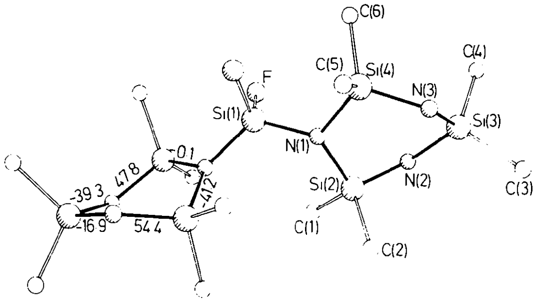

Fig. 1. View of one molecule, with the atom labelling and ring torsion angles (°) (e.s.d. = 0·3°; the sign convention is that of Klyne & Prelog, 1960).

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

$U_{eq} = \frac{1}{3}$(trace of the orthogonalized U_{ij} matrix) except for H(10).

	x	y	z	U_{eq}
Si	5698 (1)	1787 (1)	4325 (1)	477 (2)
N	6471 (3)	1578 (2)	3390 (1)	717 (8)
C(4)	5186 (3)	417 (2)	4816 (1)	496 (7)
C(1)	3773 (3)	2624 (2)	4082 (2)	677 (10)
C(11)	2572 (4)	1860 (3)	3548 (2)	1111 (16)
C(12)	3049 (5)	2952 (3)	4884 (2)	1225 (17)
C(13)	3993 (4)	3711 (3)	3572 (2)	1147 (17)
C(2)	7266 (4)	2476 (2)	5136 (1)	694 (10)
C(21)	8669 (4)	1658 (3)	5285 (3)	1287 (18)
C(22)	7889 (5)	3600 (3)	4817 (2)	1078 (15)
C(23)	6673 (5)	2691 (4)	6000 (2)	1469 (20)
C(3)	6852 (3)	613 (2)	2865 (1)	670 (10)
C(31)	7550 (6)	1089 (3)	2110 (2)	1496 (22)
C(32)	5390 (6)	−78 (3)	2566 (3)	1428 (20)
C(33)	8000 (6)	−196 (3)	3363 (3)	1349 (20)
H(10)	6435 (33)	2003 (24)	3158 (17)	1138 (78)

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

Si–N	1·706 (2)	Si–C(4)	1·851 (2)
Si–C(1)	1·905 (3)	Si–C(2)	1·909 (3)
N–H(10)	0·614 (28)	N–C(3)	1·457 (3)
C(1)–C(11)	1·529 (4)	C(1)–C(12)	1·523 (5)
C(1)–C(13)	1·525 (4)	C(2)–C(21)	1·524 (5)
C(2)–C(22)	1·522 (4)	C(2)–C(23)	1·532 (4)
C(3)–C(31)	1·501 (5)	C(3)–C(32)	1·508 (5)
C(3)–C(33)	1·507 (5)	C(4)–C(4)′	1·195 (4)
N–Si–C(4)	112·0 (1)	N–Si–C(1)	108·3 (1)
C(4)–Si–C(1)	106·6 (1)	N–Si–C(2)	109·1 (1)
C(4)–Si–C(2)	105·3 (1)	C(1)–Si–C(2)	115·6 (1)
Si–N–H(10)	113·8 (27)	Si–N–C(3)	137·6 (2)
H(10)–N–C(3)	106·5 (26)	Si–C(4)–C(4)′	174·8 (3)
Si–C(1)–C(11)	108·2 (2)	Si–C(1)–C(12)	112·8 (2)
C(11)–C(1)–C(12)	107·0 (3)	Si–C(1)–C(13)	112·0 (2)
C(11)–C(1)–C(13)	108·1 (2)	C(12)–C(1)–C(13)	108·6 (3)
Si–C(2)–C(21)	108·1 (2)	Si–C(2)–(22)	112·6 (2)
C(21)–C(2)–C(22)	106·9 (3)	Si–C(2)–C(23)	112·7 (2)
C(21)–C(2)–C(23)	107·6 (3)	C(22)–C(2)–C(23)	108·7 (3)
N–C(3)–C(31)	107·6 (2)	N–C(3)–C(32)	110·9 (3)
C(31)–C(3)–C(32)	109·9 (3)	N–C(3)–C(33)	111·2 (2)
C(31)–C(3)–C(33)	110·5 (3)	C(32)–C(3)–C(33)	106·6 (3)

atom attached to N was allowed to refine freely, with an isotropic thermal parameter. All other H atoms were constrained, such that C–H = 0·96 Å, H–C–H = 109·5° and $U(\mathrm{H}) = U_{eq}(\mathrm{C})$.

The final R is 0·058, with $R_g = (\sum w\Delta^2/\sum wF_o^2)^{1/2} = 0{\cdot}073$. Atom coordinates, bond lengths and angles are give in Tables 1 and 2.*

Discussion. This compound was prepared in the course of an investigation into the steric and electronic effects of substituents on the formation and ring geometry of cyclodisilazanes and cyclotrisilazanes, which contain Si_2N_2 and Si_3N_3 rings respectively. When the substituents on Si and N are bulky, a planar Si_3N_3 ring suffers more from steric crowding than the corresponding Si_2N_2 ring, because the external ring angles are smaller, but this crowding can be relieved by conversion to a non-planar ring conformation. The effect of large substituents on the Si_3N_3 ring conformation is shown by comparison of the structures of $(PhSiF.NMe)_3$, which has an almost planar ring (Clegg, Noltemeyer, Sheldrick & Vater, 1980), and of $(SiMe_2.NSiMe_3)_3$, where the ring has a boat conformation (Adamson & Daly, 1970). Relief of steric crowding by ring deformation is, however, not observed for Si_2N_2 rings, which are always virtually planar (Clegg, Hesse, Klingebiel, Sheldrick & Skoda, 1980, and references cited therein).

A cyclic silazane $(Bu_2Si.NBu)_n$ (Bu = *tert*-butyl) would be particularly subject to steric crowding. Preparation was attempted by a standard method for such compounds (Klingebiel & Meller, 1976*a*); $Bu_2SiF.LiNBu$ (Klingebiel & Meller, 1976*b*) was heated under reflux in dioxane. With substituent groups sterically less demanding than Bu, the reaction proceeds at room temperature, to give a cyclodisilazane. The ^1H NMR spectrum of the product could not easily be interpreted, and the crystal structure was determined in order to resolve the problem. The results show that a cyclic compound is not formed in the reaction. Under the forcing conditions, the starting material reacts with the solvent, to yield a disubstituted acetylene (Fig. 1). It seems that the *tert*-butyl-substituted cyclodisilazane cannot be formed because of the bulkiness of the substituents; nor is a ring of larger size formed.

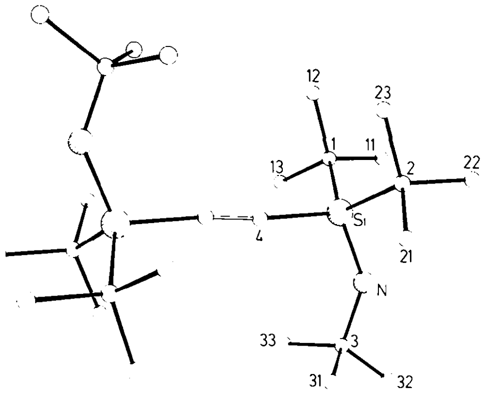

Fig. 1. View of the molecule, showing the numbering scheme for the C atoms.

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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 35833 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Bond lengths and angles are comparable to those in other silicon–nitrogen compounds and in Si-substituted acetylenes (Zeil, Haase & Dakkouri, 1969). The Bu groups are well-spaced around the molecule, with a staggered arrangement about the Si···Si line (as required by the crystallographic symmetry). Their steric bulk produces deviations of several degrees in the bond angles for Si from the ideal tetrahedral value of 109·5°.

We thank the Verband der Chemischen Industrie for financial support. All computer programs were written by WC and GMS.

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Structure of 2′-Acetyl-2′-(*p*-chlorobenzoyl)-2-(*p*-methoxyphenyl)glyoxylohydrazide (ACMGH)

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Abstract. $C_{18}H_{15}ClN_2O_5$, $M_r = 374{\cdot}785$, triclinic, $P\bar{1}$, $a = 10{\cdot}169$ (1), $b = 9{\cdot}458$ (1), $c = 9{\cdot}974$ (1) Å, $\alpha = 102{\cdot}23$ (1), $\beta = 110{\cdot}89$ (1), $\gamma = 87{\cdot}68$ (1)°, $Z = 2$, $V = 916{\cdot}15$ Å^3, λ(Mo $K\alpha$) = 0·71069 Å, $F(000) = 388$, $D_c = 1{\cdot}36$, $D_m = 1{\cdot}37$ Mg m^{-3} (by flotation, KBr solution), m.p. 390–392 K, $\mu = 0{\cdot}247$ mm^{-1}; 1477 independent non-zero reflexions. The structure was solved by direct phase determination with *MULTAN*. The positional and vibrational parameters, with anisotropic temperature factors for the non-hydrogen atoms, were refined by full-matrix least-squares calculations to a final $R = 0{\cdot}051$. The compound is an open-chain hydrazine derivative, with two characteristic planar conjugated systems, forming a small angle (13·5°) with each other.

Introduction. In the course of a study on the oxidation of bis(aroyl)hydrazones of α-dicarbonyl compounds a number of oxidation products of 1-arylglyoxal-2-aroylhydrazones with lead tetraacetate have been prepared at the Laboratory of Organic Chemistry of the Aristotle University of Thessaloniki (Rodios, 1976; Rodios & Alexandrou, 1980).

Since chemical and spectroscopic data were inconclusive as to whether these compounds contained an open chain or a heterocyclic ring, an X-ray structure analysis was considered necessary and to this end the crystal structure determination of ACMGH was carried out.

Pure, colourless crystals of ACMGH were kindly provided by Professor N. E. Alexandrou and Dr N. Rodios. A transparent prismatic single crystal, with dimensions 0·15 × 0·20 × 0·30 mm, was selected and centred on our computer-controlled Philips PW 1100 four-circle single-crystal diffractometer. With Mo $K\alpha$ radiation (λ = 0·71069 Å) the cell constants were determined by measuring the θ angles of 180 strong reflexions with large θ values directly on the diffractometer and subsequently processing them with the least-squares program *PARAM* [part of the XRAY system of crystallographic programs (Stewart, Kruger, Ammon, Dickinson & Hall, 1976)]. Intensity statistics indicated the space group $P\bar{1}$, which was confirmed by the final structure.

Three-dimensional intensity data were collected with a scintillation counter in the ω-scan mode, using Mo $K\alpha$ radiation and a graphite monochromator. The intensities of 2221 independent reflexions up to 2θ = 42° (max. hkl = 11, ±10, ±10 respectively) were examined and measured. Of these, 1477 with intensities

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