

Crystal structure of 2,2-dichloro-1-(piperidin-1-yl)butane-1,3-dione

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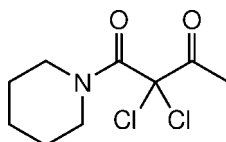
In the title compound, C₉H₁₃Cl₂NO₂, the piperidine ring shows a chair conformation and the O—C—O torsion angle between the carbonyl groups is 183.6 (4)°. In the crystal, molecules are linked into an infinite layer along the *ab* plane by a bifurcated C—H···O hydrogen bond between the carbonyl O atom adjacent to the methyl group and one of the methylene groups next to nitrogen and an additional hydrogen bond of the C—H···Cl type. These layers are connected into a three-dimensional supramolecular arrangement by O···Cl contacts [2.8979 (12) and 3.1300 (12) Å].

Keywords: crystal structure; 2,2-dichloro-1-(piperidin-1-yl)butane-1,3-dione; hydrogen bonding; O···Cl contacts.

CCDC reference: 1036594

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 X-ray structure of the starting compound, see: Schwierz *et al.* (2014).



2. Experimental

2.1. Crystal data

 C₉H₁₃Cl₂NO₂
M_r = 238.10

 Monoclinic, P2₁
a = 5.9548 (3) Å

 b = 10.5510 (4) Å
c = 8.5747 (3) Å
β = 100.568 (2)°
V = 529.60 (4) Å³
Z = 2

 Mo Kα radiation
μ = 0.59 mm⁻¹
T = 133 K
0.07 × 0.05 × 0.02 mm

2.2. Data collection

 Nonius KappaCCD diffractometer
Absorption correction: multi-scan
(SADABS; Bruker, 2002)
T_{min} = 0.616, T_{max} = 0.746

 3076 measured reflections
2402 independent reflections
2085 reflections with I > 2σ(I)
R_{int} = 0.030

2.3. Refinement

 R[F² > 2σ(F²)] = 0.024
wR(F²) = 0.059
S = 1.09
2402 reflections
128 parameters
1 restraint
All H-atom parameters refined

 Δρ_{max} = 0.33 e Å⁻³
Δρ_{min} = -0.21 e Å⁻³
Absolute structure: Flack (1983),
1115 Friedel pairs
Absolute structure parameter:
0.08 (4)

Table 1

Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C1—H1A···O1 ⁱ	0.99	2.56	3.413 (2)	145
C9—H9C···O1 ⁱ	0.98	2.53	3.494 (2)	168
C9—H9C···Cl ⁱⁱ	0.98	2.79	3.770 (2)	176

 Symmetry codes: (i) $-x + 2, y - \frac{1}{2}, -z + 2$; (ii) $x - 1, y, z$.

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.*, 2006); 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: HG5420).

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supporting information

Acta Cryst. (2015). E71, o19 [https://doi.org/10.1107/S2056989014026164]

Crystal structure of 2,2-dichloro-1-(piperidin-1-yl)butane-1,3-dione

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 1-(piperidin-1-yl)butane-1,3-dione (Schwierz *et al.*, 2014) following a modified procedure (Schank, 1967). As it is expected the piperidine ring shows a chair conformation and the amide substructure is planar (Figure 1). The dihedral angle O1—C6—C8—O2 between the carbonyl groups measures to 183.6 (4)°. The C—O bond of the amide carbonyl group is slightly elongated with respect to the other carbonyl group due to delocalization of the nitrogen lone pair (C6—O1 1.221 (3) Å *versus*. C8—O2 1.205 (3) Å). In the crystal structure, molecules are linked to infinite layers along the *ab* plane by a bifurcated hydrogen bond between one of the carbonyl oxygen atoms (O1) towards the methyl group and one of the methylene groups next to nitrogen and an additional hydrogen bond of the C—H...Cl type (Desiraju & Steiner, 1999). In addition, these layers are connected to a 3D supramolecular arrangement by oxygen chlorine contacts (Lommerse *et al.*, 1996).

S2. Experimental

25.4 g (0.15 mol) 1-(piperidin-1-yl)butane-1,3-dione were dissolved in 70 ml dichloromethane. To this solution, 24.3 ml (40.6 g, 0.3 mol) sulfur dichloride was added dropwise and the resulting mixture refluxed for 5 h. After cooling to room temperature 30 ml diethylether were added and the solution washed with brine (3 × 20 ml), dried over CaCl₂, filtered and evaporated to dryness. The resulting highly viscous product was distilled *in vacuo* (0.2 mbar). Condensation of the distillate into a Schlenk tube cooled with liquid nitrogen yielded crystalline material suitable for X-ray diffraction (Combined yield of all fractions: 32.5 g, 91%).

S3. Refinement

Hydrogen atoms have been calculated into idealized positions with C—H = 0.98 - 0.99 Å. Methylene and methyl hydrogen atoms were refined with $U_{\text{iso}} = 1.2 U_{\text{eq}}(\text{C})$ and $1.5 U_{\text{eq}}(\text{C})$ respectively.

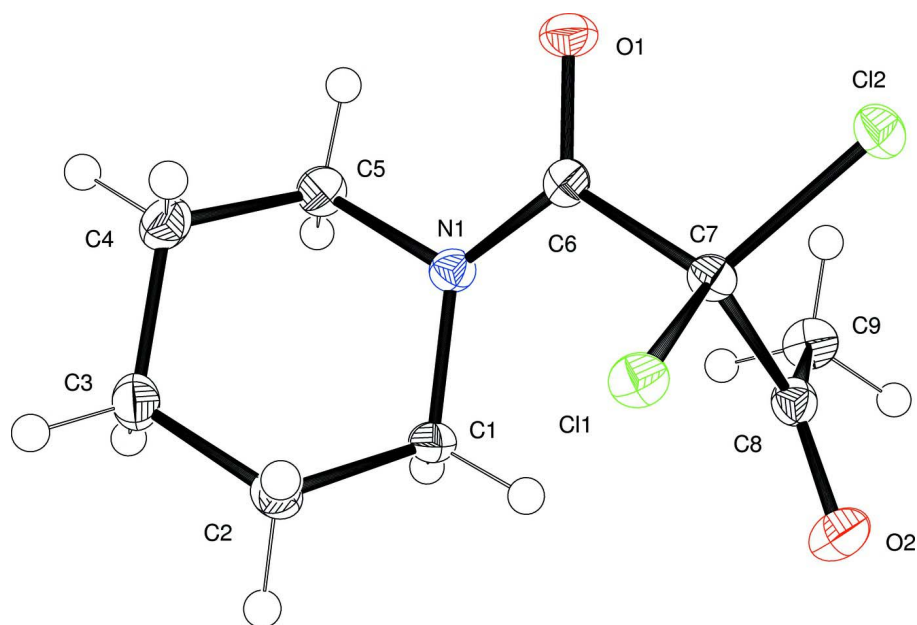


Figure 1

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

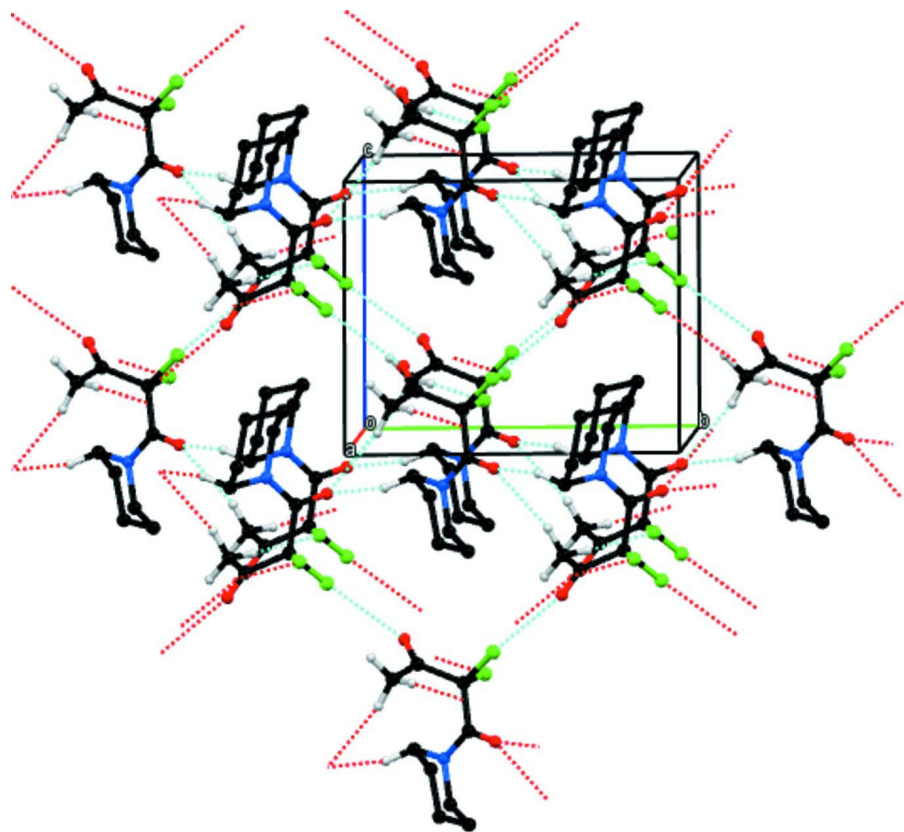


Figure 2

Crystal structure of the title compound showing a 3D supramolecular network built up by C–H···O and C–H···Cl hydrogen bonds and chlorine oxygen contacts. Hydrogen atoms at piperidine residues that are not involved in hydrogen bonding are omitted for the sake of clarity.

2,2-Dichloro-1-(piperidin-1-yl)butane-1,3-dione

Crystal data

$C_9H_{13}Cl_2NO_2$

$M_r = 238.10$

Monoclinic, $P2_1$

Hall symbol: P 2yb

$a = 5.9548$ (3) Å

$b = 10.5510$ (4) Å

$c = 8.5747$ (3) Å

$\beta = 100.568$ (2)°

$V = 529.60$ (4) Å³

$Z = 2$

$F(000) = 248$

$D_x = 1.493$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

$\mu = 0.59$ mm⁻¹

$T = 133$ K

Prism, colourless

$0.07 \times 0.05 \times 0.02$ mm

Data collection

Nonius KappaCCD

diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi- + omega-scan

Absorption correction: multi-scan

(SADABS; Bruker, 2002)

$T_{\min} = 0.616$, $T_{\max} = 0.746$

3076 measured reflections

2402 independent reflections

2085 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.030$

$\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.4^\circ$

$h = -5 \rightarrow 7$

$k = -13 \rightarrow 13$

$l = -11 \rightarrow 11$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.024$
 $wR(F^2) = 0.059$
 $S = 1.09$
 2402 reflections
 128 parameters
 1 restraint
 Primary atom site location: structure-invariant
 direct methods

Secondary atom site location: difference Fourier
 map
 Hydrogen site location: mixed
 All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.0215P)^2 + 0.1164P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.33 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.21 \text{ e } \text{\AA}^{-3}$
 Absolute structure: Flack (1983), 1115 Friedel
 pairs
 Absolute structure parameter: 0.08 (4)

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Cl1	1.44673 (6)	0.94886 (3)	0.75108 (4)	0.01711 (9)
Cl2	0.97291 (6)	1.00243 (3)	0.62597 (4)	0.01824 (9)
O1	0.9936 (2)	1.00543 (12)	0.95581 (13)	0.0203 (2)
O2	1.2365 (2)	0.72093 (11)	0.60201 (14)	0.0228 (3)
N1	1.2241 (2)	0.83853 (12)	1.03862 (15)	0.0149 (3)
C1	1.3935 (3)	0.73987 (14)	1.02007 (18)	0.0156 (3)
H1A	1.4037	0.7314	0.9066	0.019*
H1B	1.3440	0.6574	1.0572	0.019*
C2	1.6274 (3)	0.77486 (15)	1.11579 (19)	0.0183 (3)
H2A	1.6857	0.8511	1.0689	0.022*
H2B	1.7358	0.7046	1.1101	0.022*
C3	1.6153 (3)	0.80114 (17)	1.28938 (19)	0.0211 (3)
H3A	1.5787	0.7217	1.3409	0.025*
H3B	1.7656	0.8316	1.3458	0.025*
C4	1.4336 (3)	0.90029 (16)	1.30135 (19)	0.0208 (3)
H4A	1.4784	0.9824	1.2603	0.025*
H4B	1.4203	0.9120	1.4139	0.025*
C5	1.2036 (3)	0.85828 (15)	1.20554 (18)	0.0183 (3)
H5A	1.1546	0.7785	1.2501	0.022*
H5B	1.0867	0.9238	1.2120	0.022*
C6	1.1183 (3)	0.91946 (13)	0.92819 (18)	0.0140 (3)
C7	1.1618 (3)	0.90173 (14)	0.75549 (18)	0.0145 (3)
C8	1.1108 (3)	0.76732 (14)	0.68101 (18)	0.0160 (3)

C9	0.8979 (3)	0.70565 (15)	0.7144 (2)	0.0202 (3)
H9D	0.8409	0.6448	0.6300	0.030*
H9C	0.7814	0.7705	0.7187	0.030*
H9B	0.9321	0.6613	0.8164	0.030*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.01400 (17)	0.01793 (17)	0.02027 (18)	-0.00249 (13)	0.00546 (13)	-0.00093 (14)
C12	0.01831 (18)	0.01753 (16)	0.01794 (17)	0.00204 (14)	0.00086 (13)	0.00373 (14)
O1	0.0207 (6)	0.0196 (5)	0.0218 (5)	0.0062 (5)	0.0069 (5)	-0.0008 (5)
O2	0.0234 (6)	0.0232 (6)	0.0229 (6)	-0.0011 (5)	0.0071 (5)	-0.0076 (5)
N1	0.0130 (6)	0.0157 (6)	0.0162 (6)	0.0009 (5)	0.0030 (5)	0.0001 (5)
C1	0.0147 (7)	0.0140 (7)	0.0177 (8)	0.0028 (6)	0.0020 (6)	-0.0007 (5)
C2	0.0133 (7)	0.0199 (7)	0.0212 (8)	0.0014 (6)	0.0019 (6)	0.0002 (6)
C3	0.0184 (8)	0.0259 (8)	0.0178 (8)	-0.0008 (6)	-0.0001 (6)	0.0001 (6)
C4	0.0226 (9)	0.0232 (8)	0.0171 (7)	-0.0012 (7)	0.0050 (6)	-0.0035 (6)
C5	0.0179 (8)	0.0221 (8)	0.0160 (7)	0.0006 (6)	0.0062 (6)	0.0011 (6)
C6	0.0101 (7)	0.0151 (7)	0.0169 (7)	-0.0040 (5)	0.0026 (6)	-0.0014 (5)
C7	0.0115 (7)	0.0153 (7)	0.0172 (7)	-0.0009 (6)	0.0041 (6)	0.0009 (6)
C8	0.0169 (8)	0.0148 (7)	0.0152 (7)	0.0004 (6)	0.0001 (6)	0.0008 (6)
C9	0.0187 (8)	0.0177 (7)	0.0246 (8)	-0.0040 (7)	0.0047 (7)	-0.0016 (6)

Geometric parameters (Å, °)

C11—C7	1.7752 (16)	C3—H3A	0.9900
C12—C7	1.7802 (15)	C3—H3B	0.9900
O1—C6	1.2226 (19)	C4—C5	1.528 (2)
O2—C8	1.202 (2)	C4—H4A	0.9900
N1—C6	1.3431 (19)	C4—H4B	0.9900
N1—C5	1.4734 (19)	C5—H5A	0.9900
N1—C1	1.4782 (19)	C5—H5B	0.9900
C1—C2	1.527 (2)	C6—C7	1.561 (2)
C1—H1A	0.9900	C7—C8	1.562 (2)
C1—H1B	0.9900	C8—C9	1.499 (2)
C2—C3	1.529 (2)	C9—H9D	0.9800
C2—H2A	0.9900	C9—H9C	0.9800
C2—H2B	0.9900	C9—H9B	0.9800
C3—C4	1.522 (2)		
C6—N1—C5	118.90 (12)	H4A—C4—H4B	108.2
C6—N1—C1	127.81 (13)	N1—C5—C4	109.73 (13)
C5—N1—C1	112.57 (12)	N1—C5—H5A	109.7
N1—C1—C2	110.19 (12)	C4—C5—H5A	109.7
N1—C1—H1A	109.6	N1—C5—H5B	109.7
C2—C1—H1A	109.6	C4—C5—H5B	109.7
N1—C1—H1B	109.6	H5A—C5—H5B	108.2
C2—C1—H1B	109.6	O1—C6—N1	123.93 (14)

H1A—C1—H1B	108.1	O1—C6—C7	119.03 (13)
C1—C2—C3	111.45 (13)	N1—C6—C7	117.04 (12)
C1—C2—H2A	109.3	C6—C7—C8	116.30 (12)
C3—C2—H2A	109.3	C6—C7—C11	108.20 (10)
C1—C2—H2B	109.3	C8—C7—C11	111.13 (11)
C3—C2—H2B	109.3	C6—C7—C12	108.94 (10)
H2A—C2—H2B	108.0	C8—C7—C12	103.51 (10)
C4—C3—C2	110.58 (13)	C11—C7—C12	108.45 (8)
C4—C3—H3A	109.5	O2—C8—C9	124.54 (14)
C2—C3—H3A	109.5	O2—C8—C7	120.38 (14)
C4—C3—H3B	109.5	C9—C8—C7	115.07 (13)
C2—C3—H3B	109.5	C8—C9—H9D	109.5
H3A—C3—H3B	108.1	C8—C9—H9C	109.5
C3—C4—C5	110.03 (14)	H9D—C9—H9C	109.5
C3—C4—H4A	109.7	C8—C9—H9B	109.5
C5—C4—H4A	109.7	H9D—C9—H9B	109.5
C3—C4—H4B	109.7	H9C—C9—H9B	109.5
C5—C4—H4B	109.7		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C1—H1A...O1 ⁱ	0.99	2.56	3.413 (2)	145
C9—H9C...O1 ⁱ	0.98	2.53	3.494 (2)	168
C9—H9C...C11 ⁱⁱ	0.98	2.79	3.770 (2)	176

Symmetry codes: (i) $-x+2, y-1/2, -z+2$; (ii) $x-1, y, z$.