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

C(1)–C(2)	1·373 (6)	C(5)–C(6)	1·376 (5)
C(1)–C(6)	1·365 (6)	C(7)–C(8)	1·513 (5)
C(2)–C(3)	1·383 (4)	C(7)–N	1·345 (5)
C(3)–C(4)	1·383 (5)	C(7)–O	1·221 (5)
C(4)–C(5)	1·379 (5)	C(8)–C(9)	1·492 (6)
C(4)–N	1·417 (3)	C(9)–C′(9)	1·511 (4)
C(2)–C(1)–C(6)	119·3 (5)	C(1)–C(6)–C(5)	120·5 (5)
C(1)–C(2)–C(3)	121·0 (4)	C(8)–C(7)–N	114·5 (3)
C(2)–C(3)–C(4)	119·4 (4)	C(8)–C(7)–O	121·9 (4)
C(3)–C(4)–C(5)	119·2 (4)	N–C(7)–O	123·6 (4)
C(3)–C(4)–N	123·0 (4)	C(7)–C(8)–C(9)	114·0 (4)
C(5)–C(4)–N	117·8 (3)	C(8)–C(9)–C′(9)	113·2 (4)
C(4)–C(5)–C(6)	120·6 (4)	C(4)–N–C(7)	126·8 (4)
C(6)–C(1)–C(2)–C(3)	−0·7 (4)	C(5)–C(4)–N–C(7)	152·2 (3)
C(2)–C(1)–C(6)–C(5)	0·4 (4)	C(4)–C(5)–C(6)–C(1)	0·4 (4)
C(1)–C(2)–C(3)–C(4)	0·1 (4)	C(8)–C(7)–N–C(4)	−176·1 (3)
C(2)–C(3)–C(4)–C(5)	0·7 (3)	N–C(7)–C(8)–C(9)	−143·9 (3)
C(2)–C(3)–C(4)–N	−176·2 (3)	O–C(7)–C(8)–C(9)	39·5 (4)
C(3)–C(4)–C(5)–C(6)	−0·9 (4)	O–C(7)–N–C(4)	0·5 (3)
C(3)–C(4)–N–C(7)	−30·9 (3)	C(7)–C(8)–C(9)–C′(9)	−174·5 (3)
N–C(4)–C(5)–C(6)	176·1 (3)		

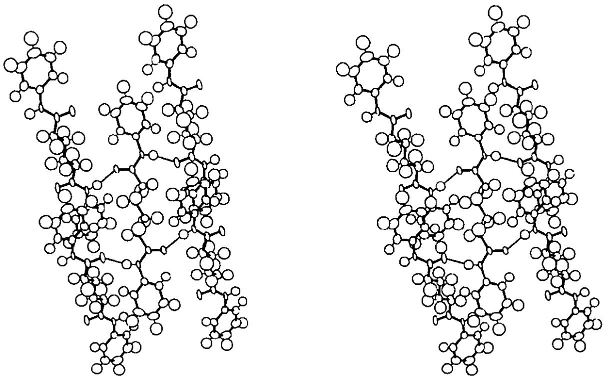

Fig. 2. Stereoscopic view of the crystal structure of DPHD.

DPTP and TMDB. Hydrogen bonds in the first group are shorter [N—H···O distances: DPHD 2·840 (4), DMDB 2·85 and PPDB (II) 2·857 (1) Å] than the hydrogen bonds in the second group [N—H···O distances: PPDB 3·111 (4), DPTP 3·118 (2) and TMDB 2·999 (4) Å]. The overall packing of the molecules, as judged from the cell volume, is better for the second group [cell volumes: PPDB 759, PPDB (II) 818 (× 2) Å^3]. Therefore it seems that stronger hydrogen bonding is possible at the expense of the efficiency of the overall packing. In the case of short hydrogen bonds, large deviations from ideal values of the torsion angles of the bonds between the amide group and the central (phenyl, tetramethylene or dimethylene) group of the molecule are found. For instance the torsion angle N—C(7)—C(8)—C(9) has the value −143·9 (3)° in DPHD. The corresponding C(7)—N—C(8)—C(9) torsion angle in TMDB is 169·5 (2)°, much closer to the expected *trans* value of 180°. Similar effects are found in DMDB and PPDB (II).

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Structure of 1,1′-Fluoroboranediylbis(3-fluorodimethylsilyl-2,2,4,4,6,6-hexamethylcyclotrisilazane), $C_{16}H_{50}BF_3N_6Si_8$

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Abstract. $M_r = 619·1$, orthorhombic, *Pbcn*, $a = 18·764$ (2), $b = 14·633$ (2), $c = 13·098$ (2) Å, $U = 3596·4$ Å^3, $Z = 4$, $D_x = 1·143$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0·32$ mm^{-1}, $F(000) = 1328$, $T =$

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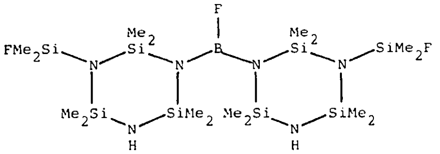
291 K. Final $R = 0{\cdot}048$ for 2474 observed reflections. Two Si_3N_3 rings, with conformation intermediate between boat and twist, are joined by a BF bridge.

Introduction. The compound is one of the products obtained from reactions of cyclotrisilazanes or their lithium salts with $BF_3.Et_2O$ (Hesse, Klingebiel & Skoda, 1981). The main interest in the structure investigation was the conformation of the cyclotrisilazane rings.



Experimental. Crystals obtained from *n*-hexane and mounted in capillaries, 0·4 × 0·4 × 0·3 mm, Stoe–Siemens AED diffractomater, unit-cell parameters derived from 2θ angles for 48 reflections centred at $\pm\omega$ ($20 < 2\theta < 25°$), intensities measured for 3705 reflections with $2\theta < 50°$ and all indices ≥ 0, profile analysis on-line (Clegg, 1981), no significant variation in intensity for three standard reflections; no absorption correction, $R_{\text{int}} = 0{\cdot}042$ (based only on 133 reflections measured twice because of a disc fault), 3168 unique reflections, 2474 with $F > 4\sigma(F)$; structure solved by automatic multisolution direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0{\cdot}00055F^2$, H atoms constrained to give C—H = 0·96 Å, H—C—H = 109·5°, N—H = 0·87 Å bisecting external Si—N—Si angle, $U(\text{H}) = 1{\cdot}2U_{\text{eq}}(\text{C})$ or $1{\cdot}2U_{\text{eq}}(\text{N})$, anisotropic thermal parameters for all non-H atoms, no extinction correction, 179 parameters, $R = 0{\cdot}048$, $wR = 0{\cdot}062$, slope of normal probability plot = 1·44, max. shift/e.s.d. = 0·06, mean = 0·005, largest peak in final difference map = 0·30 e Å^{-3}, largest hole = −0·27 e Å^{-3}, scattering factors from *International Tables for X-ray Crystallography* (1974), programs used: *SHELXTL* (Sheldrick, 1978), diffractometer-control program by WC.

Discussion. Atomic coordinates and bond lengths and angles are given in Tables 1 and 2 respectively, ring torsion angles in Fig. 1.* The B—F bond lies along a crystallographic twofold rotation axis. Coordination of B and N atoms is essentially planar [required for B by crystallographic symmetry; N(1) and N(3) lie 0·167 (3) and 0·070 (3) Å respectively out of the planes defined by the atoms bonded to them].

Table 1. *Atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å² ×10⁴)

	x	y	z	U^*
B	0	2708 (3)	2500	443 (16)
F(1)	0	1787 (2)	2500	940 (14)
N(1)	−499 (1)	3139 (1)	1830 (2)	381 (7)
Si(1)	−1081 (1)	3994 (1)	2248 (1)	430 (3)
C(11)	−892 (2)	5152 (2)	1715 (3)	662 (13)
C(12)	−1085 (2)	4060 (2)	3662 (3)	619 (12)
N(2)	−1884 (1)	3611 (2)	1784 (2)	480 (8)
Si(2)	−2172 (1)	2501 (1)	1631 (1)	436 (3)
C(21)	−3050 (2)	2538 (3)	971 (3)	686 (14)
C(22)	−2252 (2)	1918 (3)	2883 (3)	700 (15)
N(3)	−1520 (1)	1940 (2)	918 (2)	437 (8)
Si(3)	−752 (1)	2585 (1)	693 (1)	444 (3)
C(31)	−899 (2)	3440 (3)	−327 (3)	750 (15)
C(32)	5 (2)	1874 (3)	230 (3)	794 (16)
Si(4)	−1587 (1)	808 (1)	609 (1)	606 (4)
F(2)	−2373 (1)	506 (1)	923 (2)	966 (10)
C(41)	−983 (3)	66 (3)	1354 (4)	993 (20)
C(42)	−1544 (3)	587 (4)	−772 (4)	1164 (25)

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

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

B—F(1)	1·348 (5)	B—N(1)	1·430 (3)
N(1)—Si(1)	1·747 (2)	N(1)—Si(3)	1·761 (3)
Si(1)—C(11)	1·867 (3)	Si(1)—C(12)	1·855 (4)
Si(1)—N(2)	1·719 (3)	N(2)—Si(2)	1·723 (3)
Si(2)—C(21)	1·861 (4)	Si(2)—C(22)	1·856 (4)
Si(2)—N(3)	1·743 (3)	N(3)—Si(3)	1·747 (2)
N(3)—Si(4)	1·710 (3)	Si(3)—C(31)	1·852 (4)
Si(3)—C(32)	1·862 (4)	Si(4)—F(2)	1·594 (3)
Si(4)—C(41)	1·849 (5)	Si(4)—C(42)	1·839 (5)

F(1)—B—N(1)	116·2 (2)	N(1)—B—N(1)′	127·6 (2)
B—N(1)—Si(1)	122·2 (2)	B—N(1)—Si(3)	119·5 (2)
Si(1)—N(1)—Si(3)	115·2 (1)	N(1)—Si(1)—C(11)	114·4 (1)
N(1)—Si(1)—C(12)	110·7 (1)	C(11)—Si(1)—C(12)	109·1 (2)
N(1)—Si(1)—N(2)	101·8 (1)	C(11)—Si(1)—N(2)	109·3 (1)
C(12)—Si(1)—N(2)	111·5 (2)	Si(1)—N(2)—Si(2)	128·5 (1)
N(2)—Si(2)—C(21)	107·7 (1)	N(2)—Si(2)—C(22)	110·9 (2)
C(21)—Si(2)—C(22)	110·6 (2)	N(2)—Si(2)—N(3)	106·6 (1)
C(21)—Si(2)—N(3)	112·7 (2)	C(22)—Si(2)—N(3)	108·3 (2)
Si(2)—N(3)—Si(3)	114·5 (1)	Si(2)—N(3)—Si(4)	122·1 (1)
Si(3)—N(3)—Si(4)	122·9 (1)	N(1)—Si(3)—N(3)	109·2 (1)
N(1)—Si(3)—C(31)	109·8 (1)	N(3)—Si(3)—C(31)	111·4 (2)
N(1)—Si(3)—C(32)	109·1 (2)	N(3)—Si(3)—C(32)	112·5 (2)
C(31)—Si(3)—C(32)	104·8 (2)	N(3)—Si(4)—F(2)	106·0 (1)
N(3)—Si(4)—C(41)	113·5 (2)	F(2)—Si(4)—C(41)	105·5 (2)
N(3)—Si(4)—C(42)	113·6 (2)	F(2)—Si(4)—C(42)	104·3 (2)
C(41)—Si(4)—C(42)	112·9 (2)		

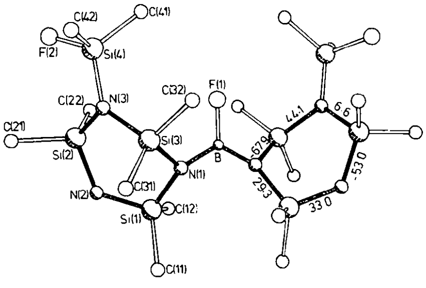


Fig. 1. View of one molecule, with atom labelling and ring torsion angles (°, e.s.d. = 0·2°).

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* Tables of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38252 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

The deviation of the ring conformation from the ideal boat form (torsion angles 0, 60, −60, 0, 60, −60° in cyclic order; Bucourt & Hainaut, 1965) is greater than that observed in previously determined structures of cyclotrisilazanes (Adamson & Daly, 1970; Clegg, Noltemeyer, Sheldrick & Vater, 1981), to the extent of approximating more closely to the twist conformation (33·1, 33·1, −70·6, 33·1, 33·1, −70·6°). Other cyclotrisilazanes have been reported with almost planar rings (Rozsondai, Hargittai, Golubinskii, Vilkov & Mastyukov, 1975; Clegg, Noltemeyer, Sheldrick & Vater, 1980).

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2,5,8-Trithia[9](2,6)-pyridinophane,* $C_{11}H_{15}NS_3$

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Abstract. $M_r = 257{\cdot}44$, monoclinic, $P2_1/c$, $a = 9{\cdot}049\,(3)$, $b = 15{\cdot}875\,(5)$, $c = 9{\cdot}523\,(4)$ Å, $\beta = 114{\cdot}09\,(2)°$, $U = 1248{\cdot}9\,(8)$ Å^3, $Z = 4$, $D_x = 1{\cdot}369$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}539$ mm^{-1}, $F(000) = 544$, $T = 291$ K. Final $R = 0{\cdot}0426$ for 1871 observed $[I > 2\sigma(I)]$ diffractometer data. The macrocycle is disordered, the major component (84%) adopting a 'chair-like' conformation. However, the minor component of the thioether chain possesses an alternative conformation which may be suitable for forming transition-metal complexes, the four heteroatoms being coplanar to within ± 0·09 Å.

Introduction. The title compound may be considered as a hetero analogue of '12-crown-4' and was reported to form crystalline complexes with $AgNO_3$, $HgCl_2$, $HAuCl_4$, $PdCl_2$, H_2PtCl_6 and $Co(SCN)_2$ (Weber & Vögtle, 1976). The present X-ray investigation was undertaken to study possible structural changes on complex formation.

Experimental. Colourless rod *ca* 0·5 × 0·15 × 0·1 mm (kindly provided by Dr E. Weber and Professor F. Vögtle, Bonn, Federal Republic of Germany) chosen for crystallographic measurements on an automated Stoe X-ray four-circle diffractometer, cell dimensions determined by least squares from settings of 38 strong reflexions in range $20 < 2\theta < 25°$; out of 3642 data collected between $2\theta = 7$ and 50° in a profile fitting mode (Clegg, 1981), 109 systematically absent ($h0l$, $l = 2n+1$; $0k0$, $k = 2n+1$) and 2190 unique ($R_{\text{int}} = 0{\cdot}0194$); structure solved by multisolution direct methods and refined anisotropically minimizing $\sum w(|F_o| - |F_c|)^2$, with scattering factors as incorporated in *SHELXTL*.

A difference map then revealed all H-atom positions, but also a minor disorder component $[f = 0{\cdot}163\,(2)]$ of atoms S(4)′ to S(10)′. Except C(3)—S(4) and C(3)—S(4)′, corresponding distances in both conformations were restrained to be equal by the method of additional observational equations with weights derived from $\sigma = 0{\cdot}005$ Å. Restraining C(3)—S(4)′ resulted in a dominant peak of 0·6 e Å^{-3} [close to S(4) and S(4)′] in the difference map, at distances of 1·48 and 1·75 Å to C(3) and C(5)′, respectively, possibly indicating some additional non-resolvable disorder. Isotropic temperature factors of primed S atoms were allowed to vary freely whilst those of C(5)′, C(6)′, C(8)′ and C(9)′ were kept fixed at U_{eq} of corresponding C atoms of the major component. Only for that part of the chain were H atoms included [in calculated positions, C—H = 0·96 Å, $U_{\text{iso}}(\text{H}_i) = 1{\cdot}2\,U_{\text{eq}}(\text{C}_i)$].

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* Nomenclature according to Vögtle & Neumann (1970).

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