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Difluorosilanediyl-1,1′-bis(2,2,4,4,6,6-hexamethylcyclotrisilazane)

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Abstract. $C_{12}H_{40}F_2N_6Si_7$, $M_r = 503\cdot1$, orthorhombic, $Pbcn$, $a = 8\cdot388$ (2), $b = 13\cdot245$ (3), $c = 25\cdot144$ (4) Å, $U = 2793\cdot5$ Å^3, $Z = 4$, $D_x = 1\cdot196$ Mg m^{-3}, final $R = 0\cdot050$ for 1715 reflexions, measured at 233 K. Two boat-conformation Si_3N_3 rings are joined by a SiF_2 bridge.

Introduction. The compound, obtained by the method of Klingebiel, Enterling & Meller (1977), was recrystallized from light petroleum spirit. All crystallographic measurements were made with a Stoe–Siemens AED diffractometer and graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot71069$ Å) (Clegg, 1981). The crystal, *ca* 0·28 × 0·38 × 0·65 mm, was maintained at 233 ± 1 K by a stream of dry air, cooled by heat exchange with refrigerated methanol (Bellard & Sheldrick, 1978). Cell dimensions were obtained from 36 centred reflexions. Intensities were measured for reflexions with $7 < 2\theta < 50°$ in a θ/ω scan mode. Absorption corrections were not applied ($\mu = 0\cdot34$ mm^{-1}). 1715 unique reflexions with $I > 2\sigma(I)$ were used for structure determination.

The structure was solved by multisolution direct methods, and refined to a minimum of $\sum w\Delta^2$ [$w^{-1} = \sigma^2(F) + 0\cdot001F^2$]. H atoms were included with constraints [C—H = N—H = 0·96 Å, H—C—H = 109·5°, N—H bisects external Si—N—Si angle; $U(\text{H}) = 1\cdot2U_{\text{eq}}(\text{N})$ or $1\cdot3U_{\text{eq}}(\text{C})$]. Anisotropic thermal parameters were refined for non-H atoms.

Table 1. *Atomic coordinates* (×10^4) *and isotropic thermal parameters* (Å^2 × 10^4)

$U_{\text{eq}} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Si(1)	10000	475 (1)	2500	450 (5)
Si(2)	8575 (1)	2058 (1)	3230 (1)	445 (3)
Si(3)	8431 (2)	1458 (1)	4386 (1)	570 (4)
Si(4)	11011 (1)	592 (1)	3631 (1)	455 (4)
F(1)	8515 (3)	−263 (1)	2470 (1)	706 (9)
N(1)	9964 (4)	1101 (2)	3086 (1)	395 (9)
N(2)	7552 (4)	1747 (2)	3796 (1)	562 (12)
N(3)	10348 (4)	1212 (2)	4189 (1)	522 (12)
C(1)	9648 (6)	3268 (3)	3324 (2)	630 (17)
C(2)	7095 (5)	2169 (3)	2693 (2)	603 (16)
C(3)	8490 (7)	2515 (4)	4870 (2)	897 (22)
C(4)	7395 (7)	382 (4)	4693 (2)	959 (23)
C(5)	13187 (5)	810 (3)	3594 (2)	679 (17)
C(6)	10595 (6)	−776 (2)	3691 (2)	688 (18)

Table 2. *Bond lengths* (Å) *and angles* (°)

Si(1)—F(1)	1·585 (2)	Si(1)—N(1)	1·690 (3)
Si(2)—N(1)	1·759 (3)	Si(2)—N(2)	1·713 (3)
Si(2)—C(1)	1·853 (4)	Si(2)—C(2)	1·840 (4)
Si(3)—N(2)	1·701 (3)	Si(3)—N(3)	1·714 (4)
Si(3)—C(3)	1·856 (5)	Si(3)—C(4)	1·839 (5)
Si(4)—N(1)	1·762 (3)	Si(4)—N(3)	1·718 (3)
Si(4)—C(5)	1·851 (4)	Si(4)—C(6)	1·851 (4)
F(1)—Si(1)—N(1)	109·2 (1)	F(1)—Si(1)—F(1)′	103·9 (2)
N(1)—Si(1)—F(1)′	106·0 (1)	F(1)—Si(1)—N(1)′	106·0 (1)
N(1)—Si(1)—N(1)′	121·3 (2)	F(1)′—Si(1)—N(1)′	109·2 (1)
N(1)—Si(2)—N(2)	109·3 (1)	N(1)—Si(2)—C(1)	109·2 (2)
N(2)—Si(2)—C(1)	110·2 (2)	N(1)—Si(2)—C(2)	110·7 (2)
N(2)—Si(2)—C(2)	106·9 (2)	C(1)—Si(2)—C(2)	110·6 (2)
N(2)—Si(3)—N(3)	101·3 (2)	N(2)—Si(3)—C(3)	114·4 (2)
N(3)—Si(3)—C(3)	108·0 (2)	N(2)—Si(3)—C(4)	109·6 (2)
N(3)—Si(3)—C(4)	114·7 (2)	C(3)—Si(3)—C(4)	108·8 (2)
N(1)—Si(4)—N(3)	106·9 (1)	N(1)—Si(4)—C(5)	113·1 (2)
N(3)—Si(4)—C(5)	106·6 (2)	N(1)—Si(4)—C(6)	110·2 (2)
N(3)—Si(4)—C(6)	109·9 (2)	C(5)—Si(4)—C(6)	110·0 (2)
Si(1)—N(1)—Si(2)	123·0 (2)	Si(1)—N(1)—Si(4)	118·8 (2)
Si(2)—N(1)—Si(4)	116·5 (1)	Si(2)—N(2)—Si(3)	124·2 (2)
Si(3)—N(3)—Si(4)	129·1 (2)		

The prime denotes an atom generated by the twofold rotation axis.

Final values of R and R_g [$= (\sum w\Delta^2/\sum wF_o^2)^{1/2}$] are 0·050 and 0·060 respectively. Refined coordinates are given in Table 1, bond lengths and angles in Table 2.*

Discussion. The molecule (Fig. 1) possesses crystallographic twofold rotation symmetry. The electron-withdrawing F atoms have a considerable effect on the geometry of the silicon–nitrogen molecular skeleton, causing shortening of the exocyclic Si—N bonds and concomitant lengthening of the nearest ring bonds, compared with the other ring bonds.

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* Lists of structure factors, anisotropic thermal parameters and H atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35832 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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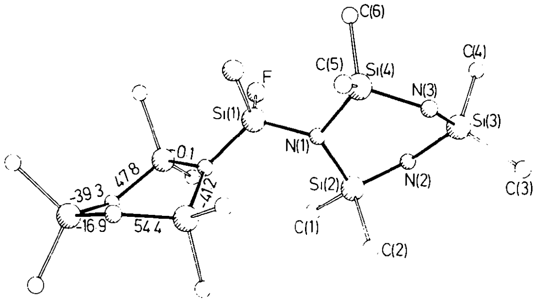

Fig. 1. View of one molecule, with the atom labelling and ring torsion angles (°) (e.s.d. = 0·3 °; the sign convention is that of Klyne & Prelog, 1960).

The Si_3N_3 ring is far from planar: ring torsion angles are shown in Fig. 1. They do not correspond to any ideal conformation of six-membered rings, but approximate most closely to those of the boat conformation (ideal values 0, 60, −60, 0, 60, −60° in cyclic order). A similar boat conformation was found for $(SiMe_2.NSiMe_3)_3$ (Adamson & Daly, 1970), while almost planar Si_3N_3 rings have been reported for $(SiMe_2.NH)_3$ in the gas phase (Rozsondai, Hargittai, Golubinskii, Vilkov & Mastyukov, 1975) and for $(PhSiF.NMe)_3$ (Clegg, Noltemeyer, Sheldrick & Vater, 1980). In contrast to Si_2N_2 four-membered rings, which are always virtually planar (Clegg, Hesse, Klingebiel, Sheldrick & Skoda, 1980, and references therein), it appears that the conformation of Si_3N_3 six-membered rings is sensitive to electronic and steric effects of the ring substituents.

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Bis[di-*tert*-butyl(*tert*-butylamino)silyl]acetylene

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Abstract. $C_{26}H_{56}N_2Si_2$, M_r = 452·9, monoclinic, $P2_1/n$, a = 8·512 (2), b = 11·659 (2), c = 15·780 (3) Å, β = 97·08 (2)°, U = 1554·1 Å^3, Z = 2, D_x = 0·968 Mg m^{-3}; final R = 0·058 for 2253 reflexions. The molecule, which has a crystallographic centre of symmetry, consists of a central C≡C bond with two $(NHBu)SiBu_2$ substituents (Bu = *tert*-butyl).

Introduction. Colourless crystals were obtained from a solution in light petroleum. A crystal *ca* 0·30 × 0·27 × 0·25 mm was used for X-ray investigation. All crystallographic measurements were made at room temperature with graphite-monochromated Mo $K\alpha$ radiation (λ = 0·71069 Å), on a Stoe–Siemens AED diffractometer. Cell dimensions were refined from the angle settings of 46 strong reflexions. Intensities for reflexions with $7 < 2\theta < 45°$ were measured in a θ/ω scan mode by a profile-fitting procedure (Clegg, 1981). No absorption corrections were applied (μ = 0·12 mm^{-1}). 2253 unique reflexions with $I > 2\sigma(I)$ were used for structure determination.

Application of multisolution direct methods, followed by difference syntheses, located all non-H atoms, which were subsequently refined with anisotropic thermal parameters to a minimum of $\sum w\Delta^2$ [$w^{-1} = \sigma^2(F) + gF^2$; g refined to a value of 0·00039]. The H

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