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Crystal structure of 2,2-dichloro-1-(piperidin-1-yl)ethanone

Markus Schwierz,[a] Helmar Görls[b] and Wolfgang Imhof[a]*

[a]University Koblenz-Landau, Institute for Integrated Natural Sciences, Universitätsstrasse 1, 56070 Koblenz, Germany, and [b]Friedrich-Schiller-University Jena, Institute of Inorganic and Analytical Chemistry, Humboldtstrasse 8, 07743 Jena, Germany. *Correspondence e-mail: Imhof@uni-koblenz.de

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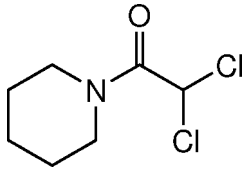
In the title compound, $C_7H_{11}Cl_2NO$, the piperidine ring shows a chair conformation and the bond-angle sum at the N atom is 359.9°. The H atom of the dichloromethyl group is in an eclipsed conformation with respect to the carbonyl group (H—C—C=O = −5°). In the crystal, inversion dimers are linked by pairs of C—H···O hydrogen bonds between the dichloromethyl group and the carbonyl O atom, which generate $R_2^2(8)$ loops. The dimers are linked into a ladder-like structure propagating in the [100] direction by short O···Cl [3.1084 (9) Å] contacts.

Keywords: crystal structure; piperidine ring; ethanone; weak hydrogen bonds; intermolecular Cl···O interactions.

CCDC reference: 1038542

1. Related literature

For the synthetic procedure, see: Schank (1967). For a survey concerning weak hydrogen bonds, see: Desiraju & Steiner (1999). For a description of the nature of intermolecular interactions between chlorine and oxygen, see: Lommerse *et al.* (1996). For the crystal structure of the starting compound, see: Schwierz *et al.* (2015).



2. Experimental

2.1. Crystal data

$C_7H_{11}Cl_2NO$ M_r = 196.07

Monoclinic, $P2_1/n$
a = 6.2972 (1) Å
b = 15.4896 (2) Å
c = 9.3709 (2) Å
β = 108.920 (1)°
V = 864.66 (3) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.69 mm^{-1}
T = 133 K
0.08 × 0.07 × 0.06 mm

2.2. Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.712, T_{max} = 0.746
5528 measured reflections
1982 independent reflections
1909 reflections with $I > 2\sigma(I)$
R_{int} = 0.014

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.051
S = 1.07
1982 reflections
144 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C7—H7···O1^{i}	0.927 (13)	2.286 (12)	3.1931 (13)	166 (1)

Symmetry code: (i) $-x+2, -y+1, -z+1$.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012) and *Mercury* (Macrae *et al.*, 2008); software used to prepare material for publication: *SHELXL97*.

Acknowledgements

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Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7336).

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supporting information

Acta Cryst. (2015). E**71**, o47 [https://doi.org/10.1107/S205698901402708X]

Crystal structure of 2,2-dichloro-1-(piperidin-1-yl)ethanone

Markus Schwierz, Helmar Görls and Wolfgang Imhof

S1. Comment

The title compound is an intermediate in the synthesis of 2,2-dimethoxy-1-(pyridin-2-yl)ethanone and has been synthesized from 2,2-dichloro-1-(piperidin-1-yl)butane-1,3-dione (Schwierz *et al.*, 2015) following a modified procedure (Schank, 1967). As it is expected the piperidine ring shows a chair conformation and the amide substructure is planar. The hydrogen atom of the dichloromethyl group is in an eclipsed conformation with respect to the carbonyl group. In the crystal structure, dimeric aggregates are formed by hydrogen bonds of the C–H···O type between the dichloromethyl group and the carbonyl oxygen atom. In addition, these dimers are linked into a ladder-like structure parallel to the *ac* plane by oxygen chlorine contacts.

S2. Experimental

22 ml methanol was cooled down to -6°C and then 1.93 g (84 mmol) sodium was slowly added in a way that the temperature is maintained. Afterwards 20.0 g (84 mmol) 2,2-dichloro-1-(piperidin-1-yl)butane-1,3-dione in 10 ml methanol was dropwise added to the solution of NaOMe. The resulting solution was stirred for 30 minutes and then neutralized with aqueous HCl at -10°C. After evaporating the mixture to dryness the amorphous material was collected on filter paper in a Büchner funnel and washed with water (yield: 13.6 g, 83%). The product has to be destilled *in vacuo* (0.2 mbar) and condensed into a Schlenk tube cooled by liquid nitrogen to obtain colourless prisms for X-ray diffraction.

S3. Refinement

The positions of all hydrogen atoms have been determined from a Fourier map and all hydrogen atoms were refined without any constraints.

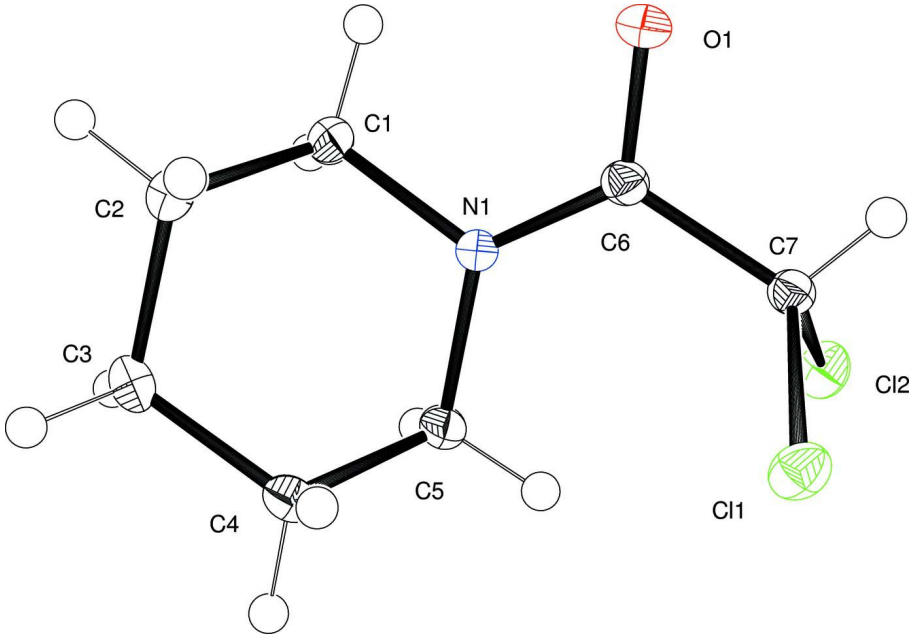

Figure 1

Molecular structure of the title compound with displacement ellipsoids drawn at the 50% probability level.

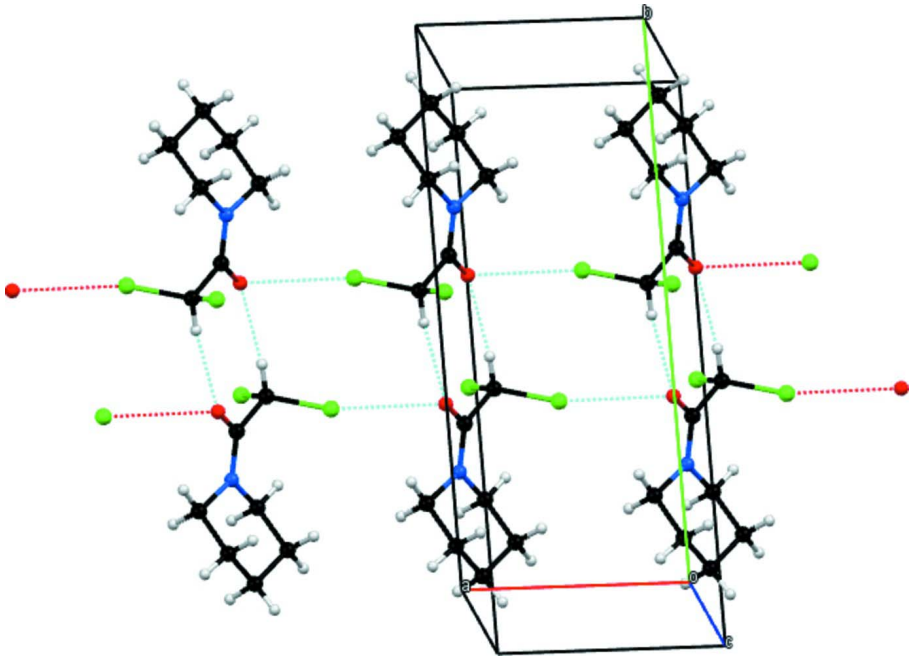

Figure 2

Crystal structure of the title compound showing ladder-like arrangement parallel to the *ac* plane.

2,2-Dichloro-1-(piperidin-1-yl)ethanone

Crystal data

$C_7H_{11}Cl_2NO$
M_r = 196.07

Monoclinic, $P2_1/n$
Hall symbol: -P 2yn

a = 6.2972 (1) Å
b = 15.4896 (2) Å
c = 9.3709 (2) Å
β = 108.920 (1)°
V = 864.66 (3) Å^3
Z = 4
F(000) = 408

D_x = 1.506 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
μ = 0.69 mm^{-1}
T = 133 K
Prism, colourless
0.08 × 0.07 × 0.06 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
phi– + ω–scan
Absorption correction: multi-scan (*SADABS*; Bruker, 2002)
T_{min} = 0.712, T_{max} = 0.746

5528 measured reflections
1982 independent reflections
1909 reflections with $I > 2\sigma(I)$
R_{int} = 0.014
θ_{max} = 27.5°, θ_{min} = 2.6°
h = −8→8
k = −17→20
l = −12→8

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.020
$wR(F^2)$ = 0.051
S = 1.07
1982 reflections
144 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 0.3796P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.18 e Å^{-3}

Special details

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

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

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

	x	y	z	U_{iso}*/U_{eq}
Cl1	0.58896 (4)	0.397515 (17)	0.60904 (3)	0.01933 (8)
Cl2	1.00866 (4)	0.453542 (17)	0.83711 (3)	0.01976 (8)
O1	1.06874 (14)	0.38479 (5)	0.48067 (9)	0.02086 (18)
N1	1.05601 (15)	0.28336 (6)	0.65192 (10)	0.01611 (18)
C1	1.20371 (19)	0.22440 (7)	0.60412 (13)	0.0191 (2)
H1B	1.333 (2)	0.2132 (9)	0.6929 (16)	0.023 (3)*
H1A	1.254 (2)	0.2541 (9)	0.5296 (16)	0.021 (3)*
C2	1.0825 (2)	0.14060 (7)	0.54290 (13)	0.0187 (2)
H2B	0.959 (2)	0.1519 (9)	0.4527 (17)	0.023 (3)*
H2A	1.189 (2)	0.1027 (9)	0.5171 (17)	0.026 (4)*

C3	0.99241 (19)	0.09891 (7)	0.65911 (13)	0.0185 (2)
H3B	0.910 (2)	0.0471 (9)	0.6184 (15)	0.019 (3)*
H3A	1.119 (2)	0.0834 (9)	0.7476 (16)	0.022 (3)*
C4	0.84334 (18)	0.16225 (7)	0.70759 (12)	0.0170 (2)
H4B	0.713 (2)	0.1755 (9)	0.6231 (15)	0.019 (3)*
H4A	0.792 (2)	0.1379 (9)	0.7849 (16)	0.022 (3)*
C5	0.96872 (19)	0.24606 (7)	0.76638 (12)	0.0167 (2)
H5B	1.098 (2)	0.2349 (9)	0.8562 (15)	0.018 (3)*
H5A	0.875 (2)	0.2867 (9)	0.7911 (15)	0.018 (3)*
C6	1.00703 (17)	0.36088 (7)	0.58641 (11)	0.0140 (2)
C7	0.87376 (17)	0.42766 (7)	0.64343 (11)	0.0141 (2)
H7	0.874 (2)	0.4785 (8)	0.5911 (14)	0.013 (3)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.01372 (13)	0.02241 (14)	0.02175 (14)	−0.00113 (10)	0.00559 (10)	−0.00364 (10)
Cl2	0.02030 (14)	0.01973 (14)	0.01757 (13)	−0.00162 (10)	0.00382 (10)	−0.00656 (9)
O1	0.0272 (4)	0.0187 (4)	0.0225 (4)	0.0016 (3)	0.0162 (3)	0.0043 (3)
N1	0.0203 (4)	0.0119 (4)	0.0204 (4)	0.0008 (3)	0.0126 (4)	0.0009 (3)
C1	0.0189 (5)	0.0149 (5)	0.0278 (6)	0.0014 (4)	0.0136 (5)	0.0003 (4)
C2	0.0213 (5)	0.0154 (5)	0.0218 (5)	0.0021 (4)	0.0103 (4)	−0.0008 (4)
C3	0.0214 (5)	0.0125 (5)	0.0214 (5)	−0.0016 (4)	0.0065 (4)	0.0003 (4)
C4	0.0181 (5)	0.0167 (5)	0.0173 (5)	−0.0017 (4)	0.0071 (4)	0.0027 (4)
C5	0.0226 (5)	0.0142 (5)	0.0160 (5)	0.0003 (4)	0.0101 (4)	0.0020 (4)
C6	0.0137 (5)	0.0138 (5)	0.0152 (5)	−0.0025 (4)	0.0054 (4)	−0.0012 (4)
C7	0.0150 (5)	0.0136 (5)	0.0146 (5)	−0.0014 (4)	0.0057 (4)	−0.0004 (4)

Geometric parameters (Å, º)

Cl1—C7	1.7786 (10)	C2—H2A	0.977 (15)
Cl2—C7	1.7823 (10)	C3—C4	1.5254 (15)
O1—C6	1.2328 (13)	C3—H3B	0.966 (14)
N1—C6	1.3383 (14)	C3—H3A	0.974 (15)
N1—C5	1.4726 (13)	C4—C5	1.5264 (15)
N1—C1	1.4731 (13)	C4—H4B	0.961 (14)
C1—C2	1.5208 (15)	C4—H4A	0.961 (14)
C1—H1B	0.973 (15)	C5—H5B	0.980 (14)
C1—H1A	0.971 (14)	C5—H5A	0.942 (14)
C2—C3	1.5249 (15)	C6—C7	1.5332 (14)
C2—H2B	0.960 (15)	C7—H7	0.927 (13)
C6—N1—C5	126.95 (9)	C3—C4—C5	110.99 (9)
C6—N1—C1	119.41 (9)	C3—C4—H4B	109.7 (8)
C5—N1—C1	113.57 (8)	C5—C4—H4B	108.7 (8)
N1—C1—C2	110.77 (9)	C3—C4—H4A	111.2 (8)
N1—C1—H1B	106.7 (8)	C5—C4—H4A	108.9 (8)
C2—C1—H1B	110.4 (8)	H4B—C4—H4A	107.2 (11)

N1—C1—H1A	108.1 (8)	N1—C5—C4	110.02 (9)
C2—C1—H1A	112.0 (8)	N1—C5—H5B	106.9 (8)
H1B—C1—H1A	108.8 (12)	C4—C5—H5B	110.5 (8)
C1—C2—C3	110.46 (9)	N1—C5—H5A	109.2 (8)
C1—C2—H2B	109.9 (9)	C4—C5—H5A	111.4 (8)
C3—C2—H2B	109.0 (8)	H5B—C5—H5A	108.8 (11)
C1—C2—H2A	107.8 (8)	O1—C6—N1	123.54 (10)
C3—C2—H2A	111.4 (8)	O1—C6—C7	115.35 (9)
H2B—C2—H2A	108.3 (12)	N1—C6—C7	121.09 (9)
C2—C3—C4	110.35 (9)	C6—C7—Cl1	113.17 (7)
C2—C3—H3B	110.4 (8)	C6—C7—Cl2	111.88 (7)
C4—C3—H3B	110.3 (8)	Cl1—C7—Cl2	111.30 (5)
C2—C3—H3A	108.8 (8)	C6—C7—H7	107.1 (8)
C4—C3—H3A	108.4 (8)	Cl1—C7—H7	107.6 (8)
H3B—C3—H3A	108.6 (11)	Cl2—C7—H7	105.4 (8)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C7—H7···O1^{i}	0.927 (13)	2.286 (12)	3.1931 (13)	166 (1)

Symmetry code: (i) −*x*+2, −*y*+1, −*z*+1.