

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

## 3,6-Dichlorocatechol

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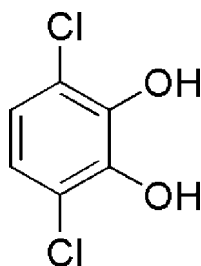
Received 24 April 2008; accepted 4 August 2008

Key indicators: single-crystal X-ray study;  $T = 296$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  $R$  factor = 0.031;  $wR$  factor = 0.119; data-to-parameter ratio = 13.4.

The title compound,  $\text{C}_6\text{H}_4\text{Cl}_2\text{O}_2$ , exhibits a two-dimensional supramolecular hydrogen-bonded network and forms a three-dimensional network supramolecular structure *via* hydrogen bonds and  $\pi$ - $\pi$  stacking of benzene rings. The  $\pi$ - $\pi$  interactions are between the benzene rings of centrosymmetrically related molecules, with centroid-centroid distances of 3.7676 (13) and 3.7107 (13) Å.

## Related literature

For related literature, see: Haigler *et al.* (1988); Kirsh & Stan (1994); Nishizawa & Satoh (1975*a,b*); Sander *et al.* (1991); Schraa *et al.* (1986); Spiess *et al.* (1995); Spain *et al.* (1989).



## Experimental

## Crystal data

$\text{C}_6\text{H}_4\text{Cl}_2\text{O}_2$   
 $M_r = 178.99$   
 Monoclinic,  $P2_1/c$   
 $a = 7.4411$  (7) Å  
 $b = 10.1283$  (10) Å  
 $c = 10.6448$  (8) Å  
 $\beta = 119.903$  (5)°

$V = 695.45$  (11) Å<sup>3</sup>  
 $Z = 4$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.86$  mm<sup>-1</sup>  
 $T = 296$  K  
 $0.36 \times 0.17 \times 0.15$  mm

## Data collection

Bruker SMART CCD area-detector diffractometer  
 Absorption correction: multi-scan (SADABS; Bruker, 1997)  
 $T_{\min} = 0.748$ ,  $T_{\max} = 0.882$   
 3531 measured reflections  
 1243 independent reflections  
 1117 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.017$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.030$   
 $wR(F^2) = 0.118$   
 $S = 1.01$   
 1243 reflections  
 93 parameters  
 H-atom parameters constrained  
 $\Delta\rho_{\max} = 0.18$  e Å<sup>-3</sup>  
 $\Delta\rho_{\min} = -0.34$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{O1}-\text{H1}\cdots\text{O2}$	0.82	2.19	2.6391 (17)	115
$\text{O1}-\text{H1}\cdots\text{Cl1}^i$	0.82	2.76	3.3980 (16)	137
$\text{O2}-\text{H2}\cdots\text{Cl2}$	0.82	2.61	3.0597 (13)	116
$\text{O2}-\text{H2}\cdots\text{O1}^{\text{ii}}$	0.82	2.13	2.8969 (19)	155

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

Data collection: SMART (Bruker, 1997); cell refinement: SMART; data reduction: SAINT (Bruker, 1997); program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: SHELXTL (Sheldrick, 2008); software used to prepare material for publication: SHELXTL.

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (20621091). The authors are also grateful to Professor Yu Tang, Lanzhou University, for her helpful guidance in the preparation of the manuscript.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2078).

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**supplementary materials**

*Acta Cryst.* (2008). E64, o1746 [ doi:10.1107/S1600536808025014 ]

### 3,6-Dichlorocatechol

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#### Comment

The compound 3,6-dichlorocatechol, (I), was a common metabolite in the microbial aerobic degradation of 1,4-dichlorobenzene. Because 1,4-dichlorobenzene was too stable to be degraded by photochemistry, biodegradation of this compound was an only way that it was eliminated from environment. 3,6-Dichlorocatechol has been reported to be an important intermediate in this process (Haigler *et al.*, 1988; Schraa *et al.*, 1986; Spain *et al.*, 1989; Sander *et al.*, 1991; Spiess *et al.*, 1995). So the title compound (I) could be used to optimize the biodegradation process of 1,4-dichlorobenzene (Kirsh *et al.*, 1994). It would be of great important significance in the protection of our surrounding and public health. Herein, we report the synthesis and structure of this compound, namely 3,6-dichlorocatechol. As shown in Fig.1, there are two hydroxyl groups in the phenyl ring. In the formation of these hydrogen bonds, one acts as donor, the other as acceptor. A two-dimensional supramolecular network was formed by O—H···Cl and O—H···O intermolecular hydrogen bonds (Table 1) [Symmetry codes (i):  $-x+2, y-1/2, -z+3/2$ ; (ii):  $x, -y+3/2, z-1/2$ ], and there are also weak  $\pi$ - $\pi$  interactions between the centrosymmetrically related phenyl rings at  $(x, y, z)$  and  $(-x, -y, -z+1)$ ,  $(-x+1, -y, -z+1)$  with a centroid-to-centroid distance of 3.7676 (13)Å and 3.7107 (13)Å, respectively (Fig. 2).

#### Experimental

3,6-Trichloro-2-hydroxycyclohex-2-en-1-one (26 g, 0.12 mol) was treated with  $\text{Li}_2\text{CO}_3$  (13.4 g, 0.18 mol) in DMF to give the title compound (I). (18.4 g) in 86% yield (Nishizawa & Satoh, 1975*a,b*). m. p. 108–109°C;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 300 MHz)  $\delta$ : 5.79 (s, 2H), 6.86 (d,  $J = 2.4$  Hz, 2H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 75 MHz)  $\delta$ : 118.7, 120.8, 140.6; MS (ESI)  $m/z$  (%): 178 ( $M^+$ , 95), 180 (49), 182 (8).

#### Refinement

All H atoms were placed in geometrically idealized positions, with C—H = 0.93 Å and O—H = 0.82 Å, and constrained to ride on their respective parent atoms, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  and  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ .

#### Figures

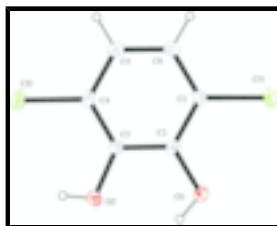


Fig. 1. A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

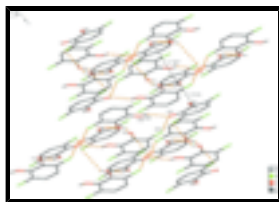


Fig. 2. The three-dimensional structure by molecular packing, showing the intermolecular hydrogen bonds as yellow dashed lines [Symmetry codes: (i)  $-x+2, y-1/2, -z+3/2$ ; (ii)  $x, -y+3/2, z-1/2$ ], and  $\pi$ - $\pi$  interactions as black dashed lines.

## 3,6-dichlorobenzene-1,2-diol

### Crystal data

$C_6H_4Cl_2O_2$	$F_{000} = 360$
$M_r = 178.99$	$D_x = 1.710 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
Hall symbol: $-P 2ybc$	$\lambda = 0.71073 \text{ \AA}$
$a = 7.4411 (7) \text{ \AA}$	Cell parameters from 2193 reflections
$b = 10.1283 (10) \text{ \AA}$	$\theta = 2.9\text{--}26.4^\circ$
$c = 10.6448 (8) \text{ \AA}$	$\mu = 0.86 \text{ mm}^{-1}$
$\beta = 119.903 (5)^\circ$	$T = 296 \text{ K}$
$V = 695.45 (11) \text{ \AA}^3$	Block, colorless
$Z = 4$	$0.36 \times 0.17 \times 0.15 \text{ mm}$

### Data collection

Bruker SMART CCD area-detector diffractometer	1243 independent reflections
Radiation source: fine-focus sealed tube	1117 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.017$
$T = 296 \text{ K}$	$\theta_{\text{max}} = 25.2^\circ$
$\varphi$ and $\omega$ scans	$\theta_{\text{min}} = 3.0^\circ$
Absorption correction: multi-scan (SADABS; Bruker, 1997)	$h = -8 \rightarrow 8$
$T_{\text{min}} = 0.748, T_{\text{max}} = 0.882$	$k = -9 \rightarrow 12$
3531 measured reflections	$l = -12 \rightarrow 12$

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.030$	H-atom parameters constrained
$wR(F^2) = 0.118$	$w = 1/[\sigma^2(F_o^2) + (0.01P)^2]$
$S = 1.01$	where $P = (F_o^2 + 2F_c^2)/3$
1243 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
93 parameters	$\Delta\rho_{\text{max}} = 0.18 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.34 \text{ e \AA}^{-3}$

Primary atom site location: structure-invariant direct methods Extinction correction: none

*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

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

	$x$	$y$	$z$	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	0.84969 (7)	1.04043 (6)	0.81747 (4)	0.0483 (3)
Cl2	0.64593 (7)	0.99288 (7)	0.17713 (4)	0.0529 (3)
O1	0.8451 (2)	0.79625 (12)	0.66807 (12)	0.0487 (4)
H1	0.8578	0.7331	0.6249	0.073*
O2	0.7560 (2)	0.76889 (12)	0.39645 (12)	0.0490 (4)
H2	0.7570	0.7708	0.3198	0.074*
C1	0.7904 (3)	1.02895 (16)	0.63843 (18)	0.0344 (4)
C2	0.7954 (2)	0.90633 (16)	0.58289 (15)	0.0335 (4)
C3	0.7515 (2)	0.89485 (16)	0.44037 (17)	0.0330 (4)
C4	0.7012 (3)	1.00694 (18)	0.35485 (17)	0.0356 (4)
C5	0.6955 (3)	1.13066 (18)	0.41095 (17)	0.0433 (4)
H5	0.6619	1.2056	0.3530	0.052*
C6	0.7397 (3)	1.14090 (18)	0.55181 (19)	0.0415 (4)
H6	0.7359	1.2230	0.5896	0.050*

*Atomic displacement parameters ( $\text{\AA}^2$ )*

$U^{11}$                        $U^{22}$                        $U^{33}$                        $U^{12}$                        $U^{13}$                        $U^{23}$

## supplementary materials

Cl1	0.0647 (4)	0.0507 (4)	0.0356 (4)	-0.00327 (18)	0.0296 (3)	-0.00797 (16)
Cl2	0.0633 (4)	0.0666 (5)	0.0307 (4)	0.0071 (2)	0.0248 (3)	0.00907 (18)
O1	0.0832 (10)	0.0343 (7)	0.0401 (7)	0.0122 (6)	0.0393 (7)	0.0089 (5)
O2	0.0835 (10)	0.0351 (7)	0.0414 (7)	-0.0021 (6)	0.0409 (7)	-0.0039 (5)
C1	0.0382 (9)	0.0370 (9)	0.0307 (8)	-0.0029 (6)	0.0192 (7)	-0.0042 (6)
C2	0.0394 (8)	0.0323 (9)	0.0317 (8)	0.0010 (7)	0.0199 (7)	0.0053 (6)
C3	0.0373 (8)	0.0334 (9)	0.0298 (7)	-0.0025 (6)	0.0177 (6)	-0.0020 (6)
C4	0.0360 (9)	0.0445 (10)	0.0276 (8)	-0.0007 (7)	0.0169 (7)	0.0042 (7)
C5	0.0488 (10)	0.0354 (9)	0.0450 (9)	0.0037 (7)	0.0230 (8)	0.0100 (7)
C6	0.0508 (10)	0.0309 (9)	0.0429 (8)	0.0009 (7)	0.0234 (7)	-0.0003 (7)

### Geometric parameters (Å, °)

O1—H1	0.8200	C3—O2	1.365 (2)
O2—H2	0.8200	C3—C4	1.385 (2)
C1—C2	1.384 (2)	C4—C5	1.398 (2)
C1—C6	1.390 (2)	C4—Cl2	1.7299 (16)
C1—Cl1	1.7326 (17)	C5—C6	1.369 (3)
C2—O1	1.3666 (18)	C5—H5	0.9300
C2—C3	1.388 (2)	C6—H6	0.9300
O1—C2—C1	120.31 (13)	C3—C4—C5	120.65 (15)
O1—C2—C3	119.68 (14)	C3—C4—Cl2	119.36 (13)
O2—C3—C4	125.85 (14)	C4—C3—C2	119.27 (15)
O2—C3—C2	114.84 (14)	C4—C5—H5	120.2
C1—C2—C3	120.02 (14)	C5—C4—Cl2	119.98 (13)
C1—C6—H6	119.9	C5—C6—C1	120.16 (16)
C2—O1—H1	109.5	C5—C6—H6	119.9
C2—C1—C6	120.32 (15)	C6—C5—C4	119.59 (15)
C2—C1—Cl1	118.94 (12)	C6—C1—Cl1	120.75 (13)
C3—O2—H2	109.5	C6—C5—H5	120.2
Cl1—C1—C2—O1	0.4 (2)	C1—C2—C3—C4	-0.5 (2)
Cl1—C1—C2—C3	-179.06 (12)	C2—C1—C6—C5	-0.3 (3)
Cl1—C1—C6—C5	179.23 (13)	C2—C3—C4—C5	0.3 (2)
Cl2—C4—C5—C6	-179.92 (13)	C2—C3—C4—Cl2	-179.90 (12)
O1—C2—C3—O2	2.1 (2)	C3—C4—C5—C6	-0.1 (3)
O1—C2—C3—C4	179.98 (15)	C4—C5—C6—C1	0.2 (3)
O2—C3—C4—C5	177.97 (16)	C6—C1—C2—O1	-179.97 (15)
O2—C3—C4—Cl2	-2.3 (2)	C6—C1—C2—C3	0.5 (2)
C1—C2—C3—O2	-178.41 (15)		

### Hydrogen-bond geometry (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H1 $\cdots$ O2	0.82	2.19	2.6391 (17)	115
O1—H1 $\cdots$ Cl1 <sup>i</sup>	0.82	2.76	3.3980 (16)	137
O2—H2 $\cdots$ Cl2	0.82	2.61	3.0597 (13)	116
O2—H2 $\cdots$ O1 <sup>ii</sup>	0.82	2.13	2.8969 (19)	155

Symmetry codes: (i)  $-x+2, y-1/2, -z+3/2$ ; (ii)  $x, -y+3/2, z-1/2$ .

Fig. 1

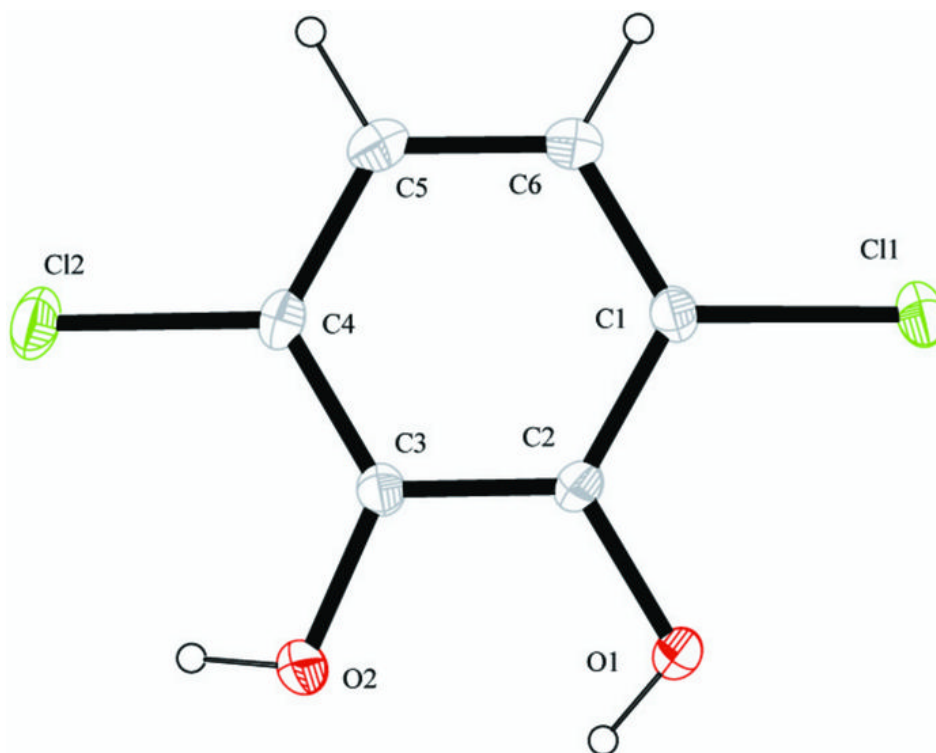


Fig. 2

