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3-Chloropropiophenone

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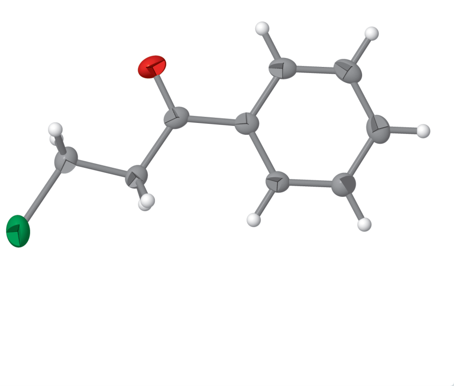
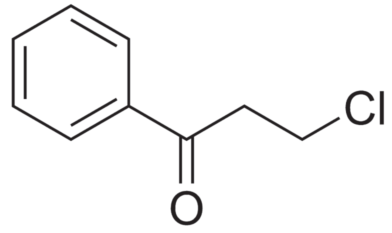
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, 3-chloropropiophenone (or 3-chloro-1-phenylpropan-1-one), C_9H_9ClO, consists of an almost planar molecule that is charaterized by very small torsion angles within the alkyl side chain (torsion angles < 6.3°). No hydrogen bonds are observed in the crystal packing. The compound exhibits a melting point of 54°C.

3D view



Chemical scheme



Structure description

β-Chloro ketones are useful building blocks for many chemical transformation reactions. They are accessible *via* different reaction schemes such as Friedel-Crafts acylation (Sartori & Maggi, 2006), Wacker-type oxidation (Liu *et al.*, 2017), or light-mediated ring opening of aryl cyclopropanes (Petzold *et al.*, 2019). The title compound was obtained in almost quantitative yield in high purity. It can be designated as a suitable building block in the ongoing efforts to synthesize feasible new ligands for Cu-based complexes (Sonneck *et al.*, 2015, 2016).

The molecular structure of 3-chloropropiophenone is almost planar with torsion angles of less than 6.3 degrees [maximum torsion angle: C1—C2—C3—O1 = −6.21 (19)°] in the side chain (Fig. 1). The main deviation out of the plane defined by the non-hydrogen atoms of the molecule is observed for O1 with −0.1091 (10) Å and for Cl1 with 0.1065 (8) Å. In addition, the layered packing prevents the formation of extended halogen or hydrogen-bonding networks. The molecules form stacks along the *c* axis. In a stack, neighbouring molecules are related by the *c* glide plane. All bond lengths and angles are within the expected range and the C═O bond is 1.2158 (18) Å.

Synthesis and crystallization

3-Chloropropiophenone was obtained as colourless crystals in quantitative yield from the Friedel–Crafts acylation of benzene and 3-chloropropionyl chloride in dichloromethane. $AlCl_3$ (38.2 g, 286.5 mmol, 1.25 eq.) was suspended in 50 ml of dry dichloromethane at 0°C. A solution of 3-chloropropionyl chloride (29.1 g, 229.2 mmol, 1.0 eq.) in 90 ml

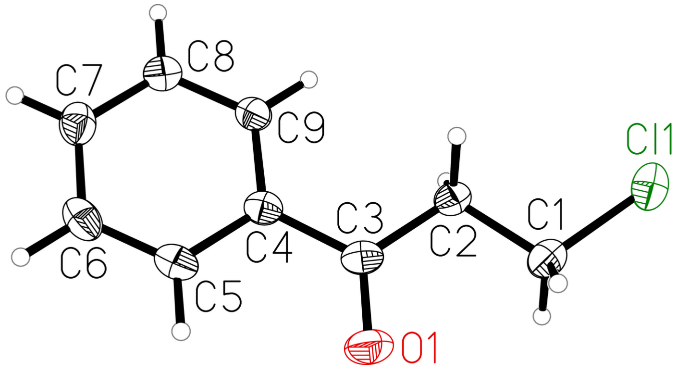


Figure 1
Molecular structure of the title compound with atom labelling and displacement ellipsoids drawn at 50% probability level.

dichloromethane was added dropwise at 0°C to the $AlCl_3$ suspension. Afterwards, a solution of benzene (17.9 g, 229.2 mmol, 1.0 eq.) in 25 mL dichloromethane was added dropwise at 0°C to the suspension and further stirred for 2 h at 0°C and 12 h at ambient conditions. The final solution was poured onto ice and concentrated hydrochloric acid (70 g:7 g) and after separation of the organic phase, the aqueous phase was extracted twice with 100 ml portions of dichloromethane. The combined organic phases were extracted twice with 150 ml portions of water and finally dried over Na_2SO_4. The solvent was removed completely under diminished pressure and the off-white crystalline solid residue was recrystallized from pentane to yield the final product (37.5 g, 97%). Colourless single crystals of 3-chloropropiophenone were obtained from a pentane solution by slow evaporation of the solvent at 4°C over the period of one week. Analytic data for C_9H_9ClO: m.p. 54°C, elemental analysis % (calculated): C 64.14 (64.11), H 5.25 (5.38); Cl 21.01 (21.02). ^{1}H NMR (400 MHz, $CDCl_3$): δ (p.p.m.) = 7.98–7.93 (*m*, 2H, ArH); 7.61–7.56 (*m*, 1H, ArH); 7.51–7.45 (*m*, 2H, ArH); 3.92 (*t*, ^3J = 6.8 Hz, 2H); 3.45 (*t*, ^3J = 6.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (p.p.m.) = 196.78 (CO); 136.45 (C); 133.65, 128.84, 128.84, 128.14, 128.14 (CH); 41.36, 38.79 (CH_2).

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1.

Table 1
Experimental details.

Crystal data	
Chemical formula	C_9H_9ClO
M_r	168.61
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	150
a, b, c (Å)	5.4485 (13), 20.347 (5), 7.4860 (17)
β (°)	102.123 (4)
V (Å^3)	811.4 (3)
Z	4
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.40
Crystal size (mm)	0.51 × 0.43 × 0.07
Data collection	
Diffractometer	Bruker APEXII CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.79, 0.97
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	9113, 1951, 1595
R_{int}	0.032
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	0.661
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.038, 0.095, 1.08
No. of reflections	1951
No. of parameters	100
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.36, −0.24

Computer programs: *APEX2* (Bruker, 2014), *SAINT* (Bruker, 2013), *SHELXS97* (Sheldrick, 2008), *SHELXL2014/7* (Sheldrick, 2015), *XP* in *SHELXTL* (Sheldrick, 2008) and *publCIF* (Westrip, 2010).

References

Bruker (2013). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2014). *APEX2* Bruker AXS Inc., Madison, Wisconsin, USA.

Krause, L., Herbst-Irmer, R., Sheldrick, G. M. & Stalke, D. (2015). *J. Appl. Cryst.* **48**, 3–10.

Liu, B., Jin, F., Wang, T., Yuan, X. & Han, W. (2017). *Angew. Chem. Int. Ed.* **56**, 12712–12717.

Petzold, D., Singh, P., Almqvist, F. & König, B. (2019). *Angew. Chem. Int. Ed.* **58**, 8577–8580.

Sartori, G. & Maggi, R. (2006). *Chem. Rev.* **106**, 1077–1104.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Sheldrick, G. M. (2015). *Acta Cryst.* C**71**, 3–8.

Sonneck, M., Peppel, T., Spannenberg, A. & Wohlrab, S. (2015). *Crystals*, **5**, 466–474.

Sonneck, M., Spannenberg, A., Wohlrab, S. & Peppel, T. (2016). *Crystals*, **6**, 66.

Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.

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full crystallographic data

IUCrData (2025). **10**, x250349 [https://doi.org/10.1107/S2414314625003499]

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3-Chloro-1-phenylpropan-1-one

Crystal data

C_9H_9ClO
$M_r = 168.61$
Monoclinic, $P2_1/c$
$a = 5.4485$ (13) Å
$b = 20.347$ (5) Å
$c = 7.4860$ (17) Å
$\beta = 102.123$ (4)°
$V = 811.4$ (3) Å^3
$Z = 4$

$F(000) = 352$
$D_x = 1.380$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2965 reflections
$\theta = 3.0$–28.7°
$\mu = 0.40$ mm^{-1}
$T = 150$ K
Plate, colourless
0.51 × 0.43 × 0.07 mm

Data collection

Bruker APEXII CCD diffractometer
Radiation source: fine-focus sealed tube
Detector resolution: 8.3333 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
$T_{\min} = 0.79$, $T_{\max} = 0.97$

9113 measured reflections
1951 independent reflections
1595 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.032$
$\theta_{\max} = 28.0°$, $\theta_{\min} = 2.0°$
$h = -7 \rightarrow 7$
$k = -26 \rightarrow 25$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.095$
$S = 1.08$
1951 reflections
100 parameters
0 restraints

Primary atom site location: structure-invariant direct methods
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0414P)^2 + 0.259P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.36$ e Å^{-3}
$\Delta\rho_{\min} = -0.24$ e Å^{-3}

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

Refinement. Hydrogen atoms were located in a difference map and refined as riding on their parent atoms with $U(H)=1.2U_{eq}(C)$.

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

	x	*y*	*z*	$U_{\rm iso}$*/$U_{\rm eq}$
C1	0.4181 (3)	0.91110 (7)	0.3732 (2)	0.0292 (3)
H1A	0.5586	0.9205	0.3120	0.035*
H1B	0.4812	0.9154	0.5067	0.035*
C2	0.3239 (3)	0.84182 (7)	0.3283 (2)	0.0243 (3)
H2A	0.1794	0.8331	0.3859	0.029*
H2B	0.2658	0.8373	0.1944	0.029*
C3	0.5285 (3)	0.79232 (7)	0.39585 (19)	0.0252 (3)
C4	0.4665 (3)	0.72090 (7)	0.38053 (19)	0.0229 (3)
C5	0.6530 (3)	0.67574 (8)	0.4561 (2)	0.0283 (3)
H5	0.8139	0.6911	0.5163	0.034*
C6	0.6055 (3)	0.60927 (8)	0.4438 (2)	0.0313 (4)
H6	0.7334	0.5789	0.4953	0.038*
C7	0.3713 (3)	0.58649 (8)	0.3564 (2)	0.0309 (3)
H7	0.3389	0.5406	0.3484	0.037*
C8	0.1843 (3)	0.63050 (8)	0.2808 (2)	0.0280 (3)
H8	0.0241	0.6148	0.2205	0.034*
C9	0.2314 (3)	0.69757 (7)	0.29323 (19)	0.0245 (3)
H9	0.1026	0.7277	0.2419	0.029*
Cl1	0.17021 (9)	0.96882 (2)	0.29882 (7)	0.04702 (17)
O1	0.7414 (2)	0.81030 (6)	0.46074 (17)	0.0399 (3)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0317 (8)	0.0274 (7)	0.0294 (8)	−0.0056 (6)	0.0081 (6)	−0.0028 (6)
C2	0.0243 (7)	0.0254 (7)	0.0237 (7)	−0.0038 (5)	0.0064 (6)	−0.0007 (5)
C3	0.0227 (7)	0.0327 (8)	0.0202 (7)	−0.0042 (6)	0.0050 (6)	0.0002 (6)
C4	0.0221 (7)	0.0290 (7)	0.0190 (6)	−0.0001 (5)	0.0074 (6)	0.0011 (5)
C5	0.0214 (7)	0.0381 (8)	0.0254 (8)	0.0028 (6)	0.0051 (6)	0.0014 (6)
C6	0.0298 (8)	0.0356 (8)	0.0303 (8)	0.0108 (6)	0.0103 (7)	0.0052 (6)
C7	0.0375 (9)	0.0266 (7)	0.0317 (8)	0.0034 (6)	0.0144 (7)	0.0011 (6)
C8	0.0256 (8)	0.0295 (7)	0.0294 (8)	−0.0017 (6)	0.0065 (6)	−0.0001 (6)
C9	0.0216 (7)	0.0277 (7)	0.0243 (7)	0.0015 (5)	0.0052 (6)	0.0027 (5)
Cl1	0.0454 (3)	0.0260 (2)	0.0684 (3)	0.00011 (18)	0.0092 (2)	−0.00376 (19)
O1	0.0255 (6)	0.0408 (7)	0.0487 (8)	−0.0080 (5)	−0.0034 (5)	0.0026 (5)

Geometric parameters (Å, º)

C1—C2	1.514 (2)	C4—C5	1.399 (2)
C1—Cl1	1.7882 (17)	C5—C6	1.377 (2)
C1—H1A	0.9900	C5—H5	0.9500
C1—H1B	0.9900	C6—C7	1.386 (2)
C2—C3	1.509 (2)	C6—H6	0.9500
C2—H2A	0.9900	C7—C8	1.385 (2)
C2—H2B	0.9900	C7—H7	0.9500

C3—O1	1.2158 (18)	C8—C9	1.388 (2)
C3—C4	1.491 (2)	C8—H8	0.9500
C4—C9	1.393 (2)	C9—H9	0.9500

C2—C1—Cl1	110.12 (11)	C5—C4—C3	118.39 (13)
C2—C1—H1A	109.6	C6—C5—C4	120.52 (14)
Cl1—C1—H1A	109.6	C6—C5—H5	119.7
C2—C1—H1B	109.6	C4—C5—H5	119.7
Cl1—C1—H1B	109.6	C5—C6—C7	120.13 (14)
H1A—C1—H1B	108.2	C5—C6—H6	119.9
C3—C2—C1	110.81 (12)	C7—C6—H6	119.9
C3—C2—H2A	109.5	C8—C7—C6	120.13 (15)
C1—C2—H2A	109.5	C8—C7—H7	119.9
C3—C2—H2B	109.5	C6—C7—H7	119.9
C1—C2—H2B	109.5	C7—C8—C9	119.92 (15)
H2A—C2—H2B	108.1	C7—C8—H8	120.0
O1—C3—C4	120.39 (14)	C9—C8—H8	120.0
O1—C3—C2	120.58 (14)	C8—C9—C4	120.33 (14)
C4—C3—C2	119.03 (12)	C8—C9—H9	119.8
C9—C4—C5	118.96 (14)	C4—C9—H9	119.8
C9—C4—C3	122.65 (13)		

Cl1—C1—C2—C3	−178.09 (10)	C3—C4—C5—C6	−179.35 (13)
C1—C2—C3—O1	−6.21 (19)	C4—C5—C6—C7	−0.1 (2)
C1—C2—C3—C4	174.28 (12)	C5—C6—C7—C8	0.1 (2)
O1—C3—C4—C9	−174.35 (14)	C6—C7—C8—C9	−0.3 (2)
C2—C3—C4—C9	5.2 (2)	C7—C8—C9—C4	0.4 (2)
O1—C3—C4—C5	5.2 (2)	C5—C4—C9—C8	−0.4 (2)
C2—C3—C4—C5	−175.26 (12)	C3—C4—C9—C8	179.21 (13)
C9—C4—C5—C6	0.2 (2)		