

for nmr or glpc analysis. The amount of chloro- and bromosilane produced was measured by integration of the methyl nmr resonances of the silanes. If the silane contained no methyl group standard glpc techniques were employed to determine the ratio of $\text{CHCl}_3/\text{HCBrcCl}_2$ formed. A duplicate run was made and the two selec-

tivity ratios $[\text{SiBr}]/[\text{SiCl}]$ were averaged. Reproducibility within $\pm 5\%$ was observed.

Acknowledgment. We thank Dow Corning Corporation for vital support which made this work possible.

Nature of the Electronic Interactions in Aryl-Substituted Polysilanes^{1a}

C. G. Pitt,*^{1b} R. N. Carey, and E. C. Toren, Jr.

Contribution from the Chemistry and Life Sciences Laboratory, Research Triangle Institute, Research Triangle Park, North Carolina 27709, The Paul Gross Chemical Laboratory, Duke University, Durham, North Carolina 27706, and the Departments of Medicine and Pathology, University of Wisconsin, Madison, Wisconsin 53706. Received August 20, 1971

Abstract: The ionization potentials and half-wave reduction potentials of a series of α -naphthyl- and phenyl-substituted polysilanes have been determined and used to elucidate the nature of the electronic interactions between aryl and polysilyanyl groups. It is shown that the relative energies of the σ and π electrons have a substantial influence on the energy and character of the highest occupied molecular orbital, and hence the electronic spectra of these compounds. The effect of extension of the $3d_\pi$ molecular orbital of the polysilane chain is found to be minimal.

Historically, interest in the electronic properties of polysilanes and the heavier group IV catenates was first stimulated by the report² of the anomalous ultraviolet absorption spectra of their phenyl derivatives. For example, whereas the phenylated monomers $(\text{C}_6\text{H}_5)_4\text{M}$, $\text{M} = \text{C}, \text{Si}, \text{Ge}, \text{Sn},$ and Pb , exhibit only a slightly perturbed $^1\text{L}_a$ transition (206–211 nm)³ associated with the benzene π system, the absorption maxima of the dimeric derivatives $(\text{C}_6\text{H}_5)_3\text{M} \cdot \text{M}(\text{C}_6\text{H}_5)_3$, $\text{M} = \text{Si}, \text{Ge}, \text{Sn},$ and Pb , are strongly red shifted (230–246.5 nm). Hague and Prince^{2a} originally favored assigning this absorption to a $\pi_{\text{C}=\text{C}} \rightarrow 3d(\pi)_{\text{Si}-\text{Si}}$ charge-transfer transition, where the π electron is excited to a molecular orbital derived from extended overlap of the adjacent $\text{Si}-3d$ orbitals of the silicon chain (Figure 1a). Subsequently, however, spectroscopic analysis was complicated by the demonstration that the permethylated catenates also absorb in the ultraviolet (Table I),⁴ and that the transition need not necessarily be directly associated with the benzenoid π electrons.

In recent publications^{4,5} the nature of the electron spectra of the permethylated polysilanes, $\text{Me}(\text{Me}_2\text{Si})_n\text{Me}$, has been discussed in some detail. The shift of the long wavelength maximum with chain length (n)

(1) (a) Work done in partial fulfillment of Ph.D. requirements of R. N. C. at Duke University. A portion of this work has been presented previously: Organosilicon Symposium, Pittsburgh, Pa., 1971. (b) Correspondence should be addressed to Research Triangle Institute.

(2) (a) D. N. Hague and R. H. Prince, *Proc. Chem. Soc.*, 300 (1962); *Chem. Ind. (London)*, 1492 (1964); *J. Chem. Soc.*, 4690 (1965); (b) H. Gilman, W. H. Atwell, and G. L. Schwebke, *Chem. Ind. (London)*, 1063 (1964).

(3) (a) G. Milazzo, *Gazz. Chim. Ital.*, 71, 73 (1941); C. N. R. Rao, J. Ramachandran, and A. Balasubramanian, *Can. J. Chem.*, 39, 171 (1961); S. R. LaPaglia, *J. Mol. Spectrosc.*, 7, 427 (1961).

(4) For a compilation and critical evaluation of the published spectra, see B. G. Ramsey, "Electronic Transitions in Organometalloids," Academic Press, New York, N. Y., 1969.

(5) (a) C. G. Pitt, *J. Amer. Chem. Soc.*, 91, 6613 (1969); (b) C. G. Pitt, M. M. Bursey, and P. F. Rogerson, *ibid.*, 92, 519 (1970).

Table I. Absorption Maxima of Methyl- and Phenylpolysilanes

n	Absorption, nm	
	$\text{Me}(\text{SiMe}_2)_n\text{Me}$	$\text{Ph}(\text{SiMe}_2)_n\text{Ph}$
2	193	236
3	216	243
4	235	250.5
5	250	257.5
6	260	265

has been shown^{5b} to correlate linearly with the ionization potential (IP), *i.e.*, the energy of the occupied highest MO, which is primarily $\sigma_{\text{Si}-\text{Si}}$ in character. In many respects the polysilanes resemble the homologous alkane series $\text{H}(\text{H}_2\text{C})_n\text{H}$, and the fact that the polysilanes absorb at longer wavelength than the alkanes is at least partially explained by the differences in IP of the two homologous series. The nature of the excited state of the polysilanes is less clear, though the fact that cyclic polysilanes form delocalized radical anions,⁶ whereas alkanes do not, does lend credence to the idea that the excited state may involve an extended MO derived from $3d_\pi\text{-Si}$ overlap.⁷ Considering the aryl-substituted polysilanes, the modified absorption spectra (Table I) can be adequately described in terms of a red shifted $\sigma_{\text{Si}-\text{Si}} \rightarrow 3d_{\text{Si}-\text{Si}}$ transition, where the excited state is stabilized by interaction of the $3d_{\text{Si}-\text{Si}}$ MO with the $p-\pi^*$ MO of the aryl group (Figure 1b). This supports the concept of a delocalized $3d_{\text{Si}-\text{Si}}$ MO. On the other hand, it has also been pointed out^{5b} that the ground state $\sigma_{\text{Si}-\text{Si}}-p_\pi$ interaction must also be considered (Figure 1b), and equally well explains the spec-

(6) E. Carberry, R. West, and G. E. Glass, *ibid.*, 91, 5446 (1969); G. R. Husk and R. West, *ibid.*, 87, 3993 (1965).

(7) This molecular orbital is unlikely to be pure $\text{Si}-3d$ and most probably contains some admixture of $\text{Si}-4p$ orbitals and $\sigma^*_{\text{Si}-\text{C}}$ orbitals of appropriate symmetry. However, $\text{Si}-3d$ serves as a convenient label.

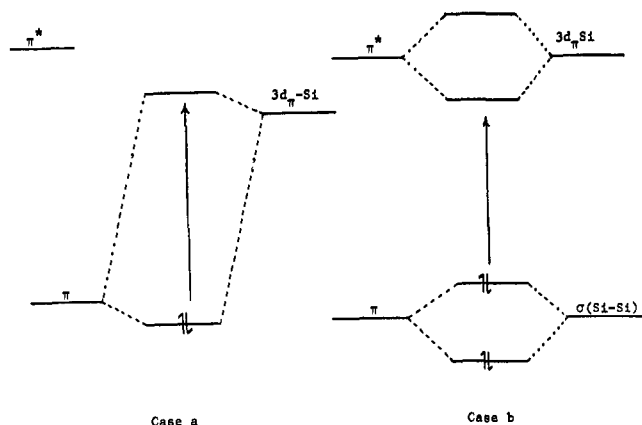


Figure 1. Qualitative MO models of the origin of the long wavelength absorption band of aryl-substituted polysilanes.

tral results. In these organometallic systems the electropositive σ framework will be of comparable energy to p_π (and lone-pair) electrons, and consequently σ - p_π interaction is energetically more favorable than d - p_π interaction.

Aryl-substituted polysilanes are ideal substrates for assessing the relative importance of these suggested mechanisms, since the effect of the interaction of the polysilane chain and the aryl π system can readily be assessed by using ionization potential and half-wave reduction potential measurements to determine changes in the energy of both the bonding and antibonding molecular orbitals. This approach has previously been used to study the effects of alkylation⁸ of aromatics and, more recently, the effects of monosilylation and germylation.^{9,10} In this paper we describe its application to various 1-naphthyl- and phenyl-substituted polysilanes.

Results and Discussion

Ionization Potentials. Koopman's theorem¹¹ equates the negative of the energy of the highest occupied MO of a molecule with the IP. It therefore follows that by comparing the IP of the aryl polysilanes with the IP's of the parent arene and polysilane it is possible to assess the extent of interaction between the two component parts. In collaboration with Professor Bock,¹² the photoelectron spectrum of $C_6H_5Si_2Me_3$ has been determined and found to exhibit bands of 8.35, 9.07, and 10.03 eV, the latter being partly obscured by the onset of a broader unresolved band at 10 eV. These values may be compared with the photoelectron spectrum bands of benzene at 9.24 eV (π , e_{1g})¹³ and hexamethyldisilane at 8.69 eV (σ_{Si-Si}).¹⁴ The band at 9.07

(8) (a) A. Streitwieser, Jr., "Molecular Orbital Theory for Organic Chemists," Wiley, London, 1961; (b) A. Streitwieser, Jr., and I. Schwager, *J. Phys. Chem.*, **66**, 2316 (1962); (c) L. H. Klemm and A. J. Kohlik, *J. Org. Chem.*, **28**, 2044 (1963); (d) E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963); (e) A. R. Lepley, *ibid.*, **86**, 2545 (1964).

(9) M. D. Curtis and A. L. Allred, *ibid.*, **87**, 2554 (1965); A. L. Allred and L. W. Bush, *ibid.*, **90**, 3352 (1968).

(10) H. Bock, H. Seidl, and M. Fochler, *Chem. Ber.*, **101**, 2815 (1968); H. Bock and H. Alt, *J. Amer. Chem. Soc.*, **92**, 1569 (1970), and references therein.

(11) T. Koopmans, *Physica*, **1**, 104 (1934).

(12) For a preliminary report and discussion, see C. G. Pitt and H. Bock, *J. Chem. Soc. D*, **28** (1970).

(13) D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, "Molecular Photoelectron Spectroscopy," Wiley-Interscience, London, 1970.

eV can clearly be assigned to the ψ_{as} MO of the originally degenerate e_{1g} MO's of benzene, for this MO is nodal at the position of substitution and so only weakly perturbed. The bands at 8.35 and 10.03 eV must therefore be assigned to the linear combinations $C_1\psi_{Si-Si} - C_2\psi_{sym}$ and $C_2\psi_{Si-Si} + C_1\psi_{sym}$, respectively (Figure 2). The 8.35 eV band can hardly be the inductively shifted ψ_{sym} MO, for only a slightly smaller shift would then be expected for the monosilyl derivative $C_6H_5SiMe_3$, whereas in fact the ψ_{sym} band for this compound is at 8.9 eV.^{15,16} The Si_2Me_3 group therefore appears to resemble the CH_2SiMe_3 group, in that there is σ - π mixing when these groups are attached to a benzene ring.¹⁷ However, the Si_2Me_3 group is unique in the sense that the IP of the σ_{Si-Si} electrons is lower than the IP of the benzene π electrons, and as a consequence the band at 8.35 eV must be assigned to a MO which is largely ψ_{Si-Si} , i.e., $C_1 > C_2$. Further evidence in support of this assignment is described elsewhere.¹²

In order to extend this study of IP's to the less volatile α -naphthyl- and *p*-methoxyphenyl-substituted polysilanes, the charge-transfer absorption spectra of the tetracyanoethylene (TCNE) complexes were determined.¹⁸ A simple molecular orbital treatment¹⁹ of charge-transfer spectra has indicated that the energy of the charge-transfer transition, which originates from the transfer of an electron from an orbital which is largely donor to the corresponding acceptor orbital, i.e., $\psi_D \rightarrow \psi_D\psi_A$, can be simply related to the difference in energy of the highest occupied MO of the donor (E_D) and the lowest unoccupied MO of the acceptor (E_A), i.e.

$$h\nu_{CT} = E_A - E_D + 2\beta \quad (1)$$

where β is the interaction energy of the two MOs. For a series of donors of related structure, and a given acceptor, both E_A and β can be treated as constant and a linear correlation of $h\nu$ and E_D is obtained. Equation 1 is equivalent to the linear expression (2) originally

$$h\nu_{CT} = IP_D - E_A - W \quad (2)$$

suggested by McConnell, *et al.*,²⁰ where E_A is the electron affinity of the acceptor and W is the dissociation energy of the excited state of the complex, and is a constant for a given series. Although more detailed theoretical treatments¹⁸ have suggested nonlinear relationships (eq 3), it appears that for the commonly

$$h\nu_{CT} = IP_D - E_A + K_1 + \frac{K_2}{IP_D - E_A + K_1} \quad (3)$$

(14) H. Bock and W. Ensslin, *Angew. Chem., Int. Ed. Engl.*, **10**, 404 (1971).

(15) H. Bock, personal communication.

(16) Y. Vignollet, J. C. Maire, A. D. Baker, and D. W. Turner, *J. Organometal. Chem.*, **18**, 349 (1969).

(17) C. Eaborn and S. H. Parker, *J. Chem. Soc.*, 939 (1954); C. Eaborn, *ibid.*, 4858 (1956); A. R. Bassindale, C. Eaborn, D. R. M. Walton, and D. J. Young, *J. Organometal. Chem.*, **20**, 49 (1969); C. G. Pitt, *ibid.*, **23**, C35 (1970); W. Hanstein, H. J. Berwin, and T. G. Traylor, *J. Amer. Chem. Soc.*, **92**, 829 (1970); T. G. Traylor, W. Hanstein, H. J. Berwin, N. A. Clinton, and R. S. Brown, *ibid.*, **93**, 5715 (1971), and references therein.

(18) For recent reviews, see R. Foster, "Organic Charge-Transfer Complexes," Academic Press, London, 1969; W. B. Person and R. S. Mulliken, "Molecular Complexes: A Lecture and Reprint Volume," Wiley, New York, N. Y., 1969.

(19) M. J. S. Dewar and A. R. Lepley, *J. Amer. Chem. Soc.*, **83**, 4560 (1961); M. J. S. Dewar and H. Rogers, *ibid.*, **84**, 395 (1962); A. R. Lepley, *ibid.*, **84**, 3577 (1962); **86**, 2545 (1964); A. R. Lepley, *Tetrahedron Lett.*, 2823 (1964); A. R. Lepley and C. C. Thompson, *J. Amer. Chem. Soc.*, **89**, 5523 (1967).

(20) H. McConnell, J. S. Ham, and J. F. Platt, *J. Chem. Phys.*, **21**, 66 (1953).

Table II. TCNE Charge-Transfer Maxima, Polarographic Half-Wave Potentials, and Ultraviolet Absorption Spectra of Naphthylpolysilanes

Substituent	—Charge-transfer spectra—		$-E_{1/2}$, eV (± 0.005), <i>vs.</i> Ag AgNO ₃	—Absorption maxima, nm—	
	λ_{\max} , nm	IP, eV		¹ L _b band	¹ L _a band
H	555	(8.12)	2.946	274.9	310.6
Me	592	7.98 ^a	2.964	281.3	313.6
SiMe ₃	578	8.03	2.845	281.6	313.1
SiMe ₂ Ar	579	8.03	2.781, 3.038	284.0	314.0
Si ₂ Me ₅	602	7.95	2.842	285.3	314.3
(SiMe ₂) ₂ Ar	610	7.91	2.816, 2.983	288.3	314.7
Si ₃ Me ₇	608	7.93	2.838	285.7	314.6
(SiMe ₂) ₃ Ar	611	7.92	2.822, 2.924	288.1	314.7
Si(SiMe ₃) ₂ Me	631	7.85		293.1	315.7
CH ₂ SiMe ₃	638	7.83	3.006	290.5	317.0

^a Reported photoionization IP, 7.96 eV (ref 22).

Table III. Charge-Transfer Maxima, Ionization Potentials, Ultraviolet Absorption Maxima, and Oscillator Strengths of *p*-MeO-C₆H₄-X

X	—Charge-transfer spectra—		—Absorption spectra, nm—			
	λ_{\max} , nm	IP, eV ^a	¹ L _a band	¹ L _b band	$f \times 10^2$ (¹ L _b)	f_X/f_H
H	508 ^b	8.18 ^c	219.5	277.5	22.9 ^d	1.00
Me	562 ^b	7.91	223.2 ^e	285.7	25.0	1.09
SiMe ₃	538	8.03	229.9 ^f	280.5	18.3 ^d	0.80
Si ₂ Me ₅	574	7.85	237.3	283.3	17.5	0.76

^a Derived from ν_{\max}^{CT} using the relationship $h\nu = 0.82IP - 4.28$ of Farrell and Newton.^{21c} ^b Reference 21b. ^c Photoionization IP, 8.20, 8.22 eV.²² ^d W. K. Musker and T. B. Savitsky, *J. Phys. Chem.*, **71**, 431 (1967). ^e Inflection point at 227 nm. ^f Shoulder at 234 nm.

studied donors and acceptors the values of K_1 and K_2 are such that a linear relationship is observed. Thus, numerous experimental studies^{10,18–21} of different π hydrocarbons and substituents have demonstrated a linear relationship between $h\nu_{CT}$ and either the IP or its theoretical counterpart, the eigenvalue of the one electron MO. Importantly Bock¹⁵ has found that ν_{CT} of the series C₆H₅X, X = H, Me, SiMe₃, Si₂Me₅, and CH₂SiMe₃, correlates well with the photoelectron spectroscopic IP's, indicating that the linear relationship is valid for these substituent groups.

The TCNE charge-transfer absorption maxima for the 1-naphthylpolysilanes are shown in Table II. The corresponding IP's were obtained using eq 2, with the constant ($E_A + W$) = 5.88 derived from the reported²² photoionization IP of naphthalene. The numbers are only intended to provide an approximate estimate of the magnitude of the changes in energy effected by the substituents. The Me₃SiCH₂ derivative is included for comparison purposes. The order of perturbation, as determined by ν_{CT} , is H < Me₃Si < Me < Me₅Si₂ < *n*-Me₇Si₃ < *i*-Me₇Si₃ < Me₃SiCH₂. An important difference between the naphthyl and phenyl series is the fact that the IP of the naphthyl π system (8.12 eV)²² is lower than that of the σ system of any of the substituents, including the polysilanes (Me₆Si₂, 8.69 eV; Me₃Si₃, 8.19 eV).¹⁴ Thus on mixing the σ and π MO's of the naphthylpolysilanes, the highest occupied MO will be predominantly π naphthyl (*i.e.*, C₁ < C₂, Figure 2). Trends in the properties of the naphthyl- and phenylpolysilanes are therefore likely to be dissimilar when the properties in question are dependent on the

nature of the highest occupied MO. The electronic spectra of the two series (*vide infra*) illustrate this point very well. The IP's of the *p*-methoxyphenyl series *p*-MeOC₆H₄X, X = H, Me, SiMe₃, and Si₂Me₅, have also been determined by means of their TCNE charge-transfer spectra. Here again the IP of the π electrons is lower than that of the σ electrons, and so the results (Table III) should primarily reflect changes in the π system.

Polarographic Half-Wave Reduction Potentials. Polarographic reduction of aromatic hydrocarbons involves the addition of an electron to the lowest unoccupied MO (ψ_{-1}) of the π system.⁸ The half-wave potential $E_{1/2}$ is given by eq 4, where D_R and $R^{\cdot-}$ are

$$E_{1/2} = \frac{\Delta F^\circ}{F} - \frac{RT}{F} \ln \frac{D_R}{D_{R^{\cdot-}}} \quad (4)$$

the diffusion constants of the hydrocarbon R and its radical anion, and ΔF° is given by

$$\Delta F^\circ = (F^\circ_R)_{\text{gas}} - (F^\circ_{R^{\cdot-}})_{\text{gas}} + (F^\circ_{\text{electron}}) + \Delta\Delta F^\circ_{\text{solvent}} \quad (5)$$

For a series of similar compounds, the diffusion term may be neglected. Therefore, in the absence of appreciable solvation energy differences ($\Delta\Delta F^\circ_{\text{solvent}}$), $E_{1/2}$ is a measure of the relative energy of ψ_{-1} ; *i.e.*, in HMO terminology^{8a}

$$E_{1/2} = -(\alpha - x_i\beta) + \text{constant}$$

The phenyl-substituted polysilanes Ph(SiMe₂)_{*n*}Me and Ph(SiMe₂)_{*n*}Ph cannot be studied polarographically, the reduction wave occurring at potentials greater than that of the solvent wave. This is not a problem with the analogous naphthylpolysilanes, and the half-wave potentials for the naphthalene series, determined in dimethylformamide using a Ag|AgNO₃ reference electrode, are shown in Table II. Cyclic voltammetry and standard line-shape criteria confirm that this reduction

(21) (a) G. Briegleb, *Angew. Chem., Int. Ed. Engl.*, **3**, 617 (1964); (b) E. M. Voigt, *J. Amer. Chem. Soc.*, **86**, 3611 (1964); E. M. Voigt and C. Reid, *ibid.*, **86**, 3930 (1964); (c) P. G. Farrell and J. Newton, *J. Phys. Chem.*, **69**, 3506 (1965); (d) A. Ledwith and H. J. Woods, *J. Chem. Soc. B*, 310 (1970).

(22) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," U. S. Department of Commerce, Washington, D. C., 1969.

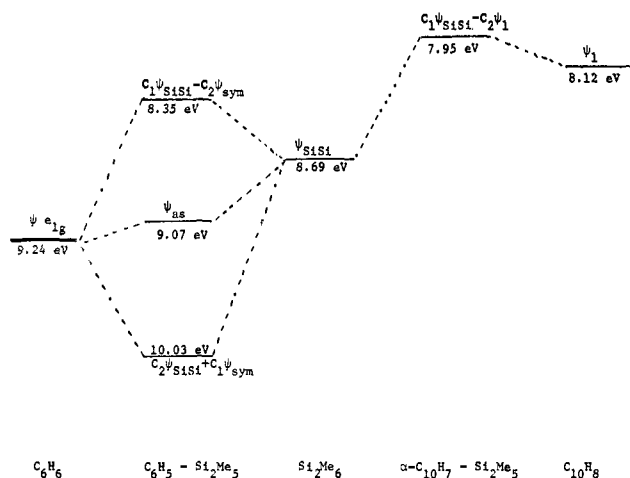


Figure 2. Molecular orbital diagram of interaction of Si_2Me_5 group with highest occupied π MO's of benzene and naphthalene.

is a one-electron reversible process (see Experimental Section).

Both the alkyl and the trialkylsilyl substituents will interact with the π system of alternate aromatic hydrocarbons by an inductomeric and a hyperconjugative (σ - π) mechanism. To a good approximation, the inductomeric effect will raise the energies of ψ_1 and ψ_{-1} equally.²³ The σ - ψ interaction will also raise the energies but, because of the larger energy separation of the σ and ψ_{-1} orbitals relative to the σ - ψ_1 separation, the perturbation of ψ_{-1} will be relatively smaller. For the silyl group, the vacant 3d (Si) orbitals can also interact with ψ_{-1} and ψ_1 , in this case lowering the energies with the major perturbation involving ψ_{-1} . These effects are summarized in Figure 3. Thus experimentally it is found^{9,10} that, whereas alkyl groups increase $E_{1/2}$, the Me_3Si group decreases $E_{1/2}$. However, the question of interest here is whether extending the silicon chain will bring about a further stabilization of ψ_{-1} .

The polarographic results are summarized in Table II. While monosilylation of naphthalene produces a decrease in the $E_{1/2}$ of 0.12 eV, a comparison with the di- and trisilyl derivatives shows that $E_{1/2}$ is virtually unchanged by the addition of a second and third silicon atom to the chain. On the basis of the increasing inductive and hyperconjugative effects of the $(\text{SiMe}_2)_n\text{Me}$ group with increasing chain length (n), as measured by the decreasing IP of ψ_1 , one might also have expected to see a corresponding but attenuated destabilization of ψ_{-1} . For example, in the cases of the Me and Me_3SiCH_2 substituents, which only interact with ψ_{-1} by an inductive and hyperconjugative mechanism, $E_{1/2}$ is increased by increments of 0.02 and 0.06 eV, respectively, relative to naphthalene. The latter increments are compatible with the relative energy changes (0.16, 0.30 eV) in ψ_1 which these two groups produce, bearing in mind the larger energy separation of the σ and ψ_{-1} orbitals relative to the σ - ψ_1 separation. Since, within experimental error, $E_{1/2}$ for the series $(\text{SiMe}_2)_n\text{Me}$, $n = 1-3$, remains constant, it is reasonable to assume that there is a very small but finite increase in stabilization (*ca.* 0.05 eV) attributable to extended 3d $_{\pi}$ overlap.

(23) J. N. Murrell, "The Theory of the Electronic Spectra of Organic Molecules," Methuen, London, 1963.

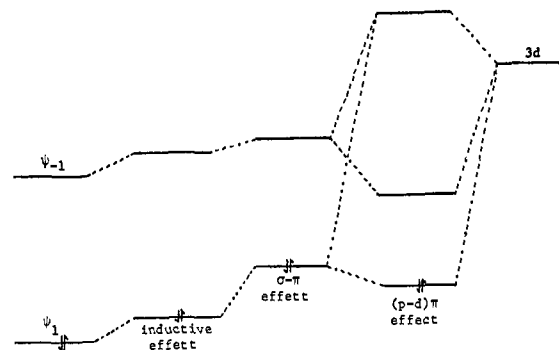


Figure 3. Perturbation of the ψ_1 and ψ_{-1} orbitals of naphthalene by (a) the inductive effect, (b) the σ - π effect, and (c) the (p-d) π effect of a substituent.

The results for the bisnaphthyl series, $\text{Ar}(\text{SiMe}_2)_n\text{Ar}$, confirm the absence of any substantial delocalization. As expected,²⁴ two overlapping waves are observed for this series, their separation ($\Delta E_{1/2}$) being a reflection of both through-space and through-bond interactions of the naphthyl radical anions. The $\Delta E_{1/2}$ is largest for the monosilane (0.26 eV), decreasing to 0.10 eV for the trisilane, showing that the two aromatic groups interact less as the chain length increases. The absolute values of $E_{1/2}$ also approach -2.84 eV, the half-wave reduction potential of the mononaphthyl series, as the chain length increases.

Finally, the half-wave reduction potentials of *p*-bis(trimethylsilyl)benzene and *p*-bis(pentamethyldisilyl)benzene were determined in order to establish the generality of the above results. Values of -3.26 and -3.23 eV, respectively, were obtained. The closeness of these waves to the solvent reduction wave leads to greater experimental uncertainty in the numbers, but again it appears that extension of the silane chain has little effect on the energy of ψ_{-1} . Permethylated polysilanes, $\text{Me}(\text{SiMe}_2)_n\text{Me}$, $n = 2-5$, are not reduced polarographically and so the above reduction processes must involve the ψ_{-1} orbitals of the aryl group.

Electronic Absorption Spectra. The electronic spectrum of naphthalene, a typical alternate cyclic hydrocarbon, consists of three bands in the ultraviolet.²⁵ The $^1\text{L}_b$ (310 nm) and ^1B (220 nm) bands originate from first-order configurational interaction of the degenerate $\psi_2 \rightarrow \psi_{-1}$ and $\psi_1 \rightarrow \psi_{-2}$ transitions, while the $^1\text{L}_a$ band (275 nm) is derived from the nondegenerate $\psi_1 \rightarrow \psi_{-1}$ transition. Since the $\psi_1 \rightarrow \psi_{-1}$ transition is subject to only minor second-order configurational interaction, the energy of the $^1\text{L}_a$ band can be related⁸ to the relative energies of ψ_{-1} and ψ_1 as determined by $E_{1/2}$ and the IP. The electronic spectrum of benzene is somewhat more complicated because of the high symmetry and the possibility of four degenerate $\psi_1 \rightarrow \psi_{-1}$ transitions. Configurational interaction leads to three transitions in the ultraviolet, at 260 ($^1\text{L}_b$), 200 ($^1\text{L}_a$), and 185 nm (^1B). The $^1\text{L}_a$ transition approximates the $\psi_1 \rightarrow \psi_{-1}$ transition, and so is comparable to the $^1\text{L}_a$ band of naphthalene.

The ability of substituents to perturb the $^1\text{L}_a$ bands of benzene and naphthalene may therefore be correlated

(24) P. Zuman, "Substituent Effects in Organic Polarography," Plenum Press, New York, N. Y., 1967, pp 206-215.

(25) For a more complete discussion of the spectra of naphthalene, benzene, and their derivatives, see, for example, ref 23.

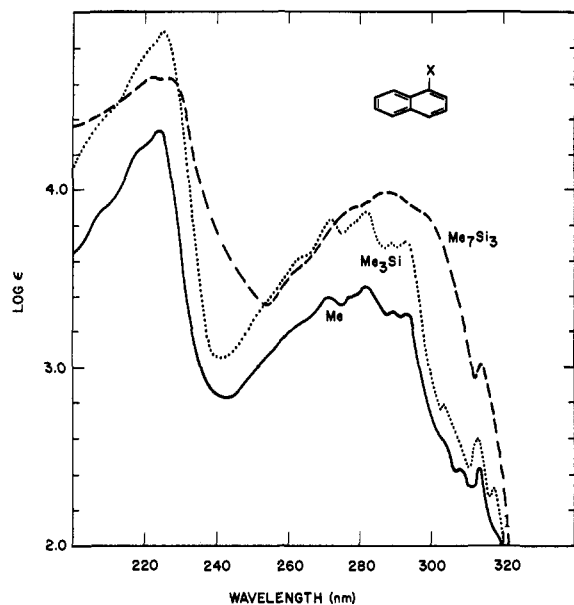


Figure 4. Absorption spectra of α -C₁₀H₇X, X = Me (—), Me₃Si (·····), and *n*-Me₇Si₃ (---). Log ϵ_{obsd} of the methyl derivative is attenuated to allow better comparison of spectra.

with their ability to modify the energies of the ψ_1 and ψ_{-1} molecular orbitals. This correlation will not hold if there is mixing of the excited state $\psi_1\psi_{-1}$ with states of comparable energy associated with the substituent, but it serves as a basis for the rationalization of the spectral trends. It is also assumed that the singlet-triplet splitting of the excited state will be the same for the series of similar substituents, and so can be neglected.

The ultraviolet absorption maxima (¹L_a, ¹L_b bands) of the naphthyl substituted polysilanes are compiled in Table II. It is immediately obvious that the spectral shifts of the naphthyl series are relatively insignificant when compared to the phenyl series (Table I) and the small changes in the energy (0.3 eV) of the ¹L_a band can be adequately accounted for by the corresponding small changes in $E_{1/2}$ and the IP. There is no evidence of any new absorption bands in the spectra of the α -naphthyl compounds, although there is loss of vibrational structure as the silicon chain increases and the D_{2h} symmetry of naphthalene is distorted. There is also an increase in end absorption (Figure 4), which is possibly related to transitions involving the polysilane chain. Essentially the same spectral results are obtained in the *p*-methoxyphenyl series, where slightly red shifted but clearly identifiable ¹L_a and ¹L_b bands are again observed (Table III). In the latter series the bathochromic shifts can be rationalized on the basis of the decreasing IP's (Me₃Si₂ > Me > Me₃Si > H (Table III)) coupled with the *expected* order of $E_{1/2}$ (Me₃Si₂ ~ Me₃Si ≪ H < Me). While this order of stabilization of the ψ_{-1} orbital by the substituents cannot be confirmed polarographically, the similarity of the Me₃Si and Me₃Si₂ groups is suggested by Goodman's²⁶ criterion that the ratio of the oscillator strengths f_X/f_H of the ¹L_b transition of *p*-MeOC₆H₄X is determined by the promotional energy difference $E(\psi_1^{\text{as}} - \psi_{-1}^{\text{sym}}) - E(\psi_1^{\text{sym}} - \psi_{-1}^{\text{as}})$, where ψ_1 and ψ_{-1} are highest occupied and lowest unoccupied MO's of the originally degenerate

(26) L. Goodman, A. H. Konstam, and L. H. Sommer, *J. Amer. Chem. Soc.*, **87**, 1012 (1965).

e_{1g} orbitals of benzene. Table III shows that this ratio is essentially the same for X = SiMe₃ and Si₂Me₅.

Considering now the phenylpolysilanes, the electronic spectra are clearly quite different. A strong absorption band is observed at relatively long wavelength which either partially or completely obscures the ¹L_b band at 260 nm. The simplest explanation of the spectra, on the basis of the data discussed in the preceding sections, is that the observed transition is again $\psi_1 \rightarrow \psi_{-1}$. However, because ψ_1 is in fact $C_1\psi_{\text{Si-Si}} - C_2\psi_{\text{aryl}}$ where $C_1 > C_2$, the ground state of the transition is largely $\sigma_{\text{Si-Si}}$. The extent of charge transfer will depend on the nature of ψ_{-1} and, since the electron affinity of benzene is probably²⁷ greater than that of linear polysilanes, it is likely that ψ_{-1} is primarily π_{aryl} . The transition therefore is substantially charge transfer, *i.e.*, $\sigma_{\text{Si-Si}} \rightarrow \pi^*_{\text{C=C}}$, although the extent of charge transfer will be modified as the chain length of the polysilane increases.

This assignment reasonably explains the large bathochromic shift associated with the phenyl series as well as the continuing red shift of the absorption as the chain length of the polysilane is increased, both features which are in marked contrast to the naphthyl series. For the latter, the ground state of the transition is largely π_{aryl} , and consequently its perturbation by the polysilane chain is, as with a (CH₂)_{*n*}Me chain,²⁸ rapidly attenuated as the chain length increases and is essentially constant for $n > 3$. The same appears to be true for the *p*-methoxyphenyl series and can be expected for any series where the highest occupied MO is predominately π_{aryl} (*i.e.*, IP_{substituent} > IP_{arene}). However, for the phenyl series the ground state of the transition is predominately $\sigma_{\text{Si-Si}}$ (*i.e.*, IP_{Si-Si} < IP_{benzene}), and the spectral shifts can be regarded as the perturbation of the polysilane absorption by the phenyl substituent. Consequently, as the chain length of the polysilane increases, the initially large perturbation of the transition diminishes until the spectrum is close to that of the unsubstituted polysilane (*cf.* Table I).

It is clear that in order to obtain polymeric group IV catenates, which absorb at substantially longer wavelengths than those presently reported,⁴ it will be necessary to attach substituents which have low-lying vacant orbitals (*e.g.*, nitroaryl) rather than high-energy occupied orbitals (*e.g.*, naphthyl, *p*-methoxyphenyl).

Experimental Section

Electronic Absorption Spectra. Absorption spectra were determined with a Cary 14 spectrophotometer, using quartz cells of 1.0-, 0.1-, or 0.01-cm path length and spectral grade isooctane (Mallinkrodt) dried over Linde 4A molecular sieve (pellets). The instrument was calibrated using benzene vapor, and the absorption maxima were measured by scanning the spectrum at a speed of 2.5 Å/sec and checking for reproducibility. The extinction coefficients, based on the error in weighing, are considered to be accurate to at least ±10%. The charge-transfer absorption spectra were determined by literature procedures,¹⁸⁻²¹ adding the substrate (10-40 mg) to 1 ml of a solution of resublimed tetracyanoethylene in chloroform (*ca.* 0.6 mg/ml) until the optical density of the long-wavelength absorption using 1-cm cells was 0.5-1.0. The spectra were scanned at least twice at a speed of 10 Å/sec, and were reproducible to within ±30 Å.

(27) Based on the ease of reduction (Me₃Si)₅ > C₆H₆ > (Me₂Si)₅ > Me(Me₂Si)_{*n*}Me: R. West, Organosilicon Symposium, Pittsburgh, Pa., 1971.

(28) M. J. Kamlet, Ed., "Organic Electronic Spectral Data," Vol. 1, Interscience, New York, N. Y., 1960.

Polarographic Data. Current potential data were obtained using a three-electrode potentiostat²⁸ and recorded on an X-Y recorder (Houston Instrument Corp., Model HR-96). All potentials were measured with reference to a silver wire in contact with 0.1 M silver nitrate in dimethylformamide, separated from the working electrode compartment by a plug of porous Vycor (thirsty glass, Corning Glass Works). A 0.05 M solution of polarographic grade tetrabutylammonium iodide (G. Frederick Smith Co.) in spectrographic dimethylformamide (Eastman) was used as the supporting electrolyte. In spite of the slow reduction of Ag⁺ to Ag⁰ in dimethylformamide,³⁰ the above reference electrode was preferred to a saturated calomel electrode (sce) because of water and potassium ion leakage from the latter, as well as uncertain junction potentials between aqueous and nonaqueous solvents.^{3b} The electrode was stored in the dark when not in use in order to prevent photodecomposition of silver ion. To compensate for the effects of the slow change in the reference electrode potential, the $E_{1/2}$ of naphthalene was measured on each day when data were collected. Over 6 weeks the $E_{1/2}$ of naphthalene decreased 24 mV, from an initial value of -2.946 to -2.970 V. The half-wave potential data were therefore corrected to the first day using the naphthalene $E_{1/2}$ as a reference. Half-wave potentials were obtained from a computerized least-squares fit³¹ of the experimental $\log(i_d - i)/i$ vs. E data to a straight line (i_d = diffusion current, i = current at potential E).

Cyclic voltammetry showed all reductions to be reversible.³² For 1-heptamethyltrisilylnaphthalene, selected for the most complete electrochemical study, the ratio of the anodic peak current to the cathodic peak current was ca. 0.85 for a potential scan rate of 100 mV/sec. The ratio of cathodic peak current to the square root of the potential scan rate was constant for variations of scan rate between 20 and 100 mV/sec. For compounds having silicon directly attached to a single naphthalene nucleus, the product of the transfer coefficient (α) and the number of electrons (n_a) was between 0.96 and 1.03. These data demonstrate that the reduction is a one-electron, reversible process. In the case of the 1-(trimethylsilylmethyl)naphthalene, $\alpha n_a = 0.87$, suggesting some slight instability of its radical anion. A diffusion controlled process for these reductions is suggested by (a) the linear relationship of the square root of the mercury column height (corrected for back pressure) vs. the limiting current and (b) the linear relationship between concentration and limiting current observed for 1-heptamethyltrisilylnaphthalene. In the case of the dinaphthyl compounds two overlapping reduction waves were observed. These were analyzed by the method of Růžic and Branica.³³ Using this method half-wave potentials obtained for 1,2-bis(1-naphthyl)tetramethyldisilane agreed to within ± 5 mV of cyclic voltammetric data, the latter being unaffected by successive reductions when $\Delta E_{1/2}$ exceeds 118/n mV.³⁴

Infrared spectra were obtained as liquid films or in carbon disulfide using the Perkin-Elmer Model 237B spectrometer. All

of the compounds showed absorption at 3000-3100 (Ar-H), 1500 (C=C), 1250 and 840 cm^{-1} (SiMe).

Nmr spectra were obtained with a Varian HA-100 spectrometer, using deuteriochloroform solvent and methylene chloride as an internal standard, but are reported relative to tetramethylsilane assuming $\delta(\text{CH}_2\text{Cl}_2) = 5.3$. Signal integration is reported to the nearest integer ratio.

1-Naphthyltrimethylsilane and bis(1-naphthyl)dimethylsilane were prepared from 1-naphthyllithium and the corresponding chlorosilane in ethereal solvent, following the published procedures.³⁵ The polysilyl derivatives were prepared by this same method using the appropriate chlorosilane. The crude products were purified by elution from silica gel with hexane containing increasing amounts of benzene (0-25%). The mononaphthyl derivatives were eluted before naphthalene, whereas the dinaphthyl derivatives were eluted after naphthalene. No attempts were made to maximize the yields which were generally about 50%. The mononaphthyl derivatives were further purified by preparative glc (2% OV17 on Chromosorb G), while the dinaphthyl derivatives were purified by crystallization from ethanol and then hexane. The melting points of the series $\text{C}_{10}\text{H}_7(\text{SiMe}_2)_n\text{C}_{10}\text{H}_7$ are $n = 1$, 133°; $n = 2$, 82-82.5°; $n = 3$, 95-96°. 1-(Trimethylsilylmethyl)naphthalene was prepared analogously, using the Grignard reagent from 1-chloromethylnaphthalene and trimethylchlorosilane, and purified by distillation (bp 90° (0.1 mm)) and preparative glc. 1,4-Bis-(trimethylsilyl)benzene, 1,4-bis(pentamethyldisilyl)benzene, *p*-trimethylsilylanisole, and *p*-(pentamethyldisilyl)anisole were prepared by published procedures.³⁶ Satisfactory elemental analyses of all new compounds were obtained by combustion analysis (Galbraith Laboratories, Knoxville, Tenn.) and high resolution mass spectrometry using an AEI Model MS902 instrument. The nmr spectra of the series 1- $\text{C}_{10}\text{H}_7\text{X}$ showed aliphatic proton absorption at X = SiMe₃, δ 0.47 (9 H); X = Si₂Me₆, δ 0.06 (9 H), 0.51 (6 H); X = Si₃Me₉, δ -0.1 (9 H), 0.11 (6 H), 0.55 (6 H); X = SiMe(SiMe₃)₂, δ 0.11 (18 H), 0.55 (3 H); X = CH₂SiMe₃, δ -0.02 (9 H), 2.58 (2 H); X = SiMe₂C₁₀H₇, δ 0.84 (6 H); X = (SiMe₂)₂C₁₀H₇, δ 0.48 (12 H); X = (SiMe₂)₃C₁₀H₇, δ 0.188 (6 H), 0.36 (12 H). All of the naphthyl derivatives showed a complex aromatic multiplet in the region δ 7.1-8.2.

Acknowledgments. This work was supported in part by NSF Grants GP-26505 and GP-9608 and by the Air Force Avionics Laboratory, Research and Technology Division, Air Force Systems Command, U. S. Air Force, under Contract No. AF 33(615)-3334. One of us (R. N. C.) expresses appreciation for a NDEA Title IV Traineeship administered by Duke University. Mass spectral data were obtained at the Research Triangle Institute Mass Spectroscopy Center under NIH Grant No. PO 7 RR 00330-03 MCHA. The authors are particularly grateful to Professor Hans Bock (Frankfurt-Main) for determining the PE spectra, communicating unpublished results, and discussion relating to this paper.

(35) M. F. Shostakovskii and Kh. I. Kondratev, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, 319 (1957); H. Gilman, R. A. Benkeser, and G. E. Dunn, *J. Amer. Chem. Soc.*, **72**, 1689 (1950).

(36) H. Sakurai, T. Imoto, N. Hayashi, and M. Kumada, *ibid.*, **87**, 4001 (1965); H. Gilman and J. F. Nobis, *ibid.*, **72**, 2629 (1950).

(29) D. D. Deford, Abstracts, 133rd National Meeting of the American Chemical Society, San Francisco, Calif., 1958; C. P. Driscoll, A.M. Thesis, Duke University, 1963.

(30) C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970, p 18.

(31) G. P. Hicks, A. A. Eggert, and E. C. Toren, Jr., *Anal. Chem.*, **42**, 729 (1970).

(32) R. S. Nicholson and J. Shain, *ibid.*, **36**, 706 (1964).

(33) I. Růžic and M. Branica, *J. Electroanal. Chem.*, **22**, 243 (1969); I. Růžic, *ibid.*, **25**, 144 (1970).

(34) D. S. Polcyn and I. Shain, *Anal. Chem.*, **38**, 370 (1966).