Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

4-Dichloromethyl-4-methyl-5-(nitromethyl)cyclohex-2-enone

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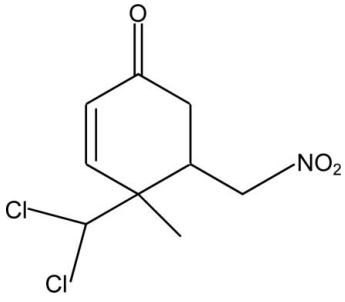
Received 1 October 2013; accepted 8 October 2013

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.005 Å; R factor = 0.073; wR factor = 0.214; data-to-parameter ratio = 15.8.

In the title compound, $C_9H_{11}Cl_2NO_3$, the six-membered ring adopts a screw-chair conformation. In the crystal, two different C—H···O hydrogen bonds involving the same acceptor atom connect the molecules into a chain extending along the c-axis direction.

Related literature

For the synthetic procedure, see: Wenkert *et al.* (1969). For polyfunctionalized products obtained by similar Michael reactions with carbanions, see: Stefanović *et al.* (1983); Solujić *et al.* (1991, 1999). For a related crystal structure, see: Yang & Carter (2010).



Experimental

Crystal data

$C_9H_{11}Cl_2NO_3$ M_r = 252.09
Monoclinic, $P2_1/c$
a = 13.8922 (7) Å
b = 10.4531 (9) Å
c = 7.8696 (5) Å
β = 101.682 (6)°
V = 1119.12 (13) Å^3
Z = 4
Cu $K\alpha$ radiation
μ = 5.14 mm^{-1}
T = 293 K
0.11 × 0.10 × 0.05 mm

Data collection

Agilent Gemini S diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
T_{min} = 0.288, T_{max} = 1.000
4083 measured reflections
2160 independent reflections
1674 reflections with $I > 2\sigma(I)$
R_{int} = 0.016

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.073
$wR(F^2)$ = 0.214
S = 1.13
2160 reflections
137 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.44 e Å^{-3}
$\Delta\rho_{min}$ = −0.46 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C8—H8···O3^{i}	0.98	2.24	3.189 (5)	164
C1—H1a···O3^{i}	0.97	2.56	3.503 (6)	164

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

Data collection: *CrysAlis PRO* (Agilent, 2013); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; 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: *WinGX* (Farrugia, 2012), *PLATON* (Spek, 2009) and *PARST* (Nardelli, 1995).

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (project Nos. 172014, 172035 and 172034).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT6936).

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supporting information

Acta Cryst. (2013). E**69**, o1638 [doi:10.1107/S1600536813027517]

4-Dichloromethyl-4-methyl-5-(nitromethyl)cyclohex-2-enone

Sladjana B. Novaković, Marko V. Rodić, Željko K. Jaćimović, Zoran Ratković and Slobodan Sukdolak

S1. Comment

4-Dichloromethyl-4-methylcyclohexa-2,5-dienone, as a conjugated enone, readily undergo Michael reaction with carbanions, giving synthetically valuable polyfunctionalized products (Wenkert *et al.*, 1969). Utilizing this reaction, some natural products (Stefanović *et al.*, 1983), as well as some bioactive compounds (Solujić *et al.*, 1991; 1999) were successfully synthesized. We report now on synthesis of the title compound (I) by the same reaction using carbanion obtained from nitromethane.

The crystal structure of (I) is shown in Figure 1. None of the oxygen atoms of the nitro group is involved in hydrogen bonding. Similarly, two chlorine atoms also remain without the appropriate intermolecular donor, while there are two bent C—H···Cl intramolecular contacts shorter then the sum of van der Waals radii for H and Cl atoms [C6—H6a = 0.97, H6···Cl1 = 2.76 Å, C6—H6···Cl1 =106 °; C2—H2 = 0.98, H2···Cl2 = 2.66 Å, C2—H2···Cl2 = 112 °]. The most significant interaction in the crystal structure is a bifurcated C—H···O hydrogen bond [C8—H8 = 0.98; H8···O3^{i} = 2.24 Å; C8—H8···O3 = 164° and C1—H1a = 0.97; H1a···O3^{i} = 2.56 Å; C1—H1a···O3 = 164°] (symmetry code: i = *x*, *y*, *z* - 1)] which connects the molecules into chains extended along the *c* axis (Figure 2).

S2. Experimental

Following the literature protocol (Wenkert *et al.*, 1969), to freshly prepared sodium methoxide in methanol a nitromethane solution of 4-(dichloromethyl)-4-methylcyclohex-2,5-dienone in dry methanol was added dropwise. After one hour stirring of the obtained solution, the solvent was evaporated and the rest quenched with diluted hydrochloric acid. The obtained mixture was extracted with toluene, the organic layer dried overnight (anh. sodium sulfate) and the solvent evaporated. The crude solid was recrystallized from hot toluene to give pure 4-(dichloromethyl)-4-methyl-5-(nitromethyl)cyclohex-2-enon.

S3. Refinement

All H atoms were placed at geometrically calculated positions and included in the refinement in the riding model approximation, with C—H lengths of 0.93 (aromatic CH), 0.96 (CH_3), 0.97 (CH_2), and 0.98 Å (CH). U_{iso} of the H atoms were set at 1.5U_{eq} of the parent C for the methyl group and at 1.2U_{eq} otherwise.

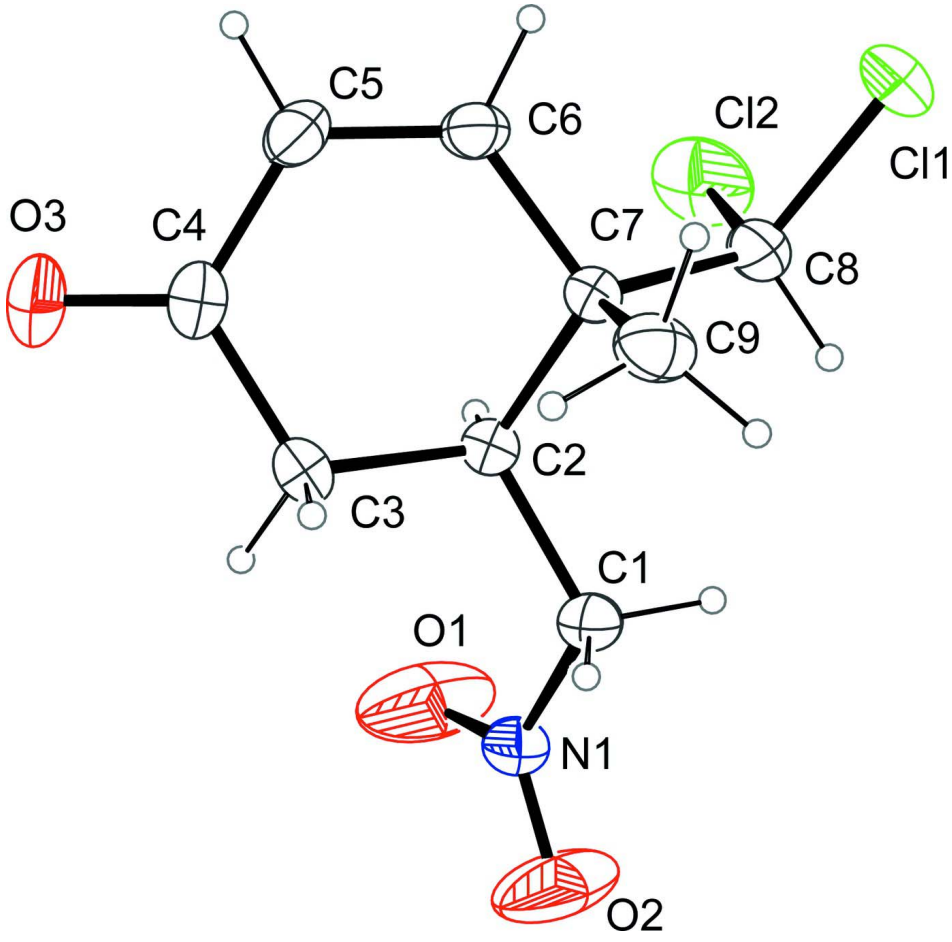

Figure 1

The molecular structure of the title compound, with atom labels and 30% probability displacement ellipsoids for non-H atoms.

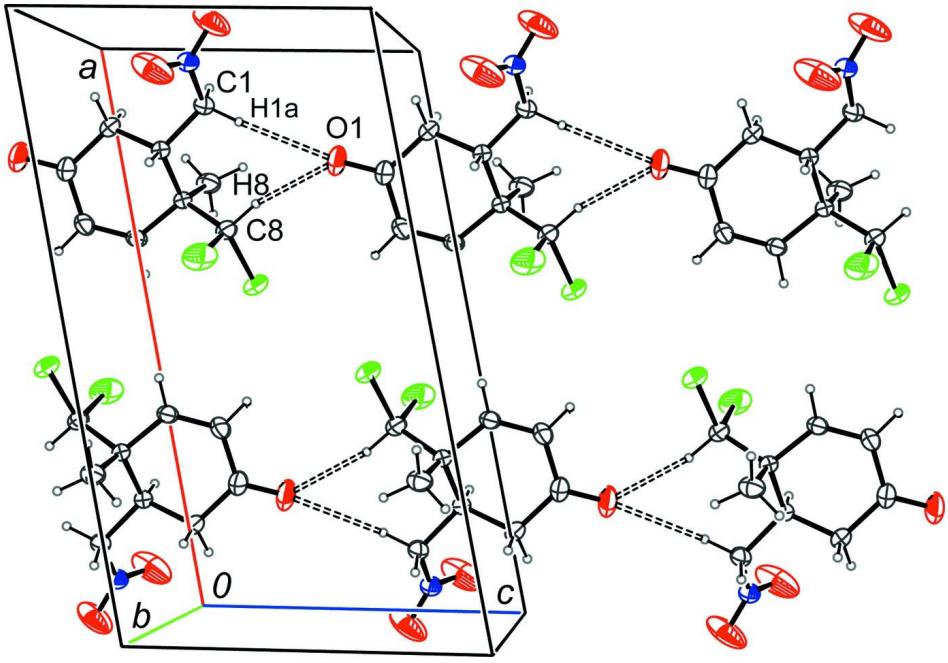

Figure 2

Segment of the crystal packing. A bifurcated C—H···O hydrogen bond connects the molecules into chains extended along *c* axis.

4-Dichloromethyl-4-methyl-5-(nitromethyl)cyclohex-2-enone

Crystal data

$C_9H_{11}Cl_2NO_3$
$M_r = 252.09$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 13.8922$ (7) Å
$b = 10.4531$ (9) Å
$c = 7.8696$ (5) Å
$\beta = 101.682$ (6)°
$V = 1119.12$ (13) Å^3
$Z = 4$
$F(000) = 520$
$D_x = 1.496$ Mg m^{-3}
Cu $K\alpha$ radiation, $\lambda = 1.54180$ Å
Cell parameters from 927 reflections
$\theta = 4.2$–$70.2°$
$\mu = 5.14$ mm^{-1}
$T = 293$ K
Prismatic, colourless
0.11 × 0.10 × 0.05 mm

Data collection

Agilent Gemini S diffractometer
Radiation source: Enhance (Cu) X-ray Source
Graphite monochromator
Detector resolution: 16.3280 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Agilent, 2013)
$T_{min} = 0.288$, $T_{max} = 1.000$
4083 measured reflections
2160 independent reflections
1674 reflections with $I > 2\sigma(I)$
$R_{int} = 0.016$
$\theta_{max} = 72.7°$, $\theta_{min} = 5.3°$
$h = -16 \rightarrow 17$
$k = -12 \rightarrow 7$
$l = -9 \rightarrow 9$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.073$
$wR(F^2) = 0.214$
$S = 1.13$
2160 reflections
137 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0912P)^2 + 0.9148P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.44$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Special details

Experimental. Empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. ′CrysAlisPro (Agilent Technologies, 2013)′

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
Cl1	0.42318 (8)	0.42826 (19)	0.16338 (17)	0.1132 (6)
Cl2	0.37776 (11)	0.67949 (16)	0.2702 (2)	0.1229 (7)
N1	0.0336 (2)	0.6681 (4)	0.1987 (4)	0.0681 (9)
O1	0.0509 (4)	0.7541 (5)	0.2925 (9)	0.184 (3)
O2	−0.0380 (4)	0.6677 (7)	0.1028 (8)	0.195 (3)
C1	0.1041 (3)	0.5609 (4)	0.1953 (5)	0.0634 (9)
H1A	0.1335	0.5699	0.0942	0.076*
H1B	0.0686	0.4804	0.1849	0.076*
C2	0.1853 (2)	0.5576 (3)	0.3579 (4)	0.0521 (8)
H2	0.2108	0.6447	0.3804	0.063*
C3	0.1430 (3)	0.5148 (5)	0.5143 (5)	0.0699 (11)
H3A	0.0917	0.5739	0.5301	0.084*
H3B	0.1135	0.4309	0.4909	0.084*
C4	0.2196 (4)	0.5091 (6)	0.6783 (5)	0.0854 (13)
C5	0.3186 (3)	0.4765 (5)	0.6616 (5)	0.0719 (11)
H5	0.3671	0.4682	0.7614	0.086*
C6	0.3420 (2)	0.4579 (4)	0.5085 (5)	0.0605 (9)
H6	0.4067	0.4358	0.5073	0.073*
C7	0.2720 (2)	0.4699 (3)	0.3368 (4)	0.0506 (8)
C8	0.3265 (3)	0.5283 (5)	0.2041 (5)	0.0746 (12)
H8	0.2791	0.5396	0.0946	0.090*
C9	0.2362 (3)	0.3356 (4)	0.2733 (6)	0.0744 (11)
H9A	0.2912	0.2782	0.2889	0.112*
H9B	0.2057	0.3394	0.1525	0.112*
H9C	0.1895	0.3056	0.3387	0.112*
O3	0.1993 (4)	0.5259 (7)	0.8183 (4)	0.165 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0604 (7)	0.1947 (17)	0.0927 (9)	0.0257 (8)	0.0351 (6)	−0.0027 (9)

Cl2	0.0976 (10)	0.1148 (12)	0.1631 (15)	−0.0342 (8)	0.0423 (9)	0.0388 (10)
N1	0.0521 (17)	0.086 (2)	0.0644 (18)	0.0131 (16)	0.0081 (14)	0.0057 (17)
O1	0.140 (4)	0.128 (4)	0.239 (6)	0.069 (3)	−0.066 (4)	−0.086 (4)
O2	0.124 (4)	0.229 (6)	0.187 (5)	0.107 (4)	−0.075 (4)	−0.105 (4)
C1	0.0504 (18)	0.080 (3)	0.058 (2)	0.0105 (17)	0.0056 (15)	−0.0045 (18)
C2	0.0448 (16)	0.063 (2)	0.0486 (16)	0.0008 (14)	0.0095 (13)	−0.0015 (14)
C3	0.0533 (19)	0.100 (3)	0.061 (2)	0.0049 (19)	0.0235 (16)	0.000 (2)
C4	0.083 (3)	0.125 (4)	0.051 (2)	0.006 (3)	0.0212 (19)	0.007 (2)
C5	0.066 (2)	0.097 (3)	0.0485 (19)	−0.004 (2)	0.0008 (16)	0.0104 (19)
C6	0.0432 (16)	0.076 (2)	0.060 (2)	−0.0024 (15)	0.0035 (14)	0.0088 (17)
C7	0.0409 (15)	0.063 (2)	0.0481 (16)	−0.0011 (13)	0.0105 (12)	−0.0021 (14)
C8	0.0508 (19)	0.115 (3)	0.060 (2)	0.004 (2)	0.0181 (16)	0.013 (2)
C9	0.060 (2)	0.069 (2)	0.092 (3)	0.0047 (18)	0.0090 (19)	−0.020 (2)
O3	0.131 (3)	0.317 (8)	0.0541 (19)	0.061 (4)	0.035 (2)	0.004 (3)

Geometric parameters (Å, º)

Cl1—C8	1.782 (4)	C3—H3B	0.9700
Cl2—C8	1.768 (5)	C4—O3	1.204 (5)
N1—O2	1.119 (5)	C4—C5	1.448 (6)
N1—O1	1.157 (5)	C5—C6	1.324 (5)
N1—C1	1.493 (5)	C5—H5	0.9300
C1—C2	1.525 (5)	C6—C7	1.502 (5)
C1—H1A	0.9700	C6—H6	0.9300
C1—H1B	0.9700	C7—C8	1.536 (5)
C2—C3	1.534 (5)	C7—C9	1.538 (5)
C2—C7	1.549 (5)	C8—H8	0.9800
C2—H2	0.9800	C9—H9A	0.9600
C3—C4	1.498 (6)	C9—H9B	0.9600
C3—H3A	0.9700	C9—H9C	0.9600
O2—N1—O1	118.3 (4)	C6—C5—C4	122.0 (3)
O2—N1—C1	118.8 (4)	C6—C5—H5	119.0
O1—N1—C1	122.8 (4)	C4—C5—H5	119.0
N1—C1—C2	112.3 (3)	C5—C6—C7	124.9 (3)
N1—C1—H1A	109.2	C5—C6—H6	117.5
C2—C1—H1A	109.2	C7—C6—H6	117.5
N1—C1—H1B	109.2	C6—C7—C8	109.0 (3)
C2—C1—H1B	109.2	C6—C7—C9	108.9 (3)
H1A—C1—H1B	107.9	C8—C7—C9	108.2 (3)
C1—C2—C3	110.0 (3)	C6—C7—C2	109.2 (3)
C1—C2—C7	112.5 (3)	C8—C7—C2	109.8 (3)
C3—C2—C7	110.2 (3)	C9—C7—C2	111.6 (3)
C1—C2—H2	108.0	C7—C8—Cl2	112.3 (3)
C3—C2—H2	108.0	C7—C8—Cl1	112.5 (3)
C7—C2—H2	108.0	Cl2—C8—Cl1	107.7 (2)
C4—C3—C2	112.5 (3)	C7—C8—H8	108.0
C4—C3—H3A	109.1	Cl2—C8—H8	108.0

C2—C3—H3A	109.1	Cl1—C8—H8	108.0
C4—C3—H3B	109.1	C7—C9—H9A	109.5
C2—C3—H3B	109.1	C7—C9—H9B	109.5
H3A—C3—H3B	107.8	H9A—C9—H9B	109.5
O3—C4—C5	121.3 (4)	C7—C9—H9C	109.5
O3—C4—C3	121.7 (5)	H9A—C9—H9C	109.5
C5—C4—C3	116.9 (3)	H9B—C9—H9C	109.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C8—H8···O3^{i}	0.98	2.24	3.189 (5)	164
C1—H1a···O3^{i}	0.97	2.56	3.503 (6)	164

Symmetry code: (i) *x*, *y*, *z*−1.