organic compounds

2,2,7-Trichloro-3,4-dihydronaphthalen-1(2H)-one

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The title compound, $C_{10}H_7Cl_3O$, obtained as a major byproduct from a classical Schmidt reaction. The cyclohexyl ring is distorted from a classical chair conformation, as observed for monocyclic analogues, presumably due to conjugation of the planar annulated benzo ring and the ketone group (r.m.s. deviation 0.024 Å). There are no significant intermolecular interactions.

Related literature

For the Schmidt reaction, see: Schmidt (1923). Lactams and their derived amidines are common structural moieties in a variety of phamaceutical agents (Fylaktakidou *et al.*, 2008), and are common in antipsychotics (Capuano *et al.*, 2002, 2008). For the conformation of the cyclohexyl ring in monocyclic analogues, see: Lectard *et al.* (1973); Lichanot *et al.* (1974).
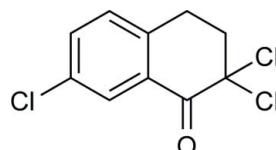
Experimental

Crystal data
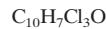
$C_{10}H_7Cl_3O$	M_r = 249.51
Monoclinic, $P2_1/c$	Z = 4
a = 8.5233 (1) Å	Mo $K\alpha$ radiation
b = 8.0182 (2) Å	μ = 0.88 mm^{-1}
c = 14.8698 (3) Å	T = 123 K
β = 102.561 (1)°	$0.28 \times 0.10 \times 0.10$ mm
V = 991.90 (3) Å^3	

Data collection

Nonius Kappa CCD diffractometer	2275 independent reflections
Absorption correction: none	1859 reflections with $I > 2\sigma(I)$
9399 measured reflections	R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.037	127 parameters
$wR(F^2)$ = 0.100	H-atom parameters constrained
S = 1.06	$\Delta\rho_{max}$ = 0.53 e Å^{-3}
2275 reflections	$\Delta\rho_{min}$ = −0.34 e Å^{-3}

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *X-SEED* (Barbour, 2001); software used to prepare material for publication: *CIFTAB* (Sheldrick, 1997).

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supplementary materials

2,2,7-Trichloro-3,4-dihydronaphthalen-1(2*H*)-one

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Comment

The reaction between hydrazoic acid and carbonyl compounds in the presence of strong acid is known as the Schmidt reaction (Schmidt, 1923) and provides a method for conversion of cyclic ketones to lactams. Lactams as well as their derived amidines are common structural moieties in a variety of phamaceutical agents (Fylaktakidou, *et al.* 2008), but are specifically of interest to our group as they are common in antipsychotics (Capuano, *et al.* 2002, 2008). In the current study, reaction of 7-chloro-1-tetralone with sodium azide and hydrochloric acid gave the desired alkyl migration lactam, 8-chloro-2,3,4,5-tetrahydro-1 *H*-2-benzazepin-1-one, but also a significant amount of the title compound. The solid state structure shows a typical bicyclic ketone framework with two fused six-membered rings and a gem-dichloro substituent in the 2 position. The cyclohexyl ring is distorted from a classical chair conformation, as observed for monocyclic analogues (Lectard, *et al.*, 1973, Lichanot, *et al.*, 1974), presumably due to conjugation of the planar annulated benzo ring and the ketone group (RMS deviation 0.024Å). There are no significant intermolecular interactions.

Experimental

Sodium azide (1.30 g, 20.0 mmol) was added to a stirred solution of 7-chloro-3,4-dihydronaphthalen-1(2*H*)-one (1.00 g, 5.54 mmol) in concentrated HCl maintained at 0 °C. After warming to room temperature and stirring overnight, the mixture was poured into water and neutralized with K_2CO_3. The crude product mixture was extracted with CH_2Cl_2 and purified by flash chromatography (silica; ethyl acetate). The fractions containing the title compound were evaporated and the residue was recrystallized from $CHCl_3$/hexane yielding beige prismatic crystals. (m.p. 435–436 K). ^{1}H NMR (300 MHz, $CDCl_3$ δ, p.p.m.): 8.12 (d, 1H, *J* = 2.5 Hz, H8), 7.52 (dd, 1H, *J* = 8.0, 2.5 Hz, H6), 7.23 (d, 1H, *J* = 8.0 Hz, H5), 3.18 (t, 2H, *J* = 6.0 Hz, H4), 2.95 (t, 2H, *J* = 6.0 Hz, H3). ^{13}C NMR (75 MHz, $CDCl_3$ δ, p.p.m.): 183.0, 140.4, 134.6, 133.9, 130.3, 129.8, 129.4, 85.7, 43.0, 27.0. *m/z* (EI, 70 ev): 254 (1%, M^+[^{37}Cl]$_3$), 252 (7, M^+[^{35}Cl][^{37}Cl]$_2$, 250 (24, M^+[^{35}Cl]$_2$[^{37}Cl]), 248 (26, M^+[^{35}Cl]$_3$), 213 (20), 152 (100), 124 (36), 89 (19). Calcd. for $C_{10}H_7Cl_3O$: C 48.1, H 2.8, Cl 42.6; found C 48.1, H 2.9, Cl 42.6%.

Refinement

All H atoms for the primary molecules were initially located in the difference Fourier map but were placed in geometrically idealized positions and constrained to ride on their parent atoms with C—H distances in the range 0.95–1.00 Å and U_{iso}(H) = 1.2–1.5 U_{eq}(C).

supplementary materials

Figures
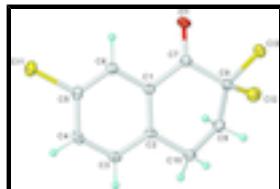
Fig. 1. Molecular diagram of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

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Crystal data

$C_{10}H_7Cl_3O$	$F_{000} = 504$
$M_r = 249.51$	$D_x = 1.671$ Mg m^{-3}
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -P 2ybc	Cell parameters from 9399 reflections
$a = 8.5233$ (1) Å	$\theta = 2.8–27.5º$
$b = 8.0182$ (2) Å	$\mu = 0.88$ mm^{-1}
$c = 14.8698$ (3) Å	$T = 123$ K
$\beta = 102.561$ (1)º	Prism, colourless
$V = 991.90$ (3) Å^3	$0.28 \times 0.10 \times 0.10$ mm
$Z = 4$	

Data collection

Nonius Kappa CCD diffractometer	1859 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.064$
Monochromator: graphite	$\theta_{max} = 27.5º$
$T = 123$ K	$\theta_{min} = 2.8º$
φ and ω scans	$h = -11 \rightarrow 11$
Absorption correction: none	$k = -10 \rightarrow 10$
9399 measured reflections	$l = -19 \rightarrow 19$
2275 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.037$	H-atom parameters constrained
$wR(F^2) = 0.100$	$w = 1/[\sigma^2(F_o^2) + (0.0478P)^2 + 0.6127P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.06$	$(\Delta/\sigma)_{max} = 0.001$
2275 reflections	$\Delta\rho_{max} = 0.53$ e Å^{-3}
127 parameters	$\Delta\rho_{min} = -0.34$ e Å^{-3}

Primary atom site location: structure-invariant direct methods

Extinction correction: none

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	−0.11870 (6)	0.58915 (7)	0.26554 (4)	0.02493 (16)
Cl2	0.48515 (6)	1.11552 (6)	0.63056 (4)	0.02410 (15)
Cl3	0.25735 (6)	0.91201 (7)	0.70159 (4)	0.02542 (16)
O1	0.20373 (18)	1.05238 (18)	0.48477 (11)	0.0256 (4)
C1	0.2039 (2)	0.7561 (2)	0.48441 (13)	0.0167 (4)
C2	0.2751 (2)	0.6089 (2)	0.52503 (14)	0.0165 (4)
C3	0.2196 (2)	0.4562 (3)	0.48443 (14)	0.0199 (4)
H3	0.2659	0.3555	0.5116	0.024*
C4	0.0986 (2)	0.4492 (3)	0.40537 (14)	0.0200 (4)
H4	0.0616	0.3449	0.3786	0.024*
C5	0.0320 (2)	0.5981 (3)	0.36575 (14)	0.0187 (4)
C6	0.0818 (2)	0.7514 (2)	0.40393 (13)	0.0180 (4)
H6	0.0346	0.8514	0.3763	0.022*
C7	0.2542 (2)	0.9236 (2)	0.52247 (14)	0.0182 (4)
C8	0.3773 (2)	0.9241 (2)	0.61578 (14)	0.0173 (4)
C9	0.4939 (2)	0.7787 (3)	0.62603 (14)	0.0200 (4)
H9A	0.5645	0.7810	0.6884	0.024*
H9B	0.5627	0.7904	0.5806	0.024*
C10	0.4060 (2)	0.6127 (2)	0.61131 (14)	0.0198 (4)
H10A	0.4845	0.5231	0.6079	0.024*
H10B	0.3583	0.5894	0.6650	0.024*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0203 (3)	0.0295 (3)	0.0223 (3)	−0.0046 (2)	−0.0012 (2)	−0.0031 (2)
Cl2	0.0264 (3)	0.0186 (3)	0.0248 (3)	−0.0065 (2)	0.0002 (2)	−0.0013 (2)
Cl3	0.0253 (3)	0.0289 (3)	0.0240 (3)	0.0017 (2)	0.0097 (2)	0.0008 (2)
O1	0.0284 (8)	0.0142 (7)	0.0295 (8)	0.0003 (6)	−0.0037 (7)	0.0008 (6)
C1	0.0165 (9)	0.0157 (10)	0.0181 (9)	−0.0002 (7)	0.0043 (8)	0.0014 (8)
C2	0.0156 (9)	0.0158 (10)	0.0188 (9)	0.0010 (7)	0.0054 (7)	0.0017 (8)

C3	0.0206 (10)	0.0152 (10)	0.0250 (10)	0.0018 (8)	0.0070 (8)	0.0012 (8)
C4	0.0207 (10)	0.0168 (9)	0.0240 (10)	−0.0026 (8)	0.0083 (8)	−0.0040 (8)
C5	0.0157 (9)	0.0225 (11)	0.0178 (9)	−0.0038 (8)	0.0035 (8)	−0.0020 (8)
C6	0.0176 (9)	0.0176 (10)	0.0190 (10)	0.0012 (8)	0.0043 (8)	0.0017 (8)
C7	0.0173 (9)	0.0169 (10)	0.0198 (10)	0.0005 (8)	0.0029 (8)	0.0006 (8)
C8	0.0190 (9)	0.0148 (9)	0.0186 (9)	−0.0027 (8)	0.0050 (8)	0.0006 (8)
C9	0.0174 (9)	0.0214 (10)	0.0203 (10)	−0.0007 (8)	0.0021 (8)	0.0012 (8)
C10	0.0208 (10)	0.0157 (10)	0.0215 (10)	0.0012 (8)	0.0018 (8)	0.0027 (8)

Geometric parameters (Å, °)

Cl1—C5	1.744 (2)	C4—C5	1.396 (3)
Cl2—C8	1.778 (2)	C4—H4	0.9500
Cl3—C8	1.803 (2)	C5—C6	1.382 (3)
O1—C7	1.208 (2)	C6—H6	0.9500
C1—C2	1.402 (3)	C7—C8	1.547 (3)
C1—C6	1.405 (3)	C8—C9	1.518 (3)
C1—C7	1.484 (3)	C9—C10	1.520 (3)
C2—C3	1.401 (3)	C9—H9A	0.9900
C2—C10	1.506 (3)	C9—H9B	0.9900
C3—C4	1.386 (3)	C10—H10A	0.9900
C3—H3	0.9500	C10—H10B	0.9900
C2—C1—C6	120.99 (18)	C1—C7—C8	115.33 (16)
C2—C1—C7	122.35 (17)	C9—C8—C7	112.93 (16)
C6—C1—C7	116.65 (17)	C9—C8—Cl2	109.90 (14)
C3—C2—C1	118.42 (18)	C7—C8—Cl2	110.16 (13)
C3—C2—C10	120.16 (17)	C9—C8—Cl3	110.33 (14)
C1—C2—C10	121.41 (17)	C7—C8—Cl3	104.88 (13)
C4—C3—C2	121.35 (19)	Cl2—C8—Cl3	108.46 (11)
C4—C3—H3	119.3	C8—C9—C10	111.50 (16)
C2—C3—H3	119.3	C8—C9—H9A	109.3
C3—C4—C5	118.84 (19)	C10—C9—H9A	109.3
C3—C4—H4	120.6	C8—C9—H9B	109.3
C5—C4—H4	120.6	C10—C9—H9B	109.3
C6—C5—C4	121.79 (19)	H9A—C9—H9B	108.0
C6—C5—Cl1	119.40 (16)	C2—C10—C9	112.99 (16)
C4—C5—Cl1	118.80 (15)	C2—C10—H10A	109.0
C5—C6—C1	118.60 (18)	C9—C10—H10A	109.0
C5—C6—H6	120.7	C2—C10—H10B	109.0
C1—C6—H6	120.7	C9—C10—H10B	109.0
O1—C7—C1	123.49 (19)	H10A—C10—H10B	107.8
O1—C7—C8	121.17 (18)		

Fig. 1