

[2]Staffane Rod as a Molecular Rack for Unraveling Conformer Properties: Proposed Singlet Excitation Localization Isomerism in *anti,anti,anti*-Hexasilanes

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Received April 3, 1997

Because of the large number and difficult separation of conformers of saturated A_nX_{2n+2} chains longer than $n = 4$,^{1,2} measurements on an individual conformer in solution are rare. Chain conformation may affect its electronic structure, as σ bond delocalization is sensitive^{3–5} to pervalent⁶ interactions, e.g., in polysilanes.⁷ We compare the temperature-dependent photophysics of a permethylated hexasilane (**1**) constrained to the all-*anti* form by racking on a transparent [2]staffane “Tinkertoy”⁸ rod^{9,10} with that of the free chain conformer mixture, Si₆Me₁₄ (**2**). Both show dual fluorescence, assigned to excited state bond-stretch isomerism.

The racked hexasilane **1**¹¹ (Figure 1),¹² obtained from Cl(SiMe₂)₆Cl¹³ and [2]staffane-3,3'-dithiol¹⁰ (Scheme 1, cyclization yield 24%), has an unstrained fully stretched silicon chain [9.79 Å from Si(1) to Si(6)]. The Si–Si bond lengths (2.345–2.355 Å), SiSiSi valence (110.8–113.9°), and SiSiSiSi dihedral angles (162.5, 178.0, 177.4°) meet expectations for the all-*anti* form.⁵ MM2¹⁴ calculations yielded only this low-energy conformation for **1** but many conformations for **2**.

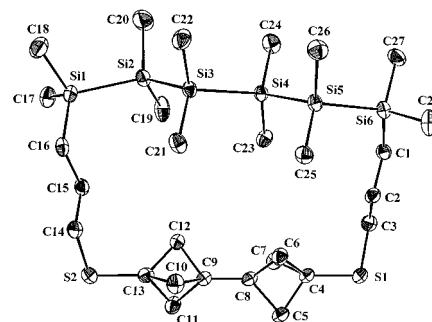


Figure 1. ORTEP plot of **1** in the solid state. The ellipsoids are plotted at the 30% probability level.

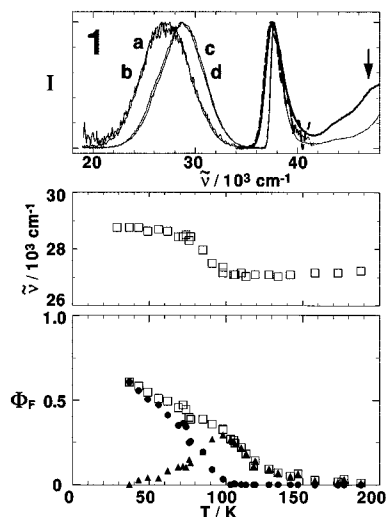
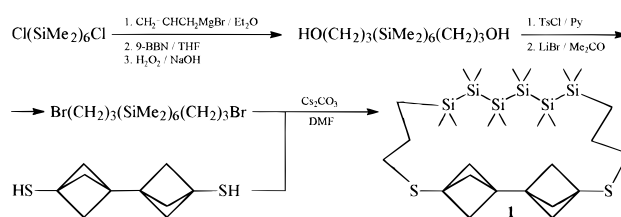


Figure 2. Photophysics of **1** in cyclopentane/isopentane (3/7). Top: normalized spectral shapes of absorption (full line) and excitation (dashed line) at 298 K (a), 110 K (b), 56 K (c), and 37 K (d). The arrow indicates absorption due to the sulfide chromophores.¹⁶ Center: ν_{\max}^{FL} . Bottom: quantum yield as a function of temperature for total fluorescence (□), higher-energy fluorescence (●), and lower-energy fluorescence (▲).

Scheme 1



Comparison of the photophysics of **1** (Figure 2) and **2** (Figure 3) in cyclopentane/isopentane (3/7)¹⁵ solution is instructive: (i) Below ~ 150 K, the absorption, fluorescence, and fluorescence excitation spectra of **2** are almost identical with those of **1**.¹⁶

(12) Crystal data: **1**, monoclinic; $a = 12.747(3)$ Å, $b = 8.055(2)$ Å, $c = 19.401(1)$ Å; $\beta = 90.437(8)^\circ$; space group $P2_1$ (no. 4); $Z = 2$; $\rho_{\text{calc}} = 1.049$ g cm⁻³; 5941 independent reflections in the range $\pm h, \pm k, \pm l$ were collected at 200 K on a CAD4 Enraf-Nonius diffractometer with graphite monochromated Mo K_{α} radiation ($\lambda = 0.71069$ Å); Lorentz and polarization but no absorption correction [$\mu(\text{Mo}) = 3.2/\text{cm}$] were made; 4075 reflections [$I > 2\sigma(I)$] were included in the final full-matrix least squares refinement of 325 parameters converging at $R = 0.052$, $R_w = 0.037$ [$w = 1/\sigma^2(F)$], an error of fit of 2.064, and a residual electron density of ± 0.5 e/Å³. The hydrogen atoms were calculated in idealized positions and not refined. Absolute structure parameter was not refined.

(13) Wojnowski, W.; Hurt, C. J.; West, R. J. *Organomet. Chem.* **1977**, *124*, 271. Middlecamp, C. H.; Wojnowski, W.; West, R. J. *Organomet. Chem.* **1977**, *140*, 133. Schuster, H. G.; Hengge, E. *Monatsh. Chem.* **1983**, *114*, 1305.

(14) Spartan Version 4.0; Wavefunction, Inc., Irvine, CA, 1995.

[†] University of Colorado.

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(1) Eliel, E. L.; Wilen, S. H. *Stereochemistry of Organic Compounds*; Wiley-Interscience: New York, 1994.

(2) Depending on the choice of A and X, there are up to three (g^+ , g^- , a), four (g^+ , g^- , a^+ , a^-), or six (g^+ , g^- , o^+ , o^- , a^+ , a^-) conformational minima for the rotation about each nonterminal backbone bond: Neumann, F.; Teramae, H.; Downing, J.; Michl, J. Submitted for publication.

(3) E.g.: Paddon-Row, M. N.; Jordan, K. D. in *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; p 115. Dewar, M. J. S. in *Modern Models of Bonding and Delocalization*; Liebman, J. F., Greenberg, A., Eds.; VCH: New York, 1988; p 1.

(4) Klingensmith, K. A.; Downing, J. W.; Miller, R. D.; Michl, J. J. *Am. Chem. Soc.* **1986**, *108*, 7438.

(5) Albinsson, B.; Teramae, H.; Downing, J. W.; Michl, J. *Chem. Eur. J.* **1996**, *2*, 529.

(6) I.e., interactions usually called *anti*- and *syn*-periplanar in the extreme limits of 180° and 0° , respectively. Some authors call them vicinal, but we reserve this term for the interaction of two orbitals located at neighboring chain atoms and pointed directly at each other.

(7) Miller, R. D.; Michl, J. *Chem. Rev.* **1989**, *89*, 1359.

(8) Tinkertoy is a trademark of Playskool, Inc., Pawtucket, RI 02862, and designates a children's toy construction set consisting of straight wooden sticks and other elements insertable into spool-like connectors.

(9) Kaszynski, P.; Michl, J. *J. Am. Chem. Soc.* **1988**, *110*, 5225. Michl, J.; Kaszynski, P.; Friedli, A. C.; Murthy, G. S.; Yang, H.-C.; Robinson, R. E.; McMurdie, N. D.; Kim, T. In *Strain and Its Implications in Organic Chemistry*; de Meijere, A., Blechert, S., Eds.; NATO ASI Series, Kluwer Academic Publishers: Dordrecht, The Netherlands, 1989; Vol. 273, p 463.

(10) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601.

(11) Mp 142 °C; ¹H NMR (CDCl₃) δ 2.44 (m, 4H), 1.79 (s, 12H), 1.59 (m, 4H), 0.66 (m, 4H), 0.23 (s, 12H), 0.16 (s, 12H), 0.05 (s, 12H); ¹³C NMR (CDCl₃) δ 54.16, 41.11, 40.82, 36.26, 29.13, 18.87, -2.37, -2.93, -3.64; ²⁹Si NMR (CDCl₃) δ -12.18, -38.82, -42.01; IR (CCL₄) ν_{\max} 2962, 2908, 1403, 1261, 1211, 1097, 1015, 687 cm⁻¹; UV (cyclopentane/isopentane, 3/7) λ_{\max} (ϵ) 267 nm (66 800); EIMS m/z 628 (M^{+2} , 2), 613 ($M - 15$, 8), 407 ($M - 221$, 8), 349 (10), 291 (34), 233 (72), 175 (93), 117 (85), 73 (100), 59 (67); CIMS (CH₄) m/z 629 (MH, 100), 613 ($M - 15$, 45); HRMS m/z (calcd for C₂₈H₆₀S₂Si₆, 628.2752) 628.2742. Anal. Calcd for C₂₈H₆₀S₂Si₆: C, 53.43; H 9.61; S, 10.19. Found: C, 53.33; H, 9.59; S, 10.19.

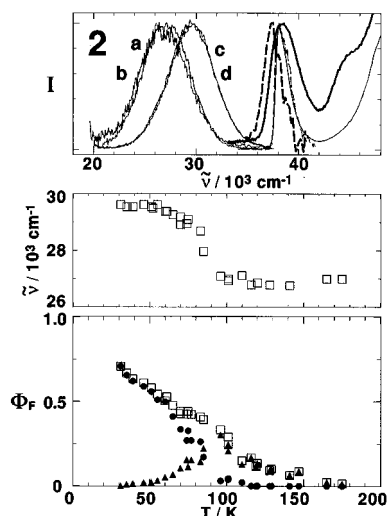


Figure 3. Photophysics of **2**. See caption to Figure 2. Fluorescence at 128 (a), 96 (b), 46 (c), and 31 (d) K.

Absorption and excitation spectra for each species agree exactly and are nearly temperature independent. Above ~ 150 K, all this is still true for **1** and the excitation spectrum of **2** but not for its absorption. The oscillator strength¹⁷ of the first transition is temperature independent for **1** (0.49 and 0.48 at 298 and 77 K, respectively) but not for **2** (0.35 and 0.43, respectively). It is concluded that below ~ 150 K, only the fluorescent all-anti conformer **2aaa** ($\tilde{\nu}_{\max}^{\text{ABS}} = \sim 38\,000\text{ cm}^{-1}$) is present in **2** (in $\text{Si}_4\text{Me}_{10}$, the anti form is also favored at low temperatures⁵). Above, nonfluorescent¹⁸ conformers are present and absorb less strongly in the region of the first transition but more strongly about 7000 cm^{-1} higher.¹⁹

(ii) The fluorescence of **1** and **2aaa** weakens at higher temperature and clearly competes with an activated nonradiative process. This was noted in a previous study of **2**²⁰ and is probably due to thermal excitation from a relaxed geometry of a hole-pair (“zwitterionic”) S_1 state²¹ to a geometry where S_1 is of dot-dot (“covalent”) nature and makes a conical intersection with S_0 , of the type computed for a trisilane.²² The Stokes-shifted emissions of **2aaa** and **1** show dual character: a temperature independent higher-energy emission from **2aaa**** ($\tilde{\nu}_{\max}^{\text{FL}} = 29\,600\text{ cm}^{-1}$) and **1**** ($\tilde{\nu}_{\max}^{\text{FL}} = 28\,800\text{ cm}^{-1}$) is observed up to 40 K and a temperature independent lower-energy emission from **2aaa*** and **1*** (both at $\tilde{\nu}_{\max}^{\text{FL}} = 27\,000\text{ cm}^{-1}$) above 100 K. Between 40 and 100 K, both partly overlapping emissions occur and $\tilde{\nu}_{\max}^{\text{FL}}$ has an intermediate

(15) Nickel, B.; Karbach, H.-J. *Chem. Phys.*, **1990**, *148*, 155.

(16) Except for a weak peak at $47\,000\text{ cm}^{-1}$ in the absorption of **1**, identified as due to the sulfide chromophore by comparison with the spectrum of 3,3'-bis(methylthio)[2]staffane.¹⁰

(17) $f = (4.319 \times 10^{-9}/n) f \epsilon d \tilde{\nu}$; in cm^{-1} ; the solvent refractive index n was measured as 1.367 at 589 nm and converted to 1.413 at 266 nm by assuming the same percent change as reported for cyclohexane at 298 K (Landolt, H.; Börnstein, R. *Landolt-Börnstein Physikalisch-chemische Tabellen*, 4th ed., Springer: Berlin, 1935). The value of n at 77 K and 266 nm was obtained as 1.79 from the 298 K value by measuring the integrated absorption for naphthalene at both temperatures and using the above equation for f , assuming that for naphthalene f is temperature independent.

(18) Perhaps because the lowest transitions of the other conformers have much lower oscillator strength, as is the case for permethylated *gauche*-tetrasilane and for permethylated tetrasilanes constrained to small dihedral angles (Imhof, R.; Teramae, H.; Michl, J. *Chem. Phys. Lett.* **1997**, *270*, 500), or because their intersystem crossing or photodecomposition rate constants are much larger.

(19) These conformers can be trapped from room temperature vapor into argon matrix and cause a series of peaks at higher energies in the absorption spectrum: Plitt, H. S.; Balaji, V.; Michl, J. *Chem. Phys. Lett.* **1993**, *213*, 158.

(20) Sun, Y.-P.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 8186.

(21) This state is believed to have very similar contributions from both zwitterionic structures and little overall polarity, since the fluorescence spectrum in acetonitrile is nearly identical with that in a hydrocarbon solvent.

(22) Venturini, A.; Vreven, T.; Bernardi, F.; Olivucci, M.; Robb, M. A. *Organometallics* **1995**, *14*, 4953.

value. Since emissions from **1** and **2aaa** are nearly identical, vastly different dihedral angles cannot be responsible for the obviously large difference in the equilibrium geometry of the emitting and the ground state. This strengthens the proposal²⁰ that this difference is a massive stretching of an SiSi bond, as suggested by fluorescence polarization²⁰ and calculations^{23,24} (self-trapped localized exciton²⁵). This interpretation naturally attributes multiple emissions to the presence of inequivalent bonds: in **2aaa**** and **1**** one bond is stretched, whereas in **2aaa*** and **1***, another bond is stretched. Small differences in $\tilde{\nu}_{\max}^{\text{FL}}$ between **1** and **2** are assigned to steric constraints in **1** imposing a larger dihedral angle at the stretched bond,²⁴ while the Si chain in **2** can relax completely. The temperature dependence of emission quantum yields is rationalized as due to initial relaxation of the Franck–Condon excited state to **2aaa****, which proceeds to **2aaa*** irreversibly over a small barrier in the potential energy surface (assuming the same S_0 potential energy curves for stretching the two SiSi bonds, **2aaa*** is 2600 cm^{-1} below **2aaa****). Three excited isomers may be present since there are three distinct SiSi bonds, if two of the emissions overlap.

Irradiation at 266 nm in fluid hexane/triethylsilane at 200 K converts **1** into the racked pentasilane²⁶ expected from the usual²⁷ chain abridgement in 27% isolated yield. This indirectly supports the proposed^{22,28} concerted nature of this reaction,²⁹ since a nonconcerted 1,20-biradical intermediate would be unlikely to perform the required $S_{\text{H}}2$ substitution to release dimethylsilylene.

In conclusion, comparison of **2** with **1** allowed us to (i) identify **2aaa** both as its only strongly fluorescent and dominant low-temperature conformer, (ii) eliminate alternatives and tentatively assign dual emission to excited bond-stretch isomers that differ by the location of the excited SiSi bond, and (iii) obtain support for concertedness in the photochemical chain abridgement reaction of peralkylated oligosilanes. It is likely that in other oligosilanes, too, the all-anti conformer is fluorescent and responsible for the intense lowest-energy absorption, as assumed earlier without proof.²³

Acknowledgment. The authors are grateful to the Japan High Polymer Center for support within the framework of the Industrial Science and Technology Frontier Program funded by the New Energy and Industrial Technology Development Organization. Partial support was provided by a grant from the USARO administered jointly with NSF/DMR (DAAH04-94-G-0018).

Supporting Information Available: Details of the crystallographic analysis of **1** (14 pages). See any current masthead page for ordering and Internet access instructions.

JA971059H

(23) Plitt, H. S.; Downing, J. W.; Raymond, M. K.; Balaji, V.; Michl, J. *J. Chem. Soc., Faraday Trans.*, **1994**, *90*, 1653.

(24) A completely optimized CASSCF(6,6)/6-31G** S_1 ($\sigma\sigma^*$) geometry is available for Si_4H_{10} : C_2 symmetry, SiSiSiSi dihedral angle, 105° , central SiSi bond stretched to 2.55 and the terminal ones to 2.44 Å (in S_0 , 2.35 Å). Increasing the dihedral angle to 180° increases the energy by only 4 kcal/mol. Teramae, H.; Michl, J. *Chem. Phys. Lett.* In press.

(25) Thorne, J. R. G.; Williams, S. A.; Hochstrasser, R. M.; Fagan, P. J. *Chem. Phys.* **1991**, *157*, 401.

(26) Mp 127 °C; $^1\text{H NMR}$ (CDCl_3) δ 2.47 (m, 4H), 1.81 (s, 12H), 1.62 (m, 4H), 0.68 (m, 4H), 0.23 (s, 6H), 0.17 (s, 12H), 0.06 (s, 12H); $^{13}\text{C NMR}$ (CDCl_3) δ 54.49, 41.20, 40.76, 36.38, 28.69, 18.46, -2.19, -2.85, -3.72; IR (CCL_4) ν_{\max} 2955, 2910, 2894, 1411, 1262, 1245, 1209, 1096, 1009, 687 cm^{-1} ; UV (cyclopentane/isopentane, 3/7) λ_{\max} (ϵ) 254 (39 100); EIMS m/z 555 ($M - 15$, 12), 429 (100), 412 (80), 349 (52). CIMS (CH_4) m/z 599 ($M + 29$, 23), 571 ($M + 1$, 90), 555 ($M - 15$, 100). Anal. Calcd for $\text{C}_{26}\text{H}_{54}\text{Si}_2$: C, 54.66; H, 9.53. Found: C, 55.02; H, 9.57. Oscillator strength f of the first transition,¹⁶ 0.32 at 298 K, 0.31 at 77 K.

(27) Steinmetz, M. G. *Chem. Rev.* **1995**, *95*, 1527.

(28) Sakurai, H.; Kobayashi, Y.; Nakadaira, Y. *J. Am. Chem. Soc.* **1974**, *96*, 2656. Ramsey, B. G. *J. Organomet. Chem.* **1974**, *67*, C67.

(29) The argument will be stronger if the chain can be abridged further by irradiation at shorter wavelengths, and this is presently under examination. In arylated oligosilanes a triplet state appears more likely to be populated and possibly provides a nonconcerted path.