	0.97	2.51	3.367 (6)	147
C8—H8*B*···*Cg*^{iii}	0.97	2.73	3.482 (5)	134

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

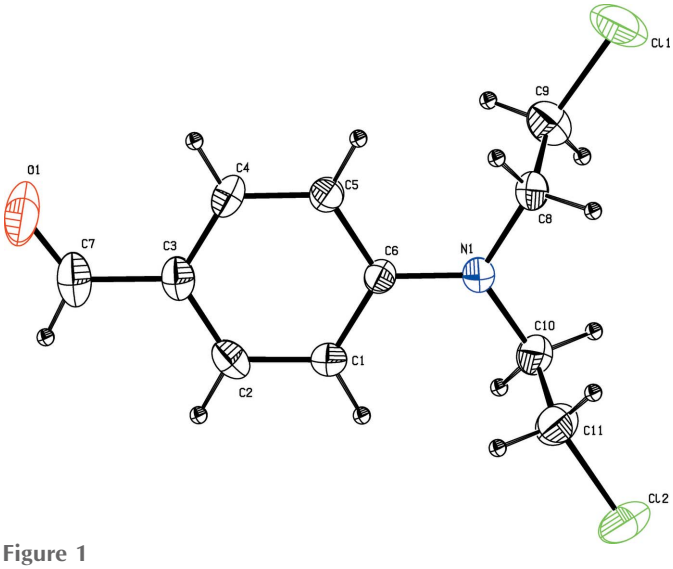


Figure 1
The molecular structure of the title compound, showing the atom labelling and 30% probability displacement ellipsoids.

Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{11}H_{13}Cl_2NO$
M_r	246.12
Crystal system, space group	Monoclinic, *Cc*
Temperature (K)	296
a, *b*, *c* (Å)	14.7725 (5), 9.3588 (3), 9.8079 (3)
β (°)	116.3080 (14)
V (Å^3)	1215.52 (7)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.51
Crystal size (mm)	0.35 × 0.22 × 0.10
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Bruker, 2014)
T_{min}, T_{max}	0.842, 0.951
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	4392, 2044, 1926
R_{int}	0.013
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.594
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, *S*	0.038, 0.103, 1.02
No. of reflections	2044
No. of parameters	136
No. of restraints	2
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.25, −0.29
Absolute structure	Flack *x* determined using 848 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	0.08 (2)

Computer programs: *APEX2* and *SAINT* (Bruker, 2014), *SHELXS97* and *SHELXTL* (Sheldrick 2008), *Mercury* (Macrae *et al.*, 2008), *SHELXL2014* (Sheldrick, 2015) and *PLATON* (Spek, 2009).

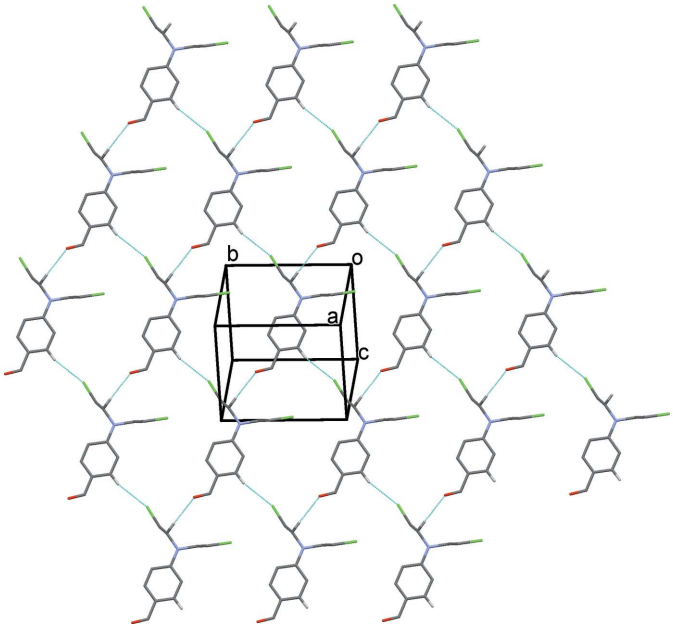


Figure 2
A view normal to plane $(20\bar{1})$ of the crystal packing of the title compound, with hydrogen bonds shown as dashed lines (see Table 1). For clarity, H atoms not involved in hydrogen bonding have been omitted.

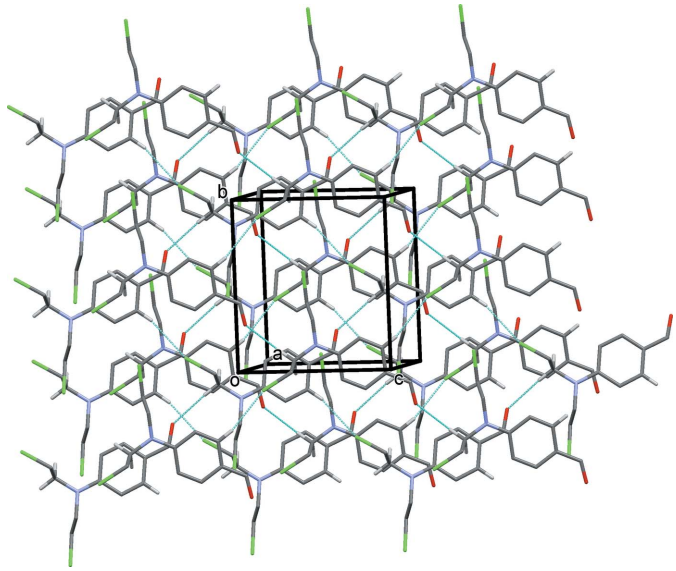


Figure 3
A view, almost along the *a* axis, of the crystal packing of the title compound, with hydrogen bonds shown as dashed lines (see Table 1). For clarity, H atoms not involved in the various intermolecular interactions have been omitted.

Synthesis and crystallization

A flask containing dimethyl formaldehyde (1 equiv) was placed in an ice bath and (1.1 equiv) of phosphorus oxychloride was added dropwise over 30 min with constant stirring at 273 K. Then *N*,*N*-bis(2-chloroethyl)aniline and 10 ml of dimethylformamide were added dropwise. After completion of the addition, the solution was stirred at 273 K for 15 min, then the reaction mixture was allowed to warm up to room temperature over a period of 3 h. After completion of the reaction, the mixture was poured into crushed ice, and a yellowish brown precipitate of the title compound formed. It was recrystallized from ethanol solution yielding violet block-like crystals.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2.

Acknowledgements

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full crystallographic data

IUCrData (2017). **2**, x162043 [https://doi.org/10.1107/S2414314616020435]

4-[Bis(2-chloroethyl)amino]benzaldehyde

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(I)

Crystal data

$C_{11}H_{13}Cl_2NO$
M_r = 246.12
Monoclinic, *Cc*
a = 14.7725 (5) Å
b = 9.3588 (3) Å
c = 9.8079 (3) Å
β = 116.3080 (14)°
V = 1215.52 (7) Å^3
Z = 4
F(000) = 512
D_x = 1.345 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2835 reflections
θ = 2.7–26.2°
μ = 0.51 mm^{-1}
T = 296 K
Block, violet
0.35 × 0.22 × 0.10 mm

Data collection

Bruker APEXII CCD diffractometer
φ and *ω* scans
Absorption correction: multi-scan (SADABS; Bruker, 2014)
T_{min} = 0.842, T_{max} = 0.951
4392 measured reflections
2044 independent reflections
1926 reflections with $I > 2\sigma(I)$
R_{int} = 0.013
θ_{max} = 25.0°, θ_{min} = 2.7°
h = −17→17
k = −11→11
l = −11→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.038
$wR(F^2)$ = 0.103
S = 1.02
2044 reflections
136 parameters
2 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
$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2 + 0.7925P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.25 e Å^{-3}
$\Delta\rho_{min}$ = −0.29 e Å^{-3}
Absolute structure: Flack *x* determined using 848 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: 0.08 (2)

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.6673 (3)	0.3236 (4)	0.2692 (4)	0.0449 (8)
H1	0.6576	0.2252	0.2634	0.054*
C2	0.7354 (3)	0.3839 (5)	0.4026 (4)	0.0514 (9)
H2	0.7704	0.3253	0.4863	0.062*
C3	0.7538 (3)	0.5297 (5)	0.4168 (4)	0.0499 (9)
C4	0.7002 (3)	0.6147 (4)	0.2902 (4)	0.0473 (9)
H4	0.7113	0.7128	0.2968	0.057*
C5	0.6309 (3)	0.5565 (4)	0.1552 (4)	0.0432 (8)
H5	0.5961	0.6159	0.0721	0.052*
C6	0.6119 (3)	0.4089 (4)	0.1410 (4)	0.0379 (7)
C7	0.8248 (4)	0.5912 (6)	0.5606 (5)	0.0729 (13)
H7	0.8581	0.5279	0.6404	0.087*
C8	0.4888 (3)	0.4367 (4)	−0.1290 (4)	0.0476 (8)
H8A	0.4717	0.3777	−0.2184	0.057*
H8B	0.5330	0.5127	−0.1306	0.057*
C9	0.3941 (4)	0.5004 (6)	−0.1334 (5)	0.0649 (11)
H9A	0.4110	0.5636	−0.0472	0.078*
H9B	0.3507	0.4252	−0.1279	0.078*
C10	0.5119 (3)	0.2010 (4)	−0.0036 (5)	0.0549 (9)
H10A	0.4420	0.1908	−0.0782	0.066*
H10B	0.5175	0.1689	0.0939	0.066*
C11	0.5779 (4)	0.1099 (5)	−0.0490 (6)	0.0673 (12)
H11A	0.6480	0.1203	0.0248	0.081*
H11B	0.5716	0.1403	−0.1474	0.081*
Cl1	0.33067 (14)	0.5973 (2)	−0.30549 (17)	0.1116 (7)
Cl2	0.54009 (14)	−0.07305 (13)	−0.0583 (2)	0.1026 (6)
N1	0.5415 (2)	0.3503 (3)	0.0072 (3)	0.0485 (8)
O1	0.8448 (3)	0.7153 (5)	0.5867 (4)	0.1042 (15)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0492 (19)	0.0381 (18)	0.0434 (18)	0.0023 (15)	0.0169 (15)	0.0023 (15)
C2	0.046 (2)	0.064 (3)	0.0378 (19)	0.0090 (17)	0.0129 (17)	0.0093 (16)
C3	0.0434 (19)	0.064 (2)	0.0401 (18)	−0.0042 (18)	0.0163 (15)	−0.0097 (18)
C4	0.054 (2)	0.044 (2)	0.049 (2)	−0.0157 (16)	0.0269 (18)	−0.0147 (17)
C5	0.050 (2)	0.0394 (19)	0.0380 (18)	−0.0018 (15)	0.0178 (17)	0.0007 (15)
C6	0.0400 (16)	0.0358 (17)	0.0372 (16)	−0.0025 (14)	0.0164 (14)	−0.0039 (13)
C7	0.061 (3)	0.096 (4)	0.049 (3)	−0.013 (3)	0.014 (2)	−0.020 (2)
C8	0.051 (2)	0.049 (2)	0.0374 (17)	−0.0015 (16)	0.0155 (16)	−0.0061 (15)
C9	0.057 (2)	0.079 (3)	0.057 (2)	0.011 (2)	0.0236 (19)	0.007 (2)
C10	0.048 (2)	0.048 (2)	0.059 (2)	−0.0081 (17)	0.0150 (17)	−0.0059 (18)
C11	0.065 (3)	0.053 (2)	0.078 (3)	−0.0001 (19)	0.027 (2)	−0.011 (2)
Cl1	0.1303 (13)	0.1108 (12)	0.0692 (8)	0.0702 (10)	0.0221 (8)	0.0210 (8)
Cl2	0.1109 (11)	0.0428 (6)	0.1303 (13)	0.0013 (6)	0.0317 (9)	−0.0175 (7)

N1	0.0513 (17)	0.0396 (16)	0.0401 (16)	−0.0029 (13)	0.0071 (14)	−0.0009 (13)
O1	0.108 (3)	0.109 (4)	0.072 (2)	−0.041 (3)	0.018 (2)	−0.040 (2)

Geometric parameters (Å, º)

C1—C2	1.370 (5)	C8—N1	1.457 (5)
C1—C6	1.405 (5)	C8—C9	1.504 (6)
C1—H1	0.9300	C8—H8A	0.9700
C2—C3	1.385 (6)	C8—H8B	0.9700
C2—H2	0.9300	C9—Cl1	1.774 (5)
C3—C4	1.389 (6)	C9—H9A	0.9700
C3—C7	1.453 (6)	C9—H9B	0.9700
C4—C5	1.377 (5)	C10—N1	1.454 (5)
C4—H4	0.9300	C10—C11	1.503 (6)
C5—C6	1.405 (5)	C10—H10A	0.9700
C5—H5	0.9300	C10—H10B	0.9700
C6—N1	1.377 (4)	C11—Cl2	1.791 (5)
C7—O1	1.197 (7)	C11—H11A	0.9700
C7—H7	0.9300	C11—H11B	0.9700
C2—C1—C6	120.7 (3)	N1—C8—H8B	109.4
C2—C1—H1	119.6	C9—C8—H8B	109.4
C6—C1—H1	119.6	H8A—C8—H8B	108.0
C1—C2—C3	122.0 (3)	C8—C9—Cl1	108.9 (3)
C1—C2—H2	119.0	C8—C9—H9A	109.9
C3—C2—H2	119.0	Cl1—C9—H9A	109.9
C2—C3—C4	117.8 (3)	C8—C9—H9B	109.9
C2—C3—C7	120.8 (4)	Cl1—C9—H9B	109.9
C4—C3—C7	121.4 (4)	H9A—C9—H9B	108.3
C5—C4—C3	121.3 (4)	N1—C10—C11	110.7 (3)
C5—C4—H4	119.4	N1—C10—H10A	109.5
C3—C4—H4	119.4	C11—C10—H10A	109.5
C4—C5—C6	120.9 (3)	N1—C10—H10B	109.5
C4—C5—H5	119.5	C11—C10—H10B	109.5
C6—C5—H5	119.5	H10A—C10—H10B	108.1
N1—C6—C5	121.3 (3)	C10—C11—Cl2	109.2 (3)
N1—C6—C1	121.4 (3)	C10—C11—H11A	109.8
C5—C6—C1	117.3 (3)	Cl2—C11—H11A	109.8
O1—C7—C3	126.6 (5)	C10—C11—H11B	109.8
O1—C7—H7	116.7	Cl2—C11—H11B	109.8
C3—C7—H7	116.7	H11A—C11—H11B	108.3
N1—C8—C9	111.0 (3)	C6—N1—C10	121.9 (3)
N1—C8—H8A	109.4	C6—N1—C8	121.6 (3)
C9—C8—H8A	109.4	C10—N1—C8	116.5 (3)
C6—C1—C2—C3	−0.9 (6)	C4—C3—C7—O1	0.1 (8)
C1—C2—C3—C4	0.2 (6)	N1—C8—C9—Cl1	−177.4 (3)
C1—C2—C3—C7	178.6 (4)	N1—C10—C11—Cl2	179.2 (3)

C2—C3—C4—C5	0.2 (6)	C5—C6—N1—C10	−172.2 (3)
C7—C3—C4—C5	−178.2 (4)	C1—C6—N1—C10	7.4 (5)
C3—C4—C5—C6	0.1 (6)	C5—C6—N1—C8	4.7 (5)
C4—C5—C6—N1	178.8 (3)	C1—C6—N1—C8	−175.8 (3)
C4—C5—C6—C1	−0.8 (5)	C11—C10—N1—C6	−90.4 (4)
C2—C1—C6—N1	−178.4 (3)	C11—C10—N1—C8	92.6 (4)
C2—C1—C6—C5	1.2 (5)	C9—C8—N1—C6	−88.8 (5)
C2—C3—C7—O1	−178.2 (5)	C9—C8—N1—C10	88.2 (4)

Hydrogen-bond geometry (Å, º)

Cg is the centroid of the C1–C6 ring.

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···Cl1^{i}	0.93	2.81	3.715 (5)	164
C8—H8*A*···O1^{ii}	0.97	2.51	3.367 (6)	147
C8—H8*B*···*Cg*^{iii}	0.97	2.73	3.482 (5)	134

Symmetry codes: (i) *x*+1/2, *y*−1/2, *z*+1; (ii) *x*−1/2, *y*−1/2, *z*−1; (iii) *x*, −*y*+1, *z*−1/2.