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(Z,Z)-5-Chloro-1,1,1,6,6,6-hexafluoro-3,4-diaza-4-hexen-2-one Oxime, Formed by the Action of Hydroxylamine on 2,5-Dichlorohexafluoro-3,4-diazahexa-2,4-diene

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Abstract

Although the chain region between the double bonds at the 2 and 4 positions in the title compound, $C_4H_2ClF_6N_3O$ [C=N 1.245 (6), 1.269 (6) Å], shows some conjugation [N—N 1.348 (6), C—N 1.356 (6) Å; C=N—N—C −172.7 (6), N—N—C=N 171.8 (3)°] there is no evidence of an alternative tautomer with a double bond in position 3. The crystal packing features hydrogen-bonded dimers in which an oxime H atom is donated to the oxime N atom of a neighbouring molecule [O···N 2.810 (6), H···N 2.04 (6) Å; O—H···N 162 (5)°].

Comment

The structure determination reported herein was carried out as part of a general investigation of the reactions of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1) with nucleophiles (Barlow, Bell, O'Reilly & Tipping, 1983; O'Reilly, 1984; Abdul-Ghani, 1988, 1992). The crystal structure determination was required in order to differentiate between the possible products (2) and (3) formed by reaction of hydroxylamine with the azine (1), and to establish the stereochemistry of the actual product (2), which is shown in Fig. 1.

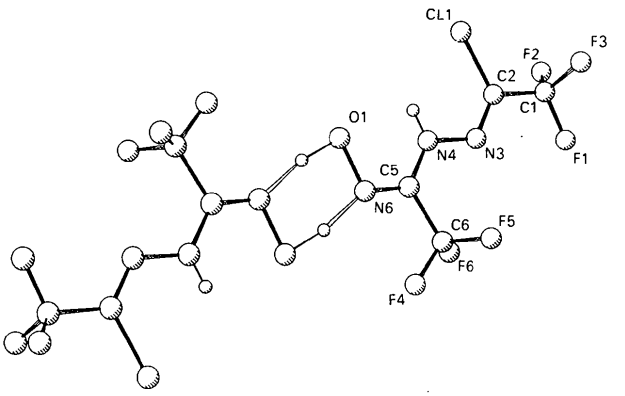


Fig. 1. The title molecule, showing the atom-numbering scheme, hydrogen-bonded to a neighbouring molecule generated by the inversion operation (2 − *x*, 1 − *y*, 2 − *z*).

Experimental

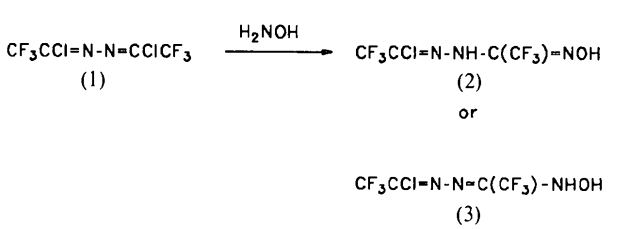
A solution of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1) (5.00 g, 19.2 mmol in diethyl ether, 15 ml) was added slowly (0.5 h) to a stirred solution of hydroxylamine hydrochloride (5.33 g, 76.7 mmol) and sodium hydroxide (3.06 g, 76.5 mmol) in diethyl ether (100 ml) and water (100 ml). The mixture was stirred for 1 d. The ether layer was separated and the aqueous layer was extracted with diethyl ether (2 × 50 ml). The combined ether extracts were dried ($MgSO_4$) and the ether was removed *in vacuo* to give a white solid (4.46 g) which was purified by sublimation *in vacuo* at 323 K to afford the title compound (2) (4.24 g, 16.4 mmol, 56%; found C 18.9, H 0.8, N 16.3, F 44.7%, M^+ 257/259; $C_4H_2N_3OClF_6$ requires C 18.6, H 0.8, N 16.3, F 44.3%, *M* 257.5; m.p. 391-393 K). The product was recrystallized from *n*-C_5H_{12}/CH_2Cl_2 1:1 (*v*/*v*).

Crystal data

$C_4H_2ClF_6N_3O$	Mo $K\alpha$ radiation
M_r = 257.52	λ = 0.71069 Å
Triclinic	Cell parameters from 25 reflections
$P\bar{1}$	θ = 6.4-8.5°
a = 5.141 (3) Å	μ = 0.50 mm^{-1}
b = 6.916 (2) Å	T = 296 K
c = 13.250 (5) Å	Prism
α = 75.08 (3)°	0.30 × 0.20 × 0.20 mm
β = 81.69 (4)°	Colourless
γ = 83.08 (4)°	
V = 448.8 (7) Å^3	
Z = 2	
D_x = 1.906 Mg m^{-3}	

Data collection

CAD-4 diffractometer	R_{int} = 0.047
$\omega/2\theta$ scans	θ_{max} = 24.99°
Absorption correction: none	h = 0 → 5
	k = −7 → 8
1610 measured reflections	l = −14 → 15



1545 independent reflections
810 observed reflections
$[I > 3\sigma(I)]$

3 standard reflections
frequency: 180 min
intensity variation: none

Refinement

Refinement on F
$R = 0.054$
$wR = 0.058$
$S = 2.40$
810 reflections
144 parameters
All H-atom parameters refined

Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{max} = 0.002$
$\Delta\rho_{max} = 0.265$ e Å^{-3}
$\Delta\rho_{min} = -0.244$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Cl(1)	0.2912 (4)	0.9492 (2)	0.6701 (2)	0.097 (1)
F(1)	0.154 (1)	0.4722 (7)	0.5933 (3)	0.129 (4)
F(2)	−0.0877 (8)	0.7370 (7)	0.5896 (3)	0.127 (4)
F(3)	0.2629 (9)	0.7428 (7)	0.4918 (3)	0.115 (4)
F(4)	0.8203 (8)	0.1053 (4)	0.9252 (3)	0.097 (3)
F(5)	0.7746 (8)	0.2068 (5)	0.7620 (3)	0.090 (3)
F(6)	0.4357 (8)	0.1703 (4)	0.8750 (3)	0.085 (3)
O(1)	0.8144 (10)	0.6752 (5)	0.9234 (4)	0.080 (3)
N(3)	0.4042 (9)	0.5570 (6)	0.7298 (3)	0.058 (3)
N(4)	0.5315 (9)	0.5930 (7)	0.8044 (4)	0.066 (4)
N(6)	0.8279 (9)	0.4699 (6)	0.9272 (3)	0.058 (3)
C(1)	0.157 (1)	0.6630 (10)	0.5860 (5)	0.071 (5)
C(2)	0.292 (1)	0.7011 (8)	0.6695 (4)	0.059 (4)
C(5)	0.680 (1)	0.4435 (7)	0.8640 (4)	0.050 (3)
C(6)	0.677 (1)	0.2284 (8)	0.8559 (5)	0.065 (5)

Table 2. *Selected geometric parameters* (Å, °)

Cl(1)—C(2)	1.718 (5)	N(4)—C(5)	1.356 (6)
O(1)—N(6)	1.402 (5)	N(6)—C(5)	1.269 (6)
N(3)—N(4)	1.348 (6)	C(1)—C(2)	1.482 (8)
N(3)—C(2)	1.245 (6)	C(5)—C(6)	1.520 (7)
N(4)—N(3)—C(2)	119.0 (5)	Cl(1)—C(2)—C(1)	115.4 (4)
N(3)—N(4)—C(5)	120.7 (5)	N(3)—C(2)—C(1)	119.3 (5)
O(1)—N(6)—C(5)	109.2 (4)	N(4)—C(5)—N(6)	124.2 (5)
Cl(1)—C(2)—N(3)	125.3 (4)	N(4)—C(5)—C(6)	119.8 (5)

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989). Cell refinement: *CAD-4 Software*. 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: *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*.

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 71823 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1073]

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(Z,Z)-5-Chloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene-2-amine, in which the Amino Group is Conjugated with a Chain Double Bond

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Abstract

The asymmetric unit of the title compound, $C_4H_2ClF_6N_3$, contains two crystallographically independent molecules which have similar C=N—N=C configurations [torsion angles −153.8 (7) and −153.6 (7)°]. Intermolecular hydrogen bonds between the amino H atoms and the diazine N atoms link the molecules into infinite chains along the *ac* diagonal [N···N 2.989 (9), 3.05 (1), H···N 2.22 (6), 2.16 (8) Å, N—H···N 156 (7), 172 (7)°].

Comment

The structure determination reported herein was carried out as part of a general investigation of the reactions of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1) with nucleophiles (Barlow, Bell, O'Reilly & Tipping, 1983; O'Reilly, 1984; Abdul-Ghani, 1988, 1992). The X-ray crystal structure was required to distinguish between the possible compounds (2) and (3) and to establish the relative stereochemistry of the substituents at the two C=N bonds.