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)

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

	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: *SHELXS*86 (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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Acta Cryst. (1994). C**50**, 722–724

(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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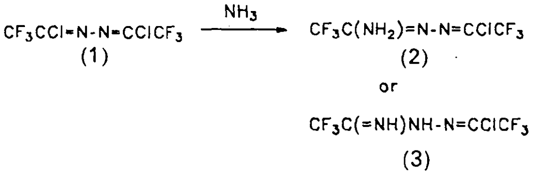
(*Received* 15 *October* 1993; *accepted* 18 *November* 1993)

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.



$$\underset{(1)}{CF_3CCl{=}N{-}N{=}CClCF_3} \xrightarrow{NH_3} \underset{(2)}{CF_3C(NH_2){=}N{-}N{=}CClCF_3}$$

or

$$\underset{(3)}{CF_3C({=}NH)NH{-}N{=}CClCF_3}$$

Acta Crystallographica Section C
ISSN 0108-2701 ©1994

The location of both H atoms on the amine N atom and the short diazahexadiene C═N bonds [1.236 (9)–1.283 (8) Å] suggest tautomer (2). However, the amine N atom has been drawn into conjugation with the adjacent double bond [C—N 1.30 (1), 1.30 (1) Å], suggesting that the molecule is better described as a mixture of tautomers (2) and (3). This situation may, in part, be a consequence of the hydrogen bonding, which offers a low-energy pathway between the two tautomers.

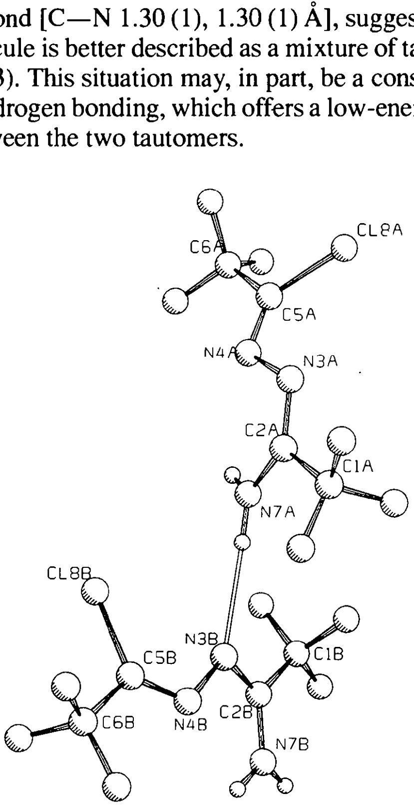


Fig. 1. The asymmetric unit, including atomic numbering scheme, drawn using *PLUTO* (Motherwell & Clegg, 1978).

Experimental

An aqueous solution of ammonia (2.23 g, 45.9 mmol, 35 wt %) in diethyl ether (25 ml) was added slowly to a stirred solution of 2,5-dichloro-1,1,1,6,6,6-hexafluoro-3,4-diazahexa-2,4-diene (1) in diethyl ether (50 ml) and water (25 ml) at 273 K (ice bath) and stirring was continued for 2 h. The ether layer was separated, dried ($MgSO_4$) and the ether removed *in vacuo* to give the title compound (2) (4.50 g, 18.63 mmol, 81%; found C 19.6, H 0.7, N 17.1%, M^+ 241/243; $C_4H_2N_3ClF_6$ requires C 19.9, H 0.8, N 17.4%, *M* 241.5; m.p. 331-333 K). The product was recrystallized from *n*-C_5H_{12}/CH_2Cl_2 1:1 (*v*/*v*).

Crystal data

$C_4H_2ClF_6N_3$
$M_r = 241.52$
Monoclinic
$P2_1/n$
$a = 10.487$ (3) Å
$b = 9.215$ (2) Å
$c = 17.472$ (8) Å
$\beta = 95.52$ (3)°
$V = 1680$ (1) Å^3
$Z = 8$
$D_x = 1.909$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 16.10$-36.07°
$\mu = 0.5160$ mm^{-1}
$T = 293$ K
Plate
0.40 × 0.40 × 0.10 mm
Colourless

Data collection

Nicolet *R3m/V* diffractometer
$\omega/2\theta$ scans with profile analysis (Siemens, 1990)
Absorption correction: refined from ΔF
$T_{\min} = 0.72$, $T_{\max} = 1.00$
2997 measured reflections
2695 independent reflections
1203 observed reflections [$I > 3\sigma(I)$]

$R_{\rm int} = 0.029$
$\theta_{\max} = 24.04$°
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 10$
$l = -19 \rightarrow 19$
3 standard reflections monitored every 150 reflections intensity variation: 0.8%

Refinement

Refinement on *F*
$R = 0.057$
$wR = 0.058$
$S = 2.199$
1203 reflections
269 parameters
All H-atom parameters refined
Weighting scheme based on measured e.s.d.'s
$(\Delta/\sigma)_{\max} = 0.1$

$\Delta\rho_{\max} = 0.485$ e Å^{-3}
$\Delta\rho_{\min} = -0.352$ e Å^{-3}
Extinction correction: Zachariasen (1967) type II Gaussian, isotropic
Extinction coefficient: 3.834×10^{-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)

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

	x	*y*	*z*	$U_{\rm eq}$
C1*A*	0.497 (1)	0.170 (1)	0.1269 (6)	0.072 (6)
C2*A*	0.4865 (8)	0.3319 (9)	0.1293 (4)	0.041 (4)
N3*A*	0.3978 (6)	0.3841 (7)	0.0827 (3)	0.039 (3)
N4*A*	0.3950 (6)	0.5348 (7)	0.0876 (3)	0.040 (3)
C5*A*	0.2897 (8)	0.5911 (9)	0.0688 (4)	0.041 (4)
C6*A*	0.279 (1)	0.752 (1)	0.0693 (8)	0.080 (7)
N7*A*	0.5663 (8)	0.3929 (9)	0.1808 (5)	0.057 (4)
Cl8*A*	0.1512 (2)	0.5057 (3)	0.0414 (1)	0.071 (1)
F11*A*	0.4263 (8)	0.1113 (7)	0.1761 (4)	0.139 (5)
F12*A*	0.6104 (7)	0.1245 (6)	0.1484 (4)	0.130 (4)
F13*A*	0.4599 (8)	0.1169 (6)	0.0616 (3)	0.129 (4)
F61*A*	0.3837 (6)	0.8142 (6)	0.0910 (5)	0.131 (4)
F62*A*	0.2007 (7)	0.7962 (8)	0.1141 (6)	0.161 (6)
F63*A*	0.2373 (10)	0.8010 (7)	0.0036 (5)	0.170 (6)
C1*B*	0.6540 (9)	0.332 (1)	0.3905 (6)	0.062 (5)
C2*B*	0.7726 (7)	0.2688 (8)	0.3647 (5)	0.034 (4)
N3*B*	0.7868 (6)	0.2858 (6)	0.2931 (3)	0.037 (3)
N4*B*	0.8993 (6)	0.2240 (7)	0.2751 (4)	0.044 (3)
C5*B*	0.9492 (9)	0.2755 (9)	0.2194 (5)	0.047 (4)
C6*B*	1.071 (1)	0.219 (1)	0.1975 (7)	0.070 (6)
N7*B*	0.8474 (8)	0.2073 (9)	0.4185 (4)	0.055 (4)
Cl8*B*	0.8921 (3)	0.4174 (3)	0.1656 (1)	0.086 (1)
F11*B*	0.6320 (6)	0.4603 (7)	0.3655 (4)	0.117 (4)
F12*B*	0.5560 (6)	0.2659 (8)	0.3596 (5)	0.161 (6)
F13*B*	0.6466 (8)	0.334 (1)	0.4598 (3)	0.187 (6)
F61*B*	1.1061 (5)	0.1002 (7)	0.2353 (3)	0.096 (3)
F62*B*	1.1636 (5)	0.3134 (7)	0.2092 (3)	0.091 (3)
F63*B*	1.0648 (5)	0.1840 (6)	0.1241 (3)	0.091 (3)

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

C1*A* —C2*A*	1.50 (1)	C1*B* —C2*B*	1.48 (1)
C2*A* —N3*A*	1.271 (8)	C2*B* —N3*B*	1.283 (8)
C2*A* —N7*A*	1.30 (1)	C2*B* —N7*B*	1.30 (1)
N3*A* —N4*A*	1.392 (8)	N3*B* —N4*B*	1.374 (8)
N4*A* —C5*A*	1.236 (9)	N4*B* —C5*B*	1.241 (9)
C5*A* —C6*A*	1.49 (1)	C5*B* —C6*B*	1.46 (1)
C5*A* —CL8*A*	1.680 (8)	C5*B* —CL8*B*	1.686 (8)

C1*A* —C2*A* —N3*A*	114.2 (8)	C1*B* —C2*B* —N3*B*	115.3 (8)
C1*A* —C2*A* —N7*A*	114.1 (8)	C1*B* —C2*B* —N7*B*	114.8 (8)
N3*A* —C2*A* —N7*A*	131.7 (8)	N3*B* —C2*B* —N7*B*	129.9 (8)
C2*A* —N3*A* —N4*A*	110.9 (6)	C2*B* —N3*B* —N4*B*	110.9 (6)
N3*A* —N4*A* —C5*A*	115.2 (7)	N3*B* —N4*B* —C5*B*	117.2 (7)
N4*A* —C5*A* —C6*A*	119.0 (8)	N4*B* —C5*B* —C6*B*	120.8 (8)

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: *TEXSAN*, *MITHRIL* (Gilmore, 1984). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *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 71831 (23 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: LI1087]

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Acta Cryst. (1994). C**50**, 724–726

Diethyl 5,6-Dihydro-2*H*-1,3-dithiolo[4,5-*b*]-[1,4]dithiin-2-ylphosphonate, $C_9H_{15}O_3PS_4$

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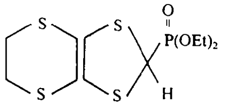
(*Received* 30 *July* 1993; *accepted* 27 *October* 1993)

Abstract

The two molecules in the asymmetric unit are very similar, apart from one P—O—C—C torsion angle. The five-membered ring is in the envelope conformation and the S—C_{sp^3} bonds [average 1.819 (7) Å] are longer than the S—C_{sp^2} bonds [average 1.76 (1) Å].

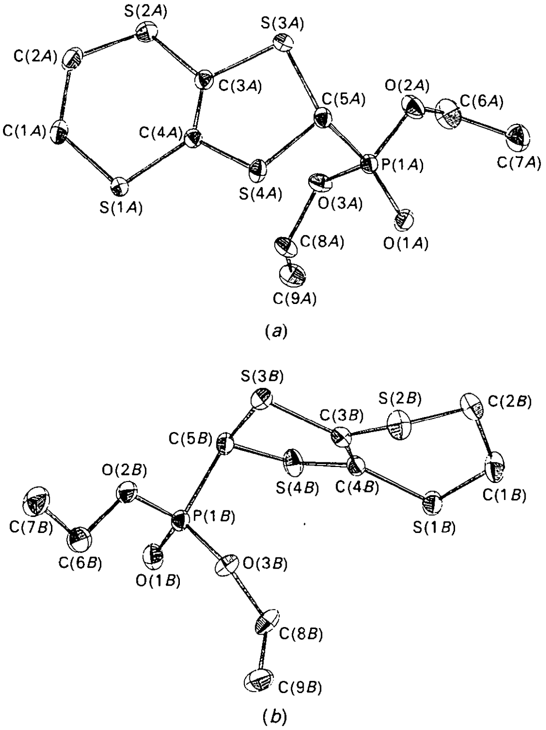
Comment

Phosphoranes of 1,3-dithiole derivatives are useful synthetic intermediates, particularly for the preparation of tetrathiafulvalene derivatives (Moore & Bryce, 1991).



(I)

The title compound (I) has been prepared previously in four steps from 4,5-ethylenedithio-1,3-dithiole-2-thione, and was reported to be an oil (Hansen, Lakshmikantham, Cava, Metzger & Becher, 1991). By heating 4,5-ethylenedithio-1,3-dithiole-2-thione in the presence of excess triethyl phosphite at 483 K for 6 h, the title compound was prepared in one step and purified by column chromatography [silica gel; 0-50% ethyl acetate/petroleum ether (40-60), gradient elution] to obtain a viscous oil. Trituration with the same solvents gave crystals (m.p. 337-338 K) and crystals suitable for X-ray examination were obtained by crystallization from ethyl acetate/petroleum ether (30/70 *v*/*v*).



(*a*)

(*b*)

Fig. 1. Views of $C_9H_{15}O_3PS_4$, showing the two molecules (*A* and *B*) in the asymmetric unit and the atom-labelling scheme. H atoms are excluded and the displacement ellipsoids are drawn at the 50% probability level.

Acta Crystallographica Section C
ISSN 0108-2701 ©1994