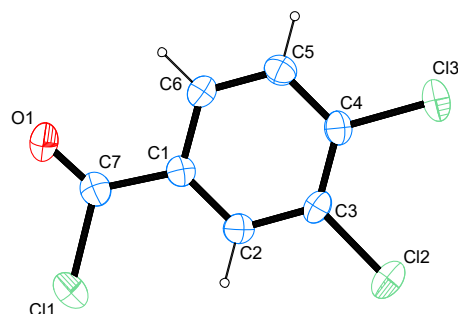


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The crystal structure of 3,4-dichlorobenzoic acid chloride, $C_7H_3Cl_3O$



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Abstract

$C_7H_3Cl_3O$, monoclinic, $P2_1/c$ (no. 14), $a = 12.0518(15)$ Å, $b = 9.7403(11)$ Å, $c = 6.9562(9)$ Å, $\beta = 99.047(4)^\circ$, $V = 806.42(17)$ Å³, $Z = 4$, $R_{gt}(F) = 0.0316$, $wR_{ref}(F^2) = 0.0793$, $T = 200$ K.

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The molecular structure is shown in the Figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

The compound was obtained commercially (Aldrich). Crystals suitable for the diffraction study were obtained upon repeated re-sublimation of the compound at room temperature. Crystal selection and mounting was conducted under

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Table 1: Data collection and handling.

Crystal:	Colourless rod
Size:	$0.55 \times 0.13 \times 0.10$ mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ :	1.07 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.3° , 80%
$N(hkl)_{\text{measured}}$, $N(hkl)_{\text{unique}}$, R_{int} :	2002, 2002, 0.043
Criterion for I_{obs} , $N(hkl)_{\text{gt}}$:	$I_{\text{obs}} > 2 \sigma(I_{\text{obs}})$, 1808
$N(\text{param})_{\text{refined}}$:	101
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

a constant stream of nitrogen to prevent the rapid hydrolysis of the compound upon contact with the atmosphere.

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.95 Å) and were included in the refinement in the riding model approximation, with $U(\text{H})$ set to $1.2U_{\text{eq}}(\text{C})$.

The compound was refined as a two-component twin with a volume ratio of 56.8:43.2.

Comment

The chlorides of carboxylic acids are useful reagents in chemical synthesis. Their high reactivity allows for the easy synthesis of a broad range of acid derivatives such as anhydrides, esters and amides. Especially benzoic acids can be converted easily into these derivatives by making use of the respective acyl chloride as an intermediate. In continuation of our interest in the structural chemistry of benzoic acids and their derivatives [7–11], the title compound was investigated. A series of fluorinated benzoic acid chlorides has been characterized by means of diffraction studies based on single crystals recently [12].

The structure solution shows the presence of a benzoic acid chloride bearing two chloro substituents in

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atom	x	y	z	U _{iso} [*] /U _{eq}
Cl1	0.35680 (6)	0.66021 (8)	0.52956 (16)	0.0565 (3)
Cl2	0.40849 (6)	0.11079 (7)	0.56444 (12)	0.0451 (2)
Cl3	0.16817 (6)	−0.01885 (6)	0.44037 (10)	0.03717 (16)
O1	0.14380 (17)	0.66732 (19)	0.4227 (4)	0.0464 (5)
C1	0.21339 (18)	0.4394 (2)	0.4596 (4)	0.0246 (4)
C2	0.30568 (19)	0.3547 (2)	0.5118 (4)	0.0271 (5)
H2	0.377974	0.393212	0.552342	0.033 [*]
C3	0.29183 (19)	0.2137 (2)	0.5044 (4)	0.0269 (5)
C4	0.1860 (2)	0.1570 (2)	0.4483 (4)	0.0267 (5)
C5	0.09342 (18)	0.2414 (3)	0.3976 (4)	0.0285 (5)
H5	0.021008	0.202565	0.359513	0.034 [*]
C6	0.10688 (19)	0.3822 (2)	0.4026 (4)	0.0276 (5)
H6	0.043666	0.440337	0.367211	0.033 [*]
C7	0.2206 (2)	0.5910 (2)	0.4619 (4)	0.0308 (5)

meta and *para* position to the acyl group. C–Cl bond lengths of 1.724(2) and 1.727(2) Å for the aromatic system and 1.768(3) Å for the acylhalide group are found in the same range of comparable bonds in other compounds whose metrical parameters have been deposited with the Cambridge Structural Database [13]. The molecule is essentially planar with the largest deviation from the least-squares plane as defined by all non-hydrogen atoms found at only 0.021(3) Å for the intracyclic carbon atom in between the acyl and chloro substituents. The plane defined by the three atoms of the acid chloride functional group and the least-squares plane as defined by the non-hydrogen atoms of the substituted aromatic system enclose an angle of only 0.8(3) Å. This is indicative of resonance spanning the halogenated carboxyl group.

In the crystal, C–H···O contacts whose range falls by more than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them are observed. These are supported by the hydrogen atom in *meta* position to the acyl group as donor and connect the molecules to zig-zag-chains along the crystallographic *b* axis. In terms of graph-set analysis [14, 15], the descriptor for this pattern is C₁¹ (6). Furthermore, dispersive Cl···O and Cl···Cl contacts with a shortening cut-off at 0.2 Å below the sum of van-der-Waals radii are present with the latter type of intermolecular interaction extending these former chains to undulated sheets along [1/2 0 1]. The structure is dominated by strong

π-stacking with the shortest distance between two centers of gravity measured at 3.6020(16) Å only.

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