

## ORGANIC COMPOUNDS

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**1,7-Dichloro-9-azatricyclo[4.3.1.0<sup>3,7</sup>]decan-8-one, a Hydrolysed Diels–Alder Cycloaddition Product from the Reaction of 3,5,6-Trichloro-1,2,4-triazine with Hexa-1,5-diene**

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**Abstract**

Although the title molecule, C<sub>9</sub>H<sub>11</sub>Cl<sub>2</sub>NO, is close to being symmetric about the plane containing the Cl and N atoms, it lies in a general position. This contrasts with the related molecule, 1,8-dichloro-5-oxa-10-azatricyclo[5.3.1.0<sup>3,8</sup>]undecan-9-one [Barlow, Pritchard, Sibous & Tipping (1992). *Acta Cryst.* C48, 1908–1909], which is bisected by a crystallographic mirror plane. However, both systems form hydrogen-bonded dimers linked *via* the amine H and ketonic O atoms [N—H...O 2.08 (3) Å, N—H...O 173 (2)°].

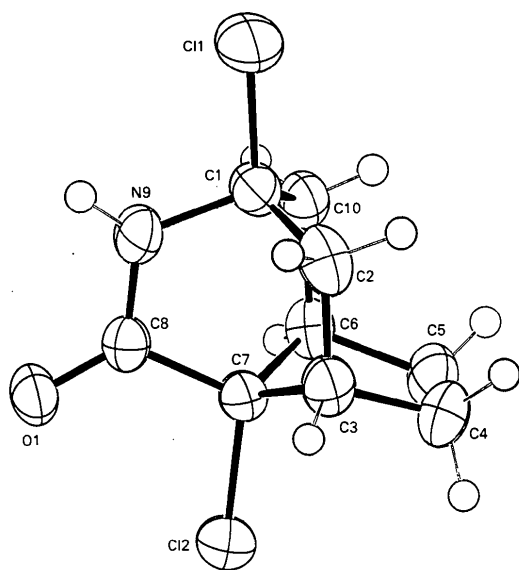
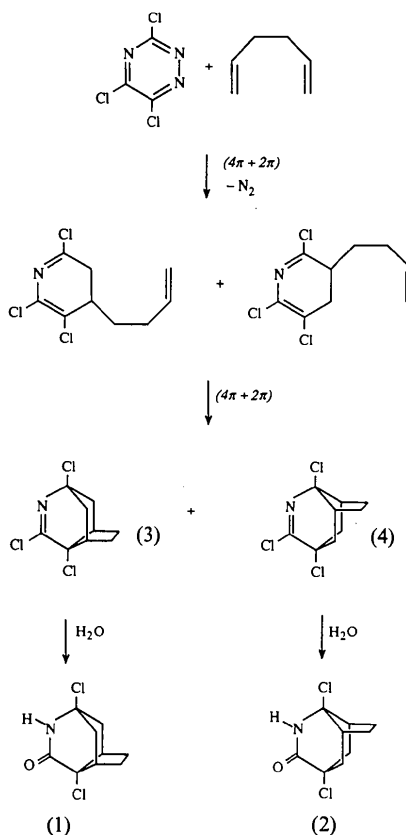


Fig. 1. The title molecule, including atomic numbering scheme.

**Comment**

This structure determination is part of an investigation into the Diels–Alder addition of diolefins to trichloro-1,2,4-triazine (Barlow, Sibous & Tipping, 1992). The initial addition involving hexa-1,5-diene was regioselective, giving two intermediate products which underwent a second intramolecular addition to afford symmetrical compounds (3) (major) and (4) (minor), which were readily hydrolysed to the isolated amides, the title compound (1) and compound (2), respectively. In contrast to the reaction with diallyl ether no products arose *via* a [1,5]-sigmatropic hydrogen shift.



**Experimental**

A mixture of 3,5,6-trichloro-1,2,4-triazine (2.00 g, 10.8 mmol) and hexa-1,5-diene (7.12 g, 86.8 mmol) was sealed *in vacuo* in a Rotaflo tube (*ca* 50 ml) and heated at 343 K for 9 d. The volatile products were identified as nitrogen (0.23 g, 8.2 mmol, 78%) and unchanged hexa-1,5-diene (6.13 g, 74.6 mmol, 86% recovered) while the residue which remained in the tube was washed out with diethyl ether and the ether removed *in vacuo* to give brown oily crystals (2.75 g). These were washed with *n*-pentane (3 × 10 ml) and then sub-

limed *in vacuo* at 343–358 K to give a mixture (2.0 g, 8.4 mmol, 78%; analysis found C 45.6, H 4.4, N 5.9, Cl 44.2%,  $M^+$  237/239/241/243; analysis calculated for  $C_9H_{10}NCl_3$  C 45.3, H 4.2, N 5.9, Cl 44.6%,  $M$  237/239/241/243) of 1,7,8-trichloro-9-azatricyclo[4.3.1.0<sup>3,7</sup>]dec-8-ene (3) and 1,7,9-trichloro-8-azatricyclo[4.3.1.0<sup>3,7</sup>]dec-8-ene (4) in the ratio *ca* 6:1 (<sup>1</sup>H NMR) as a white powder, m.p. 343–349 K.

A sample (0.5 g, 2.1 mmol) of the mixture was treated with water (10 ml) and dichloromethane (5 ml) and stirred at room temperature for 6 h. The organic layer was separated, dried (MgSO<sub>4</sub>) and the solvent removed *in vacuo* to give a mixture of the isomeric amides (1) and (2) (0.44 g, 2.0 mmol, 96%; analysis found C 49.1, H 5.3, N 6.4, Cl 32.7%,  $M^+$  219/221/223; analysis calculated for  $C_9H_{11}NOCl_2$  C 49.1, H 5.0, N 6.4, Cl 32.7%,  $M$  219/221/223) in the ratio *ca* 5:1 (<sup>1</sup>H NMR) as a white powder, m.p. 443–451 K. This mixture, separable by dry-column flash chromatography or high-pressure liquid chromatography, was dissolved in chloroform (4 ml) and the solvent slowly allowed to evaporate until crystallization occurred. The product (0.28 g) was filtered off and recrystallized from acetone to give the title compound (0.26 g, 1.2 mmol, 57%; analysis found C 48.8, H 5.1, N 6.1, Cl 32.4%,  $M^+$  219/221/223; analysis calculated for  $C_9H_{11}NOCl_2$  C 49.1, H 5.3, N 6.4, Cl 32.3%,  $M$  219/221/223) as white crystals, m.p. 465 K.

#### Crystal data

$C_9H_{11}Cl_2NO$

$M_r = 220.10$

Monoclinic

$P2_1/n$

$a = 6.241$  (2) Å

$b = 12.296$  (3) Å

$c = 12.758$  (4) Å

$\beta = 95.58$  (2)°

$V = 974.4$  (4) Å<sup>3</sup>

$Z = 4$

$D_x = 1.500$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\lambda = 0.71069$  Å

Cell parameters from 25 reflections

$\theta = 16.4$ – $27.2$ °

$\mu = 0.6248$  mm<sup>-1</sup>

$T = 296$  K

Needle

$0.40 \times 0.20 \times 0.20$  mm

Colourless

#### Data collection

Nicolet  $R3m/V$  diffractometer

$\omega/2\theta$  scans

Absorption correction: not applied

2143 measured reflections

2143 independent reflections

1539 observed reflections

$[I > 2\sigma(I)]$

$\theta_{max} = 26.11$ °

$h = 0 \rightarrow 7$

$k = 0 \rightarrow 15$

$l = -15 \rightarrow 15$

3 standard reflections

monitored every 200

reflections

intensity variation: none

#### Refinement

Refinement on  $F$

$R = 0.0478$

$wR = 0.0602$

$S = 2.057$

1539 reflections

163 parameters

All H-atom parameters refined

Weighting scheme based on measured e.s.d.'s

$(\Delta/\sigma)_{max} = 0.0517$

$\Delta\rho_{max} = 0.34$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.48$  e Å<sup>-3</sup>

Extinction correction: Zachariasen type 2

Gaussian isotropic

Extinction coefficient:

$8.4$  (9)  $\times 10^{-6}$

Atomic scattering factors

from *International Tables for X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i.a_j.$$

	x	y	z	$U_{eq}$
C11	0.6428 (2)	0.02121 (8)	0.22216 (7)	0.0829
C12	0.6647 (1)	0.30510 (7)	0.61098 (6)	0.0657
O1	0.9358 (3)	0.1171 (1)	0.5793 (1)	0.0454
N9	0.7948 (4)	0.0778 (2)	0.4134 (2)	0.0452
C1	0.6300 (4)	0.1117 (2)	0.3303 (2)	0.0416
C2	0.4131 (5)	0.1046 (3)	0.3745 (2)	0.0490
C3	0.4108 (4)	0.1847 (2)	0.4671 (2)	0.0440
C4	0.2855 (5)	0.2891 (3)	0.4350 (3)	0.0571
C5	0.4461 (5)	0.3638 (3)	0.3877 (3)	0.0514
C6	0.6595 (4)	0.3008 (2)	0.3960 (2)	0.0375
C7	0.6423 (4)	0.2273 (2)	0.4928 (2)	0.0366
C8	0.8083 (4)	0.1358 (2)	0.5020 (2)	0.0348
C10	0.6787 (5)	0.2272 (2)	0.2998 (2)	0.0417

Table 2. Selected geometric parameters (Å, °)

C11—C1	1.780 (3)	C3—C4	1.538 (4)
C12—C7	1.780 (3)	C3—C7	1.542 (4)
O1—C8	1.227 (3)	C4—C5	1.526 (5)
N9—C1	1.465 (3)	C5—C6	1.535 (4)
N9—C8	1.332 (3)	C6—C7	1.542 (3)
C1—C2	1.519 (4)	C6—C10	1.540 (4)
C1—C10	1.511 (4)	C7—C8	1.526 (3)
C2—C3	1.540 (4)		
C1—N9—C8	116.4 (2)	C3—C7—C6	99.5 (2)
N9—C1—C2	107.6 (2)	C3—C7—C8	112.4 (2)
N9—C1—C10	108.0 (2)	C6—C7—C8	113.2 (2)
C2—C1—C10	111.0 (2)		

Data collection: *P3/PC Diffractometer Program* (Siemens, 1989). Cell refinement: *P3/PC Diffractometer Program*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*. Literature search: *CSSR* (1984).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71725 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1063]

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