unchanged for 3 h; after 19 h a brown coloration developed which eventually turned to a light green, after 2 days. All the bound N_2 was evolved, as shown by the increase in gas pressure and by elemental analysis of the light green residue.

(h) Reactivity of I with N_2/H_2. A heavy-wall glass tube was charged with 200 mg of I and 4 ml of xylene. The tube was pressured with 12 atm of a mixture of 38% H_2 and 62% N_2. The initial deep blue color was discharged on standing for 4 h at 23 °C, to yield a light green solution. This was evaporated to dryness. An infrared spectrum of the residue gave bands characteristic of III and of the hydride $[(C_5H_5)_3(C_5H_4)Ti_2]\cdot H_2$ (IV). The residue contained no nitrogen (by elemental analysis—Dumas technique).

(i) **Catalytic Hydrogenation of Olefins.** The $(C_5H_5)_3(C_5H_4)Ti_2$ catalyzed hydrogenation of olefins was studied by following the drop in H_2 pressure in a closed reaction system. In a typical experiment, crystalline II (24.38 mg) was weighed under argon and transferred into a 300-ml flask. The catalyst was dissolved in *n*-octane and the solution evaporated to dryness. This procedure was then repeated so as to ensure complete removal of THF. After addition of cyclohexene (14.45 g) the flask was attached to a vacuum manifold and mercury manometer system of 466 cm^3 total volume. The reaction flask was held at 20.4 ± 0.2 °C. An initial H_2 pressure of 770 Torr was used. When the pressure had dropped to ~100 Torr fresh H_2 was introduced; the reaction kinetics were followed in this manner over four cycles of added H_2.

(j) Catalytic Isomerization of Olefins. The isomerization studies were carried out by dissolving the catalyst in the terminal olefin, contained in an NMR tube, and following the rise in the specific NMR resonances of the products. For example, in the isomerization of 1-heptene, 5 mg of $(C_5H_5)_3(C_5H_4)Ti_2$ (as obtained directly from reduction of $(C_5H_5)_2TiCl_2$) was dissolved in 0.5 ml of 1-heptene in a 5-mm o.d. NMR tube. The appearance of both the δ_{Me_4Si} 5.35 and 1.65 lines were monitored, to determine the rate of formation of 2-heptene. A Varian A-60 NMR spectrometer was used. The temperature of the probe was 30 °C.

Note Added in Proof. The olefin isomerization experiments described were done using $(C_5H_5)_3(C_5H_4)Ti_2$ (I) as obtained directly from the reduction of $(C_5H_5)_2TiCl_2$.[1] A 0.006 M solution of I (prepared from crystalline II[1]) in 1-hexene, after 1 h at 23 °C, gave a mixture containing ~52% *trans*-2-hexene and ~4% *cis*-2-hexene. No *trans*-3-hexene was detected under these conditions.

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The Synthesis and Structure of a Dispirotetrasilazane

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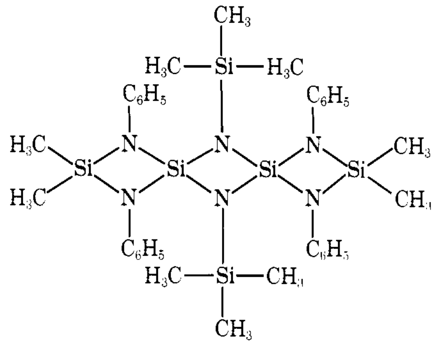
Abstract: The cyclization reaction of the tetralithio salt of 1,3-bis(trimethylsilyl)-2,2,4,4-tetrakis(anilino)cyclodisilazane, obtained from the corresponding 2,2,4,4-tetrachloro derivative, with dimethyldichlorosilane forms the novel spirocyclic derivative, 2,2,8,8-tetramethyl-1,3,7,9-tetraphenyl-5,10-bis(trimethylsilyl)dispiro[3.1.3.1]tetrasilazane. The overall synthesis is noteworthy since it proceeds through use of previously unreported tetrafunctional cyclodisilazanes. The composition and geometry of the dispirotetrasilazane have been verified by single-crystal x-ray diffraction using data collected on an automatic diffractometer. The molecular symmetry is $\bar{1}$. The four collinear silicon atoms give the molecule an extended conformation. The crystal system is monoclinic $C2/c$) with four molecules in a cell of dimensions $a = 17.384$ (7) Å, $b = 12.289$ (4) Å, $c = 19.255$ (9) Å, and $\beta = 94.68$ (2)°. The observed and calculated densities are 1.13 and 1.15 g/cm^3, respectively.

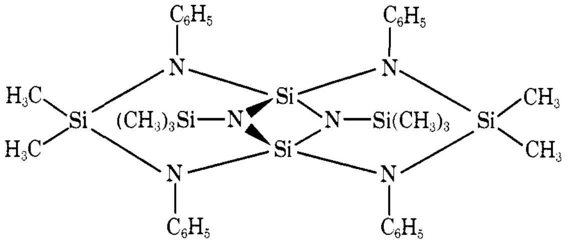
While numerous cyclodisilazanes have been reported,[2] little attention has been paid until recently to the preparation of spiro derivatives of cyclosilazanes in which silicon serves as the spiro atom. In 1964 Lienhard and Rochow[3] described the preparation of an octamethylspiro[3.3]trisilazane. The compound was characterized by elemental analysis and molecular weight but no evidence was presented for the claimed spirocyclic structure. More recently, as part of a study of polyspirocyclosilazanes, Andrianov and co-workers[4,5] reported the isolation in relatively low yields of several spirotrisilazanes and a single dispirotetrasilazane from the thermal homocondensation and cocondensation of aminosilanes at temperatures of 360–430 °C. The silazane products were characterized by elemental analysis, molecular weight, and NMR spectra. No evidence was presented for the spiro structures other than ir absorption bands at 900–915 cm^{-1} (ν_{as}(SiNSi)) as indication of the presence of the four-membered cyclodisilazane rings. Since a variety of both linear and three-dimensional condensation products are capable of being produced in these pyrolytic reactions, the analytical data presented by these Russian workers do not constitute definitive proof for the spirosilazane structures proposed for the isolated products. While x-ray crystallography has been used for the structure determination of cyclodisilazanes,[6,7] this technique has not been applied to spirosilazanes.

As part of a study of new semiorganic thermally resistant polymer systems, we investigated the preparation and characterization of spirosilazanes. Of particular concern was the development of a suitable preparative method for an oligomeric model compound containing an all-spiro structure. We now report the synthesis and structure proof of a dispirotetrasilazane: 2,2,8,8-tetramethyl-1,3,5,7-tetraphenyl-5,10-bis(trimethylsilyl)dispiro[3.1.3.1]tetrasilazane (**1**).

Although ir, NMR, and mass spectral data were all consistent with the expected structure **1,** an x-ray crystallographic analysis was necessary in order to differentiate it from at least one other dispiro structure **2.**



1



2

Experimental Section

Physical Methods. Melting points were taken on a Buchi apparatus and are uncorrected. Gas chromatographic analyses were performed on an F&M Model 500 chromatograph using a 6 ft × 0.25 in. column packed with 10% SE-30 on 60–80 Chrom W. Infrared spectra were recorded on a Perkin-Elmer Infracord Model 137B spectrophotometer. Proton NMR spectral data were obtained on a Varian A-56/60A instrument with chemical shifts reported relative to tetramethylsilane as internal standard. Integration was consistent with all assignments. Mass spectra were determined on a CEC Model 21-110B spectrometer operating at 70 eV. Mass spectral, NMR, and elemental analyses were performed by personnel of the Analytical Branch, Technical Support Division, Air Force Materials Laboratory. X-ray data were measured with a Picker FACS-1 automated diffractometer. Computer calculations were performed on the CDC 6600, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio.

1,3-Bis(trimethylsilyl)-2,2,4,4-tetrachlorocyclodisilazane (3). To a solution of 222 g (1.0 mol) of 1,1,1-trichloro-3,3,3-trimethyldisilazane[8] in 150 ml of anhydrous diethyl ether under nitrogen was added slowly 0.82 mol of *n*-butyllithium in hexane (500 ml, 1.64 M) at −40 °C. After the mixture was allowed to warm to room temperature, the ether was removed by distillation and replaced by 500 ml of dry hexane. Lithium chloride was removed by filtration and the solvent by atmospheric pressure distillation. Fractional distillation of the residue in vacuo yielded 131.0 g (85.6%) of the crude product, bp 118–125 °C. Careful purification by vacuum distillation afforded a pure crystalline sample of **3:** mp 64–65 °C; ir (KBr) 2950, 1250, 1040 cm^{-1}; NMR (CDCl$_3$) δ 0.05 ppm (s, 18, Si(CH$_3$)$_3$); mass spectrum *m/e* 355 (parent peak less a methyl group).

Anal. Calcd for $C_6H_{18}N_2Cl_4Si_4$: C, 19.34; H, 4.95; N, 7.52; Cl, 38.05; Si, 30.14. Found: C, 19.43; H, 4.87; N, 7.46; Cl, 38.09; Si, 30.09.

1,3-Bis(trimethylsilyl)-2,2,4,4-tetrakis(anilino)cyclodisilazane (4). To a solution of freshly distilled aniline (12.65 g, 0.136 mol) in 75 ml of anhydrous diethyl ether at 0 °C and under nitrogen was first added 0.135 mol of *n*-butyllithium in hexane (52 ml, 2.6 M) and then 12.63 g (0.034 mol) of **3** in 50 ml of dry toluene. After addition was complete, the reaction mixture was allowed to warm to room temperature and was heated at reflux for 0.5 h. Chloroform (150 ml) was added and the precipitated lithium chloride was removed by filtration. Evaporation of the filtrate left a solid residue which was treated with 50 ml of pentane and filtered to yield 13.0 g (64%) of crude product as beige crystals, mp 157–165 °C. Recrystallization from benzene-pentane afforded analytically pure **4:** mp 169–170 °C; ir (KBr) 1600, 1490, 1360, 1260, 1020, 900 cm^{-1}; NMR (CCl$_4$) δ 0.05 (s, 18, Si(CH$_3$)$_3$), 3.85 (s, 4, NH), and 7.00 ppm (m, 20, aromatic); mass spectrum *m/e* 598 (parent peak).

Anal. Calcd for $C_{30}H_{42}N_6Si_4$: C, 60.20; H, 7.02; N, 14.05; Si, 18.72; mol wt, 598. Found: C, 60.10; H, 7.41; N, 14.00; Si, 19.56; mol wt, 597.6 (VPO).

2,2,8,8-Tetramethyl-1,3,7,9-tetraphenyl-5,10-bis(trimethylsilyl)-dispiro[3.1.3.1]tetrasilazane (1). To a solution of 7.1 g (0.0119 mol) of **4** in 200 ml of tetrahydrofuran at −40 °C and under nitrogen was added 0.059 mol of *n*-butyllithium in hexane (28 ml, 2.1 M). After addition was complete, the reaction mixture was allowed to warm to room temprature and 4.0 g (0.031 mol) of dichlorodimethylsilane was added. The resulting mixture was stirred at room temperature while tetrahydrofuran was removed under a stream of nitrogen. Chloroform was added to the paste-like residue and the precipitated lithium chloride was removed by filtration. After evaporation of the filtrate, the residue was dissolved in hexane and filtered. Concentration of the filtrate in vacuo afforded 4.1 g (48.6%) of the crude spiro product which upon recrystallization from hexane gave analytically pure **1:** mp 272–273 °C; ir (KBr) 2950, 1585, 1485, 1290, 1245, 1020, 952, and 905 cm^{-1}; NMR (CDCl$_3$) δ 0.05 (s, 18, Si(CH$_3$)$_3$), 0.62 (s, 12, Si(CH$_3$)$_2$), and 6.75–7.01 ppm (m, 20, aromatic); mass spectrum *m/e* 710 (parent peak).

The sample used for x-ray analysis was further purified by sublimation and recrystallized from hexane as colorless plates.

Anal. Calcd for $C_{34}H_{50}N_6Si_6$: C, 57.46; H, 7.04; N, 11.83; Si, 23.66; mol wt 710. Found: C, 57.67; H, 7.01; N, 12.41; Si 24.42; mol wt, 703 (VPO).

Crystal Data. Monoclinic; $C2/c$; a = 17.383 (7), b = 12.289 (4), c = 19.255 (9) Å; β = 94.68 (2)°; Z = 4; μ(Mo Kα) = 2.33 cm^{-1}; d_m = 1.13 (by flotation in aqueous CsCl), d_c = 1.15 g cm^{-3}.

Data Collection and Structure Refinement. Preliminary Weissenberg and precession photographs were used to determine the crystal system. The absences hkl, $h + k$ even, and $h0l$, l even, indicated either space group $C2/c$ or Cc. Precise cell constants were obtained by a least-squares refinement of angular positions for 15 Friedel pairs ($25 < 2\theta < 35°$). The data crystal had dimensions 0.3 × 0.7 × 1.0 mm. Intensity data were collected using Nb-filtered Mo Kα radiation (λ 0.710 69 Å). The diffractometer control programs were adapted by Lenhert and Henry.[9]

Intensities were measured using the θ–2θ scan technique. Stationary backgrounds were measured at equal angles above and below the respective Kα peak of base width 1.1°. A dispersion factor allowing for α_1–α_2 splitting was applied to large 2θ values. Absorption factors calculated by the Oak Ridge absorption program ORABS[10] ranged from 0.8545 to 0.9373 with an average of 0.9122; 4023 reflections were measured with $2\theta < 51°$, yielding 3754 independent observations. The standard deviations of the integrated intensities were calculated as described by Miller, Lenhert, and Joesten.[11]

The selection of the space group $C2/c$ was verified by the distri-

Table I. Atomic Parameters and Estimated Standard Deviations for Dispirotetrasilazane[a]

Atom no.	x	y	z	B_{11}	B_{22}	B_{23}	B_{12}	B_{13}	B_{23}
Si(1)	17 514 (4)	36 658 (6)	16 339 (3)	5.12 (3)	5.39 (4)	3.75 (3)	0.46 (3)	1.02 (3)	−0.86 (3)
Si(2)	22 743 (3)	28 737 (5)	5 429 (3)	3.79 (3)	3.03 (3)	3.04 (3)	0.12 (2)	0.55 (2)	0.04 (2)
Si(3)	38 493 (3)	15 383 (5)	7 911 (3)	3.96 (3)	3.43 (3)	4.36 (3)	0.33 (2)	0.20 (2)	0.22 (3)
N(1)	23 196 (9)	40 959 (13)	9 858 (8)	5.04 (9)	3.35 (8)	3.61 (9)	0.12 (7)	0.82 (7)	−0.61 (7)
N(2)	17 313 (9)	24 196 (13)	11 952 (8)	4.27 (8)	4.10 (9)	3.17 (8)	−0.30 (7)	1.01 (6)	−0.11 (7)
N(3)	30 755 (8)	21 653 (12)	3 272 (8)	3.40 (7)	2.92 (7)	2.88 (7)	0.21 (6)	0.35 (6)	0.13 (6)
C(1)	27 650 (13)	50 639 (18)	9 376 (11)	6.05 (13)	3.22 (10)	3.14 (10)	0.29 (10)	0.09 (9)	−0.47 (8)
C(2)	24 136 (15)	60 797 (21)	9 226 (14)	7.00 (15)	4.15 (13)	6.90 (16)	0.87 (11)	−0.25 (12)	−1.24 (12)
C(3)	28 617 (22)	70 175 (21)	8 833 (15)	11.10 (22)	3.10 (12)	7.52 (18)	0.89 (15)	0.32 (17)	−0.96 (12)
C(4)	36 295 (21)	69 544 (23)	8 658 (15)	10.17 (21)	4.36 (15)	6.40 (16)	−1.68 (16)	0.59 (16)	−0.26 (13)
C(5)	39 862 (15)	59 687 (22)	8 846 (14)	7.21 (15)	4.77 (14)	6.34 (16)	−1.19 (12)	0.55 (12)	0.07 (12)
C(6)	35 519 (14)	50 278 (19)	9 207 (12)	6.23 (13)	3.52 (11)	4.92 (12)	0.05 (11)	0.49 (10)	0.14 (10)
C(7)	14 277 (11)	13 958 (19)	13 488 (11)	3.26 (9)	5.23 (13)	3.37 (10)	−0.35 (9)	0.35 (8)	0.41 (10)
C(8)	11 752 (14)	11 614 (22)	19 979 (12)	6.09 (13)	7.34 (16)	3.90 (12)	−1.68 (12)	1.11 (10)	0.45 (11)
C(9)	8 867 (15)	1 455 (30)	21 382 (14)	7.04 (15)	9.82 (22)	4.57 (14)	−2.70 (16)	0.81 (12)	2.29 (15)
C(10)	8 439 (16)	−6 569 (25)	16 550 (16)	7.19 (16)	7.22 (18)	6.32 (17)	−2.98 (14)	−0.29 (14)	2.55 (15)
C(11)	10 983 (14)	−4 464 (21)	10 136 (14)	7.02 (15)	5.52 (15)	6.27 (16)	−1.84 (12)	0.73 (12)	0.45 (13)
C(12)	13 894 (13)	5 687 (20)	8 644 (12)	5.87 (13)	5.21 (13)	4.24 (12)	−1.44 (11)	1.14 (10)	0.49 (11)
C(13)	7 915 (15)	43 263 (24)	16 337 (15)	6.76 (15)	9.60 (20)	7.79 (18)	2.08 (14)	2.06 (13)	−1.82 (16)
C(14)	22 335 (14)	37 258 (23)	25 172 (12)	8.09 (16)	8.91 (19)	4.08 (13)	−0.87 (14)	0.52 (12)	−1.21 (13)
C(15)	38 656 (15)	19 403 (22)	17 219 (13)	8.32 (15)	7.74 (17)	4.57 (13)	2.08 (13)	−1.52 (12)	0.11 (12)
C(16)	37 238 (14)	402 (20)	7 185 (15)	7.40 (14)	3.60 (11)	9.80 (19)	0.86 (12)	−2.33 (14)	0.72 (13)
C(17)	47 537 (12)	19 687 (23)	4 203 (15)	4.12 (12)	8.58 (18)	9.13 (19)	−0.27 (12)	0.25 (12)	0.89 (15)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
H(2)	1 878 (10)	6 090 (14)	919 (9)	5.8 (5)	H(141)	1 921 (16)	3 445 (22)	2 823 (14)	11.5 (8)
H(3)	2 606 (12)	7 588 (18)	871 (12)	9.1 (6)	H(142)	2 685 (15)	3 241 (22)	2 566 (14)	11.6 (8)
H(4)	3 959 (13)	7 535 (19)	838 (12)	9.7 (6)	H(143)	2 417 (16)	4 369 (24)	2 600 (15)	13.2 (8)
H(5)	4 540 (10)	5 197 (16)	898 (10)	7.2 (5)	H(151)	4 315 (12)	1 664 (20)	1 938 (12)	9.7 (7)
H(6)	3 811 (9)	4 352 (13)	923 (9)	4.9 (4)	H(152)	3 370 (14)	1 734 (20)	1 900 (13)	11.3 (7)
H(8)	1 163 (10)	1 745 (16)	2 298 (10)	7.1 (5)	H(153)	3 907 (15)	2 722 (23)	1 768 (13)	12.0 (8)
H(9)	710 (12)	52 (20)	2 548 (12)	9.0 (6)	H(161)	3 767 (13)	− 190 (21)	187 (14)	12.2 (8)
H(10)	628 (11)	−1 333 (16)	1 757 (11)	8.0 (6)	H(162)	4 088 (11)	− 247 (17)	987 (11)	7.8 (6)
H(11)	1 123 (12)	−1 008 (17)	668 (11)	8.1 (6)	H(163)	3 218 (18)	− 118 (27)	833 (17)	14.6 (9)
H(12)	1 564 (10)	713 (15)	412 (10)	6.2 (5)	H(171)	4 779 (16)	2 750 (24)	41 (16)	12.7 (8)
H(131)	545 (14)	4 346 (21)	1 144 (15)	12.7 (8)	H(172)	5 187 (14)	1 764 (21)	695 (13)	10.2 (7)
H(132)	472 (12)	3 865 (19)	1 865 (13)	9.8 (7)	H(173)	4 708 (17)	1 875 (26)	−28 (17)	13.4 (9)
H(133)	842 (14)	4 980 (24)	1 877 (14)	11.9 (8)					

[a] The positional parameters are ×10^5 (for the H atoms ×10^4). The anisotropic B_{ij} (Å^2) are related to the dimensionless β_{ij} employed during the least-squares refinement by $B_{ij} = 4\beta_{ij}/a_i^*a_j^*$ where β_{ij} is given by the expression: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

bution and statistical averages of the normalized structure factors. The correct structure was determined by the successful execution of the SIGMA 2 and PHASE programs of Stewart's X-RAY 70 system.[12] The initial E-map produced peaks which could be identified with the skeletal atoms. Subsequent difference syntheses revealed the remainder of the molecule and all hydrogen atoms.

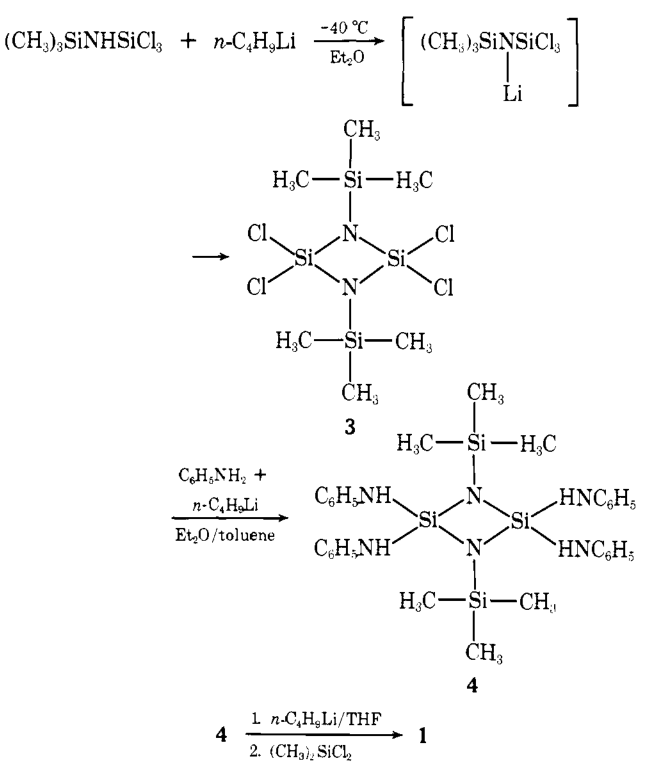
Full-matrix least-squares refinement, using anisotropic temperature factors for nonhydrogen atoms and isotropic factors for hydrogen atoms, resulted in a final R factor of 0.048 and a weighted R factor ($\omega = 1/\sigma^2(F)$) of 0.036. Table I lists the final atomic parameters with esd's. Atomic scattering factors used for nonhydrogen atoms were those of Cromer and Mann[13] and those for silicon were corrected for the real part of anomalous dispersion. Hydrogen scattering factors were those of Stewart, Davidson, and Simpson.[14] The final difference synthesis using all reflections showed a maximum residual electron density of ±0.14 e/Å^3. The observed and calculated structure factors are given in Table II.[15]

Discussion and Results

Synthesis. The preparation of the dispirotetrasilazane **1** involved a three-step reaction sequence. Although the reaction scheme involves the modification and extension of reactions generally known in organosilazane chemistry, this synthesis is significant because it incorporates the tetrafunctional cyclodisilazane **3** in the formation of a spirosilazane **1**.

By a modification of the method used by Wannagat[8] for the preparation of decachloro-N,N'-bis(silyl)cyclodisilazane, 1,1,1-trichloro-3,3,3-trimethyldisilazane[16] was readily converted to the N-lithio salt when reacted with n-butyllithium at −40 °C. Upon warming to room temperature, the salt

Scheme I



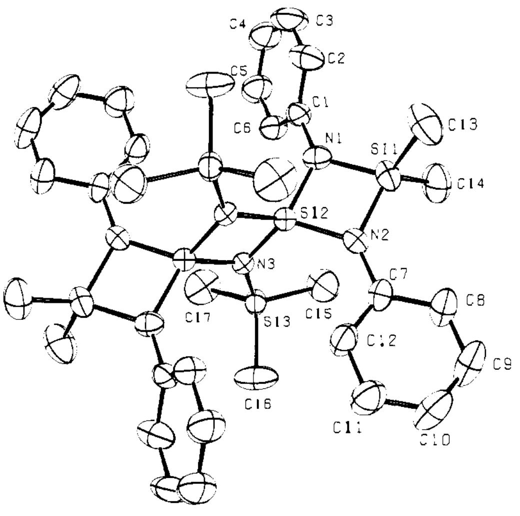


Figure 1. The 40% probability thermal ellipsoids[17] of the dispirotetrasilazane (**1**). Hydrogen atoms are omitted for clarity.

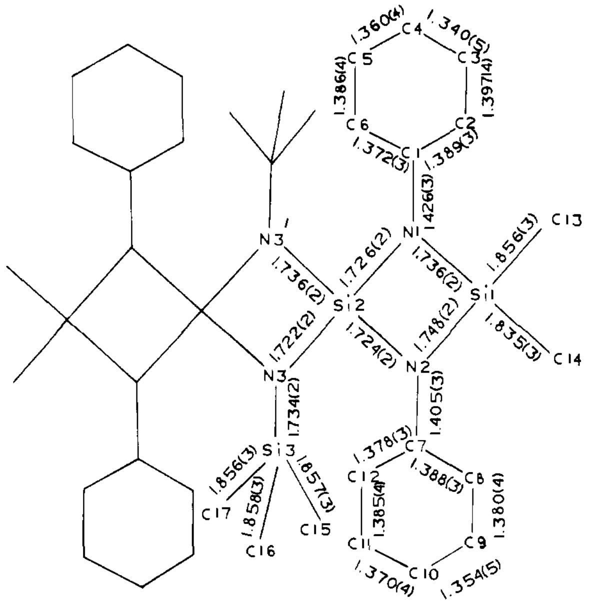


Figure 2. Bond distances (Å) with esd's for **1**.

through intermolecular-condensation and cyclization formed the first reported tetrafunctional cyclodisilazane, 1,3-bis(trimethylsilyl)-2,2,4,4-tetrachlorocyclodisilazane (**3**), in 85% yield. Treatment of **3** with *N*-lithioaniline in ether-hexane produced the corresponding tetraanilino derivative **4** in good yield. The tetramine **4**, in turn, was converted to the tetralithio salt by reaction with *n*-butyllithium in THF-hexane. Treatment of the lithium salt in situ with excess dichlorodimethylsilane resulted in the formation of the dispiro compound **1** as colorless plates. Evidence for the expected structure **1** was obtained from spectral data, including the ir 952 cm^{-1} (ν_{as}-SiN(C$_6$H$_5$)Si) and 905 cm^{-1} (ν_{as}SiNSi); NMR δ 0.05 (s, 18, Si(CH$_3$)$_3$), 0.62 (s, 12, Si(CH$_3$)$_2$), 6.75-7.01 ppm (m, 20, aromatic); and mass spectrum (M+ = 710), as well as elemental analyses. Although the chemical and spectral data were consistent with **1**, it was not possible to differentiate it from the bridged silazane **2**. The former compound, **1**, presumably was formed by the intermolecular condensation of the 1,1- and 3,3-dilithioanilino groups of **4** with two molecules of dichlorodimethylsilane.[2] However, **2**, consisting of both four- and six-membered cyclosilazane rings, could conceivably have resulted from the stepwise reaction of 1,3-dilthioanilino groups with dichlorodimethylsilane. A single-crystal x-ray crystallographic analysis was consequently performed to determine the structure of **1**.

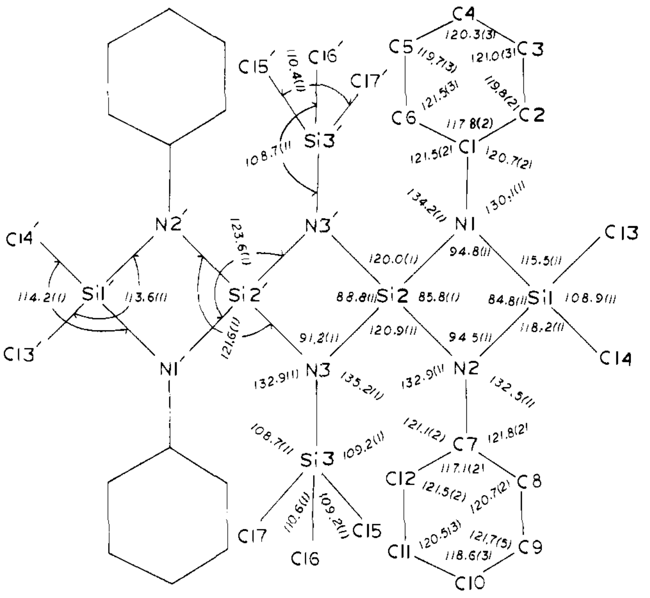


Figure 3. Bond angles (deg) with esd's for **1**.

Molecular Structure. The molecule has $\bar{1}$ molecular symmetry as demanded by the space group. The central four-membered ring of alternate silicon and nitrogen atoms is therefore planar (Figure 1). The outer disilazane rings are planar with torsion angles of 1.6°. Adjacent disilazane rings make an angle of 88°. The ring silicon atoms are collinear to within 0.03 Å. The phenyl rings are planar to within 0.006 Å and are tilted 70° to each other.

The mean Si(2)-N bond distance is 1.727 Å while the corresponding value for Si(1)-N is 1.742 Å (Figure 2). The N-Si-N angles in the exterior ring average 85.3° while the Si-N-Si angles average 94.7° (Figure 3). Hence the transannular Si(1)-Si(2) distance (2.549 (1) Å) is greater than the N(1)-N(2) distance (2.350 (2) Å). The central ring, on the other hand, has similar intra-ring distances (Si(2)-Si′(2), 2.469 (1) Å; N(3)-N′(3), 2.420 (2) Å). Wheatley,[6] in the structure determination of a substituted cyclodisilazane, also found the intra-ring distances to be nearly equal. The difference in distortion of these two four-membered rings is probably due to the interaction of the bulky trimethylsilyl and phenyl substituents. The exocyclic Si(3)-N(3) bond (1.734 Å) is not significantly different from the average endocyclic Si(2)-N(3) distance (1.729 Å). The orientation of the phenyl groups with respect to the exterior disilazane ring is best represented by the torsion angles about the C-N bonds: Si(1)-N(1)-C(1)-C(2), −61.3°, and Si(1)-N(2)-C(7)-C(8), −11.2°. As expected, the outermost atoms of the phenyl groups exhibit the largest thermal motion, resulting in short C(3)-C(4) and C(9)-C(10) bond distances. The average Si-C(Me) bond length of 1.852 Å is shorter than that reported for similar cyclodisilazanes (1.876 Å),[6,7] presumably due to the increased steric constraints in the dispirotetrasilazane.

The three valencies to the nitrogen atoms are coplanar to within 0.06 Å and the sum of the valency angles for each nitrogen atom is approximately 360°. The average C-H distance is 0.934 Å.

Supplementary Material Available: Table II, observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Studies of Propanediol–Chromium(III) Species in Acidic Solution[1]

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Abstract: The reactions of $Cr(OH_2)_6^{3+}$ in acidic water–propanediol to form species $Cr(OH_2)_wG_g^{3+}$ (G = glycol) have been studied at 60 °C to allow comparison of the properties of systems in which the chelate rings contain five atoms (1,2-propanediol) and six atoms (1,3-propanediol). For 1,3-propanediol, species with $g = 1$, 2, and 3 have been separated from equilibrated solutions by column ion-exchange procedures. Species containing a particular number of coordinated glycol molecules and different numbers of coordinated water molecules have been isolated, indicating that 1,3-propanediol bonds to chromium(III) ion as a chelated and as a nonchelated ligand. Equilibrium quotients for the reactions, which depend upon the solvent composition, have relative values close to statistical. For 1,2-propanediol, species with $g > 1$, if they form, do not survive the ion-exchange separation procedure. This system resembles the ethylene glycol system, and it is suggested that a 1,2-glycol chelated to chromium(III) labilizes the other coordination sites.

A recent study[2] of species of chromium(III) ion in acidic water–ethylene glycol mixed solvents reveals unexpected results. These are: (1) a relatively rapid spectral change which occurs when previously equilibrated solutions are diluted with a solvent component to alter the solvent composition, and (2) species containing two or more coordinated glycol molecules, *as determined by ion-exchange procedures*, are present, if at all, at much lower concentrations than expected statistically. This contrasts with the chromium(III) species involving coordinated alcohols[3] and dimethyl sulfoxide,[4] the relative stabilities of which are only moderately different from statistical.

The relatively rapid spectral change occurring upon dilution was interpreted to be due to the shifting of equilibrium in the reaction

$$Cr(OH_2)_5G^{3+} \rightleftharpoons Cr(OH_2)_4G^{3+} + H_2O$$

in which the coordinated glycol ligand, represented by G, acts as a monodentate reagent in $Cr(OH_2)_5G^{3+}$ and as a chelated bidentate reagent in $Cr(OH_2)_4G^{3+}$. The failure to isolate chromium(III) species containing two or more coordinated glycol molecules was not explained, although the possibility that such species were present at equilibrium but did not survive the ion-exchange procedure was mentioned. If the kinetic and equilibrium behavior of the chromium(III)–ethylene glycol system is attributable to specific properties of the five atom chelate ring in tetraaqua(ethylene glycol)chromium(III) ion, study of chromium(III) coordinated to the isomeric propanediols should reveal differences between the species involving 1,2-propanediol (which would form five-atom chelate rings) and those involving 1,3-propanediol (which would form six-atom chelate rings). The present paper deals with such a study, which reveals a remarkable contrast between these two systems.

The species which are possible in a system of six-coordinate chromium(III) and a ligand which can act as either a monodentate or a bidentate ligand, such as a glycol, have the composition $Cr(OH_2)_wG_g^{3+}$. The number of bidentate glycol ligands in this species is $6 - (w + g)$. Equilibrium in the solutions can be characterized by equilibrium quotients for the reactions forming each of these species from hexaaquachromium(III) ion:

$$Cr(OH_2)_6^{3+} + gG = Cr(OH_2)_wG_g^{3+} + (6 - w)H_2O$$

with

$$Q_{gw} = \frac{[Cr(OH_2)_wG_g^{3+}](1 - Z)^{6-w}}{[Cr(OH_2)_6^{3+}]Z^g}$$

in which Z is the mole fraction of propanediol in the mixed solvent. (In calculation of Z, only the solvent components are taken into account.) For many compositions of chromium species (particular values of w and g), geometric and optical isomers are possible.

Experimental Details and Results

Reagents. Reagent grade chemicals were used without additional purification unless noted otherwise. The water content of the 1,2-propanediol (Fisher Scientific Co., Laboratory Grade) and 1,3-propanediol (Eastman Kodak, Reagent Grade) was determined by Karl Fischer titrations. Solutions of chromium(III) perchlorate in per-