

1,4-Bis(4-chlorophenyl)-2-hydroxybutane-1,4-dione

Yongjun Liu,* Kuiwei Yang, Weiling Song and Yan Qi

College of Chemistry and Molecular Engineering, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China

Correspondence e-mail: pubslu@163.com

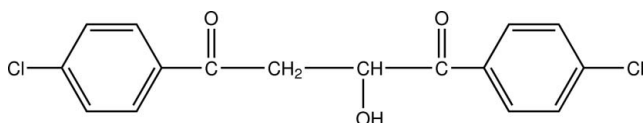
Received 30 April 2010; accepted 15 May 2010

 Key indicators: single-crystal X-ray study; $T = 273$ K; mean $\sigma(\text{C}-\text{C}) = 0.010$ Å; R factor = 0.057; wR factor = 0.163; data-to-parameter ratio = 6.6.

In the title compound, $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{O}_3$, the benzene rings form a dihedral angle of $2.0(3)^\circ$. Within the central $\text{O}=\text{C}-\text{CH}_2\text{C}(\text{H})\text{OH}-\text{C}=\text{O}$ unit, the carbonyl groups are coplanar and lie to opposite sides [$\text{O}-\text{C}\cdots\text{C}-\text{O} = -170.1(6)^\circ$]. In the crystal, intermolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds formed between the hydroxy groups lead to a supramolecular chain along the c axis. In addition, the crystal packing features some very weak $\text{C}-\text{H}\cdots\pi$ interactions.

Related literature

For the synthesis and applications of 1,4-dicarbonyl compounds, see: Ellison (1973); Hassner (1991); Ohno *et al.* (2001).



Experimental

Crystal data

 $\text{C}_{16}\text{H}_{12}\text{Cl}_2\text{O}_3$
 $M_r = 323.16$

 Monoclinic, Cc
 $a = 34.800(8)$ Å

 $b = 7.4221(14)$ Å

 $c = 5.6535(13)$ Å

 $\beta = 95.925(2)^\circ$
 $V = 1452.4(5)$ Å³
 $Z = 4$

 Mo $K\alpha$ radiation

 $\mu = 0.45$ mm⁻¹
 $T = 273$ K

 $0.12 \times 0.10 \times 0.08$ mm

Data collection

Bruker SMART CCD area-detector diffractometer

Absorption correction: multi-scan

 (*SADABS*; Sheldrick, 1996)

 $T_{\min} = 0.947$, $T_{\max} = 0.964$

3531 measured reflections

1256 independent reflections

 998 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.057$
 $wR(F^2) = 0.163$
 $S = 1.05$

1256 reflections

190 parameters

9 restraints

H-atom parameters constrained

 $\Delta\rho_{\text{max}} = 0.40$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³
Table 1

Hydrogen-bond geometry (Å, °).

$Cg1$ and $Cg2$ are the centroids of the $C1-C6$ and $C11-C16$ rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2A\cdots O2^i$	0.82	2.10	2.894 (6)	163
$C1-H1\cdots Cg1^{ii}$	0.93	2.89	3.507 (6)	125
$C4-H4\cdots Cg1^{iii}$	0.93	2.97	3.600 (6)	126
$C13-H13\cdots Cg2^{ii}$	0.93	2.88	3.517 (6)	127
$C16-H16\cdots Cg2^{iii}$	0.93	2.90	3.544 (6)	128

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINTE* (Bruker, 2001); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: TK2670).

References

- Bruker (2001). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Ellison, R. A. (1973). *Synthesis*, pp. 397–412.
- Hassner, A. (1991). *Comprehensive Organic Synthesis*, Vol. 1, edited by B. M. Trost, pp. 541–577. Oxford: Pergamon.
- Ohno, T., Sakai, M., Ishino, Y., Shibata, T., Maekawa, H. & Nishiguchi, I. (2001). *Org. Lett.* **3**, 3439–3442.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.

supplementary materials

Acta Cryst. (2010). E66, o1426 [doi:10.1107/S1600536810018027]

1,4-Bis(4-chlorophenyl)-2-hydroxybutane-1,4-dione

Y. Liu, K. Yang, W. Song and Y. Qi

Comment

1,4-Dicarbonyl compounds constitute key intermediates in various natural product syntheses, and are important synthetic precursors of cyclopentenones, cyclopenta-1,3-diones, butenolides, and derivatives of furan and pyrrole (Hassner, 1991). For this reason, a number of methods for their synthesis have been developed and applied (Ellison, 1973; Ohno *et al.*, 2001).

In the title compound, Fig. 1, the benzene rings form a dihedral angle of $2.0(3)^\circ$. Intermolecular O2—H2A \cdots O2 hydrogen bonds lead to the formation of a supramolecular chain along the *c* axis (Table 1, Fig. 2). In addition, the crystal packing is stabilized by intermolecular C—H \cdots π interactions (Table 1) and short Cl \cdots Clⁱ contacts (3.434(3) Å for *i*: 1/2+*x*, 1/2-*y*, -1/2+*z*).

Experimental

The title compound was obtained as a by-product in the coupling reaction between 4-ClC₆H₄COCH₂Br and benzaldehyde, a reaction which is being studied in our laboratory. Colourless single crystals of the title compound suitable for X-ray diffraction were obtained by slow evaporation of an ethanol solution over a period of 20 days.

Refinement

H atoms were positioned geometrically, with O—H = 0.82 Å and C—H = 0.95–0.99 Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{O})$ and $U_{\text{iso}}(\text{H}) = 1.2 U_{\text{eq}}(\text{C})$. In the absence of significant anomalous scattering effects, 1009 Friedel pairs were averaged in the final refinement.

Figures

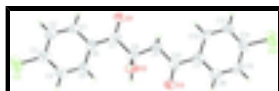


Fig. 1. The molecular structure of the title compound, showing atom labels and 50% probability displacement ellipsoids.

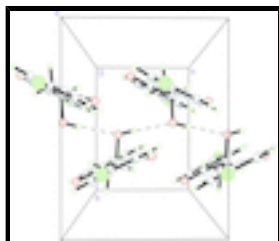


Fig. 2. The packing diagram for the title compound, viewed down the *a* axis, showing the intermolecular hydrogen bonds (dashed lines).

1,4-Bis(4-chlorophenyl)-2-hydroxybutane-1,4-dione

Crystal data

$C_{16}H_{12}Cl_2O_3$	$F(000) = 664$
$M_r = 323.16$	$D_x = 1.478 \text{ Mg m}^{-3}$
Monoclinic, Cc	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: C -2yc	Cell parameters from 1044 reflections
$a = 34.800 (8) \text{ \AA}$	$\theta = 2.4\text{--}24.4^\circ$
$b = 7.4221 (14) \text{ \AA}$	$\mu = 0.45 \text{ mm}^{-1}$
$c = 5.6535 (13) \text{ \AA}$	$T = 273 \text{ K}$
$\beta = 95.925 (2)^\circ$	Column, colourless
$V = 1452.4 (5) \text{ \AA}^3$	$0.12 \times 0.10 \times 0.08 \text{ mm}$
$Z = 4$	

Data collection

Bruker SMART CCD area-detector diffractometer	1256 independent reflections
Radiation source: fine-focus sealed tube graphite	998 reflections with $I > 2\sigma(I)$
phi and ω scans	$R_{\text{int}} = 0.025$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$\theta_{\text{max}} = 25.0^\circ$, $\theta_{\text{min}} = 2.4^\circ$
$T_{\text{min}} = 0.947$, $T_{\text{max}} = 0.964$	$h = -38 \rightarrow 40$
3531 measured reflections	$k = -7 \rightarrow 8$
	$l = -6 \rightarrow 6$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.057$	H-atom parameters constrained
$wR(F^2) = 0.163$	$w = 1/[\sigma^2(F_o^2) + (0.1063P)^2 + 0.4654P]$
$S = 1.05$	where $P = (F_o^2 + 2F_c^2)/3$
1256 reflections	$(\Delta/\sigma)_{\text{max}} < 0.001$
190 parameters	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
9 restraints	$\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	Absolute structure: nd

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.

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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
C1	1.04214 (18)	0.1713 (8)	0.3400 (11)	0.0369 (15)
H1	1.0356	0.1204	0.4809	0.044*
C2	1.0810 (2)	0.1845 (10)	0.2991 (14)	0.053 (2)
H2	1.1002	0.1385	0.4089	0.063*
C3	1.0905 (2)	0.2672 (9)	0.0921 (14)	0.049 (2)
C4	1.0605 (2)	0.3249 (10)	-0.0726 (13)	0.049 (2)
H4	1.0664	0.3745	-0.2154	0.058*
C5	1.0234 (2)	0.3116 (8)	-0.0327 (12)	0.0403 (16)
H5	1.0043	0.3556	-0.1448	0.048*
C6	1.0133 (2)	0.2332 (8)	0.1732 (12)	0.0357 (16)
C7	0.9724 (2)	0.2035 (8)	0.2253 (12)	0.0374 (16)
C8	0.9403 (2)	0.2685 (8)	0.0412 (13)	0.0383 (14)
H8	0.9443	0.2140	-0.1121	0.046*
C9	0.9007 (2)	0.2137 (9)	0.1027 (12)	0.0412 (15)
H9A	0.8999	0.0839	0.1210	0.049*
H9B	0.8961	0.2678	0.2533	0.049*
C10	0.8693 (2)	0.2712 (9)	-0.0860 (13)	0.0454 (18)
C11	0.8287 (2)	0.2621 (8)	-0.0279 (12)	0.0362 (16)
C12	0.8185 (2)	0.1854 (9)	0.1838 (11)	0.0444 (18)
H12	0.8377	0.1432	0.2964	0.053*
C13	0.7794 (2)	0.1712 (10)	0.2287 (12)	0.0465 (19)
H13	0.7725	0.1146	0.3649	0.056*
C14	0.7524 (2)	0.2427 (10)	0.0672 (14)	0.053 (2)
C15	0.7606 (2)	0.3157 (9)	-0.1456 (15)	0.0489 (18)
H15	0.7409	0.3558	-0.2564	0.059*
C16	0.7982 (2)	0.3280 (9)	-0.1908 (12)	0.0473 (18)
H16	0.8040	0.3809	-0.3319	0.057*
Cl1	1.13745 (6)	0.2822 (4)	0.0298 (3)	0.0922 (9)
Cl2	0.70386 (6)	0.2245 (4)	0.1208 (4)	0.0948 (10)
O1	0.96490 (15)	0.1328 (6)	0.4095 (9)	0.0515 (12)
O2	0.94303 (14)	0.4587 (5)	0.0178 (8)	0.0501 (10)
H2A	0.9434	0.5058	0.1492	0.075*
O3	0.87583 (16)	0.3179 (10)	-0.2824 (10)	0.084 (2)

Atomic displacement parameters (\AA^2)

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

supplementary materials

C1	0.043 (4)	0.037 (3)	0.030 (3)	-0.007 (3)	0.002 (3)	-0.001 (3)
C2	0.066 (5)	0.056 (5)	0.035 (4)	0.005 (4)	0.000 (4)	0.001 (3)
C3	0.060 (6)	0.047 (4)	0.040 (4)	-0.008 (3)	0.000 (4)	-0.012 (3)
C4	0.057 (6)	0.053 (4)	0.037 (4)	-0.006 (3)	0.008 (4)	-0.001 (3)
C5	0.047 (4)	0.033 (3)	0.040 (4)	-0.009 (3)	0.001 (3)	0.002 (3)
C6	0.042 (4)	0.033 (3)	0.033 (4)	0.009 (3)	0.008 (3)	-0.001 (3)
C7	0.057 (4)	0.026 (3)	0.030 (4)	0.006 (3)	0.009 (3)	-0.001 (3)
C8	0.048 (3)	0.033 (3)	0.033 (3)	0.011 (2)	0.000 (3)	0.002 (3)
C9	0.047 (3)	0.047 (4)	0.031 (3)	-0.007 (3)	0.008 (3)	0.003 (3)
C10	0.043 (4)	0.057 (4)	0.037 (4)	0.006 (3)	0.008 (3)	0.003 (3)
C11	0.047 (4)	0.029 (3)	0.032 (4)	-0.010 (2)	0.003 (3)	-0.004 (3)
C12	0.053 (5)	0.055 (4)	0.026 (3)	0.013 (3)	0.004 (3)	0.006 (3)
C13	0.054 (5)	0.058 (4)	0.029 (3)	-0.017 (4)	0.013 (3)	0.005 (3)
C14	0.034 (4)	0.069 (5)	0.058 (6)	-0.011 (3)	0.014 (4)	-0.004 (4)
C15	0.027 (3)	0.055 (4)	0.062 (5)	-0.008 (3)	-0.011 (3)	0.003 (4)
C16	0.061 (5)	0.042 (3)	0.037 (4)	0.001 (3)	-0.002 (4)	0.004 (3)
C11	0.0472 (14)	0.147 (3)	0.0842 (18)	-0.0177 (14)	0.0152 (13)	0.0093 (17)
C12	0.0469 (15)	0.150 (3)	0.089 (2)	-0.0122 (14)	0.0178 (13)	0.0072 (17)
O1	0.052 (3)	0.057 (3)	0.047 (3)	0.002 (2)	0.012 (2)	0.019 (2)
O2	0.064 (3)	0.039 (2)	0.048 (2)	0.0037 (19)	0.0072 (18)	0.0049 (19)
O3	0.048 (3)	0.172 (6)	0.033 (3)	0.010 (3)	0.011 (2)	0.033 (3)

Geometric parameters (Å, °)

C1—C6	1.384 (10)	C9—C10	1.507 (11)
C1—C2	1.398 (10)	C9—H9A	0.9700
C1—H1	0.9300	C9—H9B	0.9700
C2—C3	1.391 (12)	C10—O3	1.206 (9)
C2—H2	0.9300	C10—C11	1.485 (10)
C3—C4	1.393 (11)	C11—C12	1.404 (9)
C3—C11	1.711 (8)	C11—C16	1.419 (10)
C4—C5	1.334 (9)	C12—C13	1.413 (9)
C4—H4	0.9300	C12—H12	0.9300
C5—C6	1.380 (9)	C13—C14	1.349 (11)
C5—H5	0.9300	C13—H13	0.9300
C6—C7	1.499 (10)	C14—C15	1.376 (12)
C7—O1	1.218 (8)	C14—C12	1.753 (8)
C7—C8	1.525 (10)	C15—C16	1.361 (10)
C8—O2	1.422 (7)	C15—H15	0.9300
C8—C9	1.509 (7)	C16—H16	0.9300
C8—H8	0.9800	O2—H2A	0.8200
C6—C1—C2	120.7 (6)	C10—C9—H9A	109.3
C6—C1—H1	119.7	C8—C9—H9A	109.3
C2—C1—H1	119.7	C10—C9—H9B	109.3
C3—C2—C1	119.2 (7)	C8—C9—H9B	109.3
C3—C2—H2	120.4	H9A—C9—H9B	107.9
C1—C2—H2	120.4	O3—C10—C11	119.3 (6)
C2—C3—C4	118.1 (8)	O3—C10—C9	122.8 (6)
C2—C3—C11	121.1 (6)	C11—C10—C9	117.8 (6)

C4—C3—C11	120.6 (6)	C12—C11—C16	117.0 (7)
C5—C4—C3	122.3 (7)	C12—C11—C10	122.6 (6)
C5—C4—H4	118.8	C16—C11—C10	120.4 (6)
C3—C4—H4	118.8	C11—C12—C13	121.2 (6)
C4—C5—C6	120.7 (7)	C11—C12—H12	119.4
C4—C5—H5	119.7	C13—C12—H12	119.4
C6—C5—H5	119.7	C14—C13—C12	117.7 (6)
C5—C6—C1	118.9 (7)	C14—C13—H13	121.2
C5—C6—C7	124.0 (6)	C12—C13—H13	121.2
C1—C6—C7	117.1 (6)	C13—C14—C15	123.6 (7)
O1—C7—C6	121.4 (6)	C13—C14—C12	117.9 (6)
O1—C7—C8	120.9 (7)	C15—C14—C12	118.2 (6)
C6—C7—C8	117.6 (6)	C16—C15—C14	118.8 (7)
O2—C8—C9	111.2 (5)	C16—C15—H15	120.6
O2—C8—C7	109.0 (5)	C14—C15—H15	120.6
C9—C8—C7	112.3 (5)	C15—C16—C11	121.6 (7)
O2—C8—H8	108.1	C15—C16—H16	119.2
C9—C8—H8	108.1	C11—C16—H16	119.2
C7—C8—H8	108.1	C8—O2—H2A	109.5
C10—C9—C8	111.8 (5)		

Hydrogen-bond geometry (\AA , $^\circ$)

Cg1 and Cg2 are the centroids of the C1—C6 and C11—C16 rings, respectively.

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2A \cdots O2 ⁱ	0.82	2.10	2.894 (6)	163
C1—H1 \cdots Cg1 ⁱⁱ	0.93	2.89	3.507 (6)	125
C4—H4 \cdots Cg1 ⁱⁱⁱ	0.93	2.97	3.600 (6)	126
C13—H13 \cdots Cg2 ⁱⁱ	0.93	2.88	3.517 (6)	127
C16—H16 \cdots Cg2 ⁱⁱⁱ	0.93	2.90	3.544 (6)	128

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

Fig. 1

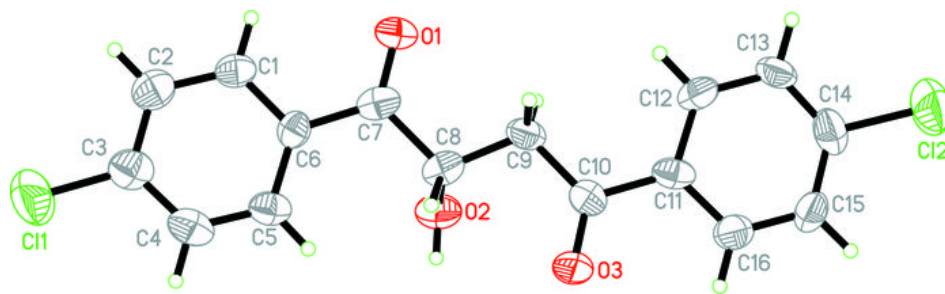


Fig. 2

