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Structures of 2,9-Di-*tert*-butyl-1,1,4,6,8,8,11,12-octamethyl-6,12-diphenyl-2,3,9,10-tetraaza-1,6,8,12-tetrasiladispiro[4.1.4.1]dodeca-3,10-diene, $C_{32}H_{52}N_4Si_4$, (1), and 1,6-Bis[bis(trimethylsilyl)amino]-3,5,8,10-tetramethyl-4,5,9,10-tetraaza-1,6-disilatricyclo[5.3.0.0^{2,6}]deca-3,8-diene, $C_{20}H_{50}N_6Si_6$, (2)

By William Clegg

Institut für Anorganische Chemie der Universität, Tammannstrasse 4, D-3400 Göttingen, Federal Republic of Germany

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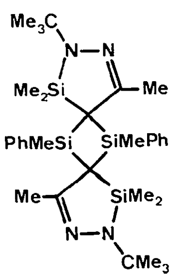
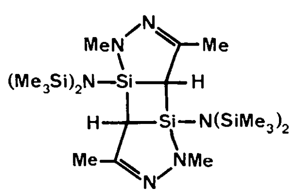
Abstract. (1): $M_r = 605{\cdot}1$, monoclinic, $P2_1/n$, $a = 11{\cdot}101$ (2), $b = 11{\cdot}442$ (2), $c = 27{\cdot}806$ (6) Å, $\beta = 97{\cdot}56$ (2)°, $U = 3501{\cdot}2$ Å^3, $Z = 4$, $D_x = 1{\cdot}148$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 0{\cdot}19$ mm^{-1}, $F(000) = 1312$, $T = 291$ K, $R = 0{\cdot}052$ for 3962 observed reflections. (2): $M_r = 543{\cdot}2$, monoclinic, $P2_1/n$, $a = 9{\cdot}263$ (2), $b = 15{\cdot}960$ (3), $c = 22{\cdot}592$ (5) Å, $\beta = 99{\cdot}30$ (2)°, $U = 3296{\cdot}1$ Å^3, $Z = 4$, $D_x = 1{\cdot}094$ Mg m^{-3}, $\mu = 0{\cdot}27$ mm^{-1}, $F(000) = 1184$, $T = 291$ K, $R = 0{\cdot}051$ for 4191 observed reflections. Two SiN_2C_2 rings are connected *via* a non-planar dispiro-C_2Si_2 ring in (1) and fused to an almost planar central C_2Si_2 ring in (2). The SiN_2C_2 rings in (2) are also virtually planar, but adopt an envelope conformation in (1), with Si out of the plane of the other atoms.

Introduction. Both compounds are formally dimers derived from intermediate silaethenes, which were not isolated (Clegg, Klingebiel, Pohlmann, Sheldrick & Werner, 1981; Clegg, Klingebiel, Sheldrick & Werner, 1981). The structures were determined in order to elucidate the course of the preparative reactions and the stereochemistry of the products. In particular, the SiN_2C_2 ring geometry is of interest for comparison with other structures containing this unit.



(1)



(2)

Experimental. Crystals obtained from n-hexane (1) or 40–60°C petroleum ether (2), mounted in capillaries, 0·15 × 0·25 × 0·5 mm (1), 0·5 × 0·5 × 0·5 mm (2), Stoe–Siemens AED diffractometer, unit-cell parameters refined from setting angles for 42 (1) and 48 (2) centred reflections ($20 < 2\theta < 25°$), 5909 reflections with $2\theta < 50°$ and $h,k \geq 0$ (1) and 6438 reflections with $2\theta < 50°$ and $h,k \geq 0$ (2), profile analysis (Clegg, 1981), no significant variation for three standard reflections, no absorption corrections, $R_{\rm int} = 0{\cdot}020$ (1) and 0·027 (2) (based only on $0kl$ reflections), 5359 (1) and 5759 (2) unique reflections, 3962 (1) and 4191 (2) with $F > 4\sigma(F)$, automatic multisolution direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + gF^2$, $g = 0{\cdot}00025$ (1), 0·00041 (2), H atoms constrained to give C—H = 0·96 Å, H—C—H = 109·5°, aromatic H on C—C—C external bisector, $U({\rm H}) = 1{\cdot}2U_{\rm eq}({\rm C})$, anisotropic thermal parameters for all non-H atoms, no extinction correction, scattering factors from *International Tables for X-ray Crystallography* (1974). (1): 403 parameters, $R = 0{\cdot}052$, $wR = 0{\cdot}051$, slope of normal probability plot = 1·38, max. shift/e.s.d. = 0·13, mean = 0·01, largest peak in final difference map = 0·31 e Å^{-3}, largest hole = −0·27 e Å^{-3}; (2): 337 parameters, $R = 0{\cdot}051$, $wR = 0{\cdot}057$, slope = 1·44, max. shift/e.s.d. = 0·02, mean = 0·005, largest peak = 0·27 e Å^{-3}, largest hole = −0·26 e Å^{-3}. Programs used: *SHELXTL* (Sheldrick, 1978), diffractometer control program by the author.

Discussion. Atomic coordinates and ring bond lengths and angles are given in Tables 1–4.* The molecular structures are shown in Figs. 1 and 2. In (1) the two SiN_2C_2 rings are connected *via* a non-planar dispiro-C_2Si_2 ring [deviations of atoms from mean plane = ±0·138 (2) Å, angle of fold about Si···Si = 22·3 (3)°]. The Si atoms of the central ring have a *cis* arrangement of substituents, but the two SiN_2C_2 rings lie mutually *trans* across this ring (Fig. 1). In (2) the two SiN_2C_2 rings are fused to a central C_2Si_2 ring, which is almost planar [deviations of atoms from mean plane = ±0·051 (2) Å]. Both SiN_2C_2 rings lie on the same side of the central C_2Si_2 ring.

* Lists of structure factors, anisotropic thermal parameters, hydrogen-atom parameters and complete bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38553 (58 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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

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

	x	*y*	*z*	U_{eq}
Si(1)	−605 (1)	−1277 (1)	1893 (1)	382 (3)
C(11)	681 (3)	−2162 (3)	2195 (1)	666 (16)
C(12)	−1545 (4)	−868 (3)	2371 (1)	643 (16)
N(2)	−1397 (2)	−2020 (2)	1400 (1)	385 (9)
C(21)	−2043 (3)	−3154 (3)	1357 (1)	506 (13)
C(22)	−2661 (4)	−3317 (4)	1807 (1)	806 (18)
C(23)	−2989 (4)	−3134 (3)	911 (1)	718 (17)
C(24)	−1157 (4)	−4146 (3)	1313 (2)	897 (20)
N(3)	−792 (2)	−1812 (2)	992 (1)	368 (9)
C(4)	−133 (3)	−887 (2)	1030 (1)	327 (11)
C(41)	500 (3)	−594 (3)	602 (1)	482 (13)
C(5)	−61 (3)	−132 (2)	1482 (1)	304 (10)
Si(6)	1235 (1)	2756 (1)	818 (1)	359 (3)
C(61)	2125 (3)	1826 (3)	446 (1)	537 (14)
C(62)	34 (3)	3441 (3)	381 (1)	612 (15)
N(7)	2153 (2)	3797 (2)	1144 (1)	438 (10)
C(71)	2928 (3)	4755 (3)	1000 (1)	522 (13)
C(72)	3299 (4)	4495 (3)	504 (1)	795 (18)
C(73)	2256 (5)	5914 (3)	979 (2)	1038 (23)
C(74)	4065 (4)	4811 (4)	1362 (1)	952 (21)
N(8)	1720 (2)	4049 (2)	1583 (1)	438 (10)
C(9)	960 (3)	3296 (2)	1707 (1)	368 (11)
C(91)	432 (3)	3587 (3)	2165 (1)	527 (14)
C(10)	656 (3)	2196 (2)	1397 (1)	309 (10)
Si(11)	−858 (1)	1367 (1)	1373 (1)	326 (3)
C(111)	−2030 (3)	1527 (2)	823 (1)	375 (11)
C(112)	−2596 (3)	2602 (3)	753 (1)	566 (14)
C(113)	−3547 (4)	2793 (3)	388 (1)	744 (17)
C(114)	−3945 (3)	1893 (4)	83 (1)	806 (18)
C(115)	−3415 (3)	822 (4)	140 (1)	780 (17)
C(116)	−2457 (3)	635 (3)	510 (1)	522 (13)
C(117)	−1739 (3)	1772 (3)	1876 (1)	487 (13)
Si(12)	1352 (1)	780 (1)	1691 (1)	340 (3)
C(121)	2861 (3)	318 (2)	1532 (1)	389 (11)
C(122)	3168 (3)	−841 (3)	1455 (1)	540 (14)
C(123)	4332 (3)	−1142 (3)	1376 (1)	708 (17)
C(124)	5206 (4)	−306 (4)	1366 (1)	767 (18)
C(125)	4929 (4)	845 (4)	1442 (1)	764 (19)
C(126)	3772 (3)	1141 (3)	1532 (1)	585 (15)
C(127)	1577 (3)	883 (3)	2368 (1)	467 (12)

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

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

	x	*y*	*z*	U_{eq}
Si(1)	6927 (1)	1852 (1)	−1562 (1)	397 (3)
N(2)	6928 (3)	2267 (2)	−2264 (1)	528 (9)
N(3)	6144 (3)	3020 (2)	−2369 (1)	608 (11)
C(4)	5517 (4)	3237 (2)	−1928 (1)	555 (12)
C(5)	5681 (3)	2709 (2)	−1362 (1)	422 (10)
Si(6)	7198 (1)	3018 (1)	−734 (1)	410 (3)
N(7)	8209 (3)	3850 (1)	−917 (1)	576 (10)
N(8)	9419 (3)	3620 (2)	−1182 (1)	631 (11)
C(9)	9569 (3)	2828 (2)	−1219 (1)	550 (12)
C(10)	8519 (3)	2244 (2)	−991 (1)	431 (10)
N(11)	6558 (2)	800 (1)	−1538 (1)	424 (8)
Si(12)	4869 (1)	425 (1)	−1913 (1)	594 (3)
C(121)	3683 (4)	1289 (2)	−2267 (2)	779 (15)
C(122)	5114 (6)	−310 (3)	−2519 (2)	1087 (21)
C(123)	3855 (5)	−66 (3)	−1354 (2)	1029 (21)
Si(13)	7817 (1)	113 (1)	−1120 (1)	542 (3)
C(131)	7782 (5)	272 (2)	−307 (1)	781 (16)
C(132)	9682 (4)	264 (2)	−1310 (2)	813 (17)
C(133)	7377 (5)	−1009 (2)	−1293 (2)	828 (17)
N(14)	6762 (2)	3038 (1)	−22 (1)	437 (8)
Si(15)	4934 (1)	2995 (1)	89 (1)	522 (3)
C(151)	4721 (5)	3206 (3)	882 (2)	888 (18)
C(152)	4185 (4)	1931 (2)	−93 (2)	723 (15)
C(153)	3843 (4)	3809 (2)	−362 (2)	688 (14)
Si(16)	8213 (1)	3095 (1)	590 (1)	531 (3)
C(161)	10028 (4)	3024 (3)	349 (2)	801 (16)
C(162)	8173 (5)	4113 (2)	982 (2)	822 (16)
C(163)	8120 (5)	2203 (2)	1112 (2)	801 (16)
C(21)	7554 (5)	1968 (2)	−2770 (2)	841 (17)
C(41)	4556 (5)	4004 (2)	−1997 (2)	916 (18)
C(71)	8026 (5)	4746 (2)	−846 (2)	953 (20)
C(91)	10856 (4)	2501 (3)	−1483 (2)	807 (17)

Table 3. *Ring bond lengths* (Å) *and angles* (°) *for* (1)

Si(1)—N(2)	1·749 (2)	Si(6)—N(7)	1·743 (2)
N(2)—N(3)	1·412 (3)	N(7)—N(8)	1·400 (4)
N(3)—C(4)	1·283 (4)	N(8)—C(9)	1·285 (4)
C(4)—C(5)	1·518 (4)	C(9)—C(10)	1·538 (4)
C(5)—Si(1)	1·890 (3)	C(10)—Si(6)	1·921 (3)
Si(11)—C(5)	1·935 (3)	Si(11)—C(10)	1·924 (3)
Si(12)—C(5)	1·909 (3)	Si(12)—C(10)	1·930 (3)
N(2)—Si(1)—C(5)	91·7 (1)	N(7)—Si(6)—C(10)	91·6 (1)
Si(1)—N(2)—N(3)	107·7 (2)	Si(6)—N(7)—N(8)	110·5 (2)
N(2)—N(3)—C(4)	113·6 (2)	N(7)—N(8)—C(9)	114·1 (2)
N(3)—C(4)—C(5)	120·3 (3)	N(8)—C(9)—C(10)	120·1 (3)
Si(1)—C(5)—C(4)	96·9 (2)	Si(6)—C(10)—C(9)	97·1 (2)
Si(11)—C(5)—Si(12)	84·5 (1)	Si(11)—C(10)—Si(12)	84·2 (1)
C(5)—Si(11)—C(10)	93·0 (1)	C(5)—Si(12)—C(10)	93·6 (1)

Table 4. *Ring bond lengths* (Å) *and angles* (°) *for* (2)

Si(1)—N(2)	1·718 (2)	Si(6)—N(7)	1·714 (3)
N(2)—N(3)	1·404 (4)	N(7)—N(8)	1·401 (4)
N(3)—C(4)	1·280 (5)	N(8)—C(9)	1·276 (4)
C(4)—C(5)	1·518 (4)	C(9)—C(10)	1·498 (4)
C(5)—Si(1)	1·892 (3)	C(10)—Si(6)	1·894 (3)
Si(1)—C(10)	1·902 (3)	Si(6)—C(5)	1·893 (3)
N(2)—Si(1)—C(5)	91·9 (1)	N(7)—Si(6)—C(10)	91·5 (1)
Si(1)—N(2)—N(3)	114·1 (2)	Si(6)—N(7)—N(8)	113·9 (2)
N(2)—N(3)—C(4)	112·8 (2)	N(7)—N(8)—C(9)	113·1 (3)
N(3)—C(4)—C(5)	120·6 (3)	N(8)—C(9)—C(10)	120·6 (3)
Si(1)—C(5)—C(4)	100·5 (2)	Si(6)—C(10)—C(9)	100·8 (2)
C(5)—Si(1)—C(10)	92·0 (1)	C(5)—Si(6)—C(10)	92·2 (1)
Si(1)—C(5)—Si(6)	87·7 (1)	Si(1)—C(10)—Si(6)	87·4 (1)

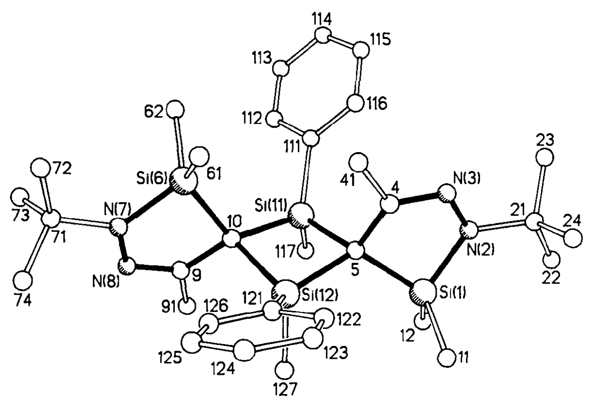


Fig. 1. Molecular structure of (1). C atoms are labelled by number only; H atoms are omitted.

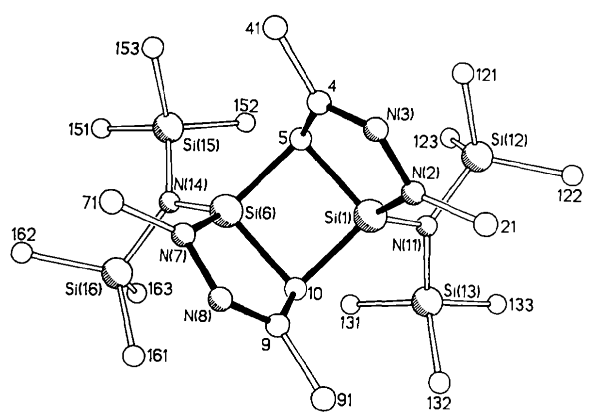
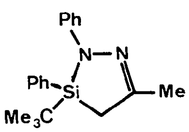


Fig. 2. Molecular structure of (2).

The SiN_2C_2 ring described here is a structural unit in five other crystal structures [(3)–(7)] (Clegg, Noltemeyer & Sheldrick, 1979; Clegg, Haase, Hesse, Klingebiel & Sheldrick, 1982; Clegg, Graalmann, Haase, Klingebiel, Sheldrick, Werner, Henkel & Krebs, 1983; Clegg, Hesse, Klingebiel & Sheldrick, 1983). In each case (ten crystallographically independent rings in seven crystal structures) the N and C atoms of the ring are virtually coplanar as a consequence of the N=C double bond (Table 5). The deviation of the Si atom from this plane varies from 0·060 (1) to 0·701 (1) Å. Conjugation of the trigonally coordinated N atom adjacent to Si with the N=C bond tends to impose coplanarity on the Si atom [(2), (3) and (7)], and this effect is enhanced when the conjugation is extended, as in (4) and (5), both of which are strongly coloured. Without such extended conjugation, however, steric interaction of substituents on the Si atom and the neighbouring C atom may cause greater deviations from coplanarity [(1) and (6)].

Table 5. *Deviations* (Å) *of atoms from* N_2C_2 *mean planes*

Structure	R.m.s.$\Delta(N_2C_2)$	Δ(Si)
(1)	0·001 (3)	0·628 (1)
	0·012 (3)	0·519 (1)
(2)	0·004 (3)	0·060 (1)
	0·001 (3)	0·065 (1)
(3)	0·002 (2)	0·263 (1)
(4)	0·007 (2)	0·071 (1)
	0·008 (2)	0·071 (1)
(5)	0·006 (2)	0·132 (1)
(6)	0·011 (3)	0·701 (1)
(7)	0·008 (2)	0·172 (1)



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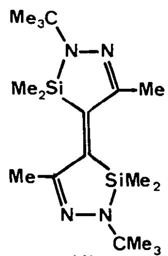

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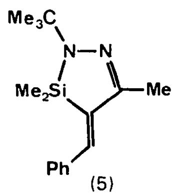

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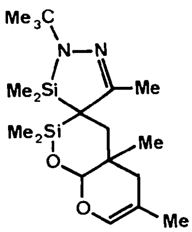

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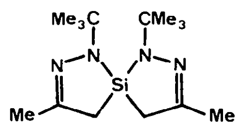

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Structure of Crogyroidine Dihydrate, $C_{20}H_{34}Br_2N_2.2H_2O$

BY R. S. SAWHNEY

Department of Biochemistry, University of Tennessee, Memphis, TN 38163, *USA*

P. K. SENGUPTA

Department of Geology, Memphis State University, Memphis, TN 38152, *USA*

AND M. B. HOSSAIN AND DICK VAN DER HELM

Department of Chemistry, University of Oklahoma, Norman, OK 73019, *USA*

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Abstract. $M_r = 498{\cdot}4$, monoclinic, $P2_1/n$, $a = 10{\cdot}965$ (3), $b = 12{\cdot}129$ (3), $c = 8{\cdot}602$ (3) Å, $\beta = 93{\cdot}78$ (2)°, $V = 1141{\cdot}5$ Å^3 at 138 (2) K and $a = 11{\cdot}090$ (5), $b = 12{\cdot}146$ (2), $c = 8{\cdot}659$ (2) Å, $\beta = 93{\cdot}15$ (3)°, $V = 1164{\cdot}6$ Å^3 at 293 K, $Z = 2$, $D_x = 1{\cdot}421$, $D_m = 1{\cdot}425$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 1{\cdot}89$ mm^{-1}, $F(000) = 516$. Final $R = 0{\cdot}046$ for 1705 observed reflections ($T = 138$ K). The

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