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 71814 (12 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1065]

References

Augustine, A., Ferguson, G. & March, F. C. (1975). *Can. J. Chem.* **53**, 1647-1650.

Beagley, B., Colburn, C. B., El-Sayrafi, O., Gott, G. A., Kelly, D. G., Mackie, A. G., McAuliffe, C. A., MacRory, P. P. & Pritchard, R. G. (1988). *Acta Cryst.* C**44**, 38-41.

Belanger, S. & Beauchamp, A. L. (1993). *Acta Cryst.* C**49**, 388-391.

Bricklebank, N., Godfrey, S. M., Mackie, A. G., McAuliffe, C. A. & Pritchard, R. G. (1992). *J. Chem. Soc. Chem. Commun.* pp. 355-356.

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual.* SERC Daresbury Laboratory, Warrington, England.

Godfrey, S. M. (1993). PhD thesis, Victoria Univ. of Manchester, England.

Godfrey, S. M., Kelly, D. G., Mackie, A. G., McAuliffe, C. A., Pritchard, R. G. & Watson, S. M. (1991). *J. Chem. Soc. Chem. Commun.* pp. 1163-1164.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software.* MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sheldrick, G. M. (1985). *SHELXS*86. *Crystallographic Computing* 3, edited by G. M. Sheldrick, C. Krüger & R. Goddard, pp. 175-189. Oxford Univ. Press.

Weller, F., Nuszhar, D., Dehnicke, K., Gingl, F. & Strahle, J. (1991). *Z. Anorg. Allg. Chem.* **602**, 7-14.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558-564.

Acta Cryst. (1994). C**50**, 719–721

(2*Z*,4*E*,6*E*)-8-Ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene-2-amine: Formation of Hydrogen-Bonded Pairs *via* an Amine–Diazine Interaction

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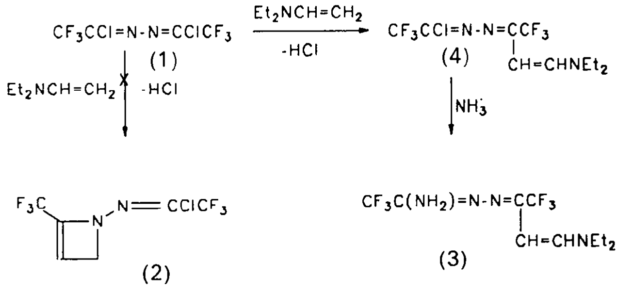
Abstract

An approximately planar conjugated region of the triazadecatriene chain in the title compound, $C_{10}H_{14}F_6N_4$, which begins at the diethylamine N atom, is disrupted by a twist between the diazo N atoms [N—N 1.405 (5) Å, C=N—N=C −144.4 (4)°]. This deformation facilitates hydrogen bonding between molecules related by a crystallographic twofold axis *via* a diazo N atom and an amine H atom [N···N 3.067 (7), H···N 2.02 (7) Å; N—H···N 157 (4)°].

Comment

The structure determination reported herein was part of an investigation of the reaction of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1) with enamines (Benomar, 1989; Abdul-Ghani, 1992). It has been reported (Benomar, O'Reilly & Tipping, 1991) that exposure of a mixture of azine (1) and triethylamine (1:2 molar ratio) to daylight gave an orange oil (40%), considered to be the Δ^2-azetine (2) on the evidence available, which was formed *via* the intermediacy of the enamine $Et_2NCH{=}CH_2$. In the present work, a solid derivative of the product was prepared by the reaction of the supposed Δ^2-azetine (2) with ammonia in order to characterize this product more fully. The ammonia derivative was subjected to an X-ray crystal structure determination and shown to be the open-chain triene (3), thus establishing that the orange oil was the chlorotriene (4) and not the Δ^2-azetine (2).



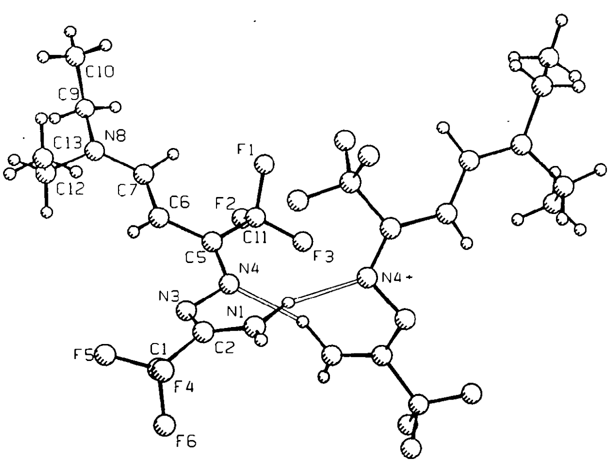


Fig. 1. The title hydrogen-bonded dimer, including atomic numbering scheme, drawn using *PLUTO* (Motherwell & Clegg, 1978).

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Experimental

Aqueous ammonia (0.6 g, 12.4 mmol, 35 wt %) was added to a stirred solution of 2-chloro-8-ethyl-1,1,1-trifluoro-5-trifluoromethyl-3,4,8-triazadeca-2,4,6-triene (4) (0.50 g, 1.55 mmol) in diethyl ether (50 ml). The flask was firmly stoppered and the contents were stirred for 20 h. The flask was then opened, stirring was continued for 5 h and water (2 ml) was added. The ether layer was separated and the aqueous layer was extracted with diethyl ether (2 x 25 ml). The combined extracts were dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the title compound (3) (0.45 g, 1.48 mmol, 96%; found C 39.6, H 4.6, N 18.4, F 37.7%, M^+ 304; $C_{10}H_{14}N_4F_6$ requires C 39.5, H 4.6, N 18.4, F 37.5%, *M* 304; m.p. 351-353 K). The product was recrystallized from n-C_6H_{14}/$CHCl_3$ 2:1 (*v*/*v*).

Crystal data

$C_{10}H_{14}F_6N_4$
$M_r = 304.24$
Monoclinic
$C2/c$
$a = 23.223\ (7)$ Å
$b = 13.044\ (3)$ Å
$c = 9.724\ (2)$ Å
$\beta = 101.46\ (3)°$
$V = 2886\ (2)$ Å^3
$Z = 8$
$D_x = 1.400$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 20.70$-$35.11°$
$\mu = 0.135$ mm^{-1}
$T = 296$ K
Needle
0.35 × 0.20 × 0.15 mm
Orange

Data collection

AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical
$T_{\min} = 0.68$, $T_{\max} = 1.00$
2741 measured reflections
2671 independent reflections
1198 observed reflections [$I > 2\sigma(I)$]

$R_{\text{int}} = 0.0303$
$\theta_{\max} = 25.00°$
$h = 0 \rightarrow 26$
$k = 0 \rightarrow 14$
$l = -10 \rightarrow 10$
3 standard reflections monitored every 150 reflections intensity variation: 4.8%

Refinement

Refinement on *F*
$R = 0.055$
$wR = 0.068$
$S = 2.46$
1198 reflections
211 parameters
H-atom parameters not refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.0046$

$\Delta\rho_{\max} = 0.34$ e Å^{-3}
$\Delta\rho_{\min} = -0.20$ e Å^{-3}
Extinction correction: Zachariasen (1967) type II Gaussian, isotropic
Extinction coefficient: $3.2\ (1) \times 10^{-7}$
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)

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

	x	y	z	U_{eq}
F(1)	1.0007 (2)	0.3988 (3)	0.5933 (4)	0.084 (2)
F(2)	1.0344 (2)	0.3295 (3)	0.4287 (4)	0.093 (2)
F(3)	1.0550 (2)	0.2668 (3)	0.6337 (4)	0.084 (2)
F(4)	0.8278 (3)	−0.0659 (5)	0.6880 (5)	0.072 (3)
F(5)	0.8195 (3)	−0.0216 (6)	0.4768 (6)	0.125 (4)
F(6)	0.8818 (3)	−0.1342 (4)	0.5618 (9)	0.122 (4)
F(7)	0.802 (2)	0.020 (3)	0.569 (6)	0.14 (2)
F(8)	0.853 (1)	−0.082 (2)	0.486 (3)	0.049 (9)
F(9)	0.853 (2)	−0.097 (3)	0.680 (5)	0.10 (2)
N(1)	0.9292 (2)	0.0389 (4)	0.7667 (5)	0.054 (2)
N(3)	0.9156 (2)	0.0886 (3)	0.5287 (4)	0.043 (2)
N(4)	0.9638 (2)	0.1545 (3)	0.5699 (4)	0.042 (2)
N(8)	0.8579 (3)	0.4085 (4)	0.2527 (6)	0.086 (3)
C(1)	0.8579 (3)	−0.0446 (5)	0.5888 (6)	0.060 (3)
C(2)	0.9048 (2)	0.0344 (3)	0.6307 (5)	0.039 (2)
C(5)	0.9578 (2)	0.2417 (4)	0.5052 (5)	0.042 (2)
C(6)	0.9072 (3)	0.2787 (4)	0.4116 (6)	0.053 (3)
C(7)	0.9038 (3)	0.3700 (5)	0.3443 (6)	0.064 (3)
C(9)	0.8625 (3)	0.5072 (5)	0.1797 (8)	0.099 (4)
C(10)	0.8278 (4)	0.5877 (6)	0.222 (1)	0.126 (5)
C(11)	1.0118 (3)	0.3074 (4)	0.5413 (6)	0.059 (3)
C(12)	0.8047 (5)	0.3465 (7)	0.203 (1)	0.131 (6)
C(13)	0.7679 (5)	0.3441 (10)	0.301 (1)	0.186 (9)

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

N(1)—C(2)	1.332 (6)	C(1)—C(2)	1.495 (7)
N(3)—N(4)	1.405 (5)	C(5)—C(6)	1.422 (7)
N(3)—C(2)	1.283 (5)	C(5)—C(11)	1.501 (7)
N(4)—C(5)	1.294 (6)	C(6)—C(7)	1.353 (7)
N(8)—C(7)	1.344 (7)	C(9)—C(10)	1.43 (1)
N(8)—C(9)	1.484 (8)	C(12)—C(13)	1.41 (1)
N(8)—C(12)	1.48 (1)		
N(4)—N(3)—C(2)	112.6 (4)	F(4)—C(1)—F(6)	104.9 (6)
N(3)—N(4)—C(5)	113.4 (4)	N(3)—C(2)—C(1)	114.4 (5)
C(7)—N(8)—C(9)	121.2 (6)	N(4)—C(5)—C(6)	127.2 (5)
C(7)—N(8)—C(12)	121.1 (6)	C(5)—C(6)—C(7)	124.8 (6)
C(9)—N(8)—C(12)	116.9 (5)	N(8)—C(7)—C(6)	127.7 (7)
F(4)—C(1)—F(5)	106.5 (6)		

Rotational disorder about C(1) was represented by a major [F(4), F(5), F(6); 86 (2)%] and a minor [F(7), F(8), F(9); 14 (2)%] conformer. The major conformer was treated anisotropically and the minor isotropically. F(4), F(5) and F(6) shared a common refined site occupancy factor, *k*, with F(7), F(8) and F(9) also having a common site occupancy factor, which was constrained to be $1-k$. Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *TEXSAN*, *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *TEXSAN*, *PLUTO* (Motherwell & Clegg, 1978). Software used to prepare material for publication: *TEXSAN FINISH*. Literature survey: *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 71820 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HU1066]

References

Abdul-Ghani, M. (1992). PhD thesis, Univ. of Manchester, England.

Benomar, S. M. (1989). MSc thesis, Univ. of Manchester, England.

Benomar, S. M., O'Reilly, N. J. & Tipping, A. E. (1991). *J. Fluorine Chem.* **51**, 207-217.

CSSR (1984). *Crystal Structure Search and Retrieval Instruction Manual*. SERC Daresbury Laboratory, Warrington, England.

Gilmore, C. J. (1984). *J. Appl. Cryst.* **17**, 42-46.

Molecular Structure Corporation (1985). *TEXSAN. TEXRAY Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Zachariasen, W. H. (1967). *Acta Cryst.* **23**, 558-564.

Acta Cryst. (1994). C**50**, 721-722

(*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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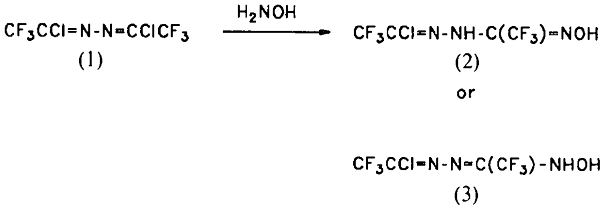
Abstract

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.



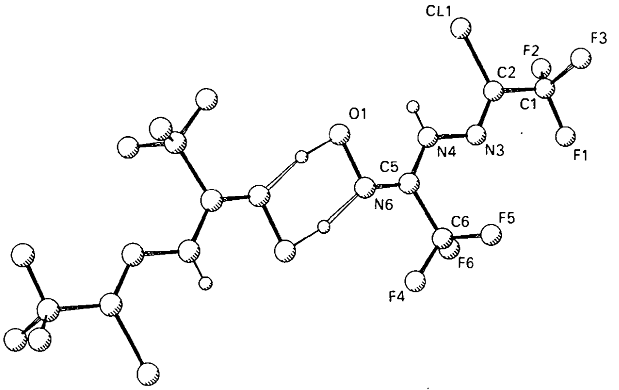


Fig. 1. The title molecule, showing the atom-numbering scheme, hydrogen-bonded to a neighbouring molecule generated by the inversion operation (2 − *x*, 1 − *y*, 2 − *z*).

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

$C_4H_2ClF_6N_3O$
M_r = 257.52
Triclinic
$P\bar{1}$
a = 5.141 (3) Å
b = 6.916 (2) Å
c = 13.250 (5) Å
α = 75.08 (3)°
β = 81.69 (4)°
γ = 83.08 (4)°
V = 448.8 (7) Å^3
Z = 2
D_x = 1.906 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71069 Å
Cell parameters from 25 reflections
θ = 6.4-8.5°
μ = 0.50 mm^{-1}
T = 296 K
Prism
0.30 × 0.20 × 0.20 mm
Colourless

Data collection

CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
1610 measured reflections

$R_{\rm int}$ = 0.047
$\theta_{\rm max}$ = 24.99°
$h = 0 \rightarrow 5$
$k = -7 \rightarrow 8$
$l = -14 \rightarrow 15$