bond angles in **7**, **8**, **10**, and **2** (Tables S7 and S8), side chain bond lengths and bond angles in **7**, **8**, **10**, and **2** (Tables S9 and S10), and solvent–solvent interactions in **7** and **8** (Table S11) and stereodiagrams of the extended unit cell packing in **8**, **10**, and **2** (Figures S1, S2, and S3) (12 pages); listing of observed and calculated structure factors for **7** (Table S1) and **8** (Table S2) (59 pages). Ordering information is given on any current masthead page.

σ,π^* Charge-Transfer Excited States of Substituted (Phenylethynyl)pentamethyldisilanes

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Abstract: A series of substituted (arylethynyl)pentamethyldisilanes was prepared by the palladium(0)-catalyzed coupling of aryl halides and ethynylpentamethyldisilane. The absorption and emission spectra of these acetylenic disilanes were measured over the temperature range from 296 to 77 K in both polar and nonpolar solvents and rigid organic glasses. At 77 K normal $^1(\pi,\pi^*)$ fluorescence and $^3(\pi,\pi^*)$ phosphorescence are observed for those (phenylethynyl)pentamethyldisilanes (**1**) bearing electron-donating substituents (e.g. 4-MeO). At 77 K those (phenylethynyl)pentamethyldisilanes bearing electron-withdrawing substituents (e.g. 4-NC, 4-CO_2Me) show only a unique intramolecular $^1(\sigma,\pi^*)$ charge-transfer (CT) fluorescence in addition to the $^3(\pi,\pi^*)$ state phosphorescence. Neither ground-state CT complex absorption bands nor exciplex emissions were observed in any of the systems studied. The singlet character of these emissive σ,π^* CT states was confirmed by picosecond lifetime measurements. The previously reported photochemical rearrangement of (phenylethynyl)pentamethyldisilanes to silacyclopropenes and silapropadienes as well as the observed photochemical cleavage of (phenylethynyl)pentamethyldisilanes to (phenylethynyl)trimethylsilanes are fully consistent with the σ,π^* CT state assignment. The general involvement of analogous $\sigma \rightarrow \pi^*$ CT or electron transfer in photoexcited polysilanes is suggested by the demonstration of intermolecular fluorescence quenching of electron-deficient benzenes and aryl acetylenes by hexamethyldisilane and dodecamethylcyclohexasilane. The general implications of this type of $\sigma \rightarrow \pi^*$ CT to polysilane photophysics and photochemistry are discussed.

Subsequent to the early reports that the photolysis of alkynyl-substituted disilane derivatives provides a convenient route to silacyclopropene derivatives,[1] photochemical[2] and photophysical[3] investigations have shown that these compounds possess unique singlet intramolecular CT emissive states which dominate their photoreactivities. In the case of (phenylethynyl)pentamethyldisilane (**1a** Y = H, n = 1), the emission spectrum at 77 K in methylcyclohexane/isopentane (MP) was reported to show a normal $^1(\pi,\pi^*)$ fluorescence at 303 nm and a normal $^3(\pi,\pi^*)$ phosphorescence at 410.5 nm. However in addition to these two bands, a third broad, featureless emission band was observed with λ_{max} at 395 nm. This latter emission band was assigned to either a $^1(2p\pi,3d\pi)$ or a $^1(2p\pi,\sigma^*)$ CT state. This band was proposed to originate from a $2p\pi^*$ (aromatic ring) to vacant $3d\pi$ (Si–Si bond) intramolecular charge transfer. The state assignment was based both on the broad, featureless structure of the emission (indicative of a CT state) and by analogy with the broad emission features of photoexcited aryldisilanes which had previously been assigned as singlet $^1(2p\pi,3d\pi)$ CT excited states.[4]

Recent picosecond spectroscopic investigations[5] of alkyl-substituted (phenylethynyl)pentamethyldisilanes have shown that the formation of these CT states occurs very rapidly (<10 ps) both at 77 K and 294 K. It was thus proposed that internal rotation about the acetylene sp hybrid C–Si σ bond is not a prerequisite for formation of the CT states in these molecules and that they are different than other twisted intramolecular charge transfer (TICT) states previously investigated. The rapid formation of these states in rigid organic matrices at 77 K also indicated that solvation changes are not important in the formation of these CT states. On the basis of these spectroscopic investigations, Shizuka and Ishikawa[4] postulated that facile intramolecular CT state formation occurs only in those molecules found in a conformation which places the Si–Si σ bond in the same plane as the phenyl ring. This conformation, it was argued, is the most favorable for $3d\pi$ to $2p\pi$ overlap. Those molecules in the conformation with the Si–Si σ bond out of the plane defined by the phenyl ring would instead only provide efficient overlap of the aromatic π orbitals with the Si–Si σ orbitals.

The decay of the fluorescence of these singlet CT states was reported to have both a fast- and a slow-decay component. For example, (phenylethynyl)pentamethyldisilane (**1a**) showed two

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decay components with τ = 320 ps and 5.8 ns at 77 K in a MP glass and τ = 20 ps and 120 ps at 294 K in MP. The origin of the two decay components was ascribed to a variation in the rate of intersystem crossing from the singlet CT state to the $^3(\pi,\pi^*)$ state depending on the conformational orientation of the disilane. Those excited states existing in the conformation twisted slightly from planar ("planarlike") were postulated to decay rapidly by intersystem crossing while those in a pure planar conformation showed a slower intersystem-crossing rate and decayed more extensively by fluorescent and radiationless deactivation pathways. Evidence for the enhancement of intersystem crossing by internal rotation or twisting was reported to include the increase in both the fast- and slow-decay rates on passing through the melting point of the MP matrix and the decrease of the ratio of the slow component of decay to that of the fast component with increasing temperature. In fluid solution at room temperature, the quantum yields for photochemical reaction were high (0.48–0.65) with the primary product being the corresponding silacyclopropene.

Recently we reported the facile synthesis of substituted (phenylethynyl)pentamethyldisilanes by the palladium(0)-catalyzed reaction of substituted aryl halides and ethynylpentamethyldisilane.[6] This methodology has allowed the facile preparation of a series of (phenylethynyl)pentamethyldisilanes having both electron-withdrawing and electron-donating substituents in multigram quantities with high purity. Previous synthetic methodologies only allowed for the preparation of derivatives of (phenylethynyl)pentamethyldisilanes bearing alkyl or other electron-donating substituents. Our initial spectroscopic investigations of these new acetylenic disilanes strongly indicated that the assignment of the CT states as $^1(2p\pi,3d\pi)$ or $^1(2p\pi,\sigma^*)$ states was incorrect and that these states are best described as $^1(\sigma,\pi^*)$ states generated by charge transfer from the Si–Si σ-bonding orbital to the localized $^1(\pi,\pi^*)$ state of the aromatic moiety. We now report our spectroscopic investigations of these new derivatives which corroborate our $^1(\sigma,\pi^*)$ CT state assignment and demonstrate that similar $\sigma \rightarrow \pi^*$ electron-transfer processes occur intermolecularly between excited singlet state aryl acetylenes and various polysilanes. The possible involvement of $^1(\sigma,\pi^*)$ states in the photochemical reactions of aromatic polysilanes and polymeric polysilanes is also discussed.

Experimental Section

General Procedures. Hexamethyldisilane (Petrarch) was purified by elution through a column of activated silica gel (100–200 mesh, Aldrich). Dodecamethylcyclohexasilane was prepared by the method of West and Carberry.[7] The crude dodecamethylcyclohexasilane was recrystallized from ethanol and then vacuum sublimed twice prior to use in the Stern–Volmer quenching experiments. Chloropentamethyldisilane and 1,2-dichlorotetramethyldisilane were prepared by the procedure of Kumada et al.[8] (**Caution!** Several violent exotherms occurred during the distillation of samples of chloropentamethyldisilane. These resulted in rapid temperature increases to greater than 220 °C in the distillation head.) Ethynylpentamethyldisilane[9] was prepared by the reaction of ethynylmagnesium bromide and chloropentamethyldisilane according to the procedure reported for ethynyltrimethylsilane.[10] 1,2-Diethynyltetramethyldisilane[11] was prepared by the reaction of ethynylmagnesium bromide with 1,2-dichlorotetramethyldisilane. (2-Naphthyl)(trimethylsilyl)acetylene (**2**), (2-naphthyl)acetylene (**3**), (4-cyanophenyl)acetylene (**4**) and (4-cyanophenyl)(trimethylsilyl)acetylene (**5**) were prepared according to the procedures given by Hagihara et al.[12] Isooctane, isopentane, and acetonitrile were Aldrich spectrophotometric gold-label materials and were used without further purification. Aldrich spectrophotometric gold-label 2-methyltetrahydrofuran was distilled prior to use to remove the inhibitor. Bis(triphenylphosphine)palladium(II) chloride, phenylacetylene (**6**), and all solvents and aromatic halides used for the synthesis of the substituted (phenylethynyl)pentamethyldisilanes were purchased from Aldrich and used as received.

Instrumentation and Procedures. NMR spectral data were obtained with a Varian Associates XL200 200-MHz spectrometer. ^{1}H and ^{29}Si chemical shifts are reported relative to internal TMS in deuteriochloroform and all ^{13}C chemical shifts are referenced to deuteriochloroform. Electron impact mass spectral data (70 eV) were obtained with a Finnigan Model 3300 instrument using direct probe sample introduction. Elemental analyses were obtained from Galbraith Laboratories, Inc., Knoxville, TN. DSC data were measured with a DuPont Model 910 Differential Scanning Calorimeter with a 9900 Computer Thermal Analyzer. Heating rates for the DSC scans were maintained at 10 °C/min. The samples were in the range of 5–10 mg and were maintained under a nitrogen atmosphere during the scan. Viscosity measurements on the EPA (ethanol/isopentane/ether (2:5:5)) and isopentane matrices as a function of temperature were measured with a Rheodynamics Nametre Direct Readout Viscometer. The matrices were solidified around the oscillating ball with a liquid-nitrogen bath and then allowed to warm to room temperature. The temperature was measured with a thermocouple inserted directly into the matrix adjacent to the oscillating ball. Infrared spectra were obtained with a Perkin-Elmer Model 983 infrared spectrophotometer. Absorption spectra were measured with a Perkin-Elmer Model 320 UV–vis spectrophotometer interfaced to a Model 3600 data station. Fluorescence emission and excitation spectra were recorded on a Perkin-Elmer 650-40 fluorescence spectrophotometer in 1-cm fluorescence cells. The emission and excitation band-pass were less than 3 nm except in the measurement of the CT emission of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at concentrations below 1×10^{-5} M. For these low-concentration spectra the emission band-pass was kept at 2 nm while the excitation band-pass was increased to 6 nm in order to maintain the signal to noise ratio. The samples were not degassed prior to the emission measurements unless otherwise indicated. The intermolecular fluorescence quenching data were obtained by monitoring the fluorescence from the substituted phenyl- and naphthylacetylenes at their emission maxima for a series of concentrations of added quencher (hexamethyldisilane or dodecamethylcyclohexasilane) and were analyzed by means of the Stern–Volmer equation. The concentrations of the aromatic acetylenes were maintained between 1×10^{-5} and 1×10^{-4} M for these quenching experiments. Low-temperature absorption and emission data were obtained with a quartz fluorescence dewar cooled with nitrogen passed through a liquid-nitrogen bath. The temperature was maintained constant to within ± 2 K by controlling the rate of flow of cold nitrogen through the dewar. The samples were contained in Spectrosil or Suprasil quartz cuvettes (ca. 7-mm path length) which have long stems for introduction of the sample and for degassing of the sample.

Synthesis of Substituted (Phenylethynyl)pentamethyldisilanes (1). The substituted (phenylethynyl)pentamethyldisilanes were prepared according to the procedure of Horn et al.[6] and purified by chromatography on silica gel (100–200 mesh, Aldrich) followed by recrystallization from ethanol. All spectroscopic data were consistent with those previously reported.

Synthesis of 1,2-Bis(phenylethynyl)tetramethyldisilane (7). Bis(triphenylphosphine)palladium(II) chloride (100 mg, 0.14 mmol) and cuprous iodide (10 mg, 0.05 mmol) were added to a solution of iodobenzene (1.88 g, 9.2 mmol) and 1,2-diethynyltetramethyldisilane (0.75 g, 4.5 mmol) in 25 mL of diethylamine under a nitrogen atmosphere. The reaction was stirred at 23 °C for 3 days and then concentrated in vacuo and chromatographed on silica gel (eluant: hexanes followed by 2% ether/hexanes). Two high R_f impurities, (phenylethynyl)pentamethyldisilane (**1a**) and biphenyl, were isolated. These were followed by 1,2-bis(phenylethynyl)tetramethyldisilane (**7**) (1.03 g, 3.2 mmol, 72%). Recrystallization from ethanol gave clear crystals, mp 78.0–79.5 °C. ^{1}H NMR δ (ppm): 7.42–7.19 (m, 10 H), 0.33 (s, 12 H). ^{13}C NMR δ (ppm): 131.92, 128.43, 128.19, 123.50, 107.79, 92.07, −2.90. ^{29}Si NMR δ (ppm): −36.84. IR (cm^{-1}), KBr: 2980 (m), 2160 (s), 1490 (s), 1440 (s), 1240 (s), 1220 (s), 1030 (w), 840 (s), 820 (s), 795 (s). MS CI, methane (*m/e*): 319 (MH$^+$), 318 (M$^+$), 303 (M$^+$ − CH$_4$), 245, 217, 159, 129. Anal. Found: C, 74.99. H, 7.27. $C_{20}H_{22}Si_2$ Calcd: C, 75.41. H, 6.96%.

EPR Spectra of the Phosphorescent Triplet State of Phenylacetylene (6) and the Substituted (Phenylethynyl)pentamethyldisilanes and (Phenylethynyl)trimethylsilanes. EPR data were obtained with a Varian Associates Model E-112 X-band spectrometer equipped with an E102 microwave bridge and a modified microwave cavity having a series of louvres on one side for sample irradiation. The sample irradiation was carried out with the broad-band UV light from a PTI Model A1000 75-W xenon-arc lamp. Spectra were obtained on samples prepared in isopentane at 77 K with concentrations in the range of 1.3×10^{-4} to 2.5×10^{-3} M. The samples were not degassed prior to irradiation. A

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representative experimental procedure for [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) follows. A 2.5 × 10^{-3} M solution of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) was prepared in isopentane in a 4-mm quartz sample tube and placed in a partially silvered dewar in the microwave cavity. The sample was cooled to 77 K and irradiated at a distance of approximately 13 in. from the PTI A1000 xenon arc lamp housing window. The spectrum was scanned from 1200 to 1600 G at 9.23 GHz while the sample was being irradiated. The arc lamp was then removed and the 1200–1600-G region was scanned again.

Fluorescence Lifetimes and Anisotropy Decays. The fluorescence lifetimes and anisotropy decays of the substituted (phenylethynyl)pentamethyldisilanes in isooctane and isopentane were obtained with a time-correlated single-photon-counting apparatus using a mode-locked argon ion laser synchronously pumped dye laser which was cavity dumped at 4 MHz. The fluorescence was monitored with an apertured JY 0.64-m monochromator. Typical instrument functions were 50 ps with the 12-μm channel plate PMT (Hammamatsu R16454-07). Data were collected with a multichannel analyzer interfaced to an IBM PC. Fluorescence data were fitted to a model of three-component exponential decay by minimizing residuals from a convolution of the instrument function with the decay model by using an interative procedure. Fluorescence decays were recorded at the magic angle. Anisotropy measurements were determined by alternately recording fluorescence decays of emission polarized parallel to and perpendicular to the incident laser light, with a computer-controlled emission polarizer. As a result of studies on test molecules having known lifetimes and picosecond time scale anisotropies, we estimate that fluorescence decays of 10–15 ps and anisotropy decays of 10–15 ps can be measured. Samples of the (phenylethynyl)pentamethyldisilanes with concentrations in the range of 1 × 10^{-5} to 1 × 10^{-4} M were prepared in isooctane, isopentane, or EPA in Suprasil quartz fluorescence cuvettes. The excitation wavelength was 282 nm. The emission was monitored at 310 nm for those samples showing localized $^1(\pi,\pi^*)$ state emissions and at 380 nm for those showing CT emissions. At 77 K static samples were used, but at 298 K where extensive photochemistry occurs to give fluorescent products (the corresponding monosilanes, vide infra) flowing samples were used. Distinct differences in the fluorescence decays were obtained for the static and flowing samples. The per pulse energy used in these experiments was 1 nJ (power = 2 mW).

The fluorescence lifetime of (2-naphthyl)acetylene (**3**) was measured with an excimer laser flash photolysis apparatus described in detail previously.[13]

Results

Synthesis of (Arylethynyl)pentamethyldisilanes. Methodology for the synthesis of (arylethynyl)pentamethyldisilanes has previously been limited to the reaction of alkali or magnesium acetylides with polysilanyl mono- or dichlorides.[14] Thus severe restrictions are placed on the functional groups which may be incorporated in the aromatic moieties used. In particular, nitrile, carbomethoxy, nitro, and keto functionalized (phenylethynyl)polysilanes cannot be synthesized by this route. Recently we reported[6] that good to excellent yields of substituted (phenylethynyl)pentamethyldisilanes can be obtained by the reaction of iodo- or bromobenzenes with ethynylpentamethyldisilane in the presence of catalytic amounts of bis(triphenylphosphine)palladium(II) chloride/cuprous iodide (eq 1).

$$\underset{X\,=\,\mathrm{Cl,\ Br,\ I}}{\mathrm{YArX}} + \mathrm{HC{\equiv}C(Si(CH_3)_2)_nSi(CH_3)_3} \xrightarrow[\mathrm{Et_2NH}]{\mathrm{CuI,\ (Ph_3P)_2PdCl_2}}$$

$$\mathrm{YArC{\equiv}C(Si(CH_3)_2)_nSi(CH_3)_3} \quad (1)$$

1a: Y = H, n = 1
1b: Y = 4-NC, n = 1
1c: Y = 4-MeO, n = 1
1d: Y = 4-MeO_2C, n = 1
1e: Y = 4-Ph, n = 1
1f: Y = 4-Cl, n = 1
1g: Y = 3-NC, n = 1
1h: Y = 4-NO_2, n = 1

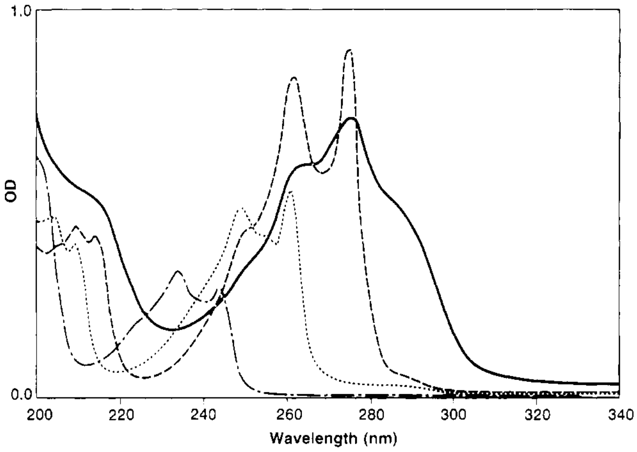

Figure 1. Absorption spectra of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) and reference compounds at 298 K in isooctane: [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**), [1.08 × 10^{-5} M], —; [(4-cyanophenyl)ethynyl]trimethylsilane (**5**), [1.01 × 10^{-5} M], – –; (4-cyanophenyl)acetylene (**4**), [9.67 × 10^{-6} M], - -; phenylacetylene (**6**), [9.79 × 10^{-6} M], - - -.

A wide range of halobenzenes can be used in this reaction and high yields are realized with either electron-donating substituents or electron-withdrawing substituents (compare e.g. [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**) (96%) and [(4-carbomethoxyphenyl)ethynyl]pentamethyldisilane (**1d**) (92%)) and also with substitution patterns involving both types of substituents (2,6-bis(ethynylpentamethyldisilanyl)-4-nitroaniline (**8**) (56%)). In addition, ortho, meta, and para halogen substitution all result in facile reaction and excellent yields. Halogenated polynuclear aromatics can also be used as is demonstrated by the synthesis of (2-naphthylethynyl)pentamethyldisilane (**9**) (55%). Si–Si bond cleavage does not occur under the mild palladium-catalyzed reaction conditions.

Absorption Spectra. The absorption spectra of a series of (phenylethynyl)pentamethyldisilanes having substituents with widely varying electronic character were investigated and compared to a series of reference acetylenes. Table I summarizes the absorption maxima, extinction coefficients, and Hammett[15] σ_p and σ_m values for the series of substituents used. Several consistent trends are seen in the absorption spectra of these substituted acetylenes. A particularly informative series of spectra including phenylacetylene (**6**), (4-cyanophenyl)acetylene (**4**), (4-cyanophenyl)(trimethylsilyl)acetylene (**5**), and [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) is shown in Figure 1. Substitution of phenylacetylene (**6**) with the electron-withdrawing 4-cyano group results in a red-shift of the two long-wavelength π,π^* maxima (233 and 243 nm) by 15 and 18 nm, respectively. Significant electronic interaction is expected for such substitution since the b_1^- HOMO (C_{2v} symmetry) and the LUMO of phenylacetylene (**6**) have large orbital coefficients in the 4-position which allow for strong interaction with the cyano substituent. Further substitution of (4-cyanophenyl)acetylene (**4**) with a trimethylsilyl group produces an additional 15-nm red-shift of both bands. An analogous red-shift is found on trimethylsilylation of phenylacetylene (**6**). In that case, PES data[18] show that the b_1^- orbital is raised in energy by 0.45 eV upon substitution [(phenylethynyl)trimethylsilane (**10**) IP = 8.37 eV, phenylacetylene (**6**) IP = 8.82 eV]. A similar raising of the LUMO must also occur since the full 0.45 eV energy change does not show up in the absorption spectrum. Substitution of the pentamethyldisilanyl group for the trimethylsilyl group of [(4-cyanophenyl)ethynyl]-

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Table I. Absorption and Emission Maxima for (Phenylethynyl)pentamethyldisilane Derivatives (**1**) and Reference Compounds in Various Solvents at Room Temperature

	absorption λ_{max}, nm (ϵ, cm^{-1} L mol^{-1})		fluorescence[a]		excitation spectrum[a]		IP (calc)[b]	
compound	isooctane	acetonitrile	λ_{max}, nm	λ_{ex}, nm	λ_{max}, nm	λ_{em}, nm	σ_p	eV
$\mathrm{YPhC{\equiv}CSi_2Me_5}$								
Y = 4-MeO, **1c**	261 (2.9×10^4)	262 (2.9×10^4)	313	263	266	316	−0.27	9.02
Y = 4-Ph, **1e**	282 (4.1×10^4)	283 (4.4×10^4)	325[c]	280[c]	283[c]	327[c]	0.01	8.79
Y = 4-H, **1a**	246, 258 (2.2×10^4)	247, 258 (2.3×10^4)	*d*	*d*	*d*	*d*	0	9.18[j] 9.05[k]
Y = 4-Cl, **1f**	261 (2.8×10^4)	261 (2.8×10^4)	*e*	*e*	*e*	*e*	0.23	9.24
Y = 4-$\mathrm{MeO_2C}$, **1d**	277 (3.0×10^4)	276 (2.4×10^4)	*f*	*f*	*f*	*f*	0.44	9.35
Y = 4-CN, **1b**	276 (3.2×10^4)	277 (3.2×10^4)	*f*	*f*	*f*	*f*	0.63	9.37
Y = 3-CN, **1g**	250 (s), *260* (1.7×10^4), 271 (s)	250 (s), *260* (1.7×10^4), 270 (s)	*g*	*g*	*g*	*g*	0.56[h]	
Y = 4-$\mathrm{NO_2}$, **1h**	300 (1.8×10^4)	306 (1.8×10^4)	*i*	*i*	*i*	*i*	0.78	
$\mathrm{2\text{-}NaphC{\equiv}CSi_2Me_5}$ (**9**)	220, 229 (s), 242 (s), *253* (1.1×10^5), 280 (s), 290, 301	221, 229 (s), 242 (s), *252*, (6.0×10^4), 281 (s), 290, 302	339, *346*, 356, 362	290	252, *292*, *305*	345		
$\mathrm{PhC{\equiv}C(SiMe_2)_2C{\equiv}CPh}$ (**7**)	248, *259* (2.0×10^4)	247, *258* (2.1×10^4)	290, *297*, 307	260	247, *257*	298		
$\mathrm{4\text{-}NCPhC{\equiv}CSiMe_3}$ (**5**)	263, *276* (3.4×10^4)		297, *306*	276	262, *276*	308	0.63	
$\mathrm{4\text{-}MeOPhC{\equiv}CSiMe_3}$ (**11**)	*257* (2.3×10^4), 285, 305		308	257	260 (s), 267	313	−0.27	
$\mathrm{4\text{-}MeO_2CPh{\equiv}CSiMe_3}$ (**12**)	*267* (3.0×10^4), 279		*f*	*f*	*f*	*f*	0.44	
$\mathrm{PhC{\equiv}CSiMe_3}$ (**10**)	*245* (2.3×10^4), 255		289, *298*, 306	245	246, *258*	301	0.0	9.16 (8.37)[l]
$\mathrm{4\text{-}CNPhC{\equiv}CH}$ (**4**)	248, *261* (2.7×10^4)	249, *261* (2.8×10^4)	296, *303*, 314	261	251, *262*	304	0.63	
$\mathrm{PhC{\equiv}CH}$ (**6**)	233 (1.5×10^4), 243		286, *295*, 303[m]	245				9.07 (8.82)[l]

[a] Data taken in isooctane. Concentrations from 1×10^{-5} M to 1×10^{-4} M. Where multiple maxima are listed, the most intense band or 0,0 band is in italic. [b] Calculated with Dewar and Thiel's MNDO[16] program from the QCPE AMPAC package #506. The most recent silicon parameterization was used.[17] [c] A new emission appears upon irradiation by the fluorometer lamp (311 nm, *325* nm). This emission is likely due to (biphenylethynyl)trimethylsilane. [d] The weak emission observed at room temperature is due to (phenylethynyl)trimethylsilane, a photoproduct of (phenylethynyl)pentamethyldisilane. [e] The emission observed at room temperature is associated with [(4-chlorophenyl)ethynyl]trimethylsilane. [f] Carefully purified samples show extremely weak fluorescence whose excitation spectrum does not match that of the parent compound. [g] The emission observed at room temperature is associated with [(3-cyanophenyl)ethynyl]trimethylsilane based on the excitation spectrum (λ_{em} = 313, λ_{max} = 225, 248, *260*, 290, 299 nm). [h] σ_m. [i] No fluorescence observed. [j] IP of the conformation with the Si–Si σ bond in the same plane as that defined by the phenyl ring. [k] IP of the conformation in which the Si–Si σ bond is perpendicular to the plane defined by the phenyl ring. [l] Reference 18. [m] Reference 20.

trimethylsilane (**5**) does not, however, result in a further red-shift. Instead the bands are broadened and a long-wavelength shoulder develops (ca. 290 nm). Little increase in oscillator strength is observed with increased substitution of the acetylene, the extinction coefficients varying from 1.5×10^4 cm^{-1} L mol^{-1} for phenylacetylene (**6**) to 3.3×10^4 cm^{-1} L mol^{-1} for [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**). Identical trends in all essential details are observed for the analogous series with strong electron-donating substituents such as the 4-methoxy group.

For the (phenylethynyl)pentamethyldisilane series, changing the 4-position substiutuent from strongly electron-donating (4-methoxy) to strongly electron-withdrawing (4-nitro) results in a 40-nm red-shift of the absorption maximum, though little change is seen in the spectral shape or bandwidth. Once again, only a small variation in transition oscillator strength is observed for the series, all values of extinction coefficients for the long-wavelength bands being between 1.8 and 3.3×10^4 cm^{-1} L mol^{-1}.

The same series of absorption spectra were also measured in acetonitrile in order to investigate the possibility of the involvement of an intramolecular CT absorption band. Such a band could provide the origin of the CT emission originally observed in substituted (phenylethynyl)pentamethyldisilanes by Shizuka et al.[2,3] If the substituted (phenylethynyl)pentamethyldisilane spectra were broadened by the formation of an intramolecular CT band or the long-wavelength shoulder were a CT band, a red-shift of the polar CT band but not the normal π,π^* bands would be expected in acetonitrile. Such effects have been observed in many classical CT complexes.[19] No shift of the absorption maximum greater than 1 nm was observed for a change of solvent from isooctane to acetonitrile for any of the substituted (phenylethynyl)pentamethyldisilanes investigated. Thus no definitive evidence was found for the existence of an intramolecular CT absorption band in this series of (phenylethynyl)pentamethyldisilane derivatives. However, since the long-wavelength shoulder observed in the spectrum of the [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) is slightly more pronounced than the same shoulder of [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**), some ground state $\sigma\pi$ orbital mixing with charge-transfer character may be involved. This interaction would involve interaction of the Si–Si σ bond with the aromatic acetylene HOMO.

No new absorption bands were observed for any of these ethynyldisilanes even at concentrations up to 10^{-3} M. Thus there are also no indications in the absorption spectra for any intermolecular CT associations. All long-wavelength absorption bands in these molecules therefore appear to be associated with transitions to $^1(\pi\pi^*)$ states with perhaps a low energy $\sigma\pi^*$ charge-transfer component.

Emission Spectra 298 K. The substituted (phenylethynyl)pentamethyldisilanes fall into two distinct categories based on their emission characteristics. The first category includes those compounds substituted with electron-donating substituents (e.g. 4-methoxy or 4-phenyl) or those which contain polynuclear aromatics (e.g. 2-naphthyl) and therefore have low IPs. These all show standard $^1(\pi,\pi^*)$ state emission spectra at 298 K in isooctane or acetonitrile. Excitation spectra for these compounds identically match their absorption spectra as expected for standard $^1(\pi,\pi^*)$ state emissions. The emission and excitation spectra of [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**) are shown in Figure 2 as a representative case for this category. The room temperature emission characteristics of the compounds in this category are essentially identical with those of phenylacetylene (**6**)[20] and (phenylethynyl)trimethylsilane (**10**) though the maxima are red-shifted due to substitution. The second category comprises

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(19) (a) Foster, R. *Organic Charge-Transfer Complexes*; Academic: New York, 1969. (b) Tamres, M.; Strong, R. L. In *Molecular Association*; Foster, R., Ed.; Academic: New York, 1979; Vol. 2, Chapter 5.

(20) Zhuravleva, T. S.; Nurmukhametov, R. M.; Kozlov, Y. I.; Shigorin, D. N. *Opt. Spektrosk.* **1965**, 489.

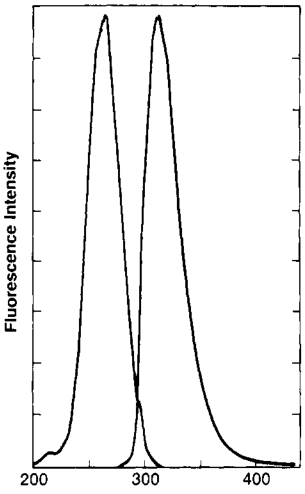

Figure 2. Emission and excitation spectra of [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**) in isooctane at 298 K. Emission: [1.98 × 10^{-5} M], λ_{ex} = 263 nm. Excitation: [1.98 × 10^{-5} M], λ_{em} = 316 nm.

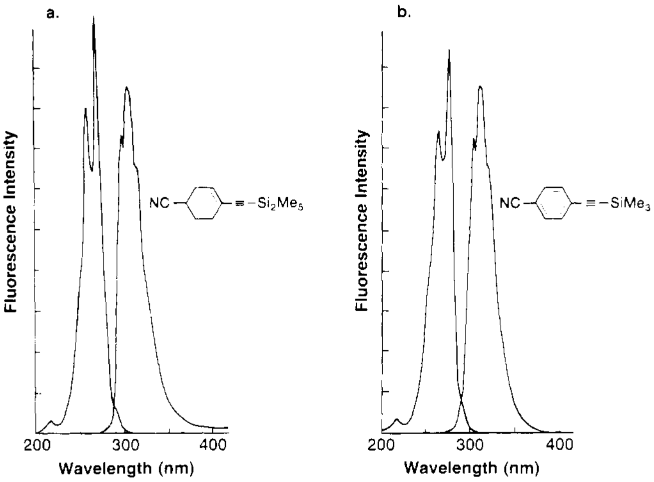

Figure 3. (a) Emission and excitation spectra of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) in isooctane at 298 K after several minutes of irradiation with 277-nm light. Emission: [1.13 × 10^{-5} M], λ_{ex} = 277 nm. Excitation: [1.13 × 10^{-5} M], λ_{em} = 307 nm. (b) Emission and excitation spectra of [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) in isooctane at 298 K are shown. Emission: [1.45 × 10^{-5} M], λ_{ex} = 277 nm. Excitation: [1.45 × 10^{-5} M], λ_{em} = 307 nm.

those ethynyldisilanes whose IPs are greater than or equal to that of (phenylethynyl)pentamethyldisilane (**1a**) and includes those (phenylethynyl)pentamethyldisilanes having electron-withdrawing substituents such as 4-cyano, 4-carbomethoxy, and 4-nitro. Freshly prepared solutions of those compounds in the second category show no emission at 298 K greater than the solvent (isooctane or isopentane) Raman band when the emission is monitored within a few seconds of placement of the sample in the fluorometer. However, even with 2-nm bandwidth excitation slits, a new emission grows in rapidly (seconds to minutes depending on the substitution). Figure 3a shows a typical emission spectrum from a solution of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) monitored after several minutes of irradiation in the fluorometer (2-nm bandwidth excitation at 277 nm). The excitation spectrum of this new emission does have a maximum at 277 nm as does the absorption spectrum of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**), but the spectral shape is not identical with the absorption spectrum of the disilane. The emission and excitation spectra of [(4-cyanophenyl)ethynyl]trimethylsilane (**5**)[12] (Figure 3b) does, however, identically match the new emission which is observed upon photolysis of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**). On the basis of the spectral match between the emission and excitation spectra of [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) and those which are observed upon photolysis of the [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) and the known photofragmentation of (phenylethynyl)pentamethyldisilanes to (phenylethynyl)trimethylsilanes,[2] the emitting species is identified as [(4-cyanophenyl)ethynyl]trimethylsilane. An identical pattern is observed for [(4-carbomethoxy)- and [(4-chlorophenyl)ethynyl]pentamethyldisilane (**1d** and **1f**). In each case the corresponding monosilane was independently synthesized and its emission and excitation spectra were compared and found to agree with the emission observed from the irradiated solutions of the disilanes.

The parent compound, (phenylethynyl)pentamethyldisilane (**1a**), has the emission characteristics of those acetylenic disilanes in the second category. Freshly prepared and purified samples or samples monitored with a flow cell show essentially no fluorescence. After a few seconds of irradiation a moderately strong emission is seen which has the same spectral features reported by Shizuka et al. for the emission of (phenylethynyl)pentamethyldisilane (**1a**) (λ_{max} = 310 nm). However, the excitation spectrum matches the absorption spectrum of (phenylethynyl)trimethylsilane (**10**) and not that of (phenylethynyl)pentamethyldisilane (**1a**). Iodobenzene which is difficult to remove from the (phenylethynyl)pentamethyldisilane (**1a**) after synthesis is also a common impurity and its characteristic excitation spectrum can be identified in some cases. Thus the emission previously observed at 298 K and previously assigned[2] as a localized $^1(\pi,\pi^*)$ excited state of (phenylethynyl)pentamethyldisilane (**1a**) appears to be that of (phenylethynyl)trimethylsilane (**10**). These emission data as well as that from the other derivatives studied and a series of reference acetylenes are summarized in Table I.

Even those compounds in category 1 show some photochemical decomposition with extended irradiation times. Thus (biphenylethynyl)pentamethyldisilane (**1e**) when irradiated eventually gives a second emission band (λ_{max} = 311 and 325 nm) which is most likely due to the corresponding monosilane. However, in this case there is a clear $^1(\pi,\pi^*)$ fluorescence from the disilane.

Emission Spectra 77 K. On the basis of their unusual emission characteristics in organic matrices at 77 K, the (phenylethynyl)pentamethyldisilane derivatives can again, without exception, be divided into the same two categories used for the room temperature emission data. The first category, which consists of those (phenylethynyl)pentamethyldisilanes which are substituted with electron-donating groups or polynuclear aromatics [[(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**), (biphenylethynyl)pentamethyldisilane (**1e**), (2-naphthylethynyl)pentamethyldisilane (**9**)], exhibits two characteristic emission bands. One is a short wavelength π,π^* fluorescence (Table II). The only significant difference between the 298 K π,π^* fluorescent emission band and that in isopentane at 77 K is the increased vibrational structure seen in the low-temperature isopentane matrix. In addition to this short-wavelength fluorescence, there is a second highly structured and significantly red-shifted emission band. In the case of [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**) the 0,0 band for this emission is at 413 nm. The striking similarity of the spectral shapes of this emission band and that of the phosphorescence of phenylacetylene (**6**) combined with the observed multisecond lifetime and unique vibrational structure of this emission at 77 K in isopentane matrices serve to identify this emission as phosphorescence from the $^3(\pi,\pi^*)$ state. The emission maxima for these low-temperature emission spectra are also summarized in Table II.

The emission spectra of the other (phenylethynyl)pentamethyldisilanes, particularly those with strong electron-withdrawing substituents, show distinctly different emission characteristics in isopentane glasses at 77 K. Figure 4a shows the emission spectrum of a 2.4 × 10^{-5} M isopentane solution of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) taken at 77 K. It provides a typical example of the emission spectra of the compounds in this second category. The three unique features of this spectrum include the conspicuous absence of any normal $^1(\pi,\pi^*)$ state fluorescent emission, the appearance of a very strong,

Table II. Normal Fluorescence, CT Fluorescence, and Phosphorescence Maxima for Substituted (Phenylethynyl)pentamethyldisilanes (**1**, $\mathrm{YPhC{\equiv}CSi_2Me_5}$) in Various Matrices at 77 K

		fluorescence				CT fluorescence				phosphorescence			
compound[a]	matrix[c]	excitation λ, nm	emission[d] λ_{max}, nm	monitor λ, nm	excitation[d] λ_{max}, nm	excitation λ, nm	emission λ_{max}, nm	monitor λ, nm	excitation[d] λ_{max}, nm	excitation λ, nm	emission[d] λ_{max}, nm	monitor λ, nm	excitation[d] λ_{max}, nm
Y = 4-MeO, **1c**	IP	265	296, *308*	309	*267*, 279		no emission detected			265	*413*, 437, 443, 455	413	*266*, 279
	2-MTHF			296	*266*, 279								
Y = 4-Ph, **1e**	IP	282	316, *328*	328	*290*, 300		no emission detected			282	*486*, 515, 527, 562	[f]	[f]
	2-MTHF	282	319, *330*	330	306		no emission detected			300	*479*, 511	[f]	[f]
Y = 4-H, **1a**	IP		weak emission detected			258	385	385	260, *272*	258	*411*, 430, 439, 449	411	*261*, 272
Y = 4-Cl, **1f**	IP		no emission detected			278	385	385	265, 276	278	*423*, 442, 451	[f]	[f]
	2-MTHF		no emission detected			262	390	390	268, *280*	262	*419*, 439, 446	[f]	[f]
Y = 4-$\mathrm{MeO_2C}$, **1d**	IP		no emission detected			277	390	390	282, *298*	277	*441*, 465, 474, 487	441	298
	2-MTHF		no emission detected			277	410	410	298	277	*435*, 458, 468	[f]	[f]
Y = 4-CN, **1b**	IP		no emission detected			277	395	395	295	276	*444*, 470, 480, 493	480	295
	2-MTHF		no emission detected			277	411	411	295	277	*440*[g]	[f]	[f]
	EPA		no emission detected			277	395	[f]	[f]	277	441[g]	[f]	[f]
	AEP		no emission detected			277	400	[f]	[f]	277	*442*, 468, 475, 490	[f]	[f]
Y = 3-CN, **1g**	IP	260	[e]	315	[e]	260	395	395	277	260	*418*, 438, 448, 460	418	262, *277*
Y = 4-$\mathrm{NO_2}$, **1h**	IP		no emission detected				no emission detected				no emission detected		
2-naph-$\mathrm{C{\equiv}CSi_2Me_5}$ (**9**)	IP	292	*332*, 341, 349, 358, 368	334	252, *292*, 306		no emission detected				(weak to none)		
$\mathrm{PhC{\equiv}C(SiMe_2)_2C{\equiv}CPh}$ (**7**)	IP		no emission detected			260	341	345	260, *285*, 300	260	*411*, 431, 439, 450, 472	[f]	[f]
4-$\mathrm{NCPhC{\equiv}CSiMe_3}$ (**5**)	IP	277	294, 297, *306*, 315	306	262, *274*		no emission detected			277	*441*, 456, 463, 472	441	265, *278*
$\mathrm{PhC{\equiv}CH}$[b] (**6**)	IP	245	*285*, 296	[f]	[f]		no emission detected			245	*398*, 417, 423	[f]	[f]
4-$\mathrm{NCPhC{\equiv}CH}$ (**4**)	IO	261	291, *302*, 314	[f]	[f]		no emission detected			261	*429*, 444, 450, 460, 470, 475, 486, 495	[f]	[f]

[a] Concentrations varied from 1.2×10^{-5} to 2.5×10^{-5} M. [b] [Phenylacetylene] = 2×10^{-3} M. [c] IP = isopentane; 2-MTHF = 2-methyltetrahydrofuran; EPA = ethanol/isopentane/ether (2:5:5); AEP = triethylamine/ether/isopentane (2:5:5); IO = isooctane (transluscent glass). [d] Where multiple maxima are listed, the most intense band or 0,0 band is in italic. [e] Emission detected with λ_{max} = 305, *315*, 322 nm, however, assignment of its origin from excitation data is not conclusive. [f] Emission not measured. [g] Other phosphorescence peaks were masked by the CT emission.

Table III. Fluorescence-Lifetime Data for (Phenylethynyl)pentamethyldisilane Derivatives (**1**) and Reference Compounds

compound 	T, K	solvent[a] or matrix	excitation wavelength λ_{ex}, nm	emission wavelength λ_{em}, nm	$10^9\tau$, s
4: Y = CN, R = H	298	IP	282	310	8.2
	77	IP	282	310	12.9
5: Y = CN, R = $\mathrm{SiMe_3}$	298	IP	282	310	7.7
	77	IP	282	310	12.2
1b: Y = CN, R = $\mathrm{Si_2Me_5}$	298	IP	282	310	<0.010[b]
	298	IP	283	380	1.4[c]
	77	IP	283	380	3[d]
	77	EPA	283	380	3[d-f]
	77	solid	280	380	0.4[d,e]
1d: Y = $\mathrm{CO_2Me}$, R = $\mathrm{Si_2Me_5}$	298	IP	282	310	[g]
	298	IP	282	380	
	77	IP	282	380	3[d,e]
	77	EPA	282	380	3[d,e]
1c: Y = MeO, R = $\mathrm{Si_2Me_5}$	298	IP	278	310	0.6
	77	IP	278	310	8.5
1a: Y = H, R = $\mathrm{Si_2Me_5}$	298	IP	278	380	[h]
	77	IP	278	380	2[d]
1e: Y = Ph, R = $\mathrm{Si_2Me_5}$	298	IP	278	330	<0.010[b]
	77	IP	278	330	0.7

[a] All solutions were prepared to be 5×10^{-5} M. IP = isopentane and EPA = ethanol/isopentane/ether (2:5:5). [b] Limit of the temporal resolution of the photon-counting apparatus. [c] CT fluorescence was very weak and may have a component of normal $\pi\pi^*$ emission convolved with it. [d] Estimate of the decay lifetime. The fluorescence decay is nonexponential and is not fit well by one, two, or three exponentials. [e] The rise time of the emission is less than 10 ps. [f] The emission intensity decreases sharply above ca. 140 K. [g] The emission is very weak and is not temporally resolvable with the available apparatus. [h] No emission observed for purified samples with a flowing sample.

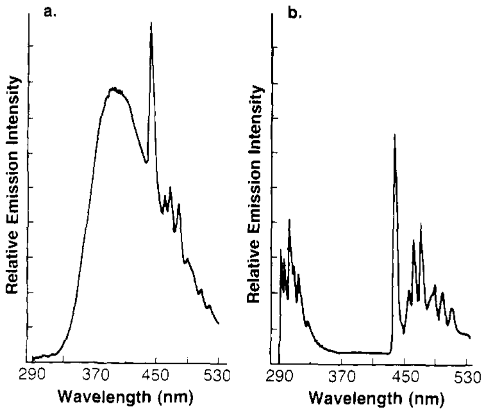

Figure 4. (a) Emission spectrum of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at 77 K in an isopentane glass; [2.4×10^{-5} M], λ_{ex} = 277 nm and (b) Emission spectrum of [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) at 77 K in an isopentane glass; [2.4×10^{-5} M], λ_{ex} = 277 nm.

broad, and featureless emission at 395 nm and a progression of sharp, distinctive emission features on the red end of this broad emission. The emission spectrum of [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) is shown in Figure 4b for comparison. The monosilane emission is analogous to that from the (phenylethynyl)pentamethyldisilanes that are substituted with electron-donating groups since only a $^1(\pi,\pi^*)$ state emission and a $^3(\pi,\pi^*)$ state phosphorescence are present and the broad, featureless long-wavelength emission is conspicuously absent. Thus, the broad, featureless emission is a characteristic only of those acetylenes substituted with both the disilane group and with aromatic moieties having relatively large IPs ($\gtrsim$8.7 eV). [(4-Carbomethoxy- and [(4-chlorophenyl)ethynyl]pentamethyldisilane (**1d** and **1f**) as well as the parent compound (phenylethynyl)pentamethyldisilane (**1a**)[2] also show low-temperature emission spectra which have both the broad, featureless emission and the progression of spectral bands on the red end of the broad emission. However, as the electron-withdrawing character of the substituent decreases from 4-cyano to hydrogen, the strength of the long-wavelength, broad emission band also decreases.

The origin of the progression of sharp spectral features beginning at 444 nm in the 77 K emission (Figure 4a) is readily identified as the $^3(\pi\pi^*)$ state of the [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**). Figure 5a shows the emission spectrum of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at 77 K in isopentane measured with a rotating-slit phosphorometer. The sharp spectral features are separated from the broad 395-nm emission on the basis of their distinctly longer ($\tau \approx$ seconds) lifetimes (vide infra). The long-wavelength phosphorescence which has a 0,0 band at 444 nm is essentially identical in shape, though red-shifted of that of the phosphorescent emissions of phenylacetylene (**6**) (0,0 band = 398 nm), (4-cyanophenyl)acetylene (**4**) (0,0 band = 429 nm), and [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) (0,0 band = 441 nm). An essentially identical vibrational structure is also seen for this emission in all four of these compounds. Moreover, the excitation spectrum of this emission band and the analogous ones from the other disilanes in the second category match the corresponding disilane absorption spectra (Table II). The emission was further identified as phosphorescence from [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) by EPR spectroscopy. Shown in Figure 5b is the $\Delta m = \pm 2$ transition of the excited $^3(\pi,\pi^*)$ state at 77 K in isopentane. This "half-field" transition (1426 G) is only observed during continuous irradiation with a xenon-arc lamp (broad band) and disappears within several seconds after the photolysis is terminated. The transition is regenerated upon repeated photolysis. The spectrum is characteristic of the triplet EPR spectra of unoriented triplet states, showing a broad distribution of resonance fields.[21] Similar spectral

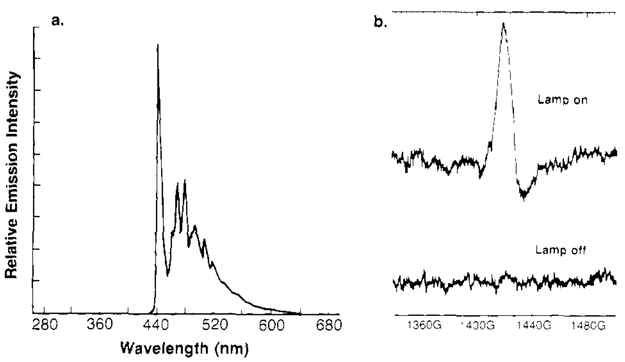

Figure 5. (a) Phosphorescent emission spectrum of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at 77 K in an isopentane glass measured with a rotating-slit phosphorometer; [9.79×10^{-5} M], λ_{ex} = 276 nm and (b) EPR spectrum of the $\Delta m = \pm 2$ transition for the phosphorescent triplet state of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at 77 K in an isopentane glass; [2.5×10^{-3} M], λ_{ex} = broad band xenon arc lamp.

transitions were observed for [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) (1420 G), (phenylethynyl)pentamethyldisilane (**1a**) (1360 G), and [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**) (1410 G) in isopentane at 77 K. The fact that this transition is observed for [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) confirms the π,π^* character of the phosphorescent triplet state since the disilane moiety is not required for the formation of this state. Several unidentified radical species were also formed on photolysis of these (phenylethynyl)pentamethyldisilanes. These all had transitions in the 3240–3310-G region and g values between 2.033 and 2.007 (comparison with DPPH). Similar radical species are observed on irradiation of phenylacetylene (**6**) in isopentane matrices and may result from hydrogen atom abstraction from the matrix.

The quantum yields for phosphorescence for [(4-cyano-, [(4-carbomethoxy-, and [(4-chlorophenyl)ethynyl]pentamethyldisilane (**1b**, **1d**, and **1f**) were determined relative to that of (phenylethynyl)pentamethyldisilane (**1a**) (ϕ_p = 0.24).[2] The phosphorescent quantum yields were determined to be 0.22, 0.30, and 0.23, respectively.

The unique, broad, featureless emission which is observed at 77 K from (phenylethynyl)pentamethyldisilane (**1a**) and from the disilanes substituted with electron-withdrawing groups (Figure 4a and Table II) can readily be assigned to a singlet intramolecular CT state. The origin of the CT emission clearly involves an excited state of (or initial excitation of) the disilane since the excitation spectrum of the emission is identical with the excitation spectrum from the phosphorescence and qualitatively agrees with the disilane's absorption spectrum at 77 K (Table II). The singlet character of the CT states is indicated by the measured lifetimes of the CT states which range from several hundred picoseconds to several nanoseconds (vide infra). The intramolecular nature of the emission is demonstrated by the fact that dilution of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) to 1×10^{-9} M in isopentane does not produce a difference in the shape of the emission at 395 nm or in the ratio of the emission intensity of the CT band at 395 nm to that of the phosphorescence at 444 nm. If the broad emission at 395 nm were due to excimer emission, the dilution would be expected to eliminate it.[22] In addition, since diffusional encounters are eliminated in the organic matrices used for these emission spectra, no diffusional encounters leading to excimer formation would be possible and only site-trapped dimers could possibly lead to this type of emission. However, in addition to the absence of a dilution effect, absorption spectra of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) in isopentane and 2-methyltetrahydrofuran at 77 K show no bands other than those observed from the monomer in solution at 298 K and no spectral shift of any band is observed. Thus there is no evidence for any

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(22) Berlman, I. B. *Handbook of Fluorescence Spectra of Aromatic Molecules*; Academic: New York, 1971; p 54.

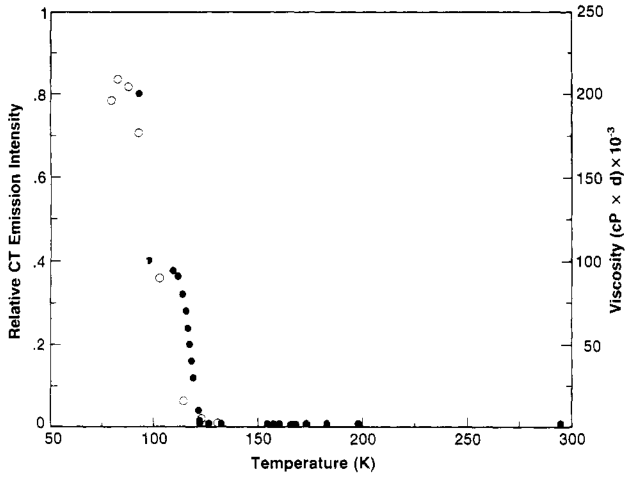

Figure 6. Comparison of the emission intensity for the CT fluorescence of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) with EPA viscosity as a function of temperature: ○, CT fluorescence; ●, EPA viscosity (cP·d).

intermolecular interaction or dimer formation in the absorption spectrum at 77 K.

The emission intensity from [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at 395 nm (λ_{max} of the CT emission band) was followed as a function of temperature in order to assess the importance of temperature and matrix viscosity effects on the CT emission intensity. Figure 6 shows a plot of the CT emission intensity as a function of temperature in an EPA matrix.[23] Above 130 K the CT emission is either nonexistent or so weak that the S/N ratio detection limit of the fluorometer is reached. As the temperature is decreased through 310 K, a very rapid growth of the CT emission is observed. Also shown in Figure 6 is a plot of the viscosity of the EPA glass as a function of temperature. The EPA glass shows a viscosity less than 400 cP·d for temperatures above ca. 130 K. However, within a few degrees of 130 K the EPA forms a rigid glass whose viscosity rapidly increases to greater than 200 000 cP·d.[24] Confirmation of the value of the glass transition temperature of the EPA was obtained with differential scanning calorimetry. A typical, though weak, glass transition endotherm was observed at 128 K. While the EPA solution and matrix were not fully thermodynamically equilibrated in these two experiments due to the relatively rapid rates of heating, the agreement of the origin of the CT emission and the glass formation temperature of the matrix is striking. In isopentane, the CT emission of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) is not observed above 110 K, the temperature at which isopentane forms a rigid matrix.[25] These data suggest that the increased viscosity of the rigid organic glass is the key parameter controlling the appearance of the CT emission rather than a simple temperature effect. This would be consistent with the known photochemistry of (phenylethynyl)pentamethyldisilanes which involves photochemical cleavage of the Si–Si σ bond.[2] The rigid matrix prevents rapid radiationless deactivation of the CT excited state by photochemical reaction thus allowing time for the singlet CT state to emit. In these organic matrices the quantum yields for emission (ϕ_{CT}) can be quite large. The emission quantum yields determined for [(4-cyano-, [(4-carbomethoxy-, and [(4-chlorophenyl)ethynyl]pentamethyldisilane (**1b**, **1d**, and **1f**) by comparison with the value for (phenylethynyl)pentamethyldisilane (**1a**) given by Shizuka et al. (0.26)[2] are 0.36, 0.49, and 0.22, respectively. For [(4-carbomethoxyphenyl)ethynyl]pentamethyldisilane (**1d**), the sum of the emission quantum yields for CT emission and phosphorescence is ca. 0.8 at 77 K, thus accounting for the majority of the decay processes.

A very large Stokes red-shift is observed for all of the CT emissions seen for the (phenylethynyl)pentamethyldisilanes substituted with electron-withdrawing groups (category 2) even though the origin of the emission occurs near the red end of the absorption spectrum. For [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) the origin of the CT emission is at 320 nm while the maximum is at 395 nm. The large Stokes shift associated with this emission indicates extensive molecular reorganization in the excited state as would be expected for a $^1(\sigma,\pi^*)$ CT excited state. However, no anomalous Stokes shift can be detected with these molecules since the CT emission does not appear until the viscosity of the matrix is increased sufficiently to prevent photochemical fragmentation. At low temperatures and high viscosity the relaxation time for the solvent is long enough that the solution cannot achieve thermal equilibrium during the lifetime of the excited state. It has been well-established that under these conditions the "general" or "polarization red-shift" of a nonpolar solute in polar solvents is proportional to $(\eta^2 - 1)/(2\eta^2 + 1)$ where η is the solvent index of refraction.[26] Thus when the organic matrix is made more polar as in the series isopentane to triethylamine/ether/isopentane[23] to EPA to 2-MTHF, only a very small shift of the maximum of the CT emission band is observed (Table II). The shifts observed are in qualitative agreement with the indices of refraction of the matrix solvents.

Emission Lifetimes. The emission lifetimes for both the $^1(\pi,\pi^*)$ fluorescence and the CT fluorescence of the (phenylethynyl)pentamethyldisilane derivatives were measured by using single-photon-counting techniques. The (phenylethynyl)pentamethyldisilanes which fall into category 1 on the basis both of their room temperature and 77 K emission characteristics only show a localized $^1(\pi,\pi^*)$ state emission in the vicinity of 310 nm. The emission lifetimes of two of these compounds, (4-methoxyphenyl)ethynyl]pentmethyldisilane (**1c**) and (biphenylethynyl)pentamethyldisilane (**1e**), were measured in isopentane at 298 K. The emission decays were fit with a single exponential to give lifetimes of 600 ps and less than 10 ps, respectively. At 77 K in an isopentane matrix, the lifetimes of these π,π^* emissions increase to 8.5 ns and 700 ps, respectively. Over multiple lifetimes, the decay curves are fit well with a single exponential. Thus a very close parallel exists between the emission behavior of these derivatives and simple phenylacetylenes. For example (4-cyanophenyl)acetylene (**4**) and [(4-cyanophenyl)ethynyl]trimethylsilane (**5**) exhibit only π,π^* emissions with lifetimes at 298 K in isopentane of ca. 8 ns. The emission lifetimes of these two reference compounds increase slightly to ca. 12 ns upon cooling to 77 K. These first-order decay lifetimes are summarized in Table III. The fact that the lifetimes of the two acetylenic disilane derivatives are similar to the reference acetylenes at 77 K but are significantly shorter at 298 K provides an indication that photochemical reaction of these derivatives is important at room temperature in fluid solution.

A very different emission behavior is observed for those compounds falling in category 2. For example, a static sample of [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) in isopentane at 298 K initially shows an extremely weak emission at ca. 310 nm upon excitation at 282 nm. However, a 5-s irradiation with the focused dye laser beam of the photon-counting apparatus (1 mW) causes a 10-fold increase in the emission intensity at 310 nm. The lifetime of the new emission which is generated by the photon counting apparatus excitation source is 7.7 ns. This lifetime is identical with that measured for [(4-cyanophenyl)ethynyl]trimethylsilane (**5**). This is fully consistent with the spectral data we have reported above which show that the monosilane is a

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[23] Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973; pp 90–92.

[24] Greenspan, H.; Fischer, E. *J. Phys. Chem.* **1965**, *69*, 2466.

[25] *CRC Handbook of Chemistry and Physics*, 60th ed.; Weast, R. C., Astle, M. J., Eds.; CRC Press: Boca Raton, Florida, 1979–1980; p C-219.

[26] For extensive discussions of solvent effects on molecular electronic spectra including classical, quantum mechanical, and perturbation theoretical treatments establishing the relationship between solvent red-shift and index of refraction under these experimental conditions, see: (a) Bayliss, N. S. *J. Chem. Phys.* **1950**, *18*, 292. (b) McRae, E. G. *J. Phys. Chem.* **1957**, *61*, 562 and references therein. For a qualitative review of these solvent effects, see: Lippert, E. *Acc. Chem. Res.* **1970**, *3*, 74. For an experimental example of the extremely small solvent-induced red-shifts at 77 K, see: Safarzadeh-Amiri, A. *J. Photochem. Photobiol., A: Chem.* **1988**, *43*, 43.

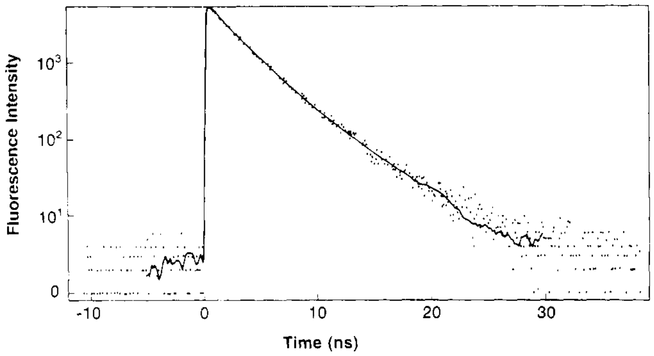

Figure 7. Charge-transfer fluorescence decay (··) of [(4-cyanophenyl)-ethynyl]pentamethyldisilane (**1b**) at 77 K in an EPA matrix, λ_{ex} = 283 nm, λ_{em} = 380 nm. The solid line fit is to two exponentials (1.9 ns, 53%; 3.8 ns, 47%: x^2 = 1.7) The instrument response function is 50 ps.

photoproduct of the photoexcitation of the corresponding disilane. Thus a flow cell was used for lifetime measurements for all of the (phenylethynyl)pentamethyldisilanes of category 2 in order to avoid monitoring photoproduct emissions. With the flow cell setup, no emission was observed at 310 nm for (phenylethynyl)pentamethyldisilane (**1a**) and only extremely weak emissions were observed for its 4-cyano and 4-carbomethoxy derivatives. In these latter cases, the emission lifetimes were extremely short (<10 ps) and thus not temporally resolvable with the current apparatus. At 77 K in isopentane matrices, these derivatives show strong CT emission at 380 nm when photoexcited at 282 nm. For (phenylethynyl)pentamethyldisilane (**1a**) and the 4-cyano and 4-carbomethoxy derivatives, the appearance of the CT emission occurred within 10 ps (the time resolution of the apparatus). Thus the formation of the CT state from the $^1(\pi,\pi^*)$ state (having, perhaps, some σ,π^* charge-transfer character, vide supra) is an extremely facile process and does not require solvent reorientation or specific molecular conformational reorientations. However, only specific subsets of possible molecular conformations may undergo CT in the matrix (vide infra). The decays of the CT emissions are nonexponential and are not fit very well by one two or three exponentials over 3 decades of decay (Figure 7). This is in contrast to the report of Shizuka et al.[2] that the decays over only approximately 1 decade of decay could be disected into two simple components, a fast and a slow process. We find that the decays are more representative of decays dependent on either matrix site variations or a spectrum of molecular conformations. The CT state lifetimes are not significantly altered by changing the matrix to the more polar EPA matrix. The lifetimes of the CT states given in Table III are the lifetimes determined with the best fit of a single exponential to the decay curves and are only meant to be representative of the time scale of the decay and not a quantitative measure of any specific individual decay process. The anisotropy of the CT emission of [(4-cyanophenyl)-ethynyl]pentamethyldisilane (**1b**) was measured and found to be 0.4 (the theoretical maximum for parallel absorbing and emitting dipoles) over the entire decay. The large value of the anisotropy indicates that the transition dipoles of both the π,π^* absorption and the CT emission are parallel. If the absorption band is associated with a $^1L_a \leftarrow {}^1A$ type allowed transition with a transition dipole along the NCPhC≡CSi axis, then the transition dipole of the CT emission also lies along the molecular long axis. A σ,π^* CT transition could have a vector component of the transition dipole moment parallel to the long molecular axis for the C_s symmetry conformation in which the Si–Si σ bond is perpendicular to the plane of the phenyl ring. In the rigid matrix at 77 K, no rotational or conformational motions which might destroy the anisotropy can occur. The CT emission can also be observed from crystalline [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) at 77 K. The lifetime of the CT state in the crystal appears to be significantly shorter than in the dilute organic matrices with an approximate lifetime of 400 ps. At 298 K the very weak emission seen at 380 nm from [(4-cyanophenyl)ethynyl]pentamethyldisilane (**1b**) may be associated with the CT state though the lifetime is shortened compared with the 77 K measurements and may also have a component of $^1(\pi,\pi^*)$ emission superimposed on it.

CT State Assignment. The CT emissions from (phenylethynyl)pentamethyldisilane (**1a**) and its alkyl-substituted derivatives have previously been assigned to emission from a $^1(2p\pi,\sigma^*)$ or $^1(2p\pi,3d\pi)$ state.[2,3] However, the pattern of emission data observed for the wide range of (arylethynyl)pentamethyldisilanes investigated in our work is clearly inconsistent with this state assignment. The data are instead consistent with a $^1(\sigma,\pi^*)$ CT emission in which the $^1(\pi,\pi^*)$ state of the aromatic moiety acts as the electron acceptor and the Si–Si σ bond acts as the electron donor. This state reassignment is also consistent with the intermolecular CT interactions observed between excited-state aromatic species and polysilanes (vide infra) and may provide an alternative explanation for the CT emission characteristics of aryl disilanes.[4] The following experimental observations provide convincing evidence for our $^1(\sigma,\pi^*)$ state assignment. The most striking feature of the emission spectra of the acetylenic disilanes investigated in this work is the absence of a CT emission from those derivatives bearing electron-donating substituents (category 1) and the observation of a strong CT emission from those derivatives bearing electron-withdrawing substituents (category 2). Since both the b_1^- HOMO and the LUMO of (phenylethynyl)pentamethyldisilane (**1a**) have large orbital coefficients in the 4-position of the phenyl ring, substitution by electron-donating substituents raises the energy of both the HOMO and the LUMO. Conversely, substitution with electron-withdrawing groups lowers both the HOMO and LUMO. Thus, the absorption λ_{max} show only minor shifts with changes in substituents from 4-methoxy to 4-cyano even though relatively large changes in IPs result. Shizuka et al. postulated that excitation of the $^1(\pi,\pi^*)$ state of these molecules decreases the energy separation between the aromatic $2p\pi^*$ orbitals and the $3d\pi$ or σ^* orbitals localized on the disilane moiety so that an exothermic CT could occur from the $^1(\pi,\pi^*)$ state to the disilane $d\pi$ orbital. However, we find that those derivatives with the highest energy LUMOs (electron-donating substituents) which would be expected to CT efficiently do not show any CT state emission, while those that have low energy LUMOs and are thus expected not to be capable of exothermic CT show extremely strong CT emissions. CT is observed even for those compounds such as [(4-cyanophenyl)ethynyl]-pentamethyldisilane (**1b**) which have estimated LUMO energies ca. 2–3 eV below the σ^* orbital energy level of the disilane chromophore.[27] Shown in Figure 8 are the estimated IPs of the substituted phenylacetylenes and disilanes one would obtain if the acetylenic disilanes investigated in this work were disected into isolated chromophores. To a first approximation this is a good representation of these compounds since the absorption spectra of all of these derivatives appear to involve primarily a localized $^1(\pi,\pi^*)$ transition. This dissection into isolated chromophores model is not meant to indicate that no ground state σ and π orbital mixing occurs but instead to provide a qualitative picture of the relative orbital orderings in these molecules. The positions of the HOMOs for these molecules are based on the PES IPs[28] for the corresponding benzenes since little data is available for substituted acetylenes. Where data is available (e.g. phenylacetylene (**6**)[18] and 2-naphthylacetylene (**3**)[29]), they support the overall trend observed for the substituted benzenes. In addition, IPs for the substituted (phenylethyl)pentamethyldisilanes calculated with

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[27] The position of the HOMOs of the (phenylethynyl)pentamethyldisilane derivatives are estimated both by MNDO calculations and by comparison with the known IPs of similarly substituted benzenes. The LUMO energies are estimated by using the measured room temperature absorption data and the calculated or measured IPs. While the positioning of the HOMOs and LUMOs are thus crude estimates, the conclusions are not affected by variations in the true energies of these MOs by up to 0.5 eV.

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[29] Gleiter, R.; Schafer, W.; Eckert-Maksic, M. *Chem. Ber.* **1981**, *114*, 2309.

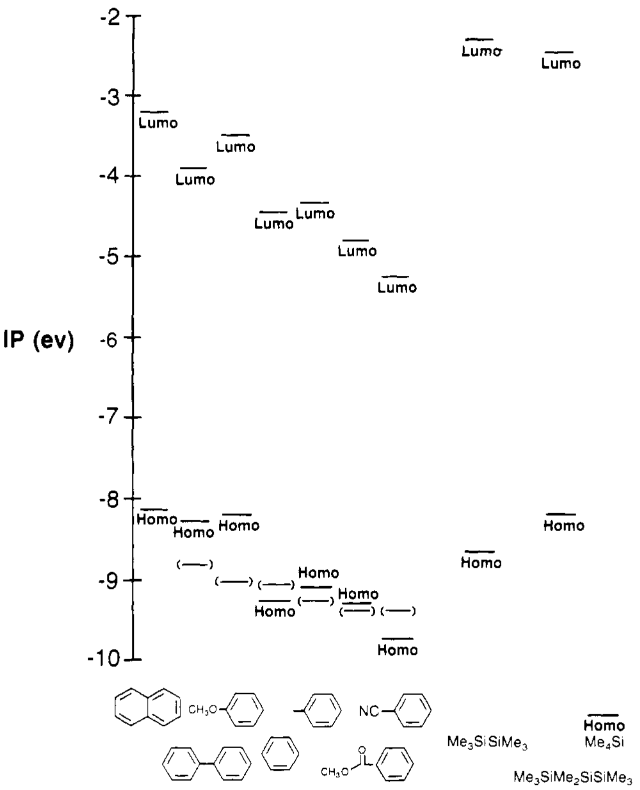
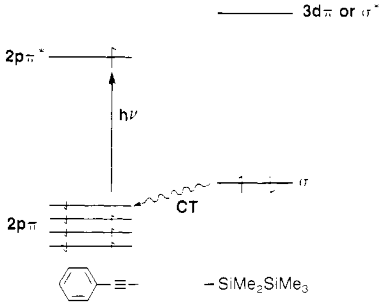


Figure 8. Graphical representation of the HOMO and LUMO positions as a function of structure of selected (arylethynyl)pentamethyldisilanes. The HOMO energies are estimated by the PES-determined IPs of the correspondingly substituted benzenes.[27,28] Bracketed values represent the MNDO calculated values for the (arylethynyl)pentamethyldisilanes.[30]

Scheme I. Proposed Mechanism of Charge Transfer in (Arylethynyl)pentamethyldisilanes



MNDO molecular orbital calculations (bracketed values in Figure 8, Table II) parallel the values for the corresponding benzenes.[30] Two distinct patterns are obvious from this data. First, all of the aromatic moieties have LUMO energies that are below the lowest spectroscopically accessible excited state of hexamethyldisilane.[31] Thus in all cases CT to this σ* orbital[32] would be endothermic. According to the CT mechanism of Shizuka and Ishikawa et al.,[2,3] none of these derivatives would have a CT emission unless a 3dπ orbital of the disilane moiety were to lie lower in energy than the σ* orbital. If this low-energy dπ orbital lies below the σ* orbital, it is inaccessible by direct excitation (e.g. symmetry or overlap forbidden). In the related phenyldisilanes the 3dπ orbital is not populated by formation of the corresponding radical anion[31d] thus indicating that either it is a high energy orbital or there is a conformational or symmetry barrier to overlap. A 2pπ* to 3dπ CT mechanism is therefore clearly inconsistent with our data. However, if one considers the positions of the HOMOs of the aromatic moieites in relationship to the HOMO of hexamethyldisilane (a model for the pentamethyldisilanyl moiety), then the derivatives investigated fall into two groups; those with IPs less than that of hexamethyldisilane [[(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**), (biphenylethynyl)pentmethyldisilane (**1e**), and (2-naphthylethynyl)pentamethyldisilane (**9**)] and those whose IPs are greater than that of hexamethyldisilane. The first group are those that do not have fluorescent CT states (category 1) and the second group includes those molecules that exhibit strong CT emissions (category 2). This pattern is typical of CT processes which involve $^1(\sigma,\pi^*)$ states or $\sigma \rightarrow \pi^*$ intermolecular CT or electron transfer.[33] A proposed mechanism for the formation of the singlet CT fluorescent states in these acetylenic disilanes is shown in Scheme I. Excitation of the localized $^1(\pi,\pi^*)$ state of the aromatic acetylene leaves a half-filled HOMO. If this orbital lies lower in energy than the Si–Si σ-bond HOMO then exothermic $\sigma \rightarrow \pi^*$ charge transfer can occur from the Si–Si σ bond to the aromatic $^1(\pi,\pi^*)$ state. Once again, the simplified model is not meant to indicate the absence of ground state σ,π orbital mixing and direct CT excitation. This energetic positioning of the aromatic HOMO and the Si–Si σ bond HOMO occurs for [(4-chloro-, [(4-carbomethoxy-, [(3-cyano-, and [(4-cyanophenyl)ethynyl]pentamethyldisilanes (**1f**, **1d**, **1g**, and **1b**). In contrast, the lowest energy singly occupied orbital (SOMO) of the π,π* state lies above that of the Si–Si σ-bond HOMO for [(4-methoxyphenyl)ethynyl]pentamethyldisilane (**1c**) or (2-naphthylethynyl)pentamethyldisilane (**9**). The CT is therefore endothermic and not as facile as other excited-state decay processes such as emission from the localized $^1(\pi,\pi^*)$ state.

Intermolecular $\sigma \rightarrow \pi^*$ Electron Transfer Analogies. The involvement of $^1(\sigma,\pi^*)$ intramolecular charge transfer states in these (phenylethynyl)pentamethyldisilanes suggests that an analogous charge transfer should occur in intermolecular reactions. The feasibility of such intermolecular CT processes is in fact suggested by earlier work as well. A series of investigations of the photochemical cleavage reactions of polysilanes in the presence of aromatic hydrocarbons like 9,10-dicyanoanthracene has indicated that the initial step in the cleavage involves charge transfer or electron transfer from the polysilane σ bond to the excited singlet π,π* state of the added aromatic.[34] Recently we[13] have investigated the fluorescence quenching of electron-deficient benzene derivatives by hexamethyldisilane and have definitively charac-

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[30] The MNDO calculations[16] were performed using the most recent Si parameterization.[17] All bond lengths and angles except those of the phenyl rings were used as optimization parameters and each calculation was initiated from the geometry with the Si–Si σ bond perpendicular to the plane of the phenyl ring unless otherwise indicated in Table II. For (biphenylethynyl)pentamethyldisilane (**1e**), the two aromatic rings were fixed at a 45° dihedral angle to each other. While the MNDO calculations probably overestimate the IPs by as much as 1 eV (compare the calculated IP for (phenylethynyl)trimethylsilane (**10**) of 9.16 eV with the experimental value of 8.37 eV), the trend in IPs is correct. A similar overestimation of the IPs of simple alkyldisilanes also occurs (Si_2Me_6 IP_{calcd} = 9.71, IP_{exp} = 8.7 eV).[17]

[31] (a) Ramsey, B. G.; Jones, L. L.; Pitt, C. G. *J. Am. Chem. Soc.* **1967**, *89*, 5471. (b) Drenth, W.; Noltes, J. G.; Bulten, E. J.; Creemers, H. M. J. C. *J. Organomet. Chem.* **1969**, *17*, 173. (c) Nagy, J. *Period. Polytech., Chem. Eng.* **1977**, *21*, 211. (d) The EPR spectrum of the radical anion of phenylpentamethyldisilane shows no delocalization of the unpaired spin density onto the second Si atom of the disilane moiety thus indicating that the bonding 3dπ orbital lies higher than the phenyl π* orbital. Gerson, F.; Heinzer, J.; Bock, H.; Alt, H.; Seidl, H. *Helv. Chim. Acta* **1968**, *51*, 707.

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[33] (a) Davidson, R. S. In *Advances in Physical Organic Chemistry*; Gold, V., Bethel, D., Eds.; Academic: New York, 1983; Vol. 19, Chapter 1. (b) Eaton, D. F. *J. Am. Chem. Soc.* **1981**, *103*, 7235 and references therein.

[34] (a) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Abstracts of Papers*, 8th International Symposium on Organosilicon Chemistry, St. Louis, MO; American Chemical Society: Washington, DC, 1987; p 89. (b) Watanabe, H.; Kato, M.; Tabei, E.; Kuwabara, H.; Hirai, N.; Sato, T.; Nagai, Y. *J. Chem. Soc., Chem. Commun.* **1986**, 1662. (c) Nakadaira, Y.; Komatsu, N.; Sakurai, H. *Chem. Lett.* **1985**, 1781. (d) Sakurai, H.; Sakamoto, K.; Kira, M. *Ibid.* **1984**, 1213.

Table IV. Stern–Volmer Data and Rate Constants for the Quenching of the Fluorescence of Aromatic Acetylenes by Hexamethyldisilane and Dodecamethylcyclohexasilane

compound	concn, M	quencher[a]	excitation wavelength λ_{ex}, nm	emission[b] wavelength λ_{em}, nm	$k_q\tau$(isooctane), M^{-1}	$10^9\tau$, s	k_q(isooctane), $M^{-1}\,s^{-1}$
PhC≡CH (**6**)	9.1×10^{-4}	Me_6Si_2	245	296	0.15 ± 0.006	6.3[d]	2.4×10^7
2-naph-C≡CH (**3**)	1.04×10^{-4}	Me_6Si_2	290	348	*c*	14[e]	*h*
2-naph-C≡CH (**3**)	9.86×10^{-5}	$Me_{12}Si_6$	295	348	28.6 ± 3.5	14[e]	2.0×10^9
4-NCPhC≡CH (**4**)	2.83×10^{-5}	Me_6Si_2	261	304	43.3 ± 0.6	8.2[f]	5.3×10^9
4-MeOPhC≡CSiMe$_3$ (**11**)	7.14×10^{-5}	Me_6Si_2	270	315	0.15 ± 0.004	*g*	
4-NCPhC≡CSiMe$_3$ (**5**)	2.61×10^{-5}	Me_6Si_2	276	306	32.3 ± 0.2	7.7[f]	4.2×10^9

[a] Me_6Si_2 = hexamethyldisilane; $Me_{12}Si_6$ = dodecamethylcyclohexasilane. [b] Emission wavelength used for monitoring the Stern–Volmer quench. [c] Concentrations of added hexamethyldisilane as high as 4.98 M did not yield any detectable quenching. [d] Isooctane. [e] Acetonitrile. [f] Isopentane. [g] Not measured. [h] Less than 1 × 10^7.

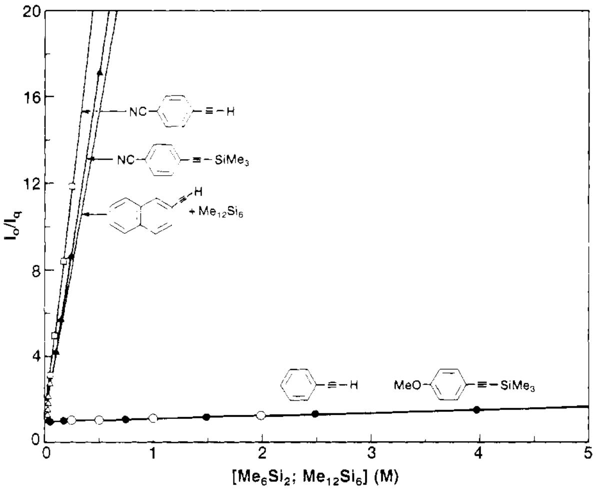

Figure 9. Stern–Volmer plots for the fluorescence quenching of substituted arylacetylenes by hexamethyldisilane and dodecamethylcyclohexasilane in air-saturated isopentane at 298 K: [(4-methoxyphenyl)ethynyl]trimethylsilane (**11**)/Me_6Si_2, ○; phenylacetylene (**6**)/Me_6Si_2; ●; (2-naphthylethynyl)trimethylsilane (**2**)/$Me_{12}Si_6$, △; [(4-cyanophenyl)ethynyl]trimethylsilane (**5**)/Me_6Si_2, ▲; (4-cyanophenyl)acetylene (**4**)/Me_6Si_2, □.

terized the quenching mechanism as involving a $\sigma \rightarrow \pi^*$ electron transfer in which the hexamethyldisilane acts as the electron donor and the $^1(\pi,\pi^*)$ state of the aromatic acts as the acceptor. Therefore in order to confirm the feasibility of our proposed $^1(\sigma,\pi^*)$ CT state fluorescence in the (phenylethynyl)pentamethyldisilanes, we have demonstrated the intermolecular fluorescence quenching of a series of aromatic acetylenes by hexamethyldisilane and dodecamethylcyclohexasilane.

The fluorescence of a series of aromatic acetylenes was quenched by hexamethyldisilane by using static quenching techniques. In each case, the quenching followed the Stern–Volmer[35] equation where I_0 and I_q are the relative fluorescent intensities

$$I_0/I_q = k_q\tau_s[Q] + 1 \qquad (2)$$

in the absence and presence of quencher Q (hexamethyldisilane), τ_s is the singlet-state lifetime of the acetylene derivative, and k_q is the bimolecular quenching rate constant. The plots of I_0/I_q vs concentration of hexamethyldisilane were linear with intercepts of 1.0 as shown in Figure 9. Values of the slopes $k_q\tau_s$ are given in Table IV along with the singlet-state lifetimes for the various acetylenes and the values obtained for the bimolecular quenching rate constants. Phenylacetylene (**6**) fluorescence and (4-methoxyphenyl)(trimethylsilyl)acetylene (**11**) fluorescence are quenched with a very small value for the bimolecular rate constant (10^7). In contrast the fluorescence of (4-cyanophenyl)acetylene (**4**) and of (4-cyanophenyl)(trimethylsilyl)acetylene (**5**) are quenched efficiently with measured bimolecular rate constants approaching the diffusion limit. These results are exactly what one would expect for a $\sigma \rightarrow \pi^*$ ET quenching mechanism, the IPs of the 4-cyano derivatives being up to 0.6 eV greater than those of phenylacetylene (**6**) and (4-methoxyphenyl)trimethylsilane (**11**) and thus having HOMOs lying below that of hexamethyldisilane (IP = 8.7 eV). As a consequence, electron transfer from the Si–Si σ bond to the lowest energy SOMO of the acetylene derivative is exothermic. 2-Naphthylacetylene (**3**) fluorescence is not quenched by hexamethyldisilane. In this case, the HOMO of 2-naphthylacetylene (**3**) (IP = 8.11 eV)[29] lies above the HOMO of hexamethyldisilane (IP = 8.7 eV) and $\sigma \rightarrow \pi^*$ electron transfer is endothermic. However, dodecamethylcyclohexasilane (IP = 7.79 eV)[36] efficiently quenches the fluorescence of (2-naphthyl)acetylene (**3**) with a bimolecular quenching rate constant near the diffusion limit. In this case the HOMO of the cyclic silane is either thermoneutral with or above that of the acetylene derivative. The quenching rates and orbital energies for these intermolecular-quenching reactions are fully analogous with the σ,π^* CT interactions observed in the (phenylethynyl)pentamethyldisilanes.

Discussion

The demonstration of the involvement of CT or ET processes in these (phenylethynyl)pentamethyldisilanes and in a variety of intermolecular fluorescence quenching reactions involving polysilanes suggests that CT or ET may play a role in the photochemical reactions of a wide variety of aromatic polysilanes.

Shizuka et al.[4] have recently investigated the emissive singlet states of a series of phenyl-substituted pentamethyldisilanes. These states are characterized by an emission usually observed in polar solvents which is broad and featureless and is red-shifted of the phenyl-substituent fluorescence. These short-lived fluorescent emissions, which are often observed in organic glasses at 77 K, have been assigned to a $^1(2p\pi,3d\pi)$ state. However, recent work by Sakurai[37] suggests that the direction of charge transfer is in fact from the disilane moiety to the $2p\pi^*$ excited state of the aromatic. He has suggested that the charge transfer requires a twisting in the excited state similar to that in the well-known TICT states.[5] However, one distinguishing feature is that the charge transfer is from a σ-bonding level and not from a lone pair of electrons. Sakurai has suggested that these systems be assigned the general name of orthogonal intramolecular charge transfer states (OICT). In fact, if one surveys the compounds studied by Shizuka and Ishikawa et al.,[3] the CT emission is only observed in those cases where the IP of the aryl substituent is sufficiently high that the charge transfer from the disilane to the $^1(\pi,\pi^*)$ state of the aromatic is exothermic. Thus the emission is observed when the aromatic ligand is phenyl, 2-methylphenyl, and 2,5-dimethylphenyl. However, when the IP is raised further by additional alkyl substitution, the band is eliminated and no charge transfer is observed for the anthyl, phenanthryl, or pyrenyl

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substituents, all of which have IPs less than that of the disilane substituent. This is exactly the prediction for a $^1(\sigma,\pi^*)$ CT state but not for the $^1(2p\pi,3d\pi)$ state postulated by Shizuka and Ishikawa. With the $^1(\sigma,\pi^*)$ state mechanism for CT, no specific conformational explanation is required to explain the absence of a CT emission from anthryl-, phenanthryl-, pyrenyl-, and mesitylpentamethyldisilane. For example, the 0.85 eV lower IP of the mesityl group compared to that of a phenyl substituent results in a HOMO which lies above that for the pentamethyldisilanyl group thus making $\sigma \rightarrow \pi^*$ charge transfer endothermic. Analogous intramolecular CT interactions have been found between peralkylpolysilanes and 1,1-dicyanoethylene linked by two or three methylene groups.[38]

A $\sigma \rightarrow \pi^*$ CT mechanism for the (phenylethynyl)pentamethyldisilane derivatives and these other aromatic polysilane systems is also most consistent with the early detailed investigations of the nature of the electronic interactions in aryl-substituted polysilanes by Pitt et al.[39] Using IP data and half-wave reduction potentials for a series of aromatic polysilanes Pitt concluded that the relative energies of the σ and π electrons have a substantial influence on the character of the HOMO and therefore the electronic spectra of these compounds. The effect of the extension of the $3d\pi$ MOs of the polysilane chain was found to be minimal.

Much effort has been extended on the determination of the mechanism of the photochemical cleavage of polysilane high polymers.[40] The investigation of these mechanisms has taken on particular importance because of the potential technological applications of these materials as photoresists and photoinitiators.[41] While the mechanism of the cleavage of alkyl-substituted polysilane high polymers has been shown to occur largely through radical- and silylene-extrusion processes, some anomalies occur with the phenyl-substituted polysilanes. For example, the quantum yield for photoscission of poly(methylphenylsilane) in solution is 5 times higher than that of poly(dodecylmethylsilane),[42] and the quantum yields for photochemical crosslinking of the aromatic polysilanes is in general higher than that for alkyl-substituted polysilanes. It has been demonstrated that in phenyl-substituted polysilanes significant orbital interactions between the σ conjugated silane HOMO and the π orbitals of the aromatic side chain occur.[43] In these systems $\sigma \rightarrow \pi^*$ charge transfer analogous to that observed in the present investigation may occur resulting in an additional photochemical degradation pathway. The extent of involvement of CT states in the photochemical cleavage reactions of phenyl-substituted polysilanes in solution will however likely be controlled by the polarity of the solvent used, increasing with increased solvent polarity. Sakurai has recently demonstrated increased involvement of CT states in the photochemical reactions of phenyldisilanes with increased solvent polarity.[37]

In polysilane films, CT processes are less likely since the polymer itself provides a significantly nonpolar environment. However, recently, a long-wavelength emission (broad, 400–500 nm) with a picosecond lifetime has been observed from poly(methylphenylsilane).[44] This emission feature, which is reminiscent of the CT emission band observed for the phenylpentamethyldisilanes and (phenylethynyl)pentamethyldisilanes, has been assigned to a $^1(\sigma,\pi^*)$ intrapolymer charge-transfer state. However, Harrah and Zeigler have demonstrated that this emission grows with emission time (313 nm) and probably involves emission from a photoproduct.[44c]

In solution, naphthyl-substituted polysilanes show only emission features associated either with the isolated naphthyl chromophore or isolated silane backbone.[43,45] Since the naphthyl chromophore's IP is lower than that of the Si–Si σ bond framework, no CT or ET occurs when the naphthyl chromophore is excited. In the phenyl-substituted case, however, the IP of the phenyl side chain is higher than that of the Si–Si framework. An electron transfer followed by a radical ion cleavage process could be involved. Interestingly, the emission quantum yields from the phenyl-substituted polysilanes are lower than those of the alkyl-substituted polymers and its phosphorescence is $^1/_{10}$ that of the naphthyl-substituted polymer. These two yield numbers clearly indicate the presence of additional nonradiative pathways in the phenyl-substituted polysilanes and perhaps include ET cleavage mechanisms.[46] Similar cleavage mechanisms might be postulated for the scission of poly[*p*-(disilanylene)phenylene].[47]

A photochemically induced $\sigma \rightarrow \pi^*$ CT or ET analogous to that observed in the (phenylethynyl)pentamethyldisilanes may also potentially explain the observed photoconductivity in phenyl-substituted polysilane high polymers. Zeigler et al.[48] have reported that poly(methylphenylsilane) is a good photoconductor in which only holes are mobile. The electronic transition which creates the carriers was initially reported to involve a $\pi^* \rightarrow \sigma^*$ transition from the excited singlet state of the aromatic side chain to the silicon backbone σ bonds. Hole migration was reported to occur via a hopping mechanism between phenyl groups. More recently the same group has demonstrated that hole migration occurs in the silane Si–Si backbone.[48b] An alternative mechanism suggested by the current investigation would involve excitation of the $^1(\pi,\pi^*)$ state of the phenyl ring followed by electron transfer from the silicon σ-bonded backbone into the lowest energy singly occupied molecular orbital of the excited phenyl group. Hole migration would then occur in the silicon σ-bonded backbone. Recent investigations have shown that hole migration occurs in the silicon framework in alkyl polysilanes.[49] This mechanism also finds analogy in the mechanisms postulated for the generation of semiconductor properties in polysilanes by doping with strong electron acceptors.[50] A CT photoconduction mechanism does not operate, however, in alkyl-substituted polysilanes where hole generation probably involves a σ–σ^* excitation mechanism and exciton migration.

Conclusion

We have demonstrated that $^1(\sigma,\pi^*)$ CT states are formed upon excitation of (phenylethynyl)pentamethyldisilanes having phenyl group IPs greater than ca. 9.2 eV. At room temperature these states do not emit due to facile scission reactions and rearrangements from these $^1(\sigma,\pi^*)$ states. In contrast, at low temperature in rigid organic matrices where rearrangement is hindered, these singlet states fluoresce efficiently, quantum yields being as high as 0.49. Analogous intermolecular ET processes were also demonstrated in the fluorescence quenching of excited-state aromatic acetylenes by simple polysilanes. A variety of other polysilane systems in which similar $\sigma \rightarrow \pi^*$ CT processes

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may play a role were also discussed.

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Registry No. 1a, 34627-92-4; **1b**, 115977-82-7; **1c**, 115977-78-1; **1d**, 115977-81-6; **1e**, 115977-79-2; **1f**, 115977-80-5; **1g**, 115977-83-8; **1h**, 115977-84-9; **4**, 3032-92-6; **5**, 75867-40-2; **6**, 536-74-3; **7**, 34627-90-2; **9**, 115977-86-1; **10**, 2170-06-1; **11**, 3989-14-8; **12**, 75867-41-3; cuprous iodide, 7681-65-4; bis(triphenylphosphine)palladium(II) chloride, 13965-03-2; iodobenzene, 591-50-4; biphenyl, 92-52-4; 1,2-diethynyltetramethyldisilane, 54773-31-8; ethynylmagnesium bromide, 4301-14-8; chloropentamethyldisilane, 1560-28-7; 1,2-dichlorotetramethyldisilane, 4342-61-4.

Rotational Barriers. 4. Dimethoxymethane. The Anomeric Effect Revisited

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Abstract: The conformational energy map for the rotamers of dimethoxymethane has been calculated using both the 3-21G and 6-31G* basis sets with complete geometry optimization in each case. Higher level calculations including electron correlation also have been performed on selected rotamers. At larger torsional angles, the map has approximate 4-fold symmetry, and this symmetry may be used to quantify the difference in the interactions in the (+sc, −sc) and (+sc, +sc) regions. Large changes in bond angles were found, and the dipole moment also changed considerably on C–O bond rotation. Calculations on equatorial and axial 2-methoxytetrahydropyran show that the axial form is favored by 1.33 kcal/mol, in fair agreement with experiment. Calculations also were carried out on the two lowest energy forms of 1,1-dimethoxyethane and on five forms of methyl propyl ether. Consideration of all these data indicates that the anomeric stabilization in dimethoxymethane is much greater than in sterically more congested systems, but the stabilization of 1,1-dimethoxyethane is similar to that of 2-methoxytetrahydropyran and other acetals.

Molecular modeling is of increasing importance in many areas of chemistry. The most commonly used method, molecular mechanics,[1] requires a knowledge of potential functions for bond length distortion, bond angle distortion, rotation about single bonds, nonbonded interactions, and atomic charges. Whereas the first two of these may be obtained from vibrational spectroscopy, the latter three frequently present experimental problems.

We have begun an analysis of rotational barriers and have presented information concerning barriers to rotation adjacent to carbonyl groups.[2-4] Here, it was possible to show that the barrier had three components: (a) dipole–induced dipole stabilizing interaction between the carbonyl and an adjacent alkyl group; (b) the 3-fold barrier characteristic of the unsubstituted compound (e.g. acetaldehyde, acetone, or acetic acid); (c) in some of the rotamers a gauche or syn repulsive interaction between the substituents attached to the carbonyl.

We now address the more general case of rotational barriers in the absence of unsaturated groups. Recently, we have studied rotational isomerism in alkanes,[5] 2-haloethanols,[6] and 1,2-dihaloethanes,[7] and in each case found that good agreement with experiment could be achieved with ab initio methods. In general, it is necessary to employ split-valence basis sets augmented by polarization functions and to correct for electron correlation.[8] Compounds in which the anomeric effect is found are of particular interest with respect to rotational barriers. This effect was first uncovered in studies of α-methyl glucosides in which it was found that the methoxy group preferred an axial orientation,[9] despite the contrary observation in the cyclohexane series.[10,11] Many experimental studies have shown that this is a general effect and also have shown that the axial C–O bond is longer than one in an equatorial position by $\sim$0.1 Å.[12]

A number of theoretical studies have been carried out in order to provide an explanation for this effect. Some semiempirical methods do not reproduce the gauche preference and bond length alterations. For instance, it was found that extended Hückel and MINDO/2 did not predict the correct global minimum for dimethoxymethane (DMM).[13] On the other hand, ab initio methods at all levels do reproduce the unusual anomeric geometries.[14,15] In one of the more comprehensive studies, Pople et al.[15] studied the rotamers of DMM using a 60° grid and the rigid rotor approximation with the 4-31G basis set. Their results were conveniently expressed with a contour plot showing the change

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