

2-Trichloroacetyl-1-(1-pyrrolidinyl)cyclopentene

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Key indicators

Single-crystal X-ray study

$T = 295\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

R factor = 0.040

wR factor = 0.124

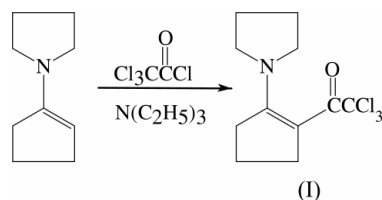
Data-to-parameter ratio = 17.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The structure of the title compound, $\text{C}_{11}\text{H}_{14}\text{Cl}_3\text{NO}$, is stabilized by intra- and intermolecular hydrogen bonds. The cyclopentene ring adopts an envelope conformation while the pyrrolidinyl moiety adopts a twist conformation.

Comment

Besides the well known methods for the acylation of enamines (Cook, 1969), we have recently investigated the synthesis of α - and α' -diacetylated enamino ketones in the presence of zinc, which is an unusual catalyst for acylation reactions (Şenöz & Tunoğlu, 2003). The crystal structures of 2,6-bis-(trichloroacetyl)-1-(1-morpholinyl)cyclohexene and 2,6-bis-(trichloroacetyl)cyclohexanone have been reported elsewhere (Özbey *et al.*, 2000, 2003). Zinc catalyses ketene formation in preference to [2 + 2]-cycloaddition reactions (Şenöz & Yıldırım, 1996; Brady, 1981). However, we obtained the diacetylated product, 2,6-bis((trichloroacetyl)-1-(1-pyrrolidinyl)cyclopentene from the corresponding cyclic enamino ketone, 1-(1-pyrrolidinyl)cyclopentene, with zinc as catalyst. The same enamine yielded the monoacetylated product, 2-trichloroacetyl-1-(1-pyrrolidinyl)cyclopentene, by the use of triethylamine to prevent salt formation without using zinc, as in the literature.



Here we report the crystal structure of 2-trichloroacetyl-1-(1-pyrrolidinyl)cyclopentene, (I), obtained by the reaction of 1-(1-pyrrolidinyl)cyclopentene with trichloroacetyl chloride. The X-ray crystal structure analysis shows that the cyclopentene ring adopts an envelope conformation, twisted at C5. Atom C5 is displaced from the C3/C4/C6/C7 mean plane by $-0.430(3)\text{ \AA}$. The puckering parameters (Cremer & Pople, 1975) of this ring are $Q = 0.299(3)\text{ \AA}$ and $\theta = 232.1(5)^\circ$. The pyrrolidinyl moiety deviates from the twist conformation, as shown by the ring-puckering parameters of $Q = 0.309(4)\text{ \AA}$ and $\theta = 273.0(5)^\circ$. The ketone group at C3 and the pyrrolidinyl ring at C7 are slightly twisted in opposite directions, with torsion angles $\text{C1}-\text{C2}-\text{C3}-\text{C7}$ and $\text{C3}-\text{C7}-\text{N1}-\text{C8}$ of $-171.5(2)$ and $177.4(2)^\circ$, respectively. The hydrogen-bond interaction between atoms O1 and C11 might be the cause of the planarity of this part of the molecule.

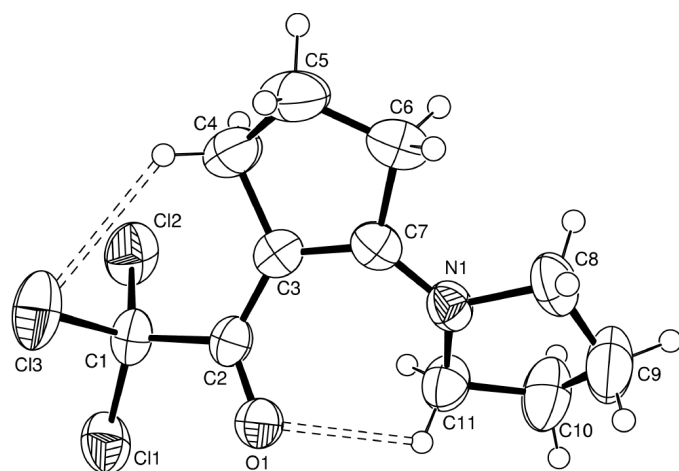


Figure 1
ORTEP-3 (Farrugia, 1997) drawing of the asymmetric unit of the molecule of the title compound, with the atomic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

The structure is stabilized by inter- and intramolecular hydrogen bonds. Details of the hydrogen-bonding geometry are given in Table 2.

Experimental

A solution of freshly distilled trichloroacetyl chloride (17.8 mmol, 3.23 g) in dry ether was added dropwise over a period of 1 h to a cooled mixture (in an ice-salt bath) of triethylamine (17.8 mmol, 1.80 g) and 1-(1-pyrrolidinyl)cyclopentene (17.8 mmol, 2.69 g) in 50 ml anhydrous ether while stirring under a nitrogen atmosphere. The reaction mixture was stirred overnight, then ammonium chloride was removed by filtration and the solvent was evaporated under reduced pressure. The residue was dissolved in hexane, dried over MgSO_4 , filtered and then the solvent was evaporated. The crude product was recrystallized from hexane to give 2.74 g (55%) 2-trichloroacetyl-1-(1-pyrrolidinyl)cyclopentene as a pure yellow solid. M.p. 363 K; IR (KBr): 1624 (C=O), 1520 (C=C) cm^{-1} ; $^1\text{H NMR}$: δ 2.90–3.00 (*t*, 4 H, NCH_2), 2.50–2.65 (*t*, 4H, NCH_2CH_2), 1.90–2.00 (*m*, 4H, $\text{CH}_2\text{CH}_2\text{CH}_2$), 1.75–1.85 (*m*, 2H, $\text{CH}_2\text{CH}_2\text{CH}_2$).

Crystal data

$\text{C}_{11}\text{H}_{14}\text{Cl}_3\text{NO}$
 $M_r = 282.58$
Orthorhombic, *Pbca*
 $a = 11.4236$ (10) Å
 $b = 10.2623$ (9) Å
 $c = 21.8899$ (3) Å
 $V = 2567.3$ (5) Å³
 $Z = 8$
 $D_x = 1.462$ Mg m⁻³

Mo $K\alpha$ radiation
Cell parameters from 25 reflections
 $\theta = 10.2$ – 18.2°
 $\mu = 0.69$ mm⁻¹
 $T = 295$ (2) K
Prism, light yellow
 $0.48 \times 0.48 \times 0.12$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
 $T_{\min} = 0.732$, $T_{\max} = 0.922$
5032 measured reflections
2597 independent reflections
1823 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.029$
 $\theta_{\text{max}} = 26.3^\circ$
 $h = 0 \rightarrow 14$
 $k = -12 \rightarrow 12$
 $l = -27 \rightarrow 0$
3 standard reflections
frequency: 120 min
intensity decay: 3%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.040$
 $wR(F^2) = 0.124$
 $S = 1.08$
2597 reflections
145 parameters
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0651P)^2 + 0.494P]$$

where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.32 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.28 \text{ e \AA}^{-3}$

Table 1
Selected geometric parameters (Å, °).

C1–C2	1.575 (3)	C5–C6	1.517 (4)
C1–C11	1.763 (3)	C6–C7	1.509 (3)
C1–C13	1.776 (2)	C7–N1	1.322 (3)
C1–C12	1.778 (2)	C8–N1	1.485 (3)
C2–O1	1.228 (3)	C8–C9	1.496 (4)
C2–C3	1.412 (3)	C9–C10	1.474 (4)
C3–C7	1.399 (3)	C10–C11	1.513 (4)
C3–C4	1.528 (3)	C11–N1	1.465 (3)
C4–C5	1.532 (4)		
C2–C1–C11	111.19 (16)	N1–C7–C3	129.9 (2)
C2–C1–C13	108.69 (16)	N1–C7–C6	118.9 (2)
C2–C1–C12	112.06 (16)	C3–C7–C6	110.9 (2)
O1–C2–C3	126.2 (2)	N1–C8–C9	104.1 (2)
O1–C2–C1	114.77 (19)	C10–C9–C8	105.9 (2)
C7–C3–C2	124.4 (2)	C9–C10–C11	105.0 (2)
C2–C3–C4	127.2 (2)	N1–C11–C10	104.1 (2)
C3–C4–C5	102.7 (2)	C7–N1–C11	125.44 (19)
C6–C5–C4	105.2 (2)	C7–N1–C8	122.4 (2)
C7–C6–C5	104.0 (2)	C11–N1–C8	110.40 (19)

Table 2
Hydrogen-bonding 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>
C4–H4A...Cl3	0.97	2.73	3.434 (3)	130
C6–H6B...O1 ⁱ	0.97	2.54	3.502 (3)	171
C8–H8B...O1 ⁱⁱ	0.97	2.50	3.388 (4)	152
C11–H11B...O1	0.97	2.32	2.792 (3)	109

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

H atoms were positioned geometrically 0.97 Å from their parent atoms, and their displacement parameters were refined isotropically, using the riding-model approximation.

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD-4 EXPRESS*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 1990).

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