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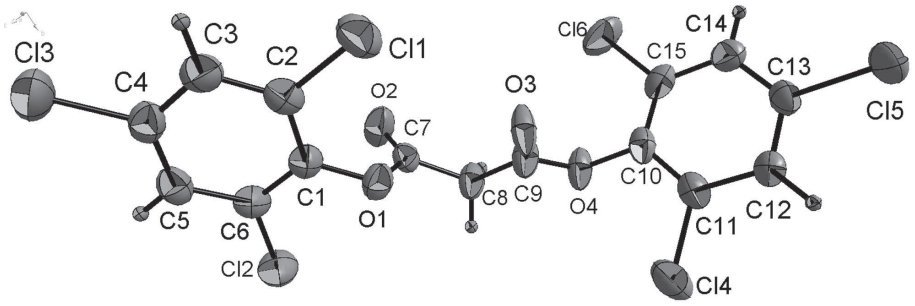
Crystal structure of bis(2,4,6-trichlorophenyl) malonate, $C_{15}H_6Cl_6O_4$



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Abstract

$[C_{15}H_6Cl_6O_4]$, monoclinic, Cc (no. 9), $a = 12.0980(11)$ Å, $b = 10.0628(9)$ Å, $c = 15.1518(14)$ Å, $\beta = 104.231(1)°$, $V = 1788.0(3)$ Å^3, $Z = 4$, $R_{gt}(F) = 0.0214$, $wR_{ref}(F^2) = 0.0568$, $T = 296(2)$ K.

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The crystal structure is shown in the figure. Tables 1 and 2 contain details on crystal structure and measurement conditions and a list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.16 × 0.14 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.0 mm^{-1}
Diffractometer, scan mode:	Bruker Apex-II, φ and ω-scans
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	6761, 3023, 0.016
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 2952
$N(param)_{refined}$:	227
Programs:	Bruker programs [1], SHELX [2]

Source of materials

Pyrimidinones are usually synthesized by using 2-aminopyridine and bis(2,4,6-trichlorophenyl)malonate. Based on the literature synthesis, we have improved the route. The synthesis process of bis(2,4,6-trichlorophenyl) malonate was carried out using malonic acid as starting material. Malonic acid (4 g, 38.46 mmol), oxalyl chloride (5.38 mL, 57.69 mmol) were added in DCM (50 mL); the mixture was stirred well for 1 h at room temperature, then we added 1 drop of DMF, and continued stirring until the mixture became clear. 2,4,6-trichlorophenol (11.3 g, 57.69 mmol) was added, the reaction solution stirred at room temperature overnight. The product was concentrated under reduced pressure. Finally, methanol (20 mL) was added until a white solid precipitated then the resulting solution was filtered under reduced pressure. The raw product (10.5 g) was recrystallied from dichloromethane. m.p: 149–152 °C. Elemental Anal. Calcd. (%) for $C_{15}H_6Cl_6O_4$ (462.90): C, 38.92; H, 1.37. Found (%): C, 38.18; H, 1.50.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with C—H = 0.90–0.97 Å with $U_{iso}(H) = 1.5\ U_{eq}(C)$ for methyl H atoms and $1.2\ U_{eq}(C)$ for all other H atoms. The Flack-Parsons parameter is 0.039(18) based on 1283 quotients [2].

Comment

Pyrimidine and pyrimidopyrimidine derivatives is an important medicine [3], and its synthesis is usually

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
C1	0.4028(2)	0.7439(3)	0.7211(2)	0.0404(6)
C2	0.3300(2)	0.6358(3)	0.7001(2)	0.0447(6)
C3	0.3337(3)	0.5341(3)	0.7616(2)	0.0492(7)
H3	0.2842	0.4621	0.7478	0.059*
C4	0.4131(3)	0.5419(3)	0.8445(2)	0.0488(7)
C5	0.4875(3)	0.6471(3)	0.8675(2)	0.0461(7)
H5	0.5403	0.6504	0.9236	0.055*
C6	0.4809(2)	0.7476(3)	0.8043(2)	0.0418(6)
C7	0.4609(2)	0.8445(3)	0.6012(2)	0.0409(6)
C8	0.4453(3)	0.9649(3)	0.5412(2)	0.0512(7)
H8A	0.4608	1.0433	0.5794	0.061*
H8B	0.5012	0.9621	0.5049	0.061*
C9	0.3289(2)	0.9783(3)	0.4783(2)	0.0507(8)
C10	0.2370(2)	1.0893(3)	0.3437(2)	0.0424(6)
C11	0.1700(2)	1.1991(3)	0.3461(2)	0.0425(6)
C12	0.0793(2)	1.2288(3)	0.2735(2)	0.0417(6)
H12	0.0345	1.3036	0.2747	0.050*
C13	0.0568(2)	1.1451(3)	0.19938(19)	0.0410(6)
C14	0.1216(3)	1.0341(3)	0.1951(2)	0.0463(7)
H14	0.1049	0.9785	0.1445	0.056*
C15	0.2121(2)	1.0079(3)	0.2683(2)	0.0475(7)
O1	0.39339(17)	0.8502(2)	0.66100(15)	0.0474(5)
O2	0.5245(2)	0.7569(3)	0.59956(17)	0.0664(7)
O3	0.2442(2)	0.9227(4)	0.4817(2)	0.0933(11)
O4	0.33483(17)	1.0684(2)	0.41368(16)	0.0538(6)
Cl1	0.23312(8)	0.62950(10)	0.59519(6)	0.0650(2)
Cl2	0.57314(7)	0.88156(8)	0.83113(6)	0.0610(2)
Cl3	0.42004(10)	0.41507(9)	0.92305(7)	0.0733(3)
Cl4	0.19913(7)	1.30229(10)	0.44010(6)	0.0663(3)
Cl5	−0.05775(7)	1.18000(8)	0.10804(6)	0.0606(2)
Cl6	0.29540(9)	0.86970(9)	0.26502(10)	0.0843(3)

performed by using 2-aminopyridine and bis(2,4,6-trichlorophenyl)malonate [4, 5].

Nowadays, many pyrimidine and pyrimidopyrimidine derivatives are of interest in the search for new pharmaceutical candidates because they may show distinguished pharmaceutical properties, such as: antiviral, antibacterial, anti-HIV, antiallergic, and antitumoral activities [6]. Pyrimidines have a prominent pharmacophore prevailing in many heterocyclic natural products. During the past two decades, several pyrimidine derivatives were found to have widespread clinical applications including chemotherapy of AIDS.

Herein we report the synthesis and crystal structure of the intermediate of the pyrimidone synthesis [7]: bis(2,4,6-trichlorophenyl) malonate. In the molecule of the title compound (Fig.), bond lengths and angles are in the expected ranges for malonates [8, 9]. Two aryl rings were bound to the both sides of malonic acid group. The dihedral angle between the benzene rings is 67.8°. Further, the dihedral angle between the central CH_2—C(O)—O segment and the phenyl ring is 83.8°.

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