organic compounds

3,6-Dichlorocatechol

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The title compound, $C_6H_4Cl_2O_2$, exhibits a two-dimensional supramolecular hydrogen-bonded network and forms a three-dimensional network supramolecular structure *via* hydrogen bonds and π–π stacking of benzene rings. The π–π 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).
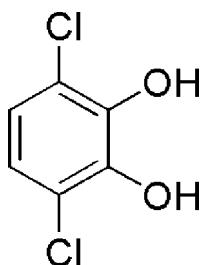
Experimental

Crystal data

$C_6H_4Cl_2O_2$
$M_r = 178.99$
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^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.86$ mm^{-1}
$T = 296$ 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 $I > 2\sigma(I)$
$R_{int} = 0.017$

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^{-3}
$\Delta\rho_{min} = -0.34$ e Å^{-3}

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$O2	0.82	2.19	2.6391 (17)	115
O1—H1$\cdots$Cl1^i	0.82	2.76	3.3980 (16)	137
O2—H2$\cdots$Cl2	0.82	2.61	3.0597 (13)	116
O2—H2$\cdots$O1^{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*.

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supporting information

3,6-Dichlorocatechol

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S1. Comment

The compound 3,6-dichlorocatechol, (I), was a common metabolite in the microbial aerobic degradation of 1,4-dichloro-benzene. 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 enviroment. 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-dichloro-benzene (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 π-π 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).

S2. Experimental

3,6,6-Tricholor-2-hydroxycyclohex-2-en-1-one (26 g, 0.12 mol) was treated with Li_2CO_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}H NMR (CDCl$_3$, 300 MHz) δ: 5.79 (s, 2H), 6.86 (d, J = 2.4 Hz, 2H); ^{13}C NMR (CDCl$_3$, 75 MHz) δ: 118.7, 120.8, 140.6; MS (ESI) m/*z* (%): 178 (*M*+, 95), 180 (49), 182 (8).

S3. 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 $U_{iso}(H) = 1.2U_{eq}(C)$ and $U_{iso}(H) = 1.5U_{eq}(O)$.
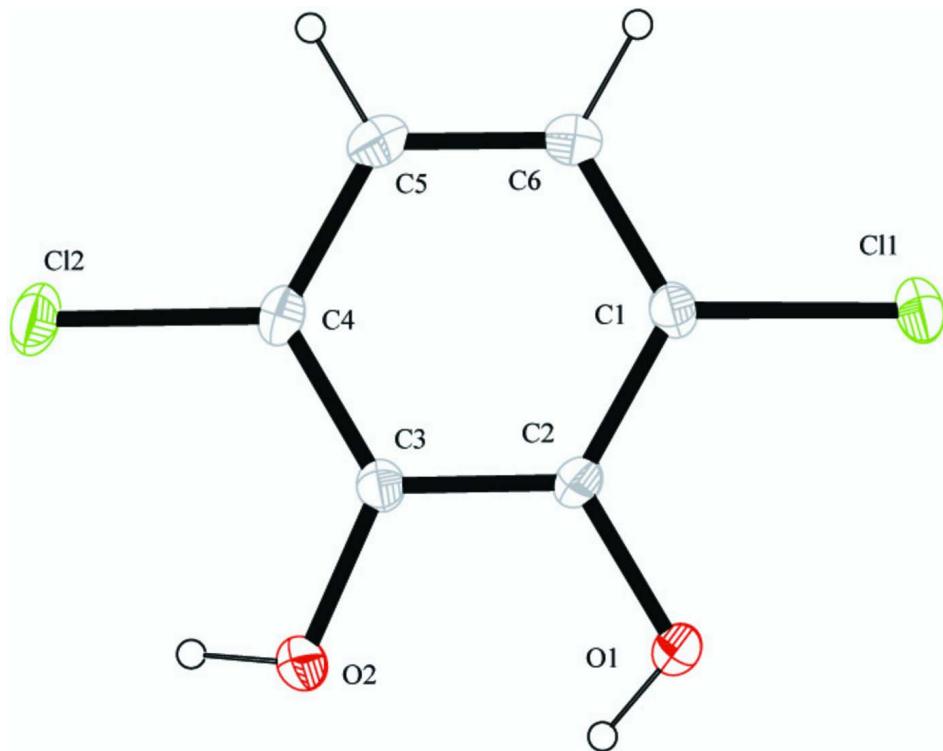
Figure 1

A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.
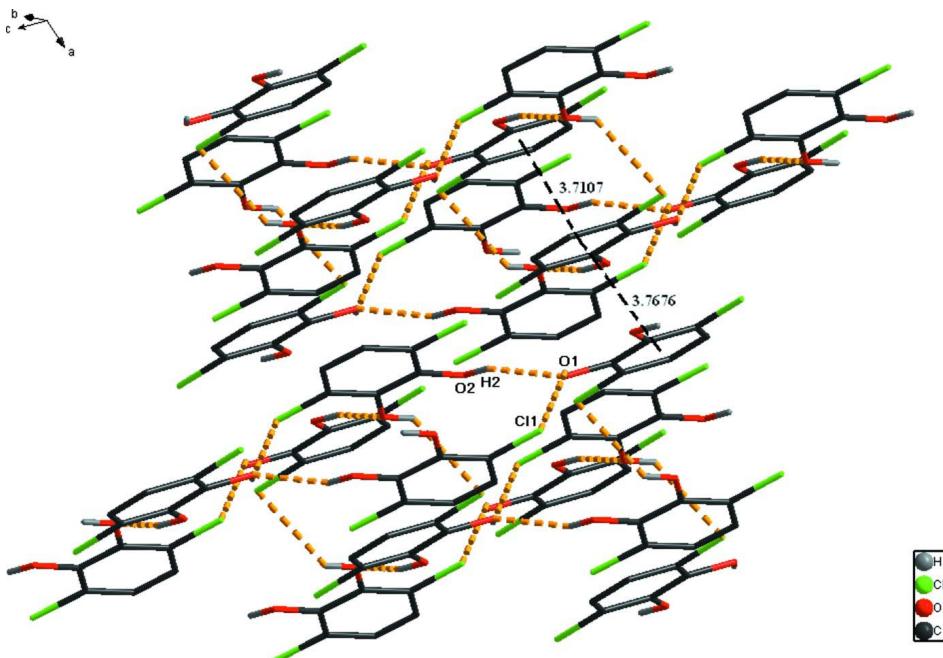
Figure 2

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 π-π interactions as black dashed lines.

3,6-dichlorobenzene-1,2-diol

Crystal data

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

Data collection

Bruker SMART CCD area-detector diffractometer	3531 measured reflections
	1243 independent reflections
Radiation source: fine-focus sealed tube	1117 reflections with $I > 2\sigma(I)$
Graphite monochromator	$R_{int} = 0.017$
φ and ω scans	$\theta_{max} = 25.2°$, $\theta_{min} = 3.0°$
Absorption correction: multi-scan (*SADABS*; Bruker, 1997)	$h = -8 \rightarrow 8$
	$k = -9 \rightarrow 12$
$T_{min} = 0.748$, $T_{max} = 0.882$	$l = -12 \rightarrow 12$

Refinement

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

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 (Å²)

	x	*y*	*z*	U_{iso}*/U_{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 (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
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, º)

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, º)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2	0.82	2.19	2.6391 (17)	115
O1—H1···Cl1[i]	0.82	2.76	3.3980 (16)	137
O2—H2···Cl2	0.82	2.61	3.0597 (13)	116
O2—H2···O1[ii]	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.