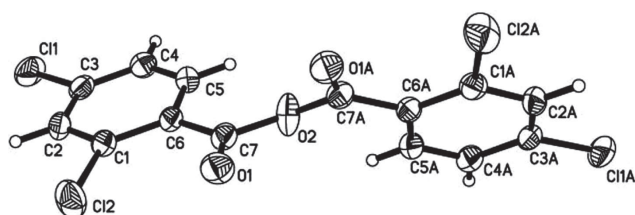


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Crystal structure of 2,4-dichlorobenzene anhydride, C₁₄H₆Cl₄O₃



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Abstract

$\text{C}_{14}\text{H}_6\text{C}_{14}\text{O}_3$ orthorhombic, Pccn (no. 56), $a = 11.884(2)$ Å, $b = 11.902(2)$ Å, $c = 10.509(2)$ Å, $V = 1235.9(5)$ Å³, $Z = 4$, $R_{\text{gt}}(F) = 0.0440$, $wR_{\text{ref}}(F^2) = 0.1047$, $T = 293$ K.

CCDC no.: 1267/4365

Table 1: Data collection and handling.

Crystal:	Colorless, block, size $0.16 \times 0.21 \times 0.23$ mm
Wavelength:	Mo K_{α} radiation ($0.71073 \text{ \AA}$)
μ :	8.00 cm^{-1}
Diffractometer, scan mode:	Rigaku RAXIS-RAPID, ω scans
$2\theta_{\text{max}}$:	50°
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$:	10417, 1303
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1033
$N(\text{param})_{\text{refined}}$:	96
Programs:	SHELXS-97 (SHELDRICK, 2008)

Source of material

The title compound was prepared according to the literature procedure [1]. 2,4-Dichlorobenzoic acid (0.04 mol) was added

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Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ($\text{\AA}^2$).

Atom	Site	x	y	z	U_{iso}
H(2)	8e	0.0039	0.3476	0.8534	0.064
H(5)	8e	0.27	0.6027	0.9912	0.058
H(4)	8e	0.2382	0.4415	1.1065	0.066

in the mixture containing *N,N'*-dicyclohexylcarbodiimide (0.02 mol) and cold acetone (45 mL). The system was stirred in ice bath for 1 h and TLC monitored, then kept overnight in a refrigerator at 4°. A white precipitate of dicyclohexylurea was filtered off and the solvent was evaporated under vacuum to give the crude anhydride product as oil. A crystalline product could be obtained from hot ethanol or methanol, in 65% yield, mp = 110–111°. Crystals suitable for the X-ray diffraction study were obtained upon free evaporation of the reaction mixture from pure ethyl acetate.

Experimental details

The C—H atoms were then constrained to an ideal geometry, with C—H distances of 0.93–0.98 Å. The U_{iso} values of the hydrogen atoms of methyl groups were set to $1.5U_{\text{eq}}$ (C_{methyl}) and the U_{iso} values of all other hydrogen atoms were set to $1.2U_{\text{eq}}(\text{C})$.

Discussion

Benzoic anhydride and its derivatives, as traditional compounds, played a significant role in the organic synthetic chemistry. It was reported that some benzoic anhydride derivatives were applied as preservatives, additives, and softeners for some polymers [2, 3]. They are also intermediates in the synthesis of some valuable compounds with special properties [4, 5]. Meanwhile, some members of this class of compounds are effective acylating reagents [4, 6]. The title compound is composed of two 2,4-dichlorobenzoyl moieties. One oxygen atom as a bridge connects the two identical moieties. The two 2,4-dichlorobenzoyl moieties of title compound are not coplanar with the dihedral angle being 64.9°. The distance between the two carbonyl oxygen atoms [O(1)—O(1A)]

Table 3: Atomic coordinates and displacement parameters (Å²).

Atom	Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₁₂	<i>U</i> ₁₃	<i>U</i> ₂₃
Cl(1)	8e	0.09041(8)	0.25896(6)	1.0762(1)	0.0793(6)	0.0437(4)	0.1170(8)	0.0035(4)	0.0163(5)	0.0221(4)
Cl(2)	8e	−0.00610(8)	0.51465(8)	0.67797(8)	0.0821(6)	0.0810(6)	0.0678(5)	−0.0140(4)	−0.0258(4)	−0.0092(4)
O(1)	8e	0.1423(2)	0.7062(2)	0.6795(2)	0.063(1)	0.064(1)	0.065(1)	0.003(1)	−0.012(1)	0.013(1)
C(1)	8e	0.0757(2)	0.4965(2)	0.8124(2)	0.047(2)	0.046(1)	0.052(2)	0.002(1)	−0.000(1)	−0.012(1)
O(2)	4d	0.2500	0.7500	0.8473(3)	0.104(2)	0.050(2)	0.043(1)	−0.033(2)	0.0	0.0
C(7)	8e	0.1789(2)	0.6794(2)	0.7799(3)	0.049(2)	0.041(1)	0.050(2)	0.003(1)	0.004(1)	−0.007(1)
C(2)	8e	0.0571(2)	0.3995(2)	0.8808(3)	0.051(2)	0.039(1)	0.070(2)	−0.006(1)	0.005(1)	−0.014(1)
C(5)	8e	0.2162(2)	0.5517(2)	0.9631(3)	0.047(2)	0.042(1)	0.055(2)	−0.003(1)	−0.003(1)	−0.002(1)
C(6)	8e	0.1564(2)	0.5749(2)	0.8518(2)	0.043(1)	0.037(1)	0.048(1)	0.001(1)	0.003(1)	−0.008(1)
C(4)	8e	0.1976(2)	0.4555(2)	1.0325(3)	0.054(2)	0.047(1)	0.064(2)	0.005(1)	−0.006(1)	0.007(1)
C(3)	8e	0.1180(2)	0.3801(2)	0.9903(3)	0.051(2)	0.035(1)	0.071(2)	0.005(1)	0.012(1)	0.002(1)

is 2.763 Å, this distance is shorter than the sum of the van der Waals radii of both atoms (3.04 Å), which suggests there are weak intramolecular interaction between two atoms. In the crystal, molecules are stabilized by weak C—H...O hydrogen bonds, C—H... π interactions, π — π interactions and van der Waals forces.

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