

Photochemistry of Dianthrylsilanes: A Study of σ, π^* -Interaction[†]

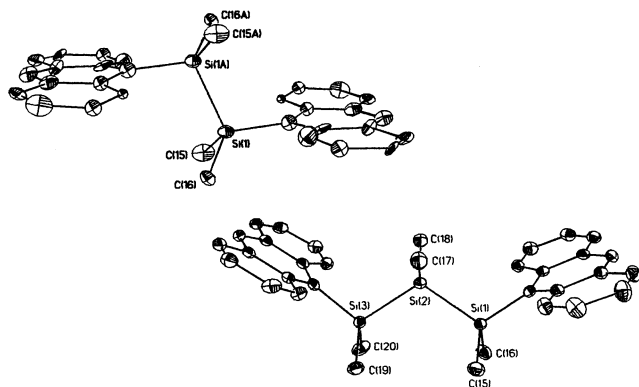
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Abstract: In this article, we demonstrated by the application of time-resolved spectroscopy, X-ray structural analysis and other spectroscopic techniques that 9-Anthrylsilanes exhibits σ, π^* -interaction between 9-anthryl group and the Si–Si linkage in anthryl-disilanes, **ASi₂**, **ASi₂A**, and **ASi₃A** which does not occur in the analogous alkyl derivatives as well as the pyrenylsilane derivatives, in spite of the fact that the 0,0-band of **PSi₂** is about 12.8 KJ more energetic than that of **ASi₂** (Figure 1). More interestingly, the X-ray structural studies reveal that **ASi₃A** exists in a butterfly-like structure in agreement with other spectroscopic analyses that the two anthryl groups do not interact in their excited states, while those in **ASi₂A** do. This is in contrast to the analogous pyrenylsilanes; the trisilanes exhibits a stronger excimer interaction than that of disilane.^{10b} Our results show that the σ, π^* -interactions in **ASi₃A** has imparted rigidity to the tri-silyl linkage. Potential applications of anthrylsilanes in material sciences will be explored.⁵ This work provides evidence that σ, π^* -interaction between the 9-anthryl group and disilyl linkage **does** play an important role in the properties of disilanes. We attribute this enhanced σ, π^* -interaction to the nature of the lowest excited state (S_1 state) of anthracenes, the L_a transition, which has a much higher oscillator strength than the S_1L_b -transition of pyrenes (Figure 1). We define the interaction in anthracene as a $\sigma, \pi^*(S_1L_a)$ interaction. This interaction lends a substantial barrier to the Si–Si bond with the excited anthryl nucleus in anthrylsilanes. The scope and potential applications of this phenomenon are discussed.

Organosilanes and polyorganosilanes often exhibit interesting properties^{2,3} and may have potential applications in material



science.³ In connection with our interest on photoinduced electron transfer,⁴ we synthesized a number of 9-anthrylsilanes including **ASi_n** and **ASi_nA** ($n = 1, 2, \text{ or } 3$),⁵ and studied their photochemistry. We discovered that anthrylsilanes exhibit UV absorptions that closely resemble their alkyl analogues, **AC_n** and **AC_nA**, except for stronger interactions in their fluorescence.

[†] Dedicated to Professor Stuart A. Rice on the occasion of his 70th Birthday.

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These results indicate that there is a σ, π^* -interaction in anthrylsilanes (Figure 1),^{6,7} a phenomenon previously proposed by Sakurai, Shizuka and their co-workers⁸ in their studies of

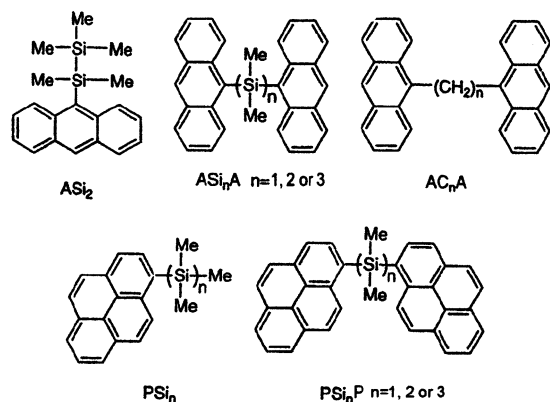
- (1) There are many excellent reviews on organosilane and organopolysilane chemistry, including: (a) West, R. Chapter 4, *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York; 1982, pp 365–398. (b) West, R. Chapter 4, *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: New York; 1995, Chapter 3, Vol. 2, pp 77–110. (c) Armitage, D. A. in 1(a), Chapter 1, p 1–204. (d) Chapter 1 in 1(a), p 1–44. (e) Patai, S., Rappoport, Z., Eds.; *The Chemistry of Organic Silicon Compounds*; John Wiley and Sons: New York, 1989, Vols. 1 and 2.
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- (5) All 9-anthrylsilanes reported in this communication were synthesized using a procedure adapted from the synthesis of 9-trimethylsilylanthracene, R. Harvey and H. Cho. The products were characterized by UV, PMR, and fluorescence spectroscopy.
- (6) This σ, π^* -transition results from the interaction of $\sigma^2(\text{Si}-\text{Si})$ with π, π^* -state of arylsilanes to give an intermediate of singular occupied $\sigma(\text{Si}-\text{Si})$ and π^* and π^2 configuration, prior to its deactivation of (π^* to σ) to the ground state. See ref 8.
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Table 1. Excimer Fluorescence of Anthrylsilanes and Related Compounds

compd	solvent	$\lambda_{\max(0,0)}(\log\epsilon)$	$\gamma_{\max}(\Phi_f)$	τ_f
ASi ₂	hexadecane	396 nm (3.97)	432 nm(0.96)	9.5 ± 0.5ns
hexane		393 nm (3.96)	432 nm(0.55)	6.1 ± 0.1ns
PSi ₂	acetonitrile	394 nm(3.95)	433 nm(0.29)	not determined
AC ₂ H ₅	alkanes	376 nm(2.50)	378 nm(0.75)	282ns ¹⁰
ASi ₂ A	hexadecane	393 nm(3.85)	414 nm(0.30)	5.1ns ¹³
	hexadecane	398 nm(4.28), 428 nm(0.03), 526 nm 32ps,	526 nm (0.12)	152ps
PSi ₂ P	alkanes	378 nm(2.7)	438 nm(0.45)	58.7ns
PSi ₃ P	alkanes	378 nm(2.7)	483 nm(0.44)	2.1,50,118.2ns ¹⁰
ACH ₂ CH ₂ A	alkanes	392 nm(4.14)	420 nm(0.22,0.10)	0.9,2.8ns ¹³
A(CH ₂) ₃ A*	alkanes ¹³	392 nm(4.4)	photodimeriation	
ASi ₃ A	hexadecane	398 nm(4.4)	434 nm(0.20 ± 0.02)	1.80ns

Legends: λ_{\max} absorption maxima; γ_{\max} ; fluorescence maxima; Φ_f , quantum yield of fluorescence; τ_f lifetime of fluorescence; τ_f/Φ_f radiative lifetime of fluorescence. *The values are for anthryl monomer.

phenylsilanes. Because of the high energy level of excited phenyl and naphthyl groups, >80 kcal/mol,⁸ and the fragility of Si–Si bonds, ca. 80 kcal/mol,^{2a} many simple phenyl- and naphthyl-silanes undergo different modes of photocleavages,³ which complicate the study of their σ,π^* -interactions. DeSchryver, Miller, and their co-workers carried out pioneering studies on the photochemistry of 1-pyrenylsilanes.^{9b} Because of their low rotational barrier¹¹ and the longer length of Si–Si bond, 3.24 Å, both 1,2-bis-[1-pyrenyl]disilane and its 1,3-homolog, **PSi₂P** and **PSi₃P** exhibit an excimer fluorescence, that of **P*Si₂P** at 438 nm vs. that of **P*Si₃P** at 483 nm (Table), because of the better π,π overlap in **P*Si₃P**.



This work provides evidence that σ,π^* -interaction between the 9-anthryl group and disilyl linkage plays an important role in the properties of anthryldisilanes although the 0,0-band of **PSi₂** is about 12.8 KJ more energetic than that of **ASi₂** (Figure 2). We attribute the enhanced intrachromophoric interaction between the Si–Si (σ -orbital) and π -orbitals of the anthryl group to the nature of the lowest excited state (**S₁L_a**) of anthracenes

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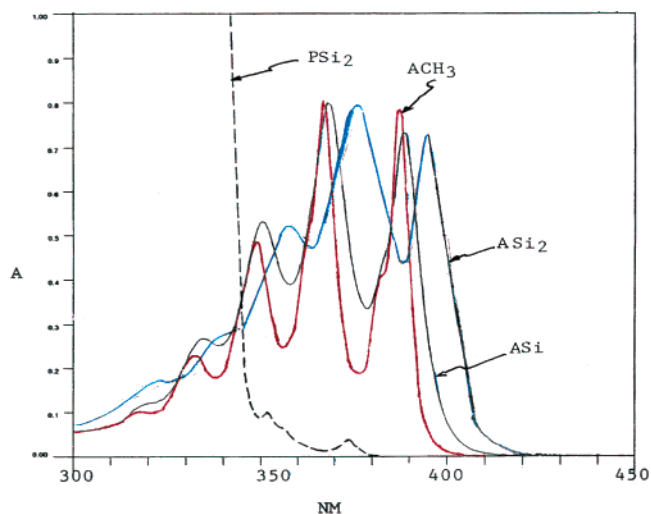


Figure 1. Absorption spectra for anthryl silanes. For comparison with anthryldisilanes, we also synthesized **ASi₂A** and **Si₃A** and studied their properties.

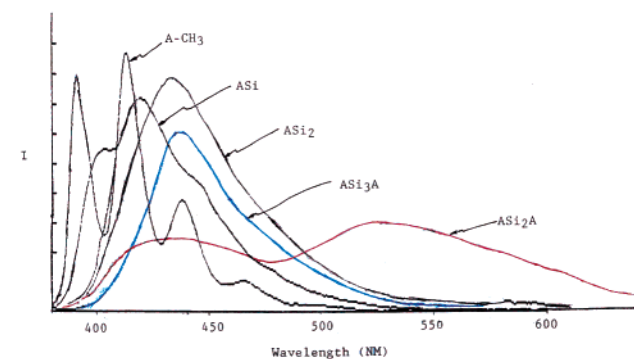


Figure 2. Fluorescence of Anthrylsilanes, the intensities are not to scale.

($\log \epsilon_{0,0} \approx 4$),⁹ which has a considerably higher oscillator strength than the **S₁L_b** state of pyrenes ($\log \epsilon_{0,0} \approx 2.5$).⁹ The $\sigma,\pi^*(S_1L_a)$ interaction is an interaction along the A–Si–Si–bonds rather than the **through-space stacked** σ,π^* -interaction in hexasilyl silane, **P Si₆**.^{9a} We found very close resemblance in the UV-absorptions of **ASi** relative to those of alkyanthracenes, **ACH₂CH₃**, which exhibit vibrational fine structures, but those in **ASi₂** are broadened. The stronger interaction in **ASi₂** than that in **ASi** suggests that the σ -orbitals of a Si–Si bond are essential for the σ,π^* -interaction.

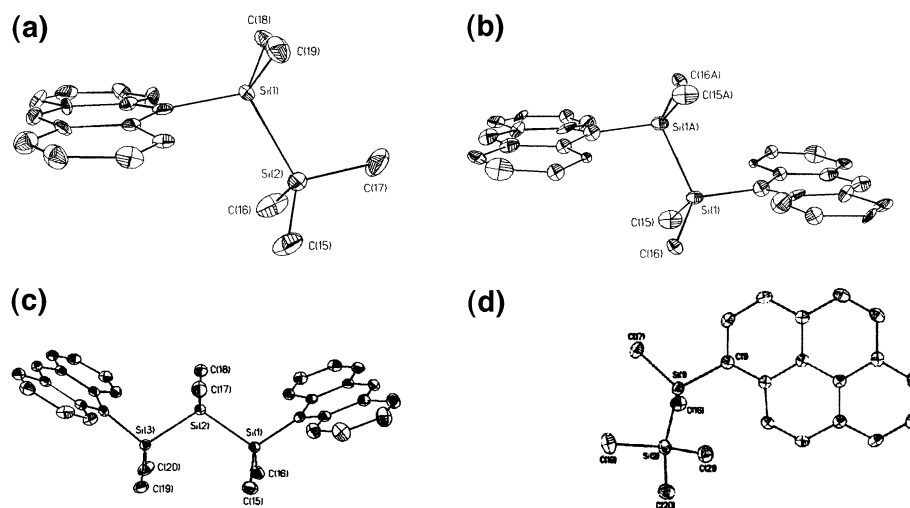


Figure 3. ORTEP representations of (a) **ASi₂**, (b) **ASi₂A**, (c) **ASi₃A**, and (d) **PSi₂**.

Fluorescence of ASi₂. 9-Anthryldisilane exhibits a broad featureless fluorescence, λ_{\max} at 432 nm, which is appreciably red-shifted from those of alkyanthracenes by 2230 cm^{-1} (0,0 to max). The fluorescence of alkyanthracenes exhibits a mirror image relationship with the absorption, both with vibrational fine structures. Our results indicate there is a σ, π^* -interaction in anthrylsilanes. The λ_{\max} , Φ , and τ of fluorescence of **ASi₂** are not apparently dependent on solvent polarity, but there is a minor dependence on solvent viscosity, which has been noted previously in the fluorescence of alkyanthracenes.¹² We assign the fluorescence of **ASi₂** at $432 \pm 1\text{ nm}$ with a radiative lifetime, τ_f/Φ_f , of 10 ns to the emission of **ASi₂** from its σ, π^* -interaction.

Because the σ, π^* -interaction may take place between the **Si-Si** linkage with both anthryl groups in **ASi₂A** and amplifies it, we synthesized both **ASi₂A** and **ASi₃A** and studied their properties. We found **ASi₂A** to be highly light and heat sensitive, mp 280° (dec), vs 98° for **ASi₂**, and it decomposes by light to a plethora of products. **ASi₂A** exhibits a dual fluorescence maxima in hexadecane (Figure 2), a major one at 526 nm, $\Phi = 0.12$; $\tau = 150\text{ ps}$ ($65 \pm 2\%$), and a minor one at 430 nm [$\Phi = 0.03$; $\tau = 32 \pm 2\text{ ps}$ (33%)]. The second anthryl group caused a large red shift in fluorescence, $>6000\text{ cm}^{-1}$ from that of **ASi₂**. Due to its sensitivities and broadness of its emissions, we were unable to resolve the origin and mutual relationship of its dual emission, nor were we able to make a detailed product analysis. Surprisingly, **ASi₃A** is a photostable solid, mp 183° . It exhibits a λ_{\max} at $396 \pm 1\text{ nm}$, and a single fluorescence maximum, λ_{\max} at 434 nm ($\Phi = 0.19 \pm 0.02$, $\tau = 1.83\text{ ns}$), results which are not very different from those of **ASi₂**, indicating that **ASi₃A** exists as a single fluorescent conformer in solution containing two noninteracting **ASi₂**-like groups. The two anthryl groups in **ASi₃A** linked by a tri-silyl linkage fail to form the traditional face-to-face excimer, clearly an anomaly among acyclic diaryls linked by three atoms.

X-ray Structures of Anthrylsilanes. The ORTEP representations of X-ray structures of anthrylsilanes and of **PSi₂** are given in Figure 3. The **Si-Si** bond angles in anthrylsilanes is $\sim 179.1^\circ$, but that in **PSi₂** is $\sim 78^\circ$. Thus, the X-ray structure, absorption, and fluorescence, are all in agreement that there is a σ, π^* -interaction in anthryldisilanes. The lack of “classical” excimer emission from **ASi₃A** is not caused by its chemical

reactivity. When samples of **ASi₃A** and of **ASi₂** in cyclohexane-*d*₁₂ were irradiated simultaneously with the same light source, there was no change in the **PMR** of **ASi₃A** when 20% of **ASi₂** was consumed. We estimated the Φ_{dec} of **ASi₃A** to be <0.02 . X-ray crystallography supports that there is a σ, π^* -interaction between each anthryl group with the **Si-Si** linkage shown in Figure 3c. This interaction also provides an activation energy barrier in the conformational flexibility of the **A-(SiMe₂)₃-A** chain in crystals as it is in solution, resulting in the butterfly-like structure, a phenomenon unknown previously in acyclic bichromophores.

Photochemistry of Anthrylsilanes. **ASi₂** photodimerizes with a Φ of 0.25 ± 0.05 in alkanes ($0.001\text{--}0.003\text{ M}$),¹³ but it photolyzes in dilute solutions ($2 \times 10^{-5}\text{ M}$ or $1\text{ mg}/180\text{ mL}$) to a mixture of products containing some unknown isomeric dihydroanthrylsilanes and other products. The threshold of **Si-Si** photocleavage is thus lowered from $<300\text{ nm}$ in silanes to 400 nm in anthrylsilanes.¹⁴

Conclusion. Photoexcited anthryldisilanes exhibit some unique interactions between the $\sigma(\text{Si-Si})$ and $\pi(\text{anthryl})^*$ groups. These interactions are absent in related pyrenyldisilanes despite its **S₁-L_b** state being more energetic by 12 KJ than the **S₁L_a** state of anthracene. The nature of low-lying **S₁** state of the aryl group, **L_a**, thus plays a significant role in σ, π^* -interaction.^{9,14} This interaction causes anthryldisilanes to exhibit novel photophysical properties e.g., the rigidity of **Si-Si** linkages in **ASi₃A**, and lowers the threshold of cleavage of **Si-Si** linkage from $<300\text{ nm}$ in silanes to 400 nm in anthrylsilanes.¹⁴

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their future work with undergraduates at the University of Chicago. They also wish to thank Ms. Lorraine Brochu for her assistance in the preparation of this manuscript. Y.Z.M. and G.R.F. wish to thank the NSF for the support at the University of California.

Supporting Information Available: Time resolved fluorescence spectroscopic information. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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