Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

2,4-Dichloro-6-(piperidin-1-ylmethyl)phenol

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Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.002 Å
R factor = 0.039
wR factor = 0.133
Data-to-parameter ratio = 17.4

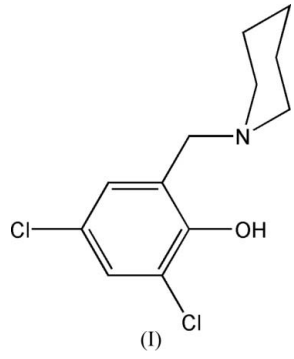
For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Received 26 September 2005
Accepted 10 October 2005
Online 15 October 2005

In the title compound, $C_{12}H_{15}Cl_2NO$, the piperidine ring adopts a chair conformation. An intramolecular O—H···N hydrogen bond is observed. The packing of the molecules in the crystal structure is stabilized by π–π interactions and Cl···Cl contacts.

Comment

The pharmacological properties of piperidine derivatives have led to many studies of the design and synthesis of these compounds (Hu *et al.*, 2002; Walker *et al.*, 2005). In addition, a number of these derivatives can act as complexing reagents with metal ions. We have previously studied the application of aminophenol derivatives as ion size recognition reagents (Hirayama *et al.*, 2001), and in this work, describe the crystal structure of 2,4-dichloro-6-(piperidin-1-ylmethyl)phenol, (I), which would be expected to act as an effective chelating reagent.



(I)

Compound (I) crystallizes in the monoclinic space group $P2_1/c$, with one molecule in the asymmetric unit. The bond lengths and angles observed in the piperidylmethyl group are all in the normal ranges and comparable with those of other related compounds (Deng *et al.*, 2001; Yuan *et al.*, 2004). The piperidine ring adopts the usual chair conformation. The torsion angles C1—C6—C7—N1 and C5—C6—C7—N1 are 44.20 (18) and −139.28 (14)°, respectively. There is an intramolecular O—H···N hydrogen bond (Table 2).

In the crystal structure, the shortest intermolecular C···C contact distance is 3.533 (2) Å for C4···C6^{i} [symmetry code: (i) $-x, -y, -z$]. In addition, weak intermolecular Cl···Cl contacts are observed. The contact distances Cl1···Cl1^{ii} and Cl1···Cl2^{iii} are 3.4596 (6) and 3.5734 (6) Å, respectively [symmetry code: (ii) $-x, -y, 1-z$; (iii) $x, -\frac{1}{2}-y, \frac{1}{2}+z$]. The packing of the molecules in the crystal structure is stabilized by π–π interactions and Cl···Cl contacts between dichlorobenzene groups.

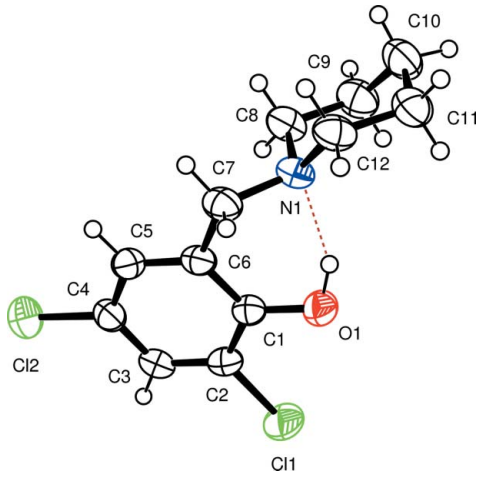


Figure 1
A view of the molecule of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. The dashed line indicates the O—H···N hydrogen bond.

Experimental

Compound (I) was prepared by the Mannich reaction. 2,4-Dichlorophenol (6.52 g, 40 mmol), piperidine (3.41 g, 40 mmol) and paraformaldehyde (1.20 g, 40 mmol) in methanol (80 ml) were refluxed for 6 h. The mixture was cooled to room temperature, then the solvent was evaporated under vacuum. The resulting oil was extracted with chloroform and evaporated to yield a solid. The product was recrystallized from methanol to give colourless crystals suitable for X-ray analysis. Yield 52.6%; m.p. 335.0–335.4 K. Analysis calculated for $C_{12}H_{15}Cl_2NO$: C 55.40, H 5.81, N 5.38%; found: C 55.49, H 5.87, N 5.37%. ^{1}H NMR ($CDCl_3$, p.p.m., 400 MHz): 1.46–1.69 (*m*, 6H, CH_2), 2.53 (*brs*, 4H, CH_2), 3.65 (*s*, 2H, CH_2), 6.85 (*d*, J = 2.5 Hz, 1H, ArH), 7.24 (*d*, J = 2.5 Hz, 1H, ArH), 10.2 (*brs*, 1H, OH).

Crystal data

$C_{12}H_{15}Cl_2NO$
M_r = 260.15
Monoclinic, $P2_1/c$
a = 9.571 (4) Å
b = 11.794 (4) Å
c = 11.345 (5) Å
β = 95.89 (3)°
V = 1273.9 (9) Å^3
Z = 4
D_x = 1.356 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 15.5–17.1°
μ = 0.49 mm^{-1}
T = 298.1 K
Prism, colourless
0.50 × 0.20 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: none
3619 measured reflections
2937 independent reflections
2773 reflections with $F^2 > 2\sigma(F^2)$
R_{int} = 0.026
θ_{max} = 27.5°
$h = -12 \rightarrow 12$
$k = -15 \rightarrow 0$
$l = -8 \rightarrow 14$
3 standard reflections
every 150 reflections
intensity decay: 2.4%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.133
S = 1.01
2776 reflections
160 parameters
H-atom parameters constrained
$w = 1/[0.0034F_o^2 + 1\sigma(F_o^2)]/(4F_o^2)$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

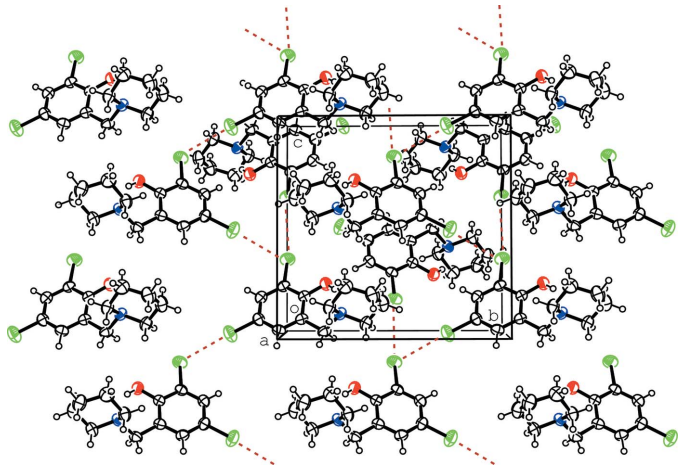


Figure 2
The packing of the molecules of (I), viewed down the *a* axis, with Cl···Cl contacts shown as dashed lines.

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.3559 (19)	N1—C8	1.466 (2)
N1—C7	1.474 (2)	N1—C12	1.472 (2)
C2···C5^{i}	3.609 (2)	Cl1···Cl1^{ii}	3.4596 (17)
C4···C6^{i}	3.533 (2)	Cl1···Cl2^{iii}	3.5734 (17)
C7—N1—C8	110.88 (12)	N1—C7—C6	111.09 (12)
C7—N1—C12	111.67 (12)	N1—C8—C9	111.12 (14)
C8—N1—C12	110.63 (12)	N1—C12—C11	109.91 (14)

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

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···N1	0.86	1.87	2.6456 (18)	149

The H atom of the hydroxyl group was found in a difference Fourier map. The other H atoms were placed in idealized positions with C—H = 0.95 Å. All the H atoms were refined as riding, with U_{iso}(H) = 1.2U_{eq}(C).

Data collection: *WinAFC* (Rigaku/MSC, 2004); cell refinement: *WinAFC*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *CRYSTALS* (Betteridge *et al.*, 2003); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure*.

This study was supported financially in part by Grants-in-Aid for Scientific Research (No.16750061) from the Japan Society for the Promotion of Science.

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supporting information

Acta Cryst. (2005). E**61**, o3706–o3708 [https://doi.org/10.1107/S1600536805032290]

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$V = 1273.9$ (9) Å^3
$Z = 4$
$F(000) = 544.00$
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Cell parameters from 25 reflections
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$S = 1.01$
2776 reflections
160 parameters
H-atom parameters constrained
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$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.52$ e Å^{-3}

Special details

Geometry. ENTER SPECIAL DETAILS OF THE MOLECULAR GEOMETRY

Refinement. Refinement using reflections with $F^2 > 2.0\ \sigma(F^2)$. The weighted *R*-factor (*wR*) and goodness of fit (*S*) are based on F^2. *R*-factor (gt) are based on *F*. The threshold expression of $F^2 > 2.0\ \sigma(F^2)$ is used only for calculating *R*-factor (gt).

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

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.00145 (5)	0.00105 (4)	0.34766 (4)	0.06163 (16)
Cl2	0.15815 (5)	−0.25596 (4)	−0.00840 (5)	0.06854 (18)

O1	0.13660 (12)	0.18416 (10)	0.23010 (10)	0.0490 (3)
N1	0.32577 (12)	0.25542 (11)	0.09257 (12)	0.0405 (3)
C1	0.13976 (13)	0.08428 (12)	0.17126 (12)	0.0365 (3)
C2	0.08247 (14)	−0.01252 (13)	0.21869 (14)	0.0386 (3)
C3	0.08777 (14)	−0.11769 (13)	0.16480 (13)	0.0413 (4)
C4	0.14981 (16)	−0.12490 (13)	0.06086 (14)	0.0430 (4)
C5	0.20396 (16)	−0.02974 (14)	0.00985 (13)	0.0426 (4)
C6	0.19853 (14)	0.07499 (13)	0.06342 (12)	0.0380 (3)
C7	0.24692 (17)	0.18072 (14)	0.00526 (12)	0.0451 (4)
C8	0.46615 (17)	0.20956 (14)	0.12827 (17)	0.0492 (4)
C9	0.5435 (2)	0.28102 (19)	0.22575 (18)	0.0598 (5)
C10	0.5516 (2)	0.40308 (18)	0.1869 (2)	0.0624 (5)
C11	0.40624 (18)	0.44785 (16)	0.1433 (2)	0.0597 (5)
C12	0.33535 (18)	0.37185 (14)	0.04735 (17)	0.0495 (4)
H1	0.2023	0.2252	0.2061	0.060*
H2	0.0502	−0.1831	0.1989	0.049*
H3	0.2455	−0.0372	−0.0623	0.051*
H4	0.1673	0.2207	−0.0302	0.054*
H5	0.3053	0.1599	−0.0541	0.054*
H6	0.4572	0.1339	0.1552	0.058*
H7	0.5188	0.2100	0.0617	0.059*
H8	0.4929	0.2777	0.2934	0.071*
H9	0.6355	0.2519	0.2454	0.071*
H10	0.5908	0.4481	0.2514	0.075*
H11	0.6098	0.4075	0.1240	0.074*
H12	0.3505	0.4484	0.2080	0.072*
H13	0.4134	0.5227	0.1137	0.072*
H14	0.3896	0.3719	−0.0182	0.060*
H15	0.2436	0.3991	0.0228	0.059*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0704 (3)	0.0678 (3)	0.0514 (3)	−0.0096 (2)	0.0291 (2)	0.0034 (2)
Cl2	0.0754 (3)	0.0506 (3)	0.0815 (4)	−0.0108 (2)	0.0169 (3)	−0.0219 (2)
O1	0.0556 (6)	0.0418 (6)	0.0522 (6)	−0.0045 (5)	0.0185 (5)	−0.0036 (5)
N1	0.0360 (6)	0.0403 (7)	0.0448 (7)	−0.0068 (5)	0.0027 (5)	0.0067 (5)
C1	0.0324 (6)	0.0399 (8)	0.0372 (7)	−0.0003 (5)	0.0035 (5)	0.0021 (6)
C2	0.0330 (7)	0.0458 (8)	0.0378 (7)	−0.0012 (5)	0.0069 (5)	0.0058 (6)
C3	0.0329 (7)	0.0424 (8)	0.0479 (8)	−0.0076 (6)	0.0012 (6)	0.0049 (6)
C4	0.0373 (7)	0.0425 (8)	0.0485 (9)	−0.0048 (6)	0.0013 (6)	−0.0056 (7)
C5	0.0372 (7)	0.0530 (9)	0.0383 (8)	−0.0058 (7)	0.0071 (6)	−0.0042 (7)
C6	0.0318 (6)	0.0460 (8)	0.0358 (7)	−0.0059 (5)	0.0022 (5)	0.0037 (6)
C7	0.0446 (8)	0.0526 (9)	0.0380 (8)	−0.0104 (7)	0.0032 (6)	0.0070 (7)
C8	0.0406 (8)	0.0426 (9)	0.0633 (11)	−0.0031 (7)	0.0004 (7)	0.0057 (8)
C9	0.0481 (9)	0.0676 (12)	0.0612 (11)	−0.0068 (8)	−0.0061 (8)	−0.0005 (9)
C10	0.0526 (10)	0.0561 (11)	0.0772 (13)	−0.0122 (8)	0.0008 (9)	−0.0112 (9)
C11	0.0570 (10)	0.0440 (10)	0.0794 (13)	−0.0071 (8)	0.0137 (9)	−0.0042 (9)

C12	0.0459 (8)	0.0433 (9)	0.0595 (10)	−0.0035 (7)	0.0074 (7)	0.0114 (8)

Geometric parameters (Å, º)

Cl1—C2	1.7323 (17)	C11—C12	1.516 (2)
Cl2—C4	1.7396 (17)	O1—H1	0.860
O1—C1	1.3559 (19)	C3—H2	0.950
N1—C7	1.474 (2)	C5—H3	0.950
N1—C8	1.466 (2)	C7—H4	0.950
N1—C12	1.472 (2)	C7—H5	0.950
C1—C2	1.398 (2)	C8—H6	0.950
C1—C6	1.402 (2)	C8—H7	0.950
C2—C3	1.386 (2)	C9—H8	0.950
C3—C4	1.376 (2)	C9—H9	0.950
C4—C5	1.387 (2)	C10—H10	0.950
C5—C6	1.380 (2)	C10—H11	0.950
C6—C7	1.506 (2)	C11—H12	0.950
C8—C9	1.521 (2)	C11—H13	0.950
C9—C10	1.510 (3)	C12—H14	0.950
C10—C11	1.523 (2)	C12—H15	0.950
C2···C5^{i}	3.609 (2)	Cl1···Cl1^{ii}	3.4596 (17)
C4···C6^{i}	3.533 (2)	Cl1···Cl2^{iii}	3.5734 (17)
C5···C2^{i}	3.609 (2)	Cl2···Cl1^{iv}	3.5734 (17)
C6···C4^{i}	3.533 (2)		
C7—N1—C8	110.88 (12)	N1—C7—H5	109.4
C7—N1—C12	111.67 (12)	C6—C7—H4	109.1
C8—N1—C12	110.63 (12)	C6—C7—H5	109.0
O1—C1—C2	119.38 (13)	H4—C7—H5	109.5
O1—C1—C6	121.91 (13)	N1—C8—H6	109.0
C2—C1—C6	118.71 (14)	N1—C8—H7	108.9
Cl1—C2—C1	118.49 (12)	C9—C8—H6	109.9
Cl1—C2—C3	119.67 (12)	C9—C8—H7	108.5
C1—C2—C3	121.84 (15)	H6—C8—H7	109.5
C2—C3—C4	118.15 (15)	C8—C9—H8	108.3
Cl2—C4—C3	119.06 (12)	C8—C9—H9	109.9
Cl2—C4—C5	119.61 (13)	C10—C9—H8	108.7
C3—C4—C5	121.33 (15)	C10—C9—H9	109.8
C4—C5—C6	120.52 (15)	H8—C9—H9	109.5
C1—C6—C5	119.39 (14)	C9—C10—H10	109.6
C1—C6—C7	119.11 (14)	C9—C10—H11	108.9
C5—C6—C7	121.41 (14)	C11—C10—H10	109.3
N1—C7—C6	111.09 (12)	C11—C10—H11	108.9
N1—C8—C9	111.12 (14)	H10—C10—H11	109.5
C8—C9—C10	110.59 (16)	C10—C11—H12	108.6
C9—C10—C11	110.66 (15)	C10—C11—H13	109.9
C10—C11—C12	110.78 (15)	C12—C11—H12	108.3

N1—C12—C11	109.91 (14)	C12—C11—H13	109.8
C1—O1—H1	106.2	H12—C11—H13	109.5
C2—C3—H2	121.00	N1—C12—H14	109.4
C4—C3—H2	121.00	N1—C12—H15	109.2
C4—C5—H3	119.00	C11—C12—H14	108.8
C6—C5—H3	120.00	C11—C12—H15	110.0
N1—C7—H4	108.7	H14—C12—H15	109.5

C7—N1—C8—C9	−175.31 (14)	Cl1—C2—C3—C4	178.40 (11)
C8—N1—C7—C6	73.99 (16)	C1—C2—C3—C4	−1.0 (2)
C7—N1—C12—C11	175.25 (13)	C2—C3—C4—Cl2	179.87 (11)
C12—N1—C7—C6	−162.14 (13)	C2—C3—C4—C5	−0.9 (2)
C8—N1—C12—C11	−60.74 (18)	Cl2—C4—C5—C6	−179.93 (11)
C12—N1—C8—C9	60.22 (19)	C3—C4—C5—C6	0.9 (2)
O1—C1—C2—Cl1	3.24 (18)	C4—C5—C6—C1	1.1 (2)
O1—C1—C2—C3	−177.40 (13)	C4—C5—C6—C7	−175.45 (13)
O1—C1—C6—C5	177.40 (13)	C1—C6—C7—N1	44.20 (18)
O1—C1—C6—C7	−6.0 (2)	C5—C6—C7—N1	−139.28 (14)
C2—C1—C6—C5	−2.9 (2)	N1—C8—C9—C10	−56.2 (2)
C2—C1—C6—C7	173.73 (12)	C8—C9—C10—C11	52.9 (2)
C6—C1—C2—Cl1	−176.51 (10)	C9—C10—C11—C12	−54.2 (2)
C6—C1—C2—C3	2.8 (2)	C10—C11—C12—N1	57.7 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
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