σ(Si-Si)-π Intramolecular Charge-Transfer Interaction and
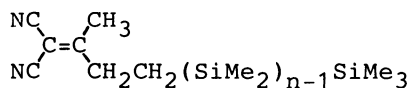X-Ray Structure of 4-Dicyanomethylene-1-silylsilacyclohexanes[1]

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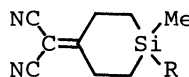Department of Chemistry, Faculty of Science, Tohoku University, Sendai 980
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4-Dicyanomethylene-1-trimethylsilylsilacyclohexane (2a) and
the trisilane analog (2b) showed the intramolecular CT bands in the
absorption spectra. In combination with the results of the X-ray
structure analysis of 2a, the origin of the σ(Si-Si)-π CT interac-
tion was ascribed to the through-bond orbital interaction.

Peralkylpolysilanes have been known to act as electron-donors and to form
charge-transfer (CT) complexes with certain π-acceptors such as TCNE.[2] Recent
efforts directed towards the elucidation of the electronic properties of poly-
silane polymers[3,4] have stimulated us to investigate the intramolecular CT
interaction of bichromophoric systems, 1 (n= 1-5), where permethylpolysilanyl
donors are separated from 1,1-dicyanoethylene acceptor by two methylene groups.
We have actually found the CT bands in the absorption spectra, but the origin of
the intramolecular σ-π CT interaction has remained still inconclusive, whereas we
have referred the through-bond rather favorably than the through-space orbital
interaction.[5] Here, we wish to report synthesis and properties of the new bi-
chromophoric systems, 4-dicyanomethylene-1-trimethylsilylsilacyclohexane (2a) and
the trisilane analog (2b), which have a conformationally rigid alicyclic framework
as a spacer of the two chromophores. The results demonstrate that the through-
bond orbital interaction is operative in the observed intramolecular CT transi-
tion. New polysilane polymers may be expected to be designed by using this
modification of the electronic properties of polysilane chains by introducing
acceptor groups.

$$NC \underset{NC}{\overset{}{>}}C=C \underset{CH_2CH_2(SiMe_2)_{n-1}SiMe_3}{\overset{CH_3}{<}}$$

1

$$NC \underset{NC}{\overset{}{>}}C= \underset{}{\overset{}{<}} Si \underset{R}{\overset{Me}{<}}$$

2a R= SiMe₃, **2b** R= SiMe₂SiMe₃

The compounds, 2 were prepared by the following sequence of reactions. In
situ reaction of a di-Grignard reagent of an acetal 3, prepared from 3-chloro-
propionyl chloride via 1,5-dichloropentane-3-one in 10% yield,[6] with 1,1-difluo-
ropermethylpolysilanes afforded the silacyclohexan-4-ones (4) in very low yields.

No cyclization products were obtained when 1,1-dichlorotetramethyldisilane was used as a dihalopolysilane. The ketones were transformed finally to dicyano-methylenesilacyclohexane, **2**, with a conventional procedure[7] in acceptable yields: **2a**, mp 73-75 °C; ^{1}H NMR (CCl$_4$) δ 0.19 (9H, s), 0.24 (3H, s), 0.99-1.21 (4H, m), and 2.78-3.00 (4H, m); ^{13}C NMR (CDCl$_3$) δ -6.1 (q), -2.2 (q), 12.7 (t), 32.3 (t), 83.6 (s), 111.8 (s), and 188.7 (s); ^{29}Si NMR (CDCl$_3$) δ -22.7 and -20.2; IR 2232 (C≡N) and 1595 (C=C); MS m/z (rel intensity) 248 (M$^+$; 5), 233 (8), 75 (8), and 73 (100). Found: m/z 248.1165. Calcd for C$_{12}$H$_{20}$N$_2$Si$_2$: M, 248.1165. **2b**, mp 50-51 °C; ^{1}H NMR (CCl$_4$) δ 0.17 (9H, s), 0.21 (6H, s), 0.28 (3H, s), 1.11 (4H, t), and 2.58-3.18 (4H, m); ^{13}C NMR (CDCl$_3$) δ -7.0 (q), -5.3 (q), -1.6 (q), 13.4 (t), 32.2 (t), 83.5 (s), 111.7 (s), and 188.6 (s); ^{29}Si NMR (CDCl$_3$) δ -49.7, -19.1, and -15.9; IR 2232 (C≡N) and 1595 (C=C); MS m/z (rel intensity) 306 (M$^+$; 6), 291 (8), 207 (21), 131 (45), and 73 (100). Found: m/z 306.1390. Calcd for C$_{14}$H$_{26}$N$_2$Si$_3$: M, 306.1404.

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1) Mg, F$_2$SiMeR, THF
2) H$^+$

4a R= SiMe$_3$, 8.6%;

4b R= SiMe$_2$SiMe$_3$, 15%.

CH$_2$(CN)$_2$, CH$_3$CO$_2$H, CH$_3$CO$_2$NH$_4$
—————————————————————
C$_6$H$_6$

2

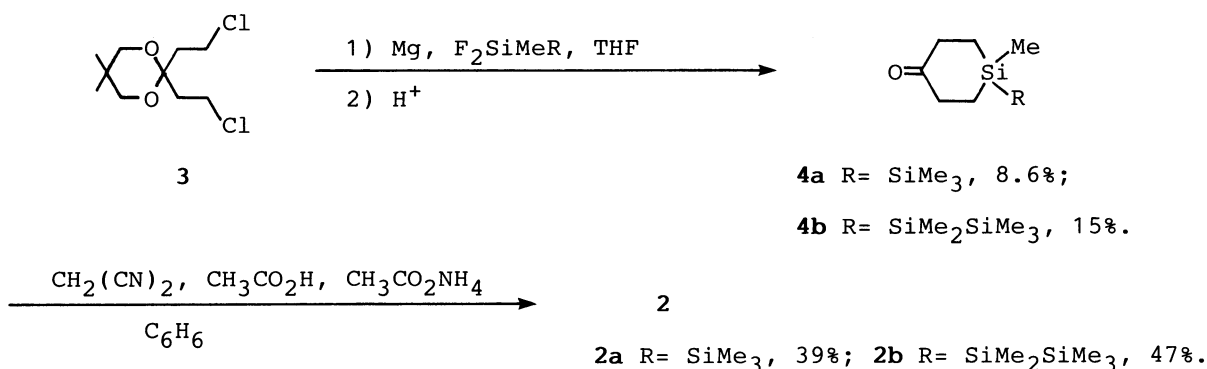**2a** R= SiMe$_3$, 39%; **2b** R= SiMe$_2$SiMe$_3$, 47%.

Figure 1 shows the absorption spectrum of **2b** in hexane and the analyzed three component bands. The two bands with the maxima at 46200 and 42100 cm^{-1} were easily assigned to the intrinsic transition bands of its component chromophores, σ-σ* and π-π* transition bands of octamethyltrisilane and 1,1-dicyanoethylene, respectively:[8] The other band with the maximum at 37300 cm^{-1} was not found in either of the component chromophores and assigned to the intramolecular CT transition from the Si-Si σ to the π* orbital of the acceptor, on the basis of the similarity of the bands with those of the acyclic systems.[5] Analogously, the spectrum of **2a** was analyzed. The band parameters are listed in Table 1 together with those of the corresponding acyclic systems (**1a**, n=2; **1b**, n=3).
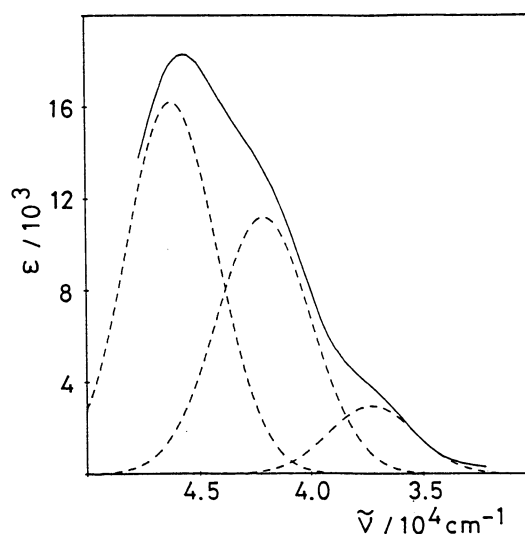
Fig. 1. Absorption spectrum of **2b** in hexane (————) and the bands resolved by assuming the Gaussian line shape (————).

The molecular structure of **2a** determined by X-ray analysis[11] supports the conclusion that the CT transition originates from the CT interaction between Si-Si σ and dicyanoethylene π* orbitals through C-C σ orbitals. The molecular structure of **2a** is illustrated in Fig. 2, together with important bond distances and angles. The conformation in crystalline state was found to be chair form in which the silyl group occupied the equatorial position. As shown in Fig. 2b, the Si(1)-Si(2) σ bond, C(1)-C(2) (and C(4)-C(5)) σ bond, and pπ orbital on C(3) are placed at the most favorable arrangement to the through-bond interaction: the dihedral angles between Si(1)-Si(2) and C(1)-C(2), and between C(1)-C(2) and pπ orbital on C(3) which were 18° and 30°, respectively, allowed the pertinent orbitals to overlap effectively. Whereas the silacyclohexane ring may be rather flexible than the parent cyclohexane ring and thus supposed to fluctuate in solution, the boat conformation required for the through-space interaction should be far less important in **2**.[12] Since the local σ-σ* and π-π* absorption bands did not shift significantly from those of the component chromophores, the through-bond interaction would be too small to change the transition energies but large enough to give the significant intensity to the CT band by intensity-borrowing from the local transitions.[14]

Further insight in the structure of the silacyclohexane was obtained as follows from the X-ray analysis. While the bond distances are rather normal, the bond angles provide interesting structural information. The bond angle C(1)-Si(1)-C(5) was significantly smaller than the tetrahedral angles but the angles Si(1)-C(1)-C(2) and C(1)-C(2)-C(3) were large. The trend is in good agreement with that derived by the force-field calculation,[13] being indicative of the lower force constants involved in bending an angle about silicon.[15]
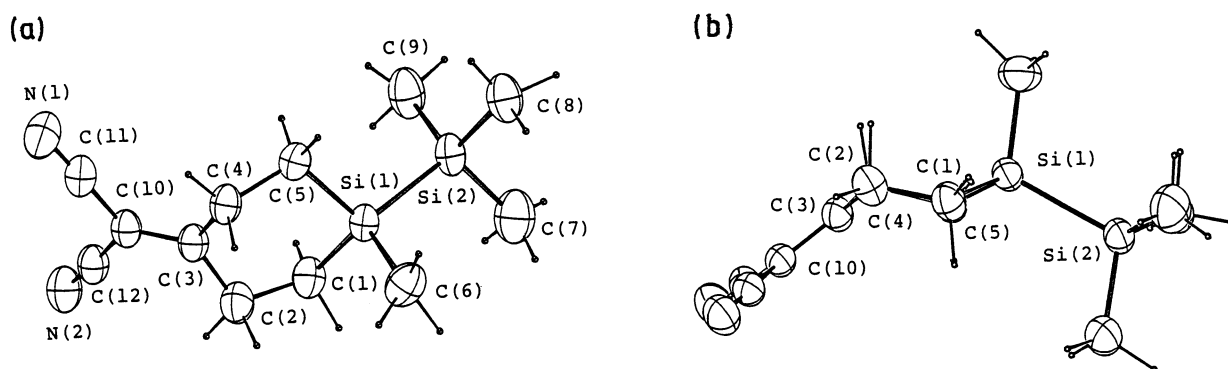

Fig. 2. (a) Molecular structure of **2a** with atom labeling scheme. (b) The side view, in which the axis through C(2) and C(4) is vertical. Selected bond distances (Å): Si(1)-Si(2)= 2.328 (1), Si(1)-C(1)= 1.878 (5), C(1)-C(2)= 1.501 (7), C(2)-C(3)= 1.502 (7), C(3)-C(10)= 1.337 (6), C(10)-C(11)= 1.430 (6), C(11)-N(1)= 1.125 (7). Selected bond angles (deg)· Si(2)-Si(1)-C(6)= 111.9 (1), C(1)-Si(1)-C(5)= 102.4 (2), Si(1)-C(1)-C(2)= 113.8 (3), C(1)-C(2)-C(3)= 114.2 (4), C(2)-C(3)-C(4)= 117.1 (3), C(2)-C(3)-C(10)= 120.7 (4).

Table 1.   Absorption Band Parameters of **1** and **2**

Compound	$\pi \rightarrow \pi^*$		$\sigma \rightarrow \sigma^*$		CT	
	$\tilde{\nu}_{max}/cm^{-1}$	ε	$\tilde{\nu}_{max}/cm^{-1}$	ε	$\tilde{\nu}_{max}/cm^{-1}$	ε
2a	43150	11500	48150	6200	38950	3800
1a[a]	42700	11500	47950	5600	39200	3700
2b	42100	11200	46200	16200	37300	2900
1b[a]	42200	11200	46600	12800	37700	3100

a) The data are taken from Ref. 5.

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8) The maxima of π-π^* band for dicyanomethylenecyclohexane[9] and σ-σ^* bands for hexamethyldisilane[10] and octamethyltrisilane[10] have been observed at 42500 (ε 18200), ca. 50000 ($\varepsilon \simeq 8000$), and 46500 cm^{-1} (ε 9020), respectively.

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11) Crystal data of **2a**, $C_{12}H_{20}N_2Si$ (fw 248.47) are as follows; monoclinic space group P2$_1$/c; a= 15.727(1), b= 8.050(1), c= 12.928(2) Å; β= 109.62(2)°; V= 1541.7(4) Å^3; D_{calcd}= 1.07 g/cm^3 (Z= 4).   A total of 2600 independent reflections were collected on a Rigaku AFC-5R diffractometer using graphite mono-chromated Mo-K$_\alpha$ radiation (crystal size= 0.2 x 0.2 x 0.2 mm^3, μ= 2.041 cm^{-1}). The final R factor was 0.066 (Rw= 0.059) for 2272 reflections with $F_o >$ 3σ(F$_o$).

12) The force-field calculation for 1,1-dimethylsilacyclohexane has shown that the skew-boat conformations are approximately 4.5 kcal/mol higher in energy than the chair conformation.[13]

13) R. J. Ouellette, J. Am. Chem. Soc., 96, 2423 (1974).

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15) More recently, X-ray analysis of a silacyclohexane, an isomer of 1-(p-bromo-phenyl-4-t-butyl-1-methylsilacyclohexane, in which the ring framework is made up of only sp^3 atoms has been achieved by our hands.   The details will be reported elsewhere.