

Acta Crystallographica Section E

## Structure Reports

Online

ISSN 1600-5368

# Dimethyl 4,5-dichlorobenzene-1,2-dicarboxylate

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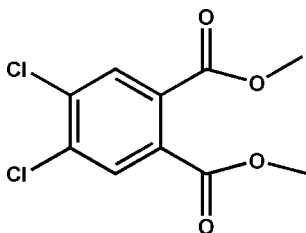
Received 20 January 2012; accepted 17 February 2012

Key indicators: single-crystal X-ray study;  $T = 295$  K; mean  $\sigma(\text{C}-\text{C}) = 0.003$  Å;  $R$  factor = 0.035;  $wR$  factor = 0.092; data-to-parameter ratio = 13.4.

In the title compound,  $\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_4$ , the two Cl atoms and one of the methoxycarbonyl groups are almost coplanar [maximum deviation =  $0.035$  (2) Å] with the benzene plane, and the other methoxycarbonyl group exhibits an almost orthogonal disposition relative to the benzene plane, with a dihedral angle of  $84.82$  (3)° between the planes. In the crystal, the molecules are connected into a chain propagating along the [011] direction through nonclassical  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds.

## Related literature

For the chemical properties and structural nature of some related benzenecarboxylate derivatives, see: Galešić *et al.* (1984); Liang *et al.* (2004); Mallinson *et al.* (2003); Rauf *et al.* (2008).



## Experimental

### Crystal data

$\text{C}_{10}\text{H}_8\text{Cl}_2\text{O}_4$	$\gamma = 91.864$ (18)°
$M_r = 263.06$	$V = 558.95$ (19) Å <sup>3</sup>
Triclinic, $P\bar{1}$	$Z = 2$
$a = 7.1906$ (14) Å	Mo $K\alpha$ radiation
$b = 7.8410$ (17) Å	$\mu = 0.58$ mm <sup>-1</sup>
$c = 10.6205$ (15) Å	$T = 295$ K
$\alpha = 97.779$ (15)°	$0.24 \times 0.20 \times 0.18$ mm
$\beta = 109.040$ (15)°	

### Data collection

Bruker SMART 1000 CCD diffractometer	3362 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	1966 independent reflections
$T_{\min} = 0.871$ , $T_{\max} = 0.902$	1663 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.010$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$	147 parameters
$wR(F^2) = 0.092$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{\text{max}} = 0.28$ e Å <sup>-3</sup>
1966 reflections	$\Delta\rho_{\text{min}} = -0.24$ e Å <sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{C6}-\text{H6}\cdots\text{O4}^i$	0.93	2.37	3.278 (2)	164

Symmetry code: (i)  $x, y - 1, z$ .

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; 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.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: RK2334).

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## supporting information

*Acta Cryst.* (2012). E68, o834 [doi:10.1107/S1600536812007167]

## Dimethyl 4,5-dichlorobenzene-1,2-dicarboxylate

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### S1. Comment

Benzenecarboxylate derivatives have been extensively studied due to their excellent chemical properties and easily modified structural natures. (Mallinson *et al.*, 2003 and Liang *et al.*, 2004). Furthermore, the investigate on single-crystal structure of benzenecarboxylate derivatives have become increasingly important in revealing precisely the relation between their chemical properties and molecular structures (Galešić *et al.*, 1984 and Rauf *et al.*, 2008). As an extension of our work on benzenecarboxylate structural characterization, the title compound, **I**, is synthesized and characterized by X-ray diffraction, as shown in Fig. 1.

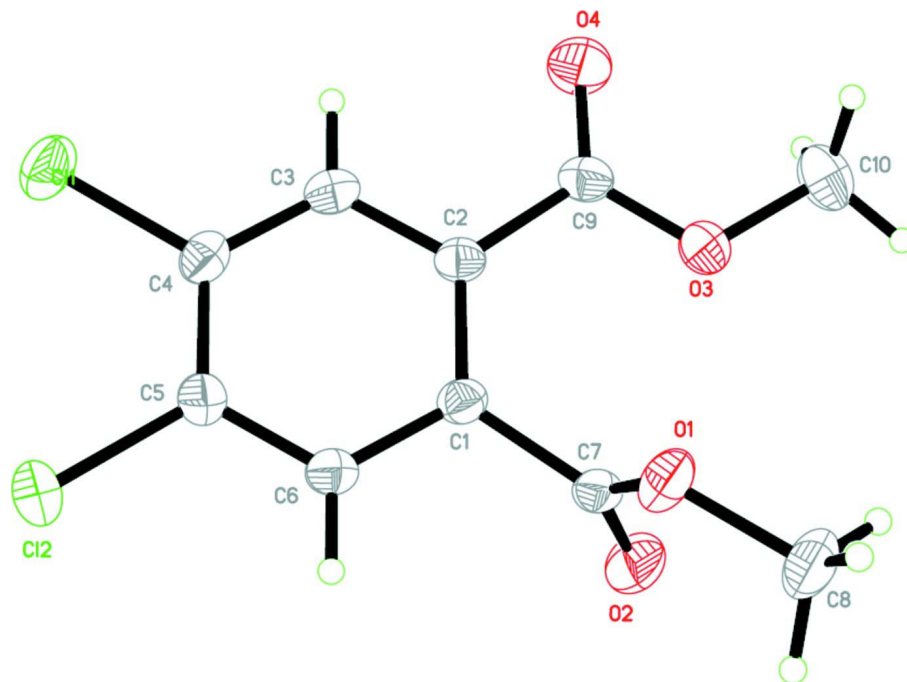
The compound **I** crystallizes in the triclinic system and consists of one phenyl framework, together with two chlorine atoms and two methoxycarbonyl groups linked to its peripheral position, respectively. Two chlorine atoms are co-planar with the benzene ring, accompanying the maximum deviation of 0.035 (2) Å from this benzene plane. Furthermore, one methoxycarbonyl group is also co-planar with this benzene plane, with the dihedral angle of 2.03 (3)° between the methoxycarbonyl plane of C9–O3–O4–C10 and the benzene plane. In contrast, the other methoxycarbonyl plane of C7–O1–O2–C8 exhibits almostly orthogonal configuration in relative to this benzene plane with the dihedral angle of 84.82 (3)° between them. As shown in Table 1, the distances of C–O (esterified hydroxyl oxygen atom) locating in the range of 1.321 (2)–1.448 (2) Å, clearly indicate their typical single-bond nature in contrast to the obviously double-bond of C=O (carbonyl oxygen atom) 1.187 (2) Å and 1.193 (2) Å, revealing the excellent flexible bridge nature of these methoxycarbonyl moieties. Furthermore, this compound molecules are connected into one-dimension chain along the [0 1 1] direction through H bond C6–H6···O4<sup>i</sup> with H6···O4<sup>i</sup> distance of 2.373 (3)°. Symmetry code: (i)  $x, y-1, z$ .

### S2. Experimental

To the solution of 4,5-dichloro-1,2-benzenedicarboxyl acid (466 mg, 2 mmol) in *MeOH* (50 ml), one drop of H<sub>2</sub>SO<sub>4</sub> was added. After refluxed for five hours under N<sub>2</sub> atmosphere, the resulting mixture was evaporated, and the residue was chromatographed on a silica gel column using CHCl<sub>3</sub> as eluent. Repeated chromatography followed by recrystallization from CHCl<sub>3</sub> and *MeOH* gave the target compound as white crystals. Yield: 182 mg, 34.6%. Anal. for C<sub>10</sub>H<sub>8</sub>Cl<sub>2</sub>O<sub>4</sub>: Calc. C, 45.66; H, 3.07; Found: C, 45.42; H, 3.17. The No. of CCDC: 863226.

### S3. Refinement

All H atoms were placed in geometrically idealized positions and treated as riding on their parent atoms with C–H distances of 0.93 Å with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  for aryl H atoms and C–H distances of 0.96 Å with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$  for methyl H atoms. The CCDC deposit number 863226.

**Figure 1**

The molecular structure of the title compound with the atom numbering scheme. Displacement ellipsoids are drawn at 30% probability level. H atoms are presented as a small spheres of arbitrary radius.

### Dimethyl 4,5-dichlorobenzene-1,2-dicarboxylate

#### Crystal data

$C_{10}H_8Cl_2O_4$   
 $M_r = 263.06$   
 Triclinic,  $P\bar{1}$   
 Hall symbol:  $-P\ 1$   
 $a = 7.1906$  (14) Å  
 $b = 7.8410$  (17) Å  
 $c = 10.6205$  (15) Å  
 $\alpha = 97.779$  (15)°  
 $\beta = 109.040$  (15)°  
 $\gamma = 91.864$  (18)°  
 $V = 558.95$  (19) Å<sup>3</sup>

$Z = 2$   
 $F(000) = 268$   
 $D_x = 1.563$  Mg m<sup>-3</sup>  
 Melting point: 389 K  
 Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å  
 Cell parameters from 1973 reflections  
 $\theta = 2.4$ – $25.0$ °  
 $\mu = 0.58$  mm<sup>-1</sup>  
 $T = 295$  K  
 Block, colourless  
 $0.24 \times 0.20 \times 0.18$  mm

#### Data collection

Bruker SMART 1000 CCD  
 diffractometer  
 Radiation source: fine-focus sealed tube  
 Graphite monochromator  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: multi-scan  
 (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.871$ ,  $T_{\max} = 0.902$

3362 measured reflections  
 1966 independent reflections  
 1663 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.010$   
 $\theta_{\text{max}} = 25.0$ °,  $\theta_{\text{min}} = 3.1$ °  
 $h = -7 \rightarrow 8$   
 $k = -9 \rightarrow 8$   
 $l = -12 \rightarrow 12$

Refinement

Refinement on  $F^2$   
 Least-squares matrix: full  
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.092$   
 $S = 1.03$   
 1966 reflections  
 147 parameters  
 0 restraints  
 Primary atom site location: structure-invariant  
 direct methods

Secondary atom site location: difference Fourier  
 map  
 Hydrogen site location: inferred from  
 neighbouring sites  
 H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0449P)^2 + 0.1781P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.28 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.24 \text{ e } \text{\AA}^{-3}$

Special details

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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	0.31371 (9)	0.97739 (8)	0.82726 (5)	0.0629 (2)
Cl2	0.25088 (11)	0.57862 (8)	0.71088 (6)	0.0693 (2)
O1	0.3423 (2)	0.70631 (19)	0.21566 (13)	0.0517 (4)
O3	0.2024 (2)	1.05587 (17)	0.22604 (14)	0.0524 (4)
C7	0.1745 (3)	0.7231 (2)	0.24061 (19)	0.0404 (4)
C9	0.2309 (3)	1.1128 (2)	0.3543 (2)	0.0414 (4)
C1	0.2123 (3)	0.7964 (2)	0.38630 (18)	0.0365 (4)
C6	0.2187 (3)	0.6771 (2)	0.47290 (19)	0.0449 (5)
H6	0.2027	0.5596	0.4397	0.054*
C3	0.2674 (3)	1.0250 (2)	0.57299 (19)	0.0401 (4)
H7	0.2835	1.1423	0.6069	0.048*
C2	0.2367 (2)	0.9725 (2)	0.43690 (18)	0.0349 (4)
C4	0.2743 (3)	0.9063 (3)	0.65837 (19)	0.0404 (4)
C5	0.2487 (3)	0.7316 (2)	0.60792 (19)	0.0431 (5)
O2	0.0140 (2)	0.6798 (2)	0.16088 (15)	0.0648 (4)
O4	0.2507 (4)	1.26184 (19)	0.39955 (19)	0.0862 (6)
C10	0.1877 (4)	1.1857 (3)	0.1392 (3)	0.0655 (7)
H13A	0.1488	1.1307	0.0470	0.098*
H13C	0.3134	1.2499	0.1630	0.098*
H13B	0.0910	1.2628	0.1499	0.098*
C8	0.3252 (4)	0.6420 (3)	0.0777 (2)	0.0654 (7)
H14C	0.2624	0.7232	0.0206	0.098*
H14A	0.2476	0.5331	0.0491	0.098*
H14B	0.4544	0.6271	0.0720	0.098*

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

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Cl1	0.0775 (4)	0.0733 (4)	0.0381 (3)	-0.0010 (3)	0.0256 (3)	-0.0048 (3)
Cl2	0.1004 (5)	0.0595 (4)	0.0460 (3)	-0.0028 (3)	0.0175 (3)	0.0212 (3)
O1	0.0606 (10)	0.0574 (9)	0.0324 (7)	0.0079 (7)	0.0121 (7)	-0.0017 (6)
O3	0.0733 (10)	0.0391 (8)	0.0445 (8)	0.0031 (7)	0.0171 (7)	0.0124 (6)
C7	0.0532 (12)	0.0281 (9)	0.0347 (10)	-0.0003 (8)	0.0077 (9)	0.0049 (7)
C9	0.0407 (11)	0.0328 (10)	0.0472 (11)	0.0020 (8)	0.0104 (9)	0.0056 (8)
C1	0.0370 (10)	0.0335 (9)	0.0339 (10)	0.0009 (7)	0.0062 (8)	0.0027 (7)
C6	0.0580 (13)	0.0320 (10)	0.0392 (11)	-0.0003 (8)	0.0104 (9)	0.0028 (8)
C3	0.0380 (10)	0.0352 (10)	0.0434 (11)	0.0014 (8)	0.0124 (8)	-0.0028 (8)
C2	0.0299 (9)	0.0330 (9)	0.0388 (10)	0.0016 (7)	0.0083 (8)	0.0034 (7)
C4	0.0346 (10)	0.0500 (11)	0.0343 (10)	0.0003 (8)	0.0112 (8)	0.0007 (8)
C5	0.0474 (11)	0.0428 (11)	0.0373 (10)	0.0000 (8)	0.0109 (9)	0.0089 (8)
O2	0.0618 (10)	0.0745 (11)	0.0412 (9)	-0.0148 (8)	0.0007 (8)	-0.0018 (8)
O4	0.159 (2)	0.0288 (8)	0.0697 (12)	0.0046 (9)	0.0378 (12)	0.0052 (8)
C10	0.0815 (17)	0.0585 (14)	0.0626 (15)	0.0099 (12)	0.0233 (13)	0.0313 (12)
C8	0.0928 (19)	0.0670 (15)	0.0366 (11)	0.0110 (13)	0.0243 (12)	0.0006 (10)

Geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Cl1—C4	1.7308 (19)	C6—C5	1.383 (3)
Cl2—C5	1.7260 (19)	C6—H6	0.9300
O1—C7	1.324 (2)	C3—C4	1.376 (3)
O1—C8	1.447 (2)	C3—C2	1.390 (3)
O3—C9	1.321 (2)	C3—H7	0.9300
O3—C10	1.448 (2)	C4—C5	1.385 (3)
C7—O2	1.193 (2)	C10—H13A	0.9600
C7—C1	1.508 (3)	C10—H13C	0.9600
C9—O4	1.187 (2)	C10—H13B	0.9600
C9—C2	1.490 (3)	C8—H14C	0.9600
C1—C6	1.390 (3)	C8—H14A	0.9600
C1—C2	1.396 (3)	C8—H14B	0.9600
C7—O1—C8	116.24 (17)	C1—C2—C9	124.47 (17)
C9—O3—C10	116.45 (16)	C3—C4—C5	119.57 (17)
O2—C7—O1	125.13 (18)	C3—C4—Cl1	119.55 (15)
O2—C7—C1	123.77 (19)	C5—C4—Cl1	120.87 (15)
O1—C7—C1	111.03 (16)	C6—C5—C4	120.08 (17)
O4—C9—O3	123.07 (18)	C6—C5—Cl2	118.90 (15)
O4—C9—C2	123.22 (19)	C4—C5—Cl2	121.02 (15)
O3—C9—C2	113.71 (15)	O3—C10—H13A	109.5
C6—C1—C2	119.35 (17)	O3—C10—H13C	109.5
C6—C1—C7	116.17 (16)	H13A—C10—H13C	109.5
C2—C1—C7	124.47 (16)	O3—C10—H13B	109.5
C5—C6—C1	120.58 (17)	H13A—C10—H13B	109.5
C5—C6—H6	119.7	H13C—C10—H13B	109.5

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C1—C6—H6	119.7	O1—C8—H14C	109.5
C4—C3—C2	121.09 (17)	O1—C8—H14A	109.5
C4—C3—H7	119.5	H14C—C8—H14A	109.5
C2—C3—H7	119.5	O1—C8—H14B	109.5
C3—C2—C1	119.31 (17)	H14C—C8—H14B	109.5
C3—C2—C9	116.21 (16)	H14A—C8—H14B	109.5

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*Hydrogen-bond geometry (Å, °)*

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<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>
C6—H6 $\cdots$ O4 <sup>i</sup>	0.93	2.37	3.278 (2)	164

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Symmetry code: (i) *x*, *y*-1, *z*.