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Electronic Spectra of Cyclotrisilane (Si_3) and Disilene (Si=Si) Frameworks

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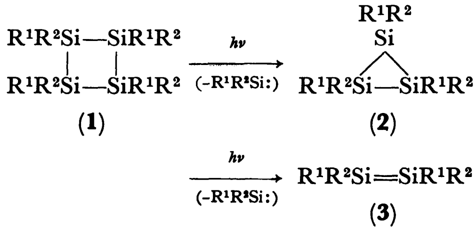
Synopsis. Photolyses of a series of octaalkylcyclotetrasilanes (**1**) in a hydrocarbon solvent successively afforded hexaalkylcyclotrisilanes (**2**) and tetraalkyldisilenes (**3**). Compounds **2** and **3** were found to exhibit their absorption bands corresponding to the lowest energy transitions at λ_{max} 300—330 and 390—440 nm, respectively.

Recently we succeeded to isolate the first peralkylcyclotrisilane, hexaneopentylcyclotrisilane $[(\mathrm{Bu}^t\mathrm{CH}_2)_2\mathrm{Si}]_3$ which gave on photolysis the first peralkyldisilene, tetraneopentyldisilene $(\mathrm{Bu}^t\mathrm{CH}_2)_2\mathrm{Si{=}Si}(\mathrm{CH}_2\mathrm{Bu}^t)_2$.[1,2] It was found that the both Si_3 and Si=Si frameworks behave as chromophores *per se,* showing their longest-wavelength absorption maxima at λ_{max} 310 and 400 nm, respectively. Further, it was also demonstrated in our subsequent work that irradiation of octaisopropylcyclotetrasilane $[\mathrm{Pr}^i_2\mathrm{Si}]_4$ successively yielded hexaisopropylcyclotrisilane $[\mathrm{Pr}^i_2\mathrm{Si}]_3$ (λ_{max} 300—330 and tetraisopropyldisilene $(\mathrm{Pr}^i_2\mathrm{Si{=}SiPr}^i_2)$ (λ_{max} 400 nm).[3] Shortly after our publication,[1] Masamune and coworkers reported that photolysis of 5,6-benzo-2,2,3,3-tetra-*t*-butyl-2,3-disilabicyclo[2.2.2]octa-5,7-diene leads to the formation of tetra-*t*-butyl-disilene $(\mathrm{Bu}^t_2\mathrm{Si{=}SiBu}^t_2)$ (λ_{max} 433 nm),[4] and also that hexakis(1-ethylpropyl)cyclotrisilane $[(\mathrm{Et_2CH})_2\mathrm{Si}]_3$ (λ_{max} 328 nm) undergoes photolysis to furnish the corresponding peralkyldisilene (λ_{max} 390 nm).[5] This note describes a photochemical reaction of peralkylcyclotetrasilanes $[\mathrm{R}^1\mathrm{R}^2\mathrm{Si}]_4$ having various alkyl groups other than isopropyl group in order to observe spectrophotometric properties of cyclotrisilane (Si_3) and disilene (Si=Si) frameworks.



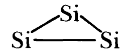
a: $\mathrm{R}^1{=}\mathrm{Bu}^t$, $\mathrm{R}^2{=}\mathrm{Me}$ **b**: $\mathrm{R}^1{=}\mathrm{Bu}^t$, $\mathrm{R}^2{=}\mathrm{Pr}^n$
c: $\mathrm{R}^1{=}\mathrm{R}^2{=}\mathrm{Bu}^s$ **d**: $\mathrm{R}^1{=}\mathrm{R}^2{=}\mathrm{Bu}^i$
e: $\mathrm{R}^1{=}\mathrm{R}^2{=}\mathrm{Me_3SiCH_2}$

Photolyses of peralkylcyclotetrasilanes (**1a**—**1e**) were carried out by using a cyclohexane solution in an evacuated UV cell, as shown previously.[3] In general, upon irradiation (254 nm) at room temperature, the longest-wavelength absorption band (290—310 nm) of a starting cyclotetrasilane diminished rapidly and a new intense band appeared at λ 300—330 nm. The intensity of the band increased and attained the highest value. This band began to diminish and instead a new weak band at λ 390—400 nm appeared. The colorless solution turned to yellow and the new band became more intense. On further irradiation, the both bands completely dissipated and the solution became colorless again, showing an absorption band in a shorter wavelength region (<275 nm). This spectral change during the irradiation was similar to that of octaisopropylcyclotetrasilane.[3] Thus, it is clearly demonstrated that the two absorption maxima at λ 300—330 nm and 390—400 nm regions in the present cases are also due to peralkylcyclotrisilanes $[\mathrm{R}^1\mathrm{R}^2\mathrm{Si}]_3$ (**2a**—**2e**) and peralkyldisilenes $[\mathrm{R}^1\mathrm{R}^2\mathrm{Si{=}SiR}^1\mathrm{R}^2]$ (**3a**—**3e**), respectively. The absorption bands observed for these cyclotrisilanes and disilenes, together with the data reported by Masamune and coworkers,[4,5] are summarized in Table 1.

The absorption wavelength for tetra-*t*-butyldisilene[4] in Table 1 is longer than those for the other disilenes and comparable with those for perarydisilenes (420—440 nm).[6] Masamune *et al.* interpreted this red shift in terms of the molecular geometry for the former disilene and also suggested that the four quaternary carbon atoms of the bulky substituents may not attain coplanality due to steric repulsion.[4]

Our previous observation that peralkylcyclotetrasilanes undergo photolysis to yield successively cyclotrisilanes and disilenes with extrusion of dialkylsilanediyls (eqn) was further confirmed in the present study.

TABLE 1. SPECTRAL BEHAVIORS OF CYCLOTRISILANES AND DISILENES (ABSORPTION BANDS CORRESPONDING TO LOWEST ENERGY TRANSITIONS)

No.	Substituents		Absorption maximum (nm)		
	R^1	R^2		Si=Si	Ref.
1	$\mathrm{Bu}^t\mathrm{CH}_2$	$\mathrm{Bu}^t\mathrm{CH}_2$	310(sh)	400	1)
2	Pr^i	Pr^i	320	400	3)
3	Bu^t	Me	328(sh)	390—400	This work
4	Bu^t	Pr^n	302	390—400	This work
5	Bu^s	Bu^s	323	400	This work
6	Bu^i	Bu^i	303	390—400	This work
7	Bu^t	Bu^t	. .	433	4)
8	$\mathrm{Me_3SiCH_2}$	$\mathrm{Me_3SiCH_2}$	316	400	This work
9	$\mathrm{Et_2CH}$	$\mathrm{Et_2CH}$	328	390	5)

Experimental

Melting points are uncorrected. UV spectra were obtained by using a Hitachi 200-100 spectrometer. IR spectra were recorded on a JASCO A-102 spectrometer. NMR spectra were recorded in $CDCl_3$ at 400 MHz for ^1H NMR and 22.6 MHz for ^{13}C NMR by using a JEOL JNM FX-400FT and a Hitachi R-90H FT spectrometer, respectively. MS spectral analyses were conducted by using a JEOL JMS-07 spectrometer.

Materials. Octaalkylcyclotetrasilanes $[R^1R^2Si]_4$ ($R^1=R^2=Pr^i$;[7] $R^1=R^2=Bu^i$;[7] $R^1=R^2=Bu^s$; $R^1={}^tBu$, $R^2=Me$;[7,8] $R^1=Bu^t$, $R^2=Pr^n$[7]) were prepared by the method described in the literatures.

$[(Me_3SiCH_2)_2Si]_4$: Bis(trimethylsilylmethyl)dichlorosilane $[(Me_3SiCH_2)_2SiCl_2]$ (bp 110—130 °C/55 Torr(1 Torr≈133.322 Pa)) (2.74 g, 10 mmol) and lithium (0.16 g, 23 mg-atom) in THF (20 ml; anhydrous and oxygen-free) was allowed, under Ar, to react with magnetic stirring at room temperature for 3 h, during which time the mixture was dark-brown in color and at the end of this time, the starting chlorosilane was consumed completely (by GLC analyses). After addition of cyclohexane (10 ml), the resulting light-yellow mixture gave on standing a yellow viscous liquid containing crystalline solid. Upon trituration with a small amount of hot ethanol, the crystalline solid was obtained, which was recrystallized from ethanol to give colorless fine needles of octakis(trimethylsilylmethyl)cyclotetrasilane $[(Me_3SiCH_2)_2Si]_4$; 0.25 g (12%), mp 290—301 °C (sealded capillary); UV (cyclohexane), λ_{max} 308 (ε 260), 263 sh (1800), and 223 nm (31000); ^1H NMR ($CDCl_3$) $\delta=0.106$ (s, 16H, CH_2) and 0.094 (s, 72H, CH_3); ^{13}C NMR ($CDCl_3$) $\delta=2.47$ ($\underline{C}H_3$, q) and 1.25 ($\underline{C}H_2$ t); IR (KBr pellet) 2960 s, 2900 m, 1440 m, 1400 w, 1350 w, 1242 vs (SiMe), 1043 sh, 1038 s, 990 w, 845 s, 770 s, 746 s, and 683 m cm^{-1}; MS (23 eV) m/z 810 M^+ (21), 289 (5), 217 (21), 201 $[(Me_3SiCH_2)_2-1]^+$ (100), 145 (19), and 73 $[Me_3Si]^+$ (14). Found; C, 47.87; H, 11.41%. Calcd for $C_{32}H_{88}Si_{12}$: C, 47.45; H, 10.95%.

$[Bu^tPr^nSi]_4$: UV (cyclohexane) λ_{max} 294 (ε 370), 257 sh (2600), and 217 nm (16900).

Photolyses of $[R^1R^2Si]_4$ giving $[R^1R^2Si]_3$ and $R^1R^2Si=SiR^1R^2$. All the photolyses of peralkylcyclotetrasilanes were performed by a similar manner to that for octaisopropylcyclotetrasilane $[Pr^i_2Si]_4$.[3]

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