

Fig. 1. The molecular geometry and atomic numbering for cheloviolen A (3). Atoms are represented as 50% probability ellipses.

119.3 (4)° whereas C(6)—C(5)—C(9) is 103.9 (3)°; C(5)—C(9)—C(10) is 116.3 (3)° whereas C(5)—C(9)—C(8) is 103.6 (3)°; C(8)—C(14)—C(13) is 116.2 (3)° whereas C(13)—C(14)—C(15) is 102.2 (3)°.

The molecules pack into the unit cell in the manner shown in the stereopair diagrams of Fig. 2. The only significant intermolecular interaction is a hydrogen bond between O(15') and O(11') [O...O 2.86 (1) Å]. Seven other intermolecular contacts are in the range 3.31–3.46 Å.

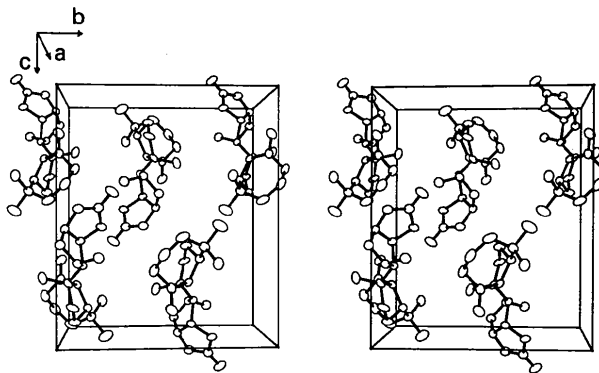


Fig. 2. Stereopair diagrams for cheloviolen A (3).

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2,2,4,4,6,6-Hexamethyl-1,3,5-triphenylcyclotrisilazane

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Abstract. $C_{24}H_{33}N_3Si_3$, $M_r = 447.81$, triclinic, $P\bar{1}$, $a = 6.8234$ (11), $b = 11.1822$ (19), $c = 17.751$ (3) Å, $\alpha = 75.900$ (12), $\beta = 79.226$ (13), $\gamma = 81.998$ (9)°, $V = 1284$ Å³, $Z = 2$, $D_x = 1.158$ Mg m⁻³, $\bar{\lambda}(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 0.194$ mm⁻¹, $F(000) = 480$, $T = 298$ K, $R = 0.0488$ for 2374 unique observed reflections. The six-membered Si_3N_3 ring is markedly non-planar and the *N*-phenyl rings are almost perpendicular to the local Si—N—Si planes.

Introduction. The structure of the title compound (I) had been incorrectly assigned to a reaction product

which was subsequently shown to be the homologous four-membered ring compound 2,2,4,4-tetramethyl-1,3-diphenylcyclodisilazane (II). The crystal structure of (II) has been published (Párkányi, Argay, Hencsei & Nagy, 1976) and since the synthesis of (I) has recently been reported (Dejak, Kulpiński, Lasocki & Piechucki, 1987), we felt that it was timely to determine the structure of this compound.

Experimental. Colourless needle (0.89 × 0.15 × 0.11 mm), Stoe Stadi-4 four-circle diffractometer, unit-cell parameters from 2θ values of 22 reflections measured at $\pm\omega$ ($2\theta = 30$ – 32°). For data collection, graphite-monochromated Mo $K\alpha$ X-radiation, ω – 2θ

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scans using the learnt-profile method (Clegg, 1981), $2\theta_{\max}$ 45° , $h - 7 \rightarrow 7$, $k - 11 \rightarrow 12$, $l 0 \rightarrow 19$. Three standard reflections showed no intensity variation, no corrections required for crystal decay or absorption; 3885 reflections measured, 3061 unique (R_{int} 0.023), giving 2374 with $F \geq 6\sigma(F)$ for structure solution [by automatic direct methods using *SHELXS86* (Sheldrick, 1986)] and refinement by *SHELX76* [using full-matrix least squares on F (Sheldrick, 1976)]. Anisotropic thermal parameters for all non-H atoms, H atoms included in fixed calculated positions. At final convergence $R = 0.0488$, $wR = 0.0696$, $S = 0.903$ for 271 parameters, $(\Delta/\sigma)_{\max}$ in final cycle 0.012, max. and min. $\Delta\rho$ in final ΔF synthesis 0.42 and -0.29 e \AA^{-3} . The weighting scheme $w^{-1} = \sigma^2(F) + 0.00554F^2$ gave satisfactory agreement analyses. Scattering factors were inlaid (Sheldrick, 1976). The atom-numbering scheme for the molecule is shown in Fig. 1, which was generated using *ORTEPII* (Mallinson & Muir, 1985). Molecular geometry calculations were performed using *CALC* (Gould & Taylor, 1985).

Discussion. Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1, while bond lengths, angles and torsion angles appear

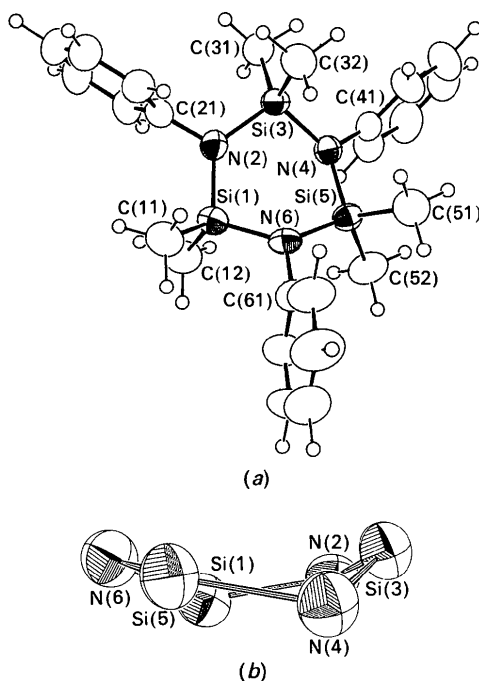


Fig. 1. (a) A view of the molecule showing the atom-numbering scheme; (b) an orthogonal view showing the conformation of the N_3Si_3 ring. All thermal ellipsoids are drawn at the 30% probability level.

Table 1. Atomic coordinates with *e.s.d.*'s

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}(\text{\AA}^2)$
Si(1)	0.32706 (14)	0.25704 (8)	0.71664 (5)	0.0503 (6)
C(11)	0.1632 (7)	0.4065 (3)	0.69657 (24)	0.074 (3)
C(12)	0.5885 (7)	0.2938 (4)	0.70754 (25)	0.079 (3)
N(2)	0.2527 (4)	0.17230 (23)	0.81020 (15)	0.0496 (17)
C(21)	0.2077 (5)	0.2353 (3)	0.87375 (19)	0.0501 (20)
C(22)	0.3555 (6)	0.2438 (3)	0.91645 (22)	0.065 (3)
C(23)	0.3075 (8)	0.2995 (3)	0.97985 (24)	0.081 (3)
C(24)	0.1186 (9)	0.3484 (4)	1.00157 (25)	0.082 (3)
C(25)	-0.0294 (8)	0.3434 (4)	0.9595 (3)	0.079 (3)
C(26)	0.0133 (6)	0.2865 (3)	0.89553 (23)	0.0645 (25)
Si(3)	0.21589 (14)	0.01559 (8)	0.83650 (5)	0.0470 (6)
C(31)	0.3098 (7)	-0.0577 (3)	0.93009 (21)	0.070 (3)
C(32)	-0.0554 (6)	-0.0019 (4)	0.8478 (3)	0.073 (3)
N(4)	0.3571 (4)	-0.05069 (22)	0.76188 (16)	0.0476 (16)
C(41)	0.4299 (5)	-0.1794 (3)	0.78348 (18)	0.0497 (21)
C(42)	0.6344 (6)	-0.2146 (3)	0.78074 (22)	0.064 (3)
C(43)	0.7043 (8)	-0.3388 (4)	0.8013 (3)	0.081 (3)
C(44)	0.5713 (9)	-0.4293 (4)	0.8272 (3)	0.086 (3)
C(45)	0.3692 (9)	-0.3947 (4)	0.8312 (3)	0.091 (4)
C(46)	0.2984 (6)	-0.2695 (3)	0.80766 (25)	0.070 (3)
Si(5)	0.35976 (13)	0.00960 (8)	0.66170 (5)	0.0466 (6)
C(51)	0.1727 (7)	-0.0601 (4)	0.62645 (24)	0.076 (3)
C(52)	0.6091 (6)	-0.0238 (4)	0.60459 (23)	0.071 (3)
N(6)	0.3001 (4)	0.16849 (24)	0.65220 (15)	0.0507 (17)
C(61)	0.2765 (6)	0.2361 (3)	0.57354 (21)	0.0588 (23)
C(62)	0.0893 (7)	0.2539 (4)	0.54958 (25)	0.081 (3)
C(63)	0.0660 (9)	0.3212 (5)	0.4749 (3)	0.101 (4)
C(64)	0.2215 (10)	0.3695 (5)	0.4232 (3)	0.098 (4)
C(65)	0.4068 (10)	0.3516 (4)	0.4451 (3)	0.097 (4)
C(66)	0.4360 (7)	0.2839 (4)	0.52043 (24)	0.078 (3)

in Table 2.* As Fig. 1 shows, the six-membered Si_3N_3 ring is puckered and the deviation from planarity is rather large. Some trisilazane rings are planar or nearly so and it has been suggested that small substituents (e.g. H or CH_3) on the N atoms favour planarity (Clegg, Sheldrick & Stalke, 1984). Relevant examples are 2,4,5-trifluoro-1,3,5-trimethyl-2,4,6-triphenylcyclotrisilazane (Clegg, Noltemeyer, Sheldrick & Vater, 1980), 2,2,4,4,6,6-hexa-*tert*-butylcyclotrisilazane (Clegg, Sheldrick & Stalke, 1984) and hexamethylcyclotrisilazane, which was found by electron diffraction to be only slightly puckered in the gas phase (Rozsondai, Hargittai, Golubinskii, Vilkov & Mastryukov, 1975). For other rings of this class the deviations from planarity are usually towards a boat conformation (Adamson & Daly, 1970; Clegg, Noltemeyer, Sheldrick & Vater, 1981). The ring in (I) does not approach any ideal conformation: in this it is similar to the condensation product of cyclotrisilazane with cyclodisilazane (Clegg, Klingebiel, Sheldrick, Skoda & Vater, 1980) and to a ring with fluorine-containing substituents on the N atoms (Clegg, 1980).

In (II) the *N*-phenyl rings are coplanar with the cyclodisilazane ring. This is in sharp contrast to the

* Lists of H-atom coordinates, structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53695 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å), angles and torsion angles (°) with *e.s.d.*'s

Si(1)—C(11)	1.873 (4)	C(41)—C(42)	1.391 (5)
Si(1)—C(12)	1.855 (5)	C(41)—C(46)	1.379 (5)
Si(1)—N(2)	1.722 (3)	C(42)—C(43)	1.386 (6)
Si(1)—N(6)	1.733 (3)	C(43)—C(44)	1.391 (7)
N(2)—C(21)	1.435 (4)	C(44)—C(45)	1.372 (7)
N(2)—Si(3)	1.741 (3)	C(45)—C(46)	1.404 (7)
C(21)—C(22)	1.396 (5)	Si(5)—C(51)	1.855 (5)
C(21)—C(26)	1.393 (5)	Si(5)—C(52)	1.851 (4)
C(22)—C(23)	1.382 (6)	Si(5)—N(6)	1.740 (3)
C(23)—C(24)	1.353 (7)	N(6)—C(61)	1.443 (5)
C(24)—C(25)	1.378 (7)	C(61)—C(62)	1.394 (6)
C(25)—C(26)	1.398 (6)	C(61)—C(66)	1.375 (6)
Si(3)—C(31)	1.852 (4)	C(62)—C(63)	1.382 (7)
Si(3)—C(32)	1.857 (4)	C(63)—C(64)	1.347 (8)
Si(3)—N(4)	1.742 (3)	C(64)—C(65)	1.366 (8)
N(4)—C(41)	1.438 (4)	C(65)—C(66)	1.401 (7)
N(4)—Si(5)	1.739 (3)		
C(11)—Si(1)—C(12)	108.22 (20)	N(4)—C(41)—C(42)	120.4 (3)
C(11)—Si(1)—N(2)	110.56 (17)	N(4)—C(41)—C(46)	120.6 (3)
C(11)—Si(1)—N(6)	109.03 (17)	C(42)—C(41)—C(46)	119.0 (3)
C(12)—Si(1)—N(2)	109.28 (17)	C(41)—C(42)—C(43)	120.3 (4)
C(12)—Si(1)—N(6)	113.03 (17)	C(42)—C(43)—C(44)	120.6 (4)
N(2)—Si(1)—N(6)	106.73 (13)	C(43)—C(44)—C(45)	119.3 (5)
Si(1)—N(2)—C(21)	118.38 (22)	C(44)—C(45)—C(46)	120.2 (5)
Si(1)—N(2)—Si(3)	126.44 (16)	C(41)—C(46)—C(45)	120.5 (4)
C(21)—N(2)—Si(3)	115.13 (21)	N(4)—Si(5)—C(51)	109.91 (17)
N(2)—C(21)—C(22)	121.0 (3)	N(4)—Si(5)—C(52)	111.27 (16)
N(2)—C(21)—C(26)	120.5 (3)	N(4)—Si(5)—N(6)	105.21 (13)
C(22)—C(21)—C(26)	118.5 (3)	C(51)—Si(5)—C(52)	108.19 (19)
C(21)—C(22)—C(23)	120.2 (4)	C(51)—Si(5)—N(6)	111.49 (17)
C(22)—C(23)—C(24)	121.4 (4)	C(52)—Si(5)—N(6)	110.79 (17)
C(23)—C(24)—C(25)	119.5 (4)	Si(1)—N(6)—Si(5)	127.65 (17)
C(24)—C(25)—C(26)	120.6 (4)	Si(1)—N(6)—C(61)	115.83 (23)
C(21)—C(26)—C(25)	119.7 (4)	Si(5)—N(6)—C(61)	114.39 (23)
N(2)—Si(3)—C(31)	109.90 (16)	N(6)—C(61)—C(62)	120.2 (3)
N(2)—Si(3)—C(32)	109.53 (17)	N(6)—C(61)—C(66)	121.5 (3)
N(2)—Si(3)—N(4)	106.41 (13)	C(62)—C(61)—C(66)	118.3 (4)
C(31)—Si(3)—C(32)	109.87 (19)	C(61)—C(62)—C(63)	120.1 (4)
C(31)—Si(3)—N(4)	108.94 (16)	C(62)—C(63)—C(64)	121.6 (5)
C(32)—Si(3)—N(4)	112.12 (17)	C(63)—C(64)—C(65)	119.2 (5)
Si(3)—N(4)—C(41)	116.92 (22)	C(64)—C(65)—C(66)	120.8 (5)
Si(3)—N(4)—Si(5)	125.08 (16)	C(61)—C(66)—C(65)	120.0 (4)
C(41)—N(4)—Si(5)	115.52 (21)		
C(11)—Si(1)—N(2)—C(21)	-44.9 (3)	Si(3)—N(4)—C(41)—C(42)	-113.1 (3)
C(11)—Si(1)—N(2)—Si(3)	132.44 (21)	Si(3)—N(4)—C(41)—C(46)	66.5 (4)
C(12)—Si(1)—N(2)—C(21)	74.1 (3)	Si(5)—N(4)—C(41)—C(42)	83.8 (4)
C(12)—Si(1)—N(2)—Si(3)	-108.55 (23)	Si(5)—N(4)—C(41)—C(46)	-96.6 (4)
N(6)—Si(1)—N(2)—C(21)	-163.37 (23)	Si(3)—N(4)—Si(5)—C(51)	-93.22 (23)
N(6)—Si(1)—N(2)—Si(3)	13.99 (23)	Si(3)—N(4)—Si(5)—C(52)	146.96 (20)
C(11)—Si(1)—N(6)—Si(5)	-160.70 (21)	Si(3)—N(4)—Si(5)—N(6)	26.93 (23)
C(11)—Si(1)—N(6)—C(61)	37.0 (3)	C(41)—N(4)—Si(5)—C(51)	68.3 (3)
C(12)—Si(1)—N(6)—Si(5)	78.9 (3)	C(41)—N(4)—Si(5)—C(52)	-51.5 (3)
C(12)—Si(1)—N(6)—C(61)	-83.4 (3)	C(41)—N(4)—Si(5)—N(6)	-171.56 (22)
N(2)—Si(1)—N(6)—Si(5)	-41.25 (23)	N(4)—C(41)—C(42)—C(43)	-179.8 (4)
N(2)—Si(1)—N(6)—C(61)	156.41 (24)	C(46)—C(41)—C(42)—C(43)	0.6 (6)
Si(1)—N(2)—C(21)—C(22)	-91.0 (4)	N(4)—C(41)—C(46)—C(45)	-177.9 (4)
Si(1)—N(2)—C(21)—C(26)	90.7 (4)	C(42)—C(41)—C(46)—C(45)	1.7 (6)
Si(3)—N(2)—C(21)—C(22)	91.3 (4)	C(41)—C(42)—C(43)—C(44)	-1.9 (7)
Si(3)—N(2)—C(21)—C(26)	-86.9 (4)	C(42)—C(43)—C(44)—C(45)	0.9 (7)
Si(1)—N(2)—Si(3)—C(31)	140.60 (21)	C(43)—C(44)—C(45)—C(46)	1.4 (7)
Si(1)—N(2)—Si(3)—C(32)	-98.60 (23)	C(44)—C(45)—C(46)—C(41)	-2.7 (7)
Si(1)—N(2)—Si(3)—N(4)	22.80 (23)	N(4)—Si(5)—N(6)—Si(1)	22.69 (24)
C(21)—N(2)—Si(3)—C(31)	-42.0 (3)	N(4)—Si(5)—N(6)—C(61)	-174.76 (23)
C(21)—N(2)—Si(3)—C(32)	78.8 (3)	C(51)—Si(5)—N(6)—Si(1)	141.78 (22)
C(21)—N(2)—Si(3)—N(4)	-159.77 (22)	C(51)—Si(5)—N(6)—C(61)	-55.7 (3)
N(2)—C(21)—C(22)—C(23)	-176.9 (4)	C(52)—Si(5)—N(6)—Si(1)	-97.66 (24)
C(26)—C(21)—C(22)—C(23)	1.4 (6)	C(52)—Si(5)—N(6)—C(61)	64.9 (3)
N(2)—C(21)—C(26)—C(25)	177.6 (4)	Si(1)—N(6)—C(61)—C(62)	-105.5 (4)
C(22)—C(21)—C(26)—C(25)	-0.7 (6)	Si(1)—N(6)—C(61)—C(66)	74.8 (4)
C(21)—C(22)—C(23)—C(24)	-0.9 (7)	Si(5)—N(6)—C(61)—C(62)	89.8 (4)
C(22)—C(23)—C(24)—C(25)	-0.4 (7)	Si(5)—N(6)—C(61)—C(66)	-89.9 (4)
C(23)—C(24)—C(25)—C(26)	1.0 (7)	N(6)—C(61)—C(62)—C(63)	178.4 (4)
C(24)—C(25)—C(26)—C(21)	-0.5 (6)	C(66)—C(61)—C(62)—C(63)	-1.9 (7)
N(2)—Si(3)—N(4)—C(41)	151.52 (23)	N(6)—C(61)—C(66)—C(65)	-178.5 (4)
N(2)—Si(3)—N(4)—Si(5)	-47.20 (22)	C(62)—C(61)—C(66)—C(65)	1.8 (6)
C(31)—Si(3)—N(4)—C(41)	33.1 (3)	C(61)—C(62)—C(63)—C(64)	1.0 (4)
C(31)—Si(3)—N(4)—Si(5)	-165.64 (20)	C(62)—C(63)—C(64)—C(65)	-0.1 (9)
C(32)—Si(3)—N(4)—C(41)	-88.7 (3)	C(63)—C(64)—C(65)—C(66)	0.0 (9)
C(32)—Si(3)—N(4)—Si(5)	72.53 (24)	C(64)—C(65)—C(66)—C(61)	-0.9 (8)

situation in (I), where they are almost perpendicular to the local Si—N—Si planes, with dihedral angles at N(2), N(4) and N(6) of 89.0, 75.5 and 82.6°. This conformation is favourable in that it minimizes strain in the molecule, but the compound is deprived of the optimal p - π overlap between the nitrogen and the benzene ring which would be afforded by coplanarity. Indeed, it has been suggested that the observed hypochromic shift and sharp fall in the intensity of the electronic absorption bands in (I) relative to (II) are due to such structural differences (Albanov, Voronkov, Dorokhova, Kulpiński, Larin, Lasocki, Piechucki, Brodskaya & Pestunovich, 1982). Consequently, the mean N—C bond length in (I) [1.439 (5) Å] is longer than in (II) [1.382 Å (Párkányi, Argay, Hencsei & Nagy, 1976)] or in hexaphenylcyclotrisilazane [1.388 Å (Párkányi, Dunaj-Jurco, Bihatsi & Hencsei, 1980)]. The Si—N bond lengths [1.722 (3)–1.742 (3) Å] and the Si—C bond lengths [1.851 (4)–1.873 (4) Å] are within the limits usually observed in silazanes (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987).

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