organic compounds

2,3,5,6-Tetrachlorobenzene-1,4-dicarboxylic acid

Qun Chen, Yingmei Xie, Chao Li, Mingyang He and Shengchun Chen*

Key Laboratory of Fine Petro-chemical Technology, Jiangsu Polytechnic University, Changzhou 213164, People's Republic of China

Correspondence e-mail: shengchunchenjpu@yahoo.com

The title compound, $C_8H_2Cl_4O_4$, was synthesized by the reaction of 2,3,5,6-tetrachlorobenzene-1,4-dicarbonitrile and sulfuric acid. The molecule is located across an inversion center. The carboxyl group is tilted with respect to the benzene ring by an angle of 72.42 (7)°. Intermolecular O—H···O hydrogen bonding helps to stabilize the crystal structure.

Related literature

For general background, see: Eufemia & Epel (1998); Meazza *et al.* (2007).
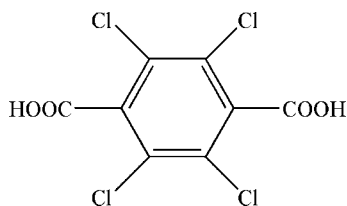
Experimental

Crystal data

$C_8H_2Cl_4O_4$	$V = 525.55$ (13) Å^3
$M_r = 303.90$	$Z = 2$
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation
$a = 5.9852$ (9) Å	$\mu = 1.12$ mm^{-1}
$b = 7.0349$ (10) Å	$T = 296$ (2) K
$c = 12.7012$ (19) Å	$0.30 \times 0.22 \times 0.20$ mm
$\beta = 100.668$ (2)°	

Data collection

Bruker SMART CCD area-detector diffractometer	4350 measured reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2002)	1213 independent reflections
	1145 reflections with $I > 2\sigma(I)$
$T_{min} = 0.734$, $T_{max} = 0.800$	$R_{int} = 0.021$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$	74 parameters
$wR(F^2) = 0.064$	H-atom parameters constrained
$S = 1.01$	$\Delta\rho_{max} = 0.32$ e Å^{-3}
1213 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^i	0.82	1.84	2.6410 (15)	166

Symmetry code: (i) $-x + \frac{1}{2}, y - \frac{1}{2}, -z - \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Bruker (2000). *SMART* (Version 5.622), *SAINT* (Version 6.02A) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Eufemia, N. A. & Epel, D. (1998). *Mar. Environ. Res.* **46**, 401–405.

Meazza, G., Bettarini, F. & Fornara, L. (2007). WO Patent No. 2007101587.

Sheldrick, G. M. (2002). *SADABS*. Version 2.03. University of Göttingen, Germany.

supplementary materials

2,3,5,6-Tetrachlorobenzene-1,4-dicarboxylic acid

Q. Chen, Y. Xie, C. Li, M. He and S. Chen

Comment

2,3,5,6-Tetrachlorobenzene-1,4-dicarboxylic acid is an important intermediate which can be used for the synthesis of herbicides (Eufemia & Epel, 1998; Meazza *et al.*, 2007). This paper presents the results of the single-crystal X-ray diffraction analysis of the title compound. A perspective view of the title compound is shown in Fig. 1. The bond lengths and angles are within normal ranges. In the molecule, the carboxyl group forms a dihedral angle of 72.42 (7)° with the central benzene ring. Classical intermolecular O—H···O hydrogen bonding occurs in the crystal structure (Table 1 and Fig. 2), which may be effective in the stabilization of the crystal structure. Short intermolecular Cl···Cl($1/2 − x, 1/2 + y, 1/2 − z$) contact of 3.62 (8)Å is observed in the crystal structure.

Experimental

2,3,5,6-Tetrachlorobenzene-1,4-dicarbonitrile (26.5 g, 100 mmol) was mixed with concentrated sulfuric acid (240 ml) and water (60 ml) under reflux at 463 K for 36 h. Upon standing this solution yielded crystalline 2,3,5,6-tetrachlorobenzene-1,4-dicarboxylic acid, which was filtered, washed with water (2× 50 ml), and dried under vacuum for 24 h (19.2 g, 63.2% yield). Single crystals were obtained by slow evaporation of the aqueous solution.

Refinement

H atom was placed in calculated position with O—H = 0.82 Å and refined in riding mode, $U_{iso}(H) = 1.5U_{eq}(O)$.
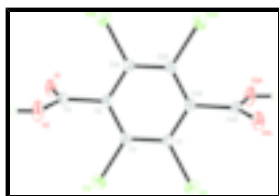
Figures

Fig. 1. The molecular structure of (I) (thermal ellipsoids are shown at 30% probability levels) [symmetry code: (A) −*x*, 2 − *y*, −*z*].
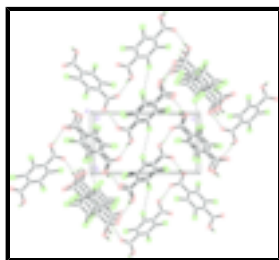

Fig. 2. A packing diagram for (I). Dashed lines indicate hydrogen bonds and short intermolecular Cl···Cl contacts.

2,3,5,6-Tetrachlorobenzene-1,4-dicarboxylic acid

Crystal data

$C_8H_2Cl_4O_4$	$F_{000} = 300.0$
$M_r = 303.90$	$D_x = 1.920$ Mg m^{-3}
Monoclinic, $P2_1/n$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
Hall symbol: -P 2yn	Cell parameters from 3424 reflections
$a = 5.9852$ (9) Å	$\theta = 3.3–27.6º$
$b = 7.0349$ (10) Å	$\mu = 1.12$ mm^{-1}
$c = 12.7012$ (19) Å	$T = 296$ (2) K
$\beta = 100.668$ (2)º	Block, colorless
$V = 525.55$ (13) Å^3	$0.30 \times 0.22 \times 0.20$ mm
$Z = 2$	

Data collection

Bruker SMART CCD area-detector diffractometer	1213 independent reflections
Radiation source: fine-focus sealed tube	1145 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{int} = 0.021$
$T = 296(2)$ K	$\theta_{max} = 27.6º$
φ and ω scans	$\theta_{min} = 3.3º$
Absorption correction: multi-scan (SADABS; Sheldrick, 2002)	$h = -7 \rightarrow 7$
$T_{min} = 0.734$, $T_{max} = 0.800$	$k = -9 \rightarrow 8$
4350 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.024$	H-atom parameters constrained
$wR(F^2) = 0.064$	$w = 1/[\sigma^2(F_o^2) + (0.03P)^2 + 0.2817P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.01$	$(\Delta/\sigma)_{max} < 0.001$
1213 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
74 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-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 $F^2 > 2\text{sigma}(F^2)$ 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 ($Å^2$)

	x	y	z	$U_{iso}*/U_{eq}$
Cl1	0.27187 (7)	1.04641 (6)	0.19970 (3)	0.04105 (13)
Cl2	0.10264 (7)	0.73074 (6)	0.02950 (3)	0.03963 (13)
O1	0.4028 (2)	0.53756 (15)	−0.12663 (9)	0.0455 (3)
H1	0.3466	0.4605	−0.1724	0.068*
O2	0.2347 (2)	0.74573 (15)	−0.24712 (9)	0.0395 (3)
C2	0.3240 (2)	0.87853 (19)	0.01385 (10)	0.0272 (3)
C1	0.3983 (2)	1.01943 (19)	0.08955 (10)	0.0270 (3)
C3	0.4255 (2)	0.85885 (18)	−0.07583 (10)	0.0265 (3)
C4	0.3431 (2)	0.70930 (19)	−0.15941 (11)	0.0289 (3)

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0506 (2)	0.0444 (2)	0.0328 (2)	−0.00380 (17)	0.01984 (16)	−0.00767 (15)
Cl2	0.0409 (2)	0.0375 (2)	0.0414 (2)	−0.01307 (15)	0.00999 (16)	−0.00066 (15)
O1	0.0733 (8)	0.0230 (5)	0.0330 (6)	0.0063 (5)	−0.0091 (5)	−0.0043 (4)
O2	0.0572 (7)	0.0265 (5)	0.0294 (5)	−0.0020 (5)	−0.0064 (5)	0.0004 (4)
C2	0.0303 (6)	0.0229 (6)	0.0280 (6)	−0.0014 (5)	0.0044 (5)	0.0008 (5)
C1	0.0325 (7)	0.0256 (6)	0.0232 (6)	0.0019 (5)	0.0063 (5)	−0.0010 (5)
C3	0.0340 (7)	0.0207 (6)	0.0234 (6)	0.0017 (5)	0.0015 (5)	−0.0012 (5)
C4	0.0376 (7)	0.0230 (6)	0.0256 (6)	−0.0002 (5)	0.0041 (5)	−0.0015 (5)

Geometric parameters (Å, °)

Cl1—C1	1.7199 (14)	C2—C3	1.3936 (19)
Cl2—C2	1.7243 (14)	C2—C1	1.3951 (18)
O1—C4	1.3060 (17)	C1—C3^i	1.394 (2)
O1—H1	0.8200	C3—C4	1.5110 (18)
O2—C4	1.2084 (18)		
C4—O1—H1	109.5	C2—C3—C1^i	119.70 (12)
C3—C2—C1	120.15 (12)	C2—C3—C4	120.56 (12)
C3—C2—Cl2	119.66 (10)	C1^i—C3—C4	119.73 (12)

C1—C2—Cl2	120.18 (10)	O2—C4—O1	123.97 (13)
C3^i—C1—C2	120.15 (12)	O2—C4—C3	123.35 (12)
C3^i—C1—Cl1	119.39 (10)	O1—C4—C3	112.69 (11)
C2—C1—Cl1	120.45 (11)		
Cl2—C2—C1—C3^i	−178.81 (10)	Cl2—C2—C3—C4	0.05 (18)
C3—C2—C1—Cl1	179.28 (10)	C2—C3—C4—O2	107.13 (17)
Cl2—C2—C1—Cl1	0.47 (16)	C1^i—C3—C4—O2	−71.6 (2)
Cl2—C2—C3—C1^i	178.82 (10)	C2—C3—C4—O1	−73.18 (17)
C1—C2—C3—C4	−178.76 (12)	C1^i—C3—C4—O1	108.05 (15)

Symmetry codes: (i) −x+1, −y+2, −z.

Hydrogen-bond geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H1···O2^{ii}	0.82	1.84	2.6410 (15)	166

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

Fig. 1

Fig. 2