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(4E,8Z,12E)-13,16-Dichloro-14-azabicyclo[10.4.0]hexadeca-4,8,12-trien-15-one: a Thermal Cycloaddition Product

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Abstract. $C_{15}H_{19}Cl_2NO$, $M_r = 300.23$, monoclinic, $P2_1/c$, $a = 13.978 (8)$, $b = 7.467 (9)$, $c = 16.452 (9)$ Å, $\beta = 114.11 (4)°$, $V = 1567 (2)$ Å^3, $Z = 4$, $D_x = 1.272$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.41$ mm^{-1}, $F(000) = 632$, $T = 293$ K, $R = 0.052$, 1468 unique reflexions [$F \geq 4\sigma(F)$]. The 12-membered ring is sufficiently flexible to accommodate a planar *cis*-alkene link [C—C=C—C $-2 (1)°$]; however, the *trans*-alkene is distorted [C—C=C—C 171.2 (5)°]. The smaller ring adopts a twist conformation, severely flattened in part by the combined effect of a double bond and the amide group. Pairs of molecules are linked across an inversion centre by hydrogen bonds between the amide H atom and ketonic O atom [H···O = 2.06 (4) Å, N—H···O = 170.0 (4)°].

Experimental. A mixture of 3,5,6-trichloro-1,2,4-triazine (2.00 g, 10.8 mmol) and (1*E*,5*E*,9*Z*)-1,5,9-dodecatriene (6.15 g, 38.0 mmol) was sealed *in vacuo* in a Rotaflo tube (*ca* 50 ml) and heated at 343 K for 4 d. This gave a volatile mixture of hydrogen chloride (0.11 g, 3.0 mmol, 39%) and nitrogen together with a brown residue (7.5 g), which was extracted with diethyl ether (3 × 20 ml). The filtrate, on removal of the ether, gave a reddish oil (7.22 g), which was separated by DCFC (dry column flash chromatography) [silica (Merck Kieselgel 60 H); eluant CH_2Cl_2 and *n*-C_5H_{12} (1:1 *v/v*)] to afford (i) unchanged triene (4.75 g, 29.3 mmol, 77%), (ii) a yellow oil (R_F 0.63) comprising a mixture (0.91 g, 3.2 mmol, 42%) of (*E,Z*)- and (*Z,E*)-1,3-dichloro-

5,6,9,10,13,14-hexahydrododeca[c]pyridine, and (iii) a solid (1.22 g). The solid was sublimed *in vacuo* to give unchanged triazine (0.59 g, 3.2 mmol, 30% recovered) and a residue (R_F 0.57; 0.62 g, 1.7 mmol, 22%; analysis found: C 60.0, H 6.4, N 4.7, Cl 23.6%; M^+ 299/301/303; analysis calculated for $C_{15}H_{19}$-NOCl$_2$: C 59.8, H 6.4, N 4.6, Cl 23.6%; M 299/301/303) comprising two isomers in the ratio 4:1 (^{1}H NMR). Recrystallization from chloroform produced a small amount of the title compound (major isomer) (1) {formed by hydrolysis of (4*E*,8*Z*,12*E*,14*E*)-13,15,16-trichloro-14-azabicyclo[10.4.0]hexadeca-4,8,12,14-tetraene}.
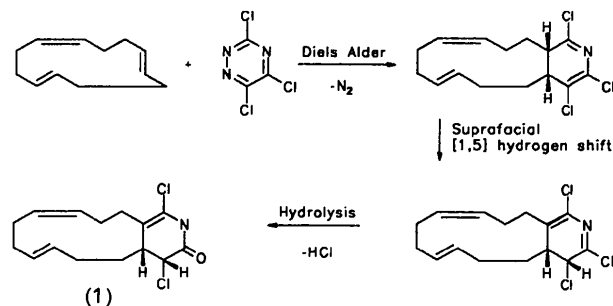
A colourless block crystal, 0.3 × 0.25 × 0.25 mm, was used for data collection on a Rigaku AFC-6*S* diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions were determined from setting angles of 16 accurately centred reflections ($20.2 \leq 2\theta \leq 24.1°$). Data were

Table 1. *Positional parameters and equivalent isotropic vibrational parameters* (Å^2)

$$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Cl(13)	0.7459 (1)	1.1574 (2)	0.4641 (1)	5.82 (6)
Cl(16)	0.7596 (1)	0.5970 (2)	0.59389 (9)	6.08 (7)
C(1)	0.6702 (4)	0.6314 (6)	0.4129 (3)	3.5 (2)
C(2)	0.5679 (4)	0.5988 (8)	0.3278 (4)	5.0 (3)
C(3)	0.5817 (5)	0.5864 (9)	0.2419 (4)	5.9 (3)
C(4)	0.6577 (5)	0.4439 (8)	0.2428 (4)	5.3 (3)
C(5)	0.7376 (5)	0.4655 (9)	0.2220 (4)	5.8 (3)
C(6)	0.8214 (6)	0.3275 (10)	0.2352 (5)	6.8 (3)
C(7)	0.9188 (5)	0.3613 (9)	0.3214 (5)	6.5 (3)
C(8)	0.9690 (5)	0.5375 (10)	0.3253 (5)	6.3 (3)
C(9)	0.9635 (4)	0.6803 (10)	0.3694 (4)	6.5 (3)
C(10)	0.9028 (5)	0.7006 (10)	0.4246 (4)	5.6 (3)
C(11)	0.8054 (4)	0.8211 (7)	0.3782 (4)	4.4 (2)
C(12)	0.7237 (3)	0.8092 (5)	0.4151 (3)	3.2 (2)
C(13)	0.6940 (3)	0.9438 (5)	0.4506 (3)	3.5 (2)
N(14)	0.6162 (3)	0.9301 (5)	0.4836 (3)	3.7 (2)
C(15)	0.5824 (4)	0.7728 (6)	0.5016 (3)	3.7 (2)
C(16)	0.6429 (4)	0.6137 (6)	0.4921 (3)	3.9 (2)
O(15)	0.5087 (3)	0.7604 (4)	0.5234 (2)	5.0 (2)

Table 2. *Selected bond lengths* (Å) *and angles* $(°)$

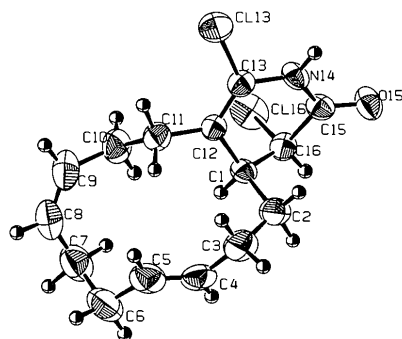|				
Cl(13)—C(13)	1.729 (5)		C(7)—C(8)	1.480 (9)
Cl(16)—C(16)	1.803 (5)		C(8)—C(9)	1.310 (8)
C(1)—C(2)	1.558 (7)		C(9)—C(10)	1.483 (8)
C(1)—C(12)	1.517 (6)		C(10)—C(11)	1.548 (7)
C(1)—C(16)	1.505 (6)		C(11)—C(12)	1.498 (6)
C(2)—C(3)	1.506 (8)		C(12)—C(13)	1.311 (6)
C(3)—C(4)	1.500 (8)		C(13)—N(14)	1.404 (5)
C(4)—C(5)	1.305 (8)		N(14)—C(15)	1.344 (5)
C(5)—C(6)	1.509 (8)		C(15)—C(16)	1.503 (6)
C(6)—C(7)	1.533 (9)		C(15)—O(15)	1.224 (5)
C(2)—C(1)—C(12)	114.9 (4)		C(12)—C(13)—N(14)	123.5 (4)
C(12)—C(1)—C(16)	110.7 (4)		C(13)—N(14)—C(15)	123.2 (4)
C(1)—C(12)—C(11)	119.5 (4)		N(14)—C(15)—C(16)	113.8 (4)
C(1)—C(12)—C(13)	116.0 (4)		C(1)—C(16)—C(15)	111.9 (4)

Fig. 1. The title molecule drawn using *ORTEP*II (Johnson, 1976).

(*CSSR*, 1984). Fractional atomic coordinates and vibrational parameters for non-H atoms are presented in Table 1* and selected bond lengths and angles in Table 2. The title molecule, including atomic labelling, is displayed in Fig. 1.

Related literature. Further details of the reactions between trichloro-1,2,4-triazine and olefins have been presented by Barlow, Haszeldine & Simpkin (1982). The current work supports their view that the general reaction is initiated *via* a Diels–Alder addition and loss of N_2 to give a dihydropyridine followed by a [1,5] sigmatropic hydrogen shift and HCl elimination to give a pyridine. The last step was prevented in the present case by an unfavourable *cis* disposition of H and Cl atoms and was replaced by hydrolysis of the susceptible N=CCl group to give an amide.

collected using ω–2θ scans, with ω-scan width (1.78 + 0.30tanθ)° and scan speed of 8° min^{-1} with up to two additional scans of weak reflexions [$I < 10\sigma(I)$], for $0 \le h \le 16$, $0 \le k \le 8$, $-17 \le l \le 17$ and $0 \le \theta \le 25°$. 3111 reflexions were measured ($R_{int} = 0.027$), of which 2985 were unique and 1468 observed [$F \ge 4\sigma(F)$]. Intensity standards (211, 11$\bar{3}$, 11$\bar{1}$) remained constant. Lp and absorption (azimuthal scans, maximum/minimum transmission 0.96/1.0) corrections were applied. *MITHRIL* (Gilmore, 1984) was used to solve the phase problem. All non-H atoms were found in Fourier maps, and H atoms from ΔF synthesis. Full-matrix least-squares refinement was based on F using *TEXSAN* crystallographic software (Molecular Structure Corporation, 1985). Final $R = 0.052$ {$wR = 0.050$, $w = 1/[\sigma^2(F_o) + (0.03F_o)^2]$}, using anisotropic thermal parameters for heavier atoms, and isotropic for H atoms. Maximum fluctuations in the final ΔF map were in the range -0.27– 0.23 e Å^{-3}. Maximum Δ/σ was 0.01. Scattering factors were obtained from Cromer & Waber (1974). Computation was carried out on a Digital VAX station 3520. A literature survey was performed *via* the Cambridge Structural Database using the *Crystal Structure Search and Retrieval* interactive system

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