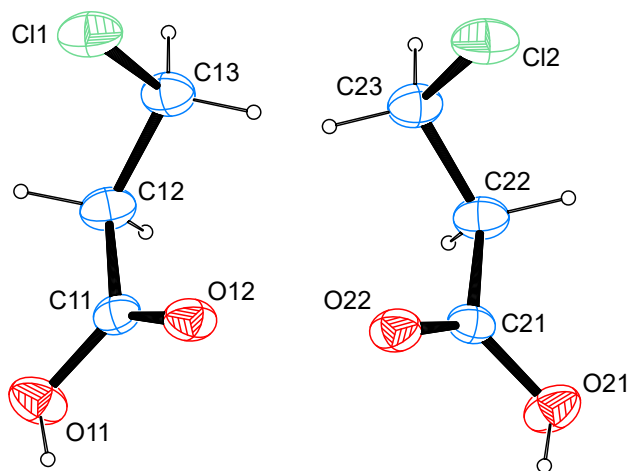


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The crystal structure of 3-chloropropionic acid, $C_3H_5ClO_2$



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Abstract

$C_3H_5ClO_2$, monoclinic, $P2_1/c$ (no. 14), $a = 5.2011(4)$ Å, $b = 7.4362(4)$ Å, $c = 24.1175(15)$ Å, $\beta = 94.594(3)^\circ$, $V = 929.78(10)$ Å³, $Z = 8$, $R_{gt}(F) = 0.0333$, $wR_{ref}(F^2) = 0.0795$, $T = 200$ 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 (Fluka). Crystals suitable for the diffraction study were taken directly from the provided product.

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Table 1: Data collection and handling.

Crystal:	Colourless platelet
Size:	0.60 × 0.46 × 0.25 mm
Wavelength:	Mo K α radiation (0.71073 Å)
μ :	0.67 mm ⁻¹
Diffractometer, scan mode:	Bruker APEX-II, φ and ω
θ_{max} , completeness:	28.4°, 99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int} :	7885, 2269, 0.017
Criterion for I_{obs} , $N(hkl)_{gt}$:	$I_{obs} > 2 \sigma(I_{obs})$, 1926
$N(param)_{refined}$:	111
Programs:	Bruker [1, 2], SHELX [3], WinGX/ORTEP [4], Mercury [5], PLATON [6]

Experimental details

Carbon-bound H atoms were placed in calculated positions (C–H 0.99 Å) and were included in the refinement in the riding model approximation, with $U(H)$ set to $1.2U_{eq}(C)$.

The H atoms of the hydroxyl groups were allowed to rotate with a fixed angle around the C–O bond to best fit the experimental electron density (HFIX 147 in the SHELX program suite [3]), with $U(H)$ set to $1.5U_{eq}(O)$.

Comment

While the first members of the homologous series of aliphatic carboxylic acids constitute a family of liquid substances at room temperature, the introduction of chlorine atoms in the backbone quickly results in a marked increase of melting points and subsequent tendency to form crystalline substances at ambient conditions. However, there is no uniform trend as the stepwise introduction of chlorine atoms into the methyl group of acetic acid to the respective trihalo acid shows with melting points of 17, 63, 14 and 58 °C (values rounded) in the order of increasing chlorine content [7]. An even stronger increase in melting point is observed for the introduction of the first terminal chlorine atom in propionic acid with a change from –21 to 41 °C. In continuation of our interest in the structures of functionalized carboxylic acids [8–15], the crystal and

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

Atom	x	y	z	<i>U</i> _{iso} [*] / <i>U</i> _{eq}
Cl1	0.74346 (8)	-0.00203 (7)	0.05634 (2)	0.03771 (13)
O11	1.0112 (2)	-0.08791 (18)	0.22569 (5)	0.0342 (3)
H11	0.914093	-0.072739	0.251507	0.051*
O12	0.7817 (2)	0.14062 (17)	0.18727 (5)	0.0300 (3)
C11	0.9545 (3)	0.0306 (2)	0.18626 (6)	0.0233 (3)
C12	1.1290 (3)	0.0165 (2)	0.13971 (7)	0.0282 (3)
H12A	1.157037	-0.112232	0.131684	0.034*
H12B	1.298420	0.069505	0.152212	0.034*
C13	1.0273 (3)	0.1085 (2)	0.08684 (7)	0.0296 (4)
H13A	1.161931	0.107960	0.060057	0.035*
H13B	0.985905	0.235247	0.094967	0.035*
Cl2	0.24696 (9)	0.58842 (7)	0.05642 (2)	0.04071 (13)
O21	0.5109 (2)	0.67876 (18)	0.22677 (5)	0.0336 (3)
H21	0.408194	0.667580	0.251715	0.050*
O22	0.2794 (2)	0.45188 (17)	0.18805 (5)	0.0297 (3)
C21	0.4530 (3)	0.5612 (2)	0.18719 (6)	0.0232 (3)
C22	0.6285 (3)	0.5747 (3)	0.14072 (6)	0.0283 (3)
H22A	0.654470	0.703369	0.132188	0.034*
H22B	0.798596	0.523582	0.153590	0.034*
C23	0.5297 (3)	0.4800 (3)	0.08820 (7)	0.0307 (4)
H23A	0.488195	0.353689	0.096891	0.037*
H23B	0.665796	0.479118	0.061771	0.037*

molecular structure of the title compound was determined to gain an understanding for this drastic change in physical properties. The structure of propionic acid has been reported earlier [16].

The structure solutions shows the expected connectivity of a propionic acid derivative bearing one chlorine atom in terminal position. The asymmetric unit comprises two complete molecules. C–Cl bond lengths of 1.7941(18) and 1.7950(17) Å are almost equal and found in good agreement with other compounds containing chloromethylene groups whose metrical parameters (determined by diffraction studies performed on single crystals) have been deposited with the Cambridge Structural Database [17]. Absolute values for the Cl–C–C–C dihedral angles differ only slightly with values of -66.78(17)° and 67.51(18)°, respectively.

In the crystal, classical hydrogen bonds of the O–H...O type are observed next to C–H...O and C–H...Cl contacts with the latter falling slightly less than 0.1 Å below the sum of van-der-Waals radii of the atoms participating in them. The classical hydrogen bonds connect the two molecules present in the asymmetric unit to the well-known carboxylic acid dimer pattern. The C–H...O contacts are supported by one hydrogen atom of the methylene group in each of the two individual molecules as donor and have exclusively the keto-type oxygen atom of one of its own

symmetry-generated equivalents as acceptor. The C–H...Cl contacts stem from the remaining hydrogen atom of the methylene group in each of the two individual molecules as donor; however, the acceptor atom is provided by the chlorine atom of the other molecule present in the asymmetric unit. In terms of graph-set analysis [18, 19], the descriptor for the classical hydrogen bonds is $R_2^2(8)$ at the binary level while the descriptor for the C–H supported intermolecular contacts can be described by means of a $DDC_1^1(4)C_1^1(4)$ descriptor at the unary level. In total, the molecules are connected to double layers perpendicular to the crystallographic *c* axis.

While the less-pronounced shortening of the C–H...O contacts with regards to their sum of van-der-Waals radii suggests a weaker bonding interaction, in the context of a comparison with the crystal structure of plain propionic acid [16], the presence of the additional C–H...Cl contacts would allow for rationalizing the observed increase in melting points when going from propionic acid to 3-chloropropionic acid.

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