Electronic spectra of (amino)(phenyl)disilanes

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(Received December 8, 1993)

Abstract

Two UV absorption maxima, around 220 and 280 nm, characteristic of a series of (amino)(phenyl)disilanes are interpreted in terms of the n-σ conjugation between the nonbonding electrons on nitrogens and the Si–Si σ-bonding electrons which are activated by the σ–π conjugation with the phenyl groups. The X-ray crystal structure of a 1,1,2,2-tetraamino-1,2,-diphenyldisilane has also been determined.

Key words: Silane; Electronic spectra; (Amino)disilane; Crystal structure; Silyllithium; σ-π conjugation

1. Introduction

Polysilanes have been extensively studied because of their unique electronic properties due to the so-called σ-conjugation [1]. The Ph–Si–Si system also has interesting electronic properties in that the Si–Si bond conjugates with the phenyl group. The conjugating properties have been rationalized at first in terms of d–π^* interaction in the excited state, and later, in addition to this, in terms of σ–π interaction in the ground state [2–5]. This σ–π interaction raises the HOMO level of the Ph–Si–Si system, the first ionization energy (IE) being estimated to be 8.35 eV [6].

Functional oligo- and polysilanes [7], however, have been little examined in terms of the electronic structure. Only a few reports have described UV spectra of heteroatom (X)-substituted permethylated oligosilanes including aminodisilanes [8,9]. The spectra were interpreted in terms of p_X–σ_{Si-Si} (n–σ) and p_X–d_{Si} (pπ–dπ) interactions.

If a functional group such as an amino group is attached to the Ph–Si–Si system, a p_N orbital of the amino group (IE = 8.06 eV) [10] is expected to interact with the activated HOMO orbital (σ_{Si-Si}–π_s) of the Ph–Si–Si system (IE = 8.35 eV) to give a novel electronic structure, as shown in Fig. 1. (Throughout this paper, π_s and π_{as} denote the symmetrical and asymmetrical highest occupied π orbitals of benzene, respectively, and π^* denotes the lowest unoccupied π orbital of the Ph–Si–Si system.) However, the functionalized Ph–Si–Si system has been little studied so far in terms of the electronic structure because of a difficulty in the synthesis of such compounds [11]. Recently, we have found a systematic method for the preparation of (amino)(phenyl)disilanes, which involves coupling of (amino)(phenyl)silyllithiums with appropriate (amino)chlorosilanes [12]. We have now started to examine the electronic spectra of the (amino)(phenyl)disilanes in order to clarify the electronic effect of amino groups on the Ph–Si–Si system.

2. Results and discussion

2.1. Synthesis of (amino)(phenyl)disilanes

1,2-(Diamino)tetraphenyl- (**1**), 1,1,2-(triamino)triphenyl- (**2**), 1,1,2,2-(tetraamino)diphenyl- (**3**) and 1,1,2,2-(tetraamino)methylphenyldisilane (**4**) were prepared by coupling between appropriate (amino)silyllithiums and (amino)chlorosilanes, as shown in Scheme 1.

2.2. UV spectra

Table 1 summarizes absorption maxima for **1–4**, together with data for 1,1,2,2-(tetraamino)dimethyldi-

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0022-328X/94/$7.00
SSDI 0022-328X(94)24552-T

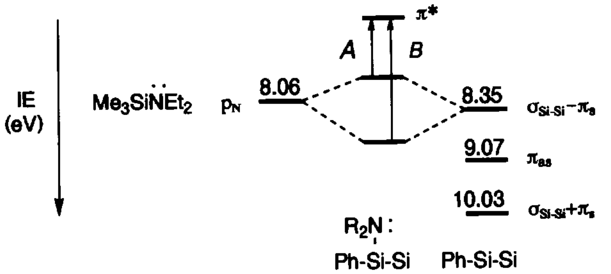


Fig. 1. Qualitative MO model for the origin of two absorptions of (amino)(phenyl)disilanes.

silane (**5**) and 1,2-dimethyltetraphenyldisilane (**6**) for reference. Some selected spectra are shown in Fig. 2.

All the (amino)(phenyl)disilanes exhibit two absorption maxima: a strong band around 220 nm and a weak band around 280 nm. They are different from those of (amino)(methyl)disilane (**5**), which shows only one weak absorption at 238 nm, and of 1,2-dimethyltetraphenyldisilane (**6**), which exhibits a strong absorption around 240 nm and weak bands around 270 nm characteristic of a typical Ph–Si–Si system. No solvent effect is observed for **3** on changing the solvent from cyclohexane to acetonitrile (Table 1).

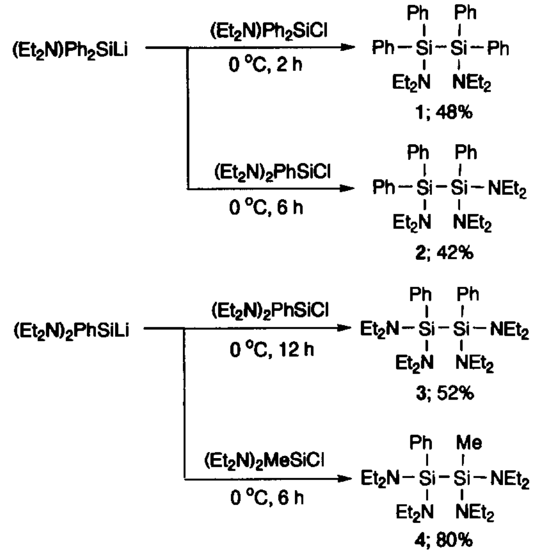
The two absorptions observed for (amino)(phenyl)disilanes are compatible with our expectations (Fig. 1). Thus, the energetically favourable interaction between the p_N orbital (Ψ(N)) and the $\sigma_{Si-Si}-\pi_s$ orbital (Ψ(Si)), *i.e.* n–σ conjugation, will form two energy levels which lead to two electronic transitions *A* and *B*. Judging from the energy levels, the HOMO is primarily of p_N character. Since a transition from the p_N orbital to π^* is locally forbidden, the transition from the HOMO will be forbidden to the extent that Ψ(N) contributes to the wave function. The weak band around 280 nm can thus be ascribed to a locally forbidden transition from the HOMO (*A* in Fig. 1). Since an increase in the number of amino groups results in more effective n–σ conjugation making the HOMO higher in energy, red shifts of the 280 nm absorptions are observed in the order of **1**, **2** and **3** with some reduction in the intensity. The insensitivity of the band to the solvent polarity, as observed for **3**, shows the electron density of p_N to be delocalized through n–σ^* or pπ–dπ conjugation. This insensitivity of the UV absorption of aminosilanes has been reported previously [8]. The bands are broad since they are overlapped by bands arising from transitions associated with the phenyl groups.

The absorption around 220 nm can be ascribed to a transition from the next HOMO (*B* in Fig. 1). This transition may thus be regarded as a blue shift of transition from the $\sigma_{Si-Si}-\pi_s$ orbital to π^* in the Ph–Si–Si system.

TABLE 1. Absorption maxima of some disilanes in cyclohexane

Disilane	λ_{max} nm(ϵ)	
$(Et_2N)Ph_2SiSiPh_2(NEt_2)$ (**1**)	227 (27900)	274 (6050)
$(Et_2N)Ph_2SiSiPh(NEt_2)_2$ (**2**)	222 (30400)	277 (5090) sh
$(Et_2N)_2PhSiSiPh(NEt_2)_2$ (**3**)	220 (27100)	285 (3600)
	217 (25000) [a]	285 (3120) [a]
$(Et_2N)_2PhSiSiMe(NEt_2)_2$ (**4**)	218 (17000)	277 (1690) sh
$(Et_2N)_2MeSiSiMe(NEt_2)_2$ (**5**)	< 210	238 (7560) sh
$MePh_2SiSiPh_2Me$ (**6**)	239 (26900)	268 (3560) sh
		273 (2310) sh

[a] In acetonitrile.



Scheme 1.

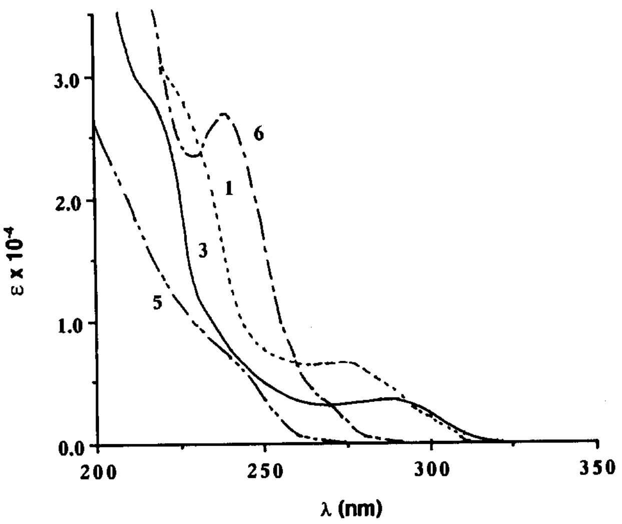


Fig. 2. UV spectra of **1**, **3**, **5** and **6** in cyclohexane.

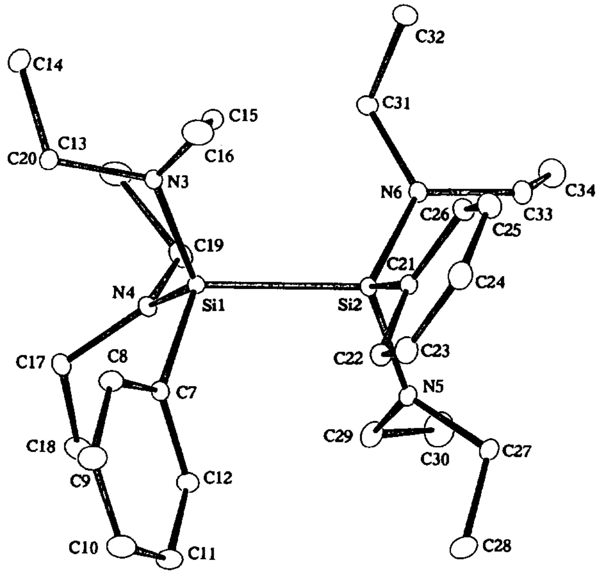


Fig. 3. Crystal structure of 3. Hydrogen atoms are omitted for clarity.

2.3. X-Ray structure of 3

To obtain further insight into the n–σ conjugation, we determined the X-ray crystal structure of 3. The structure is shown in Fig. 3 and selected bond lengths and angles are listed in Table 2.

The geometry around all nitrogen atoms is nearly planar as generally observed [13,14] (sum of three angles around nitrogen: N(3), 357.9°; N(4), 359.3°; N(5), 359.3°; N(6), 359.7°). The p_N orbital on nitrogen is thus assumed to be perpendicular to the plane. The dihedral angle (θ) between two planes defined by the Si–Si–N and C–N–C fragments implies the degree of interaction between the p orbitals and the σ_{Si-Si} orbital (n–σ conjugation): $\theta = 90°$ makes these orbitals parallel, resulting in the strongest interaction. The observed angles θ are as follows: N(3), 17°; N(4), 45°; N(5), 43°; N(6), 13°. The data suggest that the p_N orbitals on N(4) and N(5) have a greater possibility of interacting with the σ_{Si-Si} orbital than those on N(3) and N(6). However, all Si–N bond distances are normal, having an average value 1.73 Å. The Si–Si bond length of 2.391 Å is slightly longer than the normal range (2.33–2.37 Å) [14]. There is therefore no structural bias which might be anticipated by the n–σ conjugation.

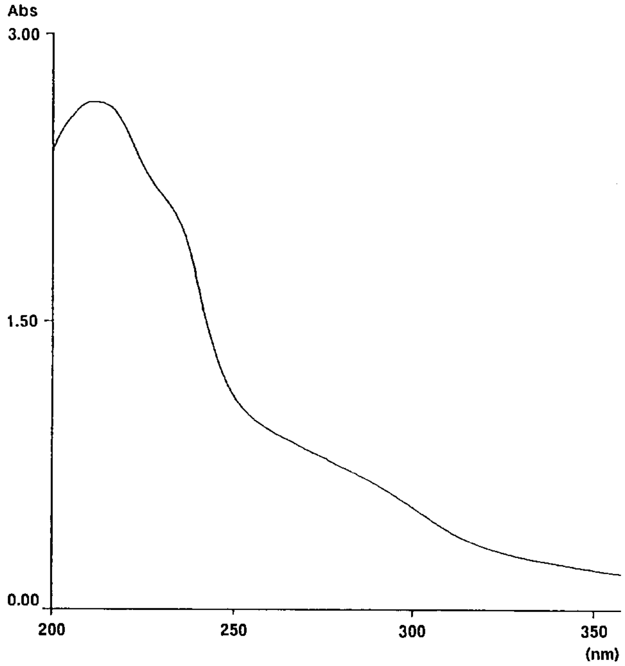


Fig. 4. UV spectrum of 3 in the solid state (KBr pellet).

We next examined the UV spectrum of 3 in the solid state (Fig. 4). The observed absorptions are not significantly different from those observed in solution (Fig. 2). We could not obtained evidence for an angle dependence of the n–σ conjugation. The high planarity of all four nitrogen atoms might rather imply angle independence of the n–σ conjugation. To clarify this point, we are currently synthesizing aminodisilanes with fixed angles between the p_N and σ_{Si-Si} orbitals and measuring the ionization potentials of the aminodisilanes.

TABLE 2. Selected bond distances (Å), angles (°) and dihedral angles (°) for 3

Bond distances			
Si(1)–N(3)	1.727(1)	Si(1)–N(4)	1.724(2)
Si(2)–N(5)	1.724(1)	Si(2)–N(6)	1.729(2)
Si(1)–Si(2)	2.391(6)		
Bond angles			
N(3)–Si(1)–Si(2)	110.02(6)	N(4)–Si(1)–Si(2)	112.88(5)
N(5)–Si(2)–Si(1)	108.76(6)	N(6)–Si(2)–Si(1)	113.35(6)
Dihedral angles			
Si(1)Si(2)N(3)–C(13)N(3)C(15)	17.31		
Si(1)Si(2)N(4)–C(17)N(4)C(19)	45.01		
Si(1)Si(2)N(5)–C(27)N(5)C(29)	43.38		
Si(1)Si(2)N(6)–C(31)N(6)C(33)	13.38		

3. Experimental details

3.1. General

^1H (200 MHz), ^{13}C (50.29 MHz) and ^{29}Si (39.73 MHz) NMR spectra were recorded on a Varian VXR-200 spectrometer equipped with a VX-4000 computer. ^1H and ^{13}C chemical shifts are referenced to internal benzene-d_6 (^1H δ7.200 ppm and ^{13}C δ 128.00 ppm). ^{29}Si chemical shifts are referenced to external Me_4Si (0 ppm). Mass spectra were recorded on a JEOL JMS-D300 mass spectrometer. UV spectra in solution were measured with a Hitachi U-3410 spectrometer. UV spectra in the solid state (KBr pellet) were measured with a Jasco Uvidec-610B spectrometer. Infrared spectra were recorded with a Hitachi 270-30 spectrometer. Melting points were measured with a Yanaco-MP-S3 apparatus. Elemental analyses were performed at the Microanalysis Centre of the Department of Pharmaceutical Sciences, Kyoto University: analytical samples were purified by recrystallization or preparative GLC. Granular lithium was purchased from Chemetall. Lithium dispersion (25 wt.% in mineral oil) was purchased from Aldrich. Tetrahydrofuran (THF) was distilled under nitrogen from sodium–benzophenone. Hexane and cyclohexane were distilled under nitrogen from sodium. Dichloromethane and acetonitrile were distilled under nitrogen from CaH_2. All reactions were carried out under nitrogen.

3.2. Preparation of (amino)chlorosilanes: a typical procedure

A solution of diethylamine (11.7 ml, 110 mmol) in dry THF (10 ml) was added to a mixture of triethylamine (15.5 ml, 110 mmol) and dichlorodiphenylsilane (20.7 ml, 100 mmol) in dry THF (150 mmol) at room temperature over 30 min with stirring. During the addition, a large amount of white salt ($Et_3N \cdot HCl$) precipitated. After the addition was complete, the mixture was stirred at room temperature for 6 h. The mixture was diluted with hexane (100 ml) and then filtered. The filtrate was concentrated under reduced pressure. The residue was distilled under reduced pressure to give 24.9 g (86% yield) of (diethylamino)diphenylchlorosilane as a viscous, colourless to pale yellow oil, b.p. 129–133°C/0.55 mmHg.

3.4. Preparation of (amino)phenylsilyllithiums [12a]

To a suspension of lithium dispersion (13 mg-atom; commercial 25 wt.% in mineral oil was washed with dry hexane three times) in dry THF (4.0 ml) was added dropwise bis(diethylamino)phenylchlorosilane (815 mg, 2.86 mmol) at room temperature with stirring. After a few minutes, the resulting greenish mixture was stirred at 0°C for 4 h to give a solution of bis(diethylamino)phenylsilyllithium. The solution was used in the next reaction without titration on the assumption of the quantitative yield [12a]. (Diethylamino)diphenylsilyllithium was prepared similarly from (diethylamino)diphenylchlorosilane and granular lithium in quantitative yield [12a].

3.5. Preparation of (amino)(phenyl)disilanes: a typical procedure: 1,1,2,2-tetrakis(diethylamino)-1,2-diphenyldisilane (3)

A solution of bis(diethylamino)phenylsilyllithium in THF (4.0 ml; 2.86 mmol), prepared as above, was separated from the excess lithium metal by transferring it via a syringe to another flask. To the solution was added bis(diethylamino)phenylchlorosilane (785 mg, 2.70 mmol) over 5 min at 0°C and then the solution was stirred at 0°C for 12 h. After warming to room temperature, the solvent was evaporated under reduced pressure. The residue was diluted with dry n-hexane and filtered. The filtrate was evaporated. The resulting white solid was recrystallized from dichloromethane to give the disilane 3 (700 mg, 52% yield) as white crystals, m.p. 145°C (dec.). ^1H NMR (C_6D_6): δ 1.06 (t, $J = 7.0$ Hz, 24H), 3.15 (q, $J = 7.0$ Hz, 16H), 7.27–7.31 (m, 6H), 7.77–7.82 (m, 4H). ^{13}C NMR (C_6D_6): δ 14.29, 39.74, 127.62, 128.93, 135.75, 141.89. ^{29}Si NMR (C_6D_6): δ −16.31. MS: m/e 498 (M^+, 1), 249 ($(Et_2N)_2PhSi^+$, 100). IR (KBr): 2972, 2940, 2856, 1380, 1202, 1170, 1098, 1020, 926, 704, 490 cm^{-1}. Anal. Calc. for

TABLE 3. Crystal data and experimental details for structure determination of 3

Chemical formula	$C_{28}H_{50}Si_2N_4$
Formula weight	498.90
Crystal size (mm)	0.30×0.40×0.35
Crystal system	Monoclinic
Space group	$P2_1/a$
Unit cell dimensions	
a (Å)	18.900(4)
b (Å)	10.365(3)
c (Å)	16.254(4)
β (degrees)	104.33(2)
V (Å^3)	3085(1)
Z	4
ρ_{calc} (g cm^{-3})	1.07
Temperature (°C)	25
Radiation	Cu Kα ($\lambda = 1.54178$ Å)
μ (Cu Kα) (cm^{-1})	11.07
No. of unique reflections	5094
No. of reflections used	4786
No. of variables	467
R	0.042
R_w	0.051
S	2.36

$C_{28}H_{50}N_4Si_2$: C, 67.41, H, 10.10. Found: C, 67.40, H, 10.01%.

3.6. *1,2-Bis(diethylamino)-1,1,2,2-tetraphenyldisilane (1)*

This compound was obtained similarly as white crystals (dichloromethane) in 48% yield, m.p. 149–150.5°C. ^{1}H NMR (C_6D_6): δ 0.96 (t, J = 7.0 Hz, 12H), 3.14 (q, J = 7.0 Hz, 8H), 7.20–7.24 (m, 12H), 7.71–7.76 (m, 8H). ^{13}C NMR (C_6D_6): δ 14.77, 41.69, 128.00, 129.39, 136.23, 139.02. ^{29}Si NMR (C_6D_6): δ −14.30. MS: *m/e* 508 (M^+, 28), 436 (M^+ − Et_2N, 39), 254 ((Et_2N)Ph_2Si^+, 100). IR (KBr): 2972, 2936, 2860, 1430, 1376, 1202, 1170, 1100, 1022, 736, 702, 498 cm^{-1}. Anal. Calc. for $C_{32}H_{40}N_2Si_2$: C, 75.53, H, 7.92. Found: C, 75.58, H, 8.00%.

TABLE 4. Atomic coordinates and equivalent isotropic thermal parameters with estimated standard deviations in parentheses for **3**

Atom	x	y	z	B_{eq}
Si(1)	0.05891(2)	−0.24847(5)	−0.23899(3)	3.46(2)
Si(2)	0.18390(2)	−0.26119(5)	−0.24475(3)	3.43(2)
N(3)	0.00460(8)	−0.3337(2)	−0.32234(9)	4.08(5)
N(4)	0.04575(8)	−0.2938(2)	−0.14182(9)	4.05(4)
N(5)	0.23570(8)	−0.1669(2)	−0.16481(9)	4.04(4)
N(6)	0.21637(8)	−0.4176(1)	−0.2412(1)	4.19(4)
C(7)	0.03596(9)	−0.0710(2)	−0.2479(1)	3.90(5)
C(8)	−0.0150(1)	−0.0201(2)	−0.3170(1)	5.21(6)
C(9)	−0.0268(2)	0.1114(2)	−0.3264(2)	6.72(8)
C(10)	0.0118(2)	0.1954(2)	−0.2673(2)	7.00(9)
C(11)	0.0624(1)	0.1483(2)	−0.1977(2)	6.14(8)
C(12)	0.0738(1)	0.0172(2)	−0.1885(1)	4.77(6)
C(13)	−0.0744(1)	−0.3452(2)	−0.3304(2)	5.14(6)
C(14)	−0.1056(1)	−0.4775(3)	−0.3540(2)	6.60(9)
C(15)	0.0279(1)	−0.3674(2)	−0.3995(1)	4.87(6)
C(16)	0.0013(2)	−0.2790(3)	−0.4746(2)	7.6(1)
C(17)	−0.0049(1)	−0.2310(2)	−0.0995(1)	4.92(6)
C(18)	0.0307(2)	−0.1777(3)	−0.0127(2)	7.3(1)
C(19)	0.0762(1)	−0.4139(2)	−0.1009(2)	5.75(7)
C(20)	0.0230(2)	−0.5236(3)	−0.1114(2)	8.6(1)
C(21)	0.19114(9)	−0.1798(2)	−0.3466(1)	3.80(5)
C(22)	0.1701(1)	−0.0518(2)	−0.3646(1)	4.73(6)
C(23)	0.1720(1)	0.0054(2)	−0.4411(2)	5.84(7)
C(24)	0.1948(1)	−0.0641(3)	−0.5017(2)	6.16(8)
C(25)	0.2158(1)	−0.1900(3)	−0.4863(1)	6.18(8)
C(26)	0.2137(1)	−0.2476(2)	−0.4099(1)	4.89(6)
C(27)	0.2958(1)	−0.0836(2)	−0.1747(2)	4.98(6)
C(28)	0.2862(2)	0.0583(3)	−0.1580(2)	7.8(1)
C(29)	0.2303(1)	−0.1791(3)	−0.0769(1)	6.02(8)
C(30)	0.2923(2)	−0.2475(4)	−0.0176(2)	9.4(1)
C(31)	0.1717(1)	−0.5344(2)	−0.2565(2)	4.94(6)
C(32)	0.1781(2)	−0.6127(3)	−0.3334(2)	6.99(9)
C(33)	0.2950(1)	−0.4384(2)	−0.2315(2)	5.53(7)
C(34)	0.3306(2)	−0.5329(3)	−0.1629(2)	8.0(1)
H(8)	−0.040(1)	0.077(2)	−0.357(2)	6.78(0)
H(9)	−0.064(2)	0.143(3)	−0.376(2)	6.78(0)
H(10)	0.006(2)	0.291(3)	−0.275(2)	6.99(0)
H11	0.088(2)	0.202(3)	−0.157(2)	6.12(0)
H(12)	0.112(1)	−0.013(2)	−0.141(2)	4.72(0)
H(13A)	−0.104(1)	−0.279(2)	−0.373(2)	5.08(0)
H(13B)	−0.082(1)	−0.317(2)	−0.273(2)	5.08(0)
H(14A)	−0.160(2)	−0.484(3)	−0.358(2)	6.49(0)
H(14B)	−0.099(2)	−0.508(3)	−0.407(2)	6.49(0)
H(14C)	−0.083(2)	−0.538(3)	−0.313(2)	6.49(0)
H(15A)	0.014(1)	−0.459(2)	−0.415(2)	4.77(0)
H(15B)	0.084(1)	−0.367(2)	−0.383(1)	4.77(0)
H(16A)	0.012(2)	−0.191(3)	−0.462(2)	7.46(0)
H(16B)	−0.054(2)	−0.266(3)	−0.462(2)	7.46(0)
H(16C)	0.016(2)	−0.311(3)	−0.522(2)	7.46(0)
H(17A)	−0.046(1)	−0.295(2)	−0.098(1)	4.72(0)
H(17B)	−0.031(1)	−0.162(2)	−0.138(2)	4.72(0)
H(18A)	0.057(2)	−0.242(3)	0.020(2)	7.00(0)
H(18B)	−0.005(2)	−0.140(3)	0.010(2)	7.00(0)
H(18C)	0.068(2)	−0.107(3)	−0.019(2)	7.00(0)
H(19A)	0.120(1)	−0.442(2)	−0.123(2)	5.51(0)
H(19B)	0.100(1)	−0.412(2)	−0.037(2)	5.51(0)
H(20A)	0.052(2)	−0.602(3)	−0.078(2)	8.26(0)
H(20B)	0.012(2)	−0.539(3)	−0.172(2)	8.26(0)
H(20C)	−0.019(2)	−0.499(3)	−0.088(2)	8.26(0)
H(22)	0.151(1)	−0.001(2)	−0.322(1)	4.60(0)
H(23)	0.157(1)	0.092(3)	−0.450(2)	5.71(0)
H(24)	0.193(1)	−0.026(3)	−0.558(2)	6.03(0)
H(25)	0.230(1)	−0.245(3)	−0.529(2)	5.95(0)
H(26)	0.227(1)	−0.334(2)	−0.402(2)	4.72(0)
H(27A)	0.301(1)	−0.098(2)	−0.236(2)	4.90(0)
H(27B)	0.342(1)	−0.113(2)	−0.134(2)	4.90(0)
H(28A)	0.329(2)	0.101(3)	−0.161(2)	7.70(0)
H(28B)	0.237(2)	0.091(3)	−0.197(2)	7.70(0)
H(28C)	0.278(2)	0.068(3)	−0.100(2)	7.70(0)
H(29A)	0.183(2)	−0.222(3)	−0.076(2)	5.97(0)
H(29B)	0.235(1)	−0.099(3)	−0.034(2)	5.97(0)
H(30A)	0.284(2)	−0.246(3)	0.043(2)	9.38(0)
H(30B)	0.338(2)	−0.208(4)	−0.016(2)	9.38(0)
H(30C)	0.277(2)	−0.329(4)	−0.051(2)	9.38(0)
H(31A)	0.120(1)	−0.507(2)	−0.264(1)	4.76(0)
H(31B)	0.185(1)	−0.590(2)	−0.202(2)	4.76(0)
H(32A)	0.146(2)	−0.680(3)	−0.341(2)	6.78(0)
H(32B)	0.227(2)	−0.645(3)	−0.326(2)	6.78(0)
H(32C)	0.166(2)	−0.562(3)	−0.388(2)	6.78(0)
H(33A)	0.320(1)	−0.354(3)	−0.218(2)	5.42(0)
H(33B)	0.306(1)	−0.473(2)	−0.287(2)	5.42(0)
H(34A)	0.386(2)	−0.537(3)	−0.157(2)	7.98(0)
H(34B)	0.305(2)	−0.619(3)	−0.176(2)	7.98(0)
H(34C)	0.319(2)	−0.513(3)	−0.112(2)	7.98(0)

3.7. *1,1,2-Tris(diethylamino)-1,2,2-triphenyldisilane (2)*

This compound was obtained similarly as white crystals (benzene) in 42% yield, m.p. 155–158°C. ^{1}H NMR (C_6D_6): δ 0.96–1.05 (m, 18H), 3.07–3.19 (m, 12H), 7.23–7.28 (m, 6H), 7.71–7.81 (m, 9H). ^{13}C NMR (C_6D_6): δ 14.30, 14.69, 39.93, 41.48, 127.54, 127.85, 129.13, 129.17, 135.78, 136.17, 139.95, 141.02. ^{29}Si NMR (C_6D_6): δ −14.84, 15.95. MS: *m/e* 503 (M^+, 6), 254 ((Et_2N)Ph_2Si^+, 5), 249 ((Et_2N)$_2$PhSi$^+$, 100). IR (KBr): 2976, 2936, 2856, 1430, 1380, 1204, 1170, 1098, 1022, 928, 738, 702, 494 cm^{-1}. Anal. Calc. for $C_{30}H_{45}N_3Si_2$: C, 71.51, H, 9.00. Found: C, 71.32, H, 9.03%.

3.8. 1,1,2,2-Tetrakis(diethylamino)-1-methyl-2-phenyldisilane (4)

This compound was prepared similarly and isolated by bulb-to-bulb distillation in 80% yield as a white solid, b.p. 225–245°C/1.30 mmHg (bath temperature), m.p. 123.5–125°C. ^{1}H NMR (C_6D_6): δ 0.41 (s, 3H), 1.03 (t, $J = 7.0$ Hz, 12H), 1.13 (t, $J = 7.0$ Hz, 12H), 2.99 (q, $J = 7.0$ Hz, 8H), 3.14 (q, $J = 7.0$ Hz, 8H), 7.26–7.40 (m, 3H), 7.87–7.91 (m, 2H). ^{13}C NMR (C_6D_6): δ 1.57, 14.63, 14.88, 39.49, 39.84, 127.72, 128.79, 135.63, 141.59. ^{29}Si NMR (C_6D_6): δ −10.05, 14.80. MS: m/e 436 (M^+, 10), 249 ($(Et_2N)_2PhSi^+$, 73), 187 ($(Et_2N)_2MeSi^+$, 100). IR (KBr): 2975, 2940, 2860, 1375, 1202, 1175, 1022, 928. Anal. Calc. for $C_{23}H_{48}N_4Si_2$: C, 63.24, H, 11.08. Found: C, 63.14, H, 11.25%.

3.9. 1,1,2,2-Tetrakis(diethylamino)-1,2-dimethyldisilane (5)

This compound was prepared as described in a previous paper [12b]. Additional data. ^{13}C NMR (C_6D_6): δ 1.12, 15.43, 39.83. ^{29}Si NMR (C_6D_6): δ −10.87. MS: m/z 374 (M^+, 5), 187 ($(Et_2N)_2MeSi^+$, 100). IR (neat): 2960, 2925, 2850, 1370, 1200, 1175, 1020, 925 cm^{-1}.

3.10. X-Ray crystal structure analysis of 3

The single crystals were obtained by recrystallization from dichloromethane. Intensity data were collected on Mac Science MXC3 diffractometer using an ω–2θ scan technique, and unique reflections within $3 \le 2\theta \le 130°$ were collected. The structure was solved by the direct method [15] and refined anisotropically by the full-matrix least-squares method. The thermal parameter of each hydrogen atom was assumed to be isotropic and equal to that of the bonded atom [16*]. The crystal data and analytical condition are listed in Table 3 and the final atomic coordinates and isotropic temperature factors in Table 4.

3.11. UV spectra of 3 in solid state

The UV spectrum was measured on a KBr pellet of 3 with no reference and the absorbance was uncorrected. The concentration of the sample was 2.7×10^{-6} mol cm^{-3} and the pellet had a 0.70 mm thickness. KBr (crystal) was purchased from Shimadzu.

Acknowledgements

We are grateful to Professors H. Ogoshi and K. Komatsu for measurement of the UV spectra in solution and in the solid state, respectively. We thank the Ministry of Education, Science, and Culture of Japan for a Grant-in-Aid for Scientific Research on Priority Area Organic Unusual Valency (No. 03233104) and Shin-etsu Chemical Co. for a gift of some chlorosilanes.

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16 Thermal parameters and observed and calculated structure factors are available on request from the authors.

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