

The *N*-oxide and amino groups of the cation are bridged by an intramolecular O...H...N hydrogen bond, O...N 2.551 (4) Å, which closes a six-membered ring in the central part of the cation. This ring has a sofa conformation with C(1) moved out of the relatively flat N(1)O(1)...H(O1)...N(2)C(2) moiety. According to its geometry, the intramolecular H bond can be classified as very strong (Novak, 1974). The O...H...N angle (126°) is far from linear but it is within the limits acceptable for H bonds (Jaskólski, 1984). According to the H(O1) position determined from a difference-Fourier map (O...H and H...N being respectively 1.35 and 1.52 Å), the H atom is nearly centrally located in the O...H...N bridge and therefore the energy barrier between the O—H...N and O...H—N minima must be relatively low.

The PEtP(NO).H⁺ cations are involved in intermolecular H bonds with water molecules. Each water molecule links two adjacent cations *via* HO—H...O(H)—N hydrogen bonds resulting in infinite ...H₂O...PEtP(NO).H⁺... chains running helically along **b** (Fig. 2). The *N*-oxide O atom is therefore involved in three H bonds: in the intramolecular O...H...N bridge and (as an acceptor) in two bonds with water molecules, 2.782 (4) and 2.837 (4) Å. The water molecule is an acceptor in a weak C(1)—H...O(W) hydrogen bond, 3.383 (5) Å. The donor of this C—H...O hydrogen bond [C(1)] is adjacent to a nitrogen atom bearing partial positive charge [N(1)] in agreement with the observation by Taylor & Kennard (1982) that such C atoms are especially likely to form H bonds.

The mean Cl—O bond length of the perchlorate ion is 1.416 (5) Å. The anion is not involved in H bonding and its O atoms show relatively high thermal motion (Table 1).

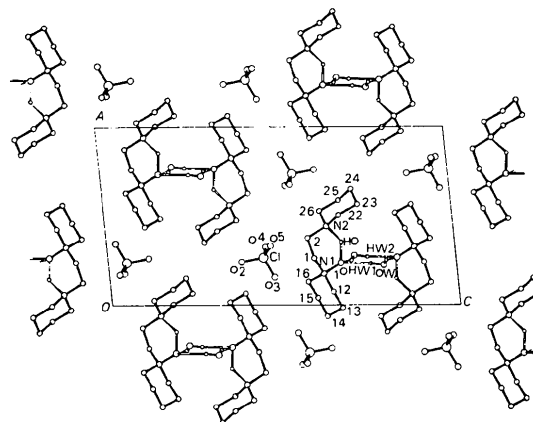


Fig. 2. Projection of the structure down **b**.

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Structure of 1,3-Di-*tert*-butyl-2,2,4,4-tetraisopropylcyclodisilazane, C₂₀H₄₆N₂Si₂

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Abstract. $M_r = 370.8$, monoclinic, $P2_1/n$, $a = 8.842(2)$, $b = 15.842(3)$, $c = 9.266(2)$ Å, $\beta = 115.89(3)^\circ$, $V = 1167.7(4)$ Å³, $Z = 2$, $D_x = 1.055(1)$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.15$ mm⁻¹, $F(000) = 416$, $T = 291$ K, $R = 0.041$ for 1670 observed reflections. The molecule has crystallographic inversion symmetry, with a central planar

Si₂N₂ ring of dimensions Si—N 1.747(2) and 1.748(2) Å, Si—N—Si 93.9(1) and N—Si—N 86.1(1)°. Consideration of the arrangement of the substituents and comparison with the structures of other cyclodisilazanes suggests that the homologous compound fully substituted with *tert*-butyl groups may be unattainable for steric reasons.

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> _{eq}
Si(1)	4353 (1)	4806 (1)	3514 (1)	284 (2)
C(1)	2380 (3)	5254 (1)	1820 (2)	410 (8)
C(11)	2616 (3)	5573 (2)	372 (3)	601 (11)
C(12)	1435 (3)	5912 (2)	2315 (3)	599 (11)
C(2)	5140 (3)	4007 (1)	2473 (2)	403 (8)
C(21)	3826 (3)	3364 (1)	1402 (3)	612 (12)
C(22)	6768 (3)	3555 (2)	3545 (3)	656 (12)
N(1)	4123 (2)	4492 (1)	5214 (2)	291 (6)
C(3)	3114 (3)	3828 (1)	5501 (2)	392 (8)
C(31)	2701 (3)	4071 (2)	6874 (3)	621 (12)
C(32)	4064 (3)	2992 (1)	5903 (3)	645 (13)
C(33)	1462 (3)	3702 (2)	4002 (3)	650 (11)

Table 2. Bond lengths (\AA) and angles ($^\circ$)

Si(1)—N(1)	1.747 (2)	Si(1)—N(1)'	1.748 (2)
Si(1)—C(1)	1.902 (2)	Si(1)—C(2)	1.897 (3)
C(1)—C(11)	1.531 (4)	C(1)—C(12)	1.526 (4)
C(2)—C(21)	1.538 (3)	C(2)—C(22)	1.524 (3)
N(1)—C(3)	1.477 (3)	C(3)—C(31)	1.518 (4)
C(3)—C(32)	1.525 (3)	C(3)—C(33)	1.526 (3)
N(1)—Si(1)—N(1)'	86.1 (1)	N(1)—Si(1)—C(1)	115.1 (1)
N(1)—Si(1)—C(2)	118.8 (1)	N(1)′—Si(1)—C(1)	118.5 (1)
N(1)′—Si(1)—C(2)	114.9 (1)	C(1)—Si(1)—C(2)	103.7 (1)
Si(1)—N(1)—Si(1)′	93.9 (1)	Si(1)—N(1)—C(3)	133.0 (1)
Si(1)′—N(1)—C(3)	132.9 (1)	Si(1)—C(1)—C(11)	114.8 (2)
Si(1)—C(1)—C(12)	115.6 (1)	C(11)—C(1)—C(12)	109.9 (2)
Si(1)—C(2)—C(21)	115.3 (2)	Si(1)—C(2)—C(22)	115.7 (2)
C(21)—C(2)—C(22)	110.0 (2)	N(1)—C(3)—C(31)	110.8 (2)
N(1)—C(3)—C(32)	110.5 (2)	C(31)—C(3)—C(32)	108.9 (2)
N(1)—C(3)—C(33)	110.0 (2)	C(31)—C(3)—C(33)	108.1 (2)
C(32)—C(3)—C(33)	108.4 (2)		

Introduction. The thermal elimination of LiF from lithiated aminofluorosilanes ($R_2\text{SiF.NR}'\text{Li}$) provides a convenient synthetic route to a variety of cyclodisilazanes. Depending on the nature of the substituents *R* and *R'*, several reaction mechanisms are available, some involving molecular rearrangements, leading to symmetrically and unsymmetrically substituted Si_2N_2 rings (Clegg, Klingebiel, Sheldrick & Stalke, 1983). The compound $\text{Bu}_2\text{SiF.NBuLi}$, with *Bu* = *tert*-butyl, does not form a cyclodisilazane even under drastic conditions (Clegg, Klingebiel, Neemann & Sheldrick, 1983). $\text{Pr}_2\text{SiF.NBuLi}$ (*Pr* = isopropyl) does, however, undergo a simple LiF elimination and dimerization above 323 K in *n*-hexane/tetrahydrofuran (THF) to produce $(\text{Pr}_2\text{Si.NBu})_2$. The symmetrical nature of this cyclodisilazane has been established by X-ray crystallography.

Experimental. Colourless crystals from *n*-hexane/THF, sealed in capillaries, $0.3 \times 0.3 \times 0.7$ mm, Stoe-Siemens AED diffractometer, unit-cell parameters refined from 2θ values of 40 reflections ($20 < 2\theta < 25^\circ$), 4432 reflections with $2\theta < 50^\circ$, range of *hkl*: *h* $-10 \rightarrow 10$, *k* $0 \rightarrow 18$, *l* $-11 \rightarrow 11$, on-line profile analysis (Clegg, 1981), no significant intensity variation for three

standard reflections, no absorption corrections, 2047 unique reflections, 1670 with $F > 4\sigma(F)$, $R_{int} = 0.033$; automatic multisolution direct methods, blocked-cascade refinement on *F*, anisotropic thermal parameters for non-H atoms, rigid methyl groups, $\text{C—H} = 0.96 \text{\AA}$, $\text{H—C—H} = 109.5^\circ$, $U(\text{H}) = 1.2U_{eq}(\text{C})$, scattering factors from *International Tables for X-ray Crystallography* (1974). 130 parameters, $R = 0.041$, $wR = 0.048$, $w^{-1} = \sigma^2(F) + 0.00033F^2$, $(\Delta/\sigma)_{\text{mean}} = 0.001$, $(\Delta/\sigma)_{\text{max}} = 0.004$, largest peak in final difference map = 0.21 e \AA^{-3} , largest hole = -0.18 e \AA^{-3} , slope of normal probability plot = 1.46, programs: *SHELXTL* (Sheldrick, 1978), diffractometer control program by WC.

Discussion. Atomic coordinates are given in Table 1, bond lengths and angles in Table 2.* The molecular structure is shown in Fig. 1. As in almost all cases of symmetrically substituted cyclodisilazanes (Clegg, Hesse, Klingebiel, Sheldrick & Skoda, 1980; Clegg, Klingebiel, Sheldrick & Vater, 1981; Wheatley, 1962), the molecule has crystallographic inversion symmetry. As is commonly observed for simple cyclodisilazanes, the Si_2N_2 ring is almost square, the N—Si—N angles being slightly below and the Si—N—Si angles slightly above 90° (Clegg, Klingebiel, Krampe & Sheldrick, 1980; Clegg, Klingebiel & Sheldrick, 1982). The variation in ring geometry of cyclodisilazanes is small, with a range of $1.72\text{--}1.77 \text{\AA}$ for the Si—N bond length, $85\text{--}90^\circ$ for the N—Si—N angle and $90\text{--}95^\circ$ for the Si—N—Si angle. These parameters appear to be rather insensitive to the nature of the ring substituents. Within the *Pr* groups, the wide C—C—C and Si—C—C angles are caused by the relatively minor steric requirements of the tertiary C—H H atoms.

* 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 39171 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

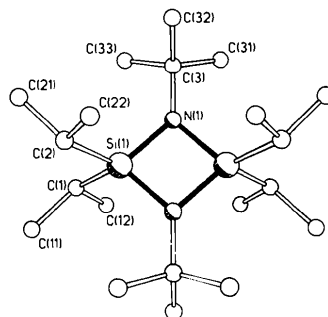


Fig. 1. The molecular structure (H atoms omitted), showing the labelling scheme for the asymmetric unit.

The insensitivity of the ring geometry to substituent effects raises the question of whether the compound $(\text{Bu}_2\text{Si.NBu})_2$ is sterically too crowded to be stable, or whether the steric bulk of the substituents has simply prevented a synthesis by the direct methods so far attempted. In this context, we note that the cyclotrisiloxane $(\text{Bu}_2\text{SiO})_3$ cannot be prepared by elimination of water from $\text{Bu}_2\text{Si}(\text{OH})_2$ (a reaction which normally occurs very readily for such compounds) and necessitates a multi-step synthetic route (Sommer & Tyler, 1954; Klingebiel, 1981). We have performed simple calculations in which the Pr groups of $(\text{Pr}_2\text{Si.NBu})_2$ are replaced by Bu groups with $\text{C}-\text{C} = 1.53 \text{ \AA}$ and ideal tetrahedral angles at the central C atom, while retaining the $(\text{C}_2\text{Si.NBu})_2$ part of the molecule unchanged. We find several $\text{C}\cdots\text{C}$ distances under 3 \AA for methyl C atoms in different Bu groups. Concerted rotation about the Si-C bonds reduces the steric interference between Bu groups attached to each Si atom [as is observed in $(\text{Bu}_2\text{SiO})_3$, where all the Bu groups fit snugly together (Clegg, 1982; Puff, Franken, Schuh & Schwab, 1983)], but the short contacts between Bu groups attached to Si and N are not relieved by such Si-C or N-C rotations. In $(\text{Pr}_2\text{Si.NBu})_2$ the substituents are oriented to avoid all such short contacts (Fig. 1), and the shortest $\text{C}\cdots\text{C}$ between methyl groups on different Bu substituents is $2.99 (1) \text{ \AA}$. We conclude that $(\text{Bu}_2\text{Si.NBu})_2$ is probably too crowded to be stable, at least with a planar central Si_2N_2 ring of the form always observed so far for cyclodisilazanes. In contrast, $(\text{Bu}_2\text{Si.PBu})_2$ has been prepared and structurally characterized (Clegg, Haase, Klingebiel & Sheldrick, 1983); in this molecule,

however, the mean Si-P bond length is 2.259 \AA , so steric crowding is much smaller.

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Structure of 2-(1,2-Dihydro-1-methyl-2-pyridylidene)-3-(4-ethoxyphenyl)-3-oxopropanenitrile, $\text{C}_{17}\text{H}_{16}\text{N}_2\text{O}_2^*$

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Abstract. $M_r = 280.2$, triclinic, $P\bar{1}$, $Z = 2$, $a = 7.199 (2)$, $b = 8.473 (1)$, $c = 12.360 (1) \text{ \AA}$, $\alpha = 101.73 (1)$, $\beta = 94.37 (2)$, $\gamma = 100.10 (2)^\circ$, $V = 721.9 \text{ \AA}^3$, $D_m(\text{floatation}) = 1.24$, $D_x = 1.25 \text{ Mg m}^{-3}$, $\mu(\text{Mo } K\alpha) = 7.18 \text{ mm}^{-1}$, $\lambda(\text{Mo } K\alpha) = 0.7107 \text{ \AA}$, $F(000) = 496.0$, $T = 293 \text{ K}$, $R = 0.052$ for 1082 observed reflections. The molecular structure obtained from the present study is in agreement with that obtained

from spectral data. The $\text{C}=\text{C}$ distance is $1.438 (6) \text{ \AA}$, appreciably longer than normal. The steric and electronic effects result in rotation about the $\text{C}=\text{C}$ bond, the rotation angle being $40.7 (6)^\circ$.

Introduction. The title compound (I) was obtained during an attempt to prepare substituted 2-azabarelenones by cycloaddition reactions between 1-methyl-2(1H)-pyridone and 3-substituted propyne-nitrile (Yadla & Madhusudhana Rao, 1984). The

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