at −80 °C) reacted with 1-alkenes (propylene, 1-butene, 1-pentene) to form mixtures of C–H insertion and π-coordination compounds. In all cases examined, the C–H insertion products[12] predominated (>90%) at low temperature, and on warming, the thermodynamically more stable π-complexes were formed.

The C–H vs. π reactivity described here is similar to that which has been reported in reactions of carbenes with alkenes[13] and lends support to the analogy which has been drawn between carbenes and coordinatively unsaturated transition-metal complexes.[14] The iron bis(diphosphine) systems differ significantly from the (η^5-Me$_5$C$_5$)IrPMe$_3$ system previously reported and would suggest that the type of reactivity exhibited by the coordinatively unsaturated complexes of iron and iridium toward alkenes is probably widespread among the other transition-metal complexes.

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[12] For propylene, 1-butene, and 1-pentene only metalation at the terminal C–H bonds was observed.

[13] See, for example: Kirmse, W. In *Carbene Chemistry*, 2nd ed.; Blomquist, A. T., Wasserman, H., Eds.; Academic Press: New York, 1971, Chapters 7, 8 and references cited therein.

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Electronic Excitation in Poly(di-*n*-hexylsilane)

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The saturated chain of silicon atoms in the potential photoresists,[2] polysilanes, acts as a near-UV chromophore (λ_{max} = 300–400 nm). The nature of the excited states is important for their photochemistry. Herein we report experimental and theoretical results for a model peralkylpolysilane.

Figure 1 shows the solution excitation–emission spectrum of $[(n\text{-}C_6H_{13})_2Si]_n$ ($M_w = 1.1 \times 10^6$, $M_w/M_n = 2.4$) (**1**), with a fluorescence band independent of λ_{exc} and narrower than the excitation band, which is similar to the absorption band. At λ_{exc} = 335 nm, the decay is exponential, $\tau_F = 130 \pm 10$ ps. The polarization degree P ranges from values near the theoretical limit 0.5 at long λ_{exc} (absorbing and emitting transition moments parallel) to about zero at short λ_{exc} (the moments uncorrelated). The ridge of highest P runs near $\lambda_{exc} = \lambda_{em}$ and peaks at long wavelengths.

These results fit expectations for the random-coil geometry[3] of **1**: electronic excitation localizes in chain segments of various lengths, leading to a distribution of excited states of differing energies, although the σ-conjugated nature of the backbone precludes full interruption of conjugation, possible in the analogous π-conjugated polyacetylene.[4] Energy transfer from short to long segments must be fast on the 10^{-10} s time scale, since emission occurs primarily from the longest segments, regardless of λ_{exc}. An increase in the average transfer distance ($\lambda_{exc} < \lambda_{em}$) reduces the correlation between the directions of absorbing and emitting moments, presumably parallel to chain segments.

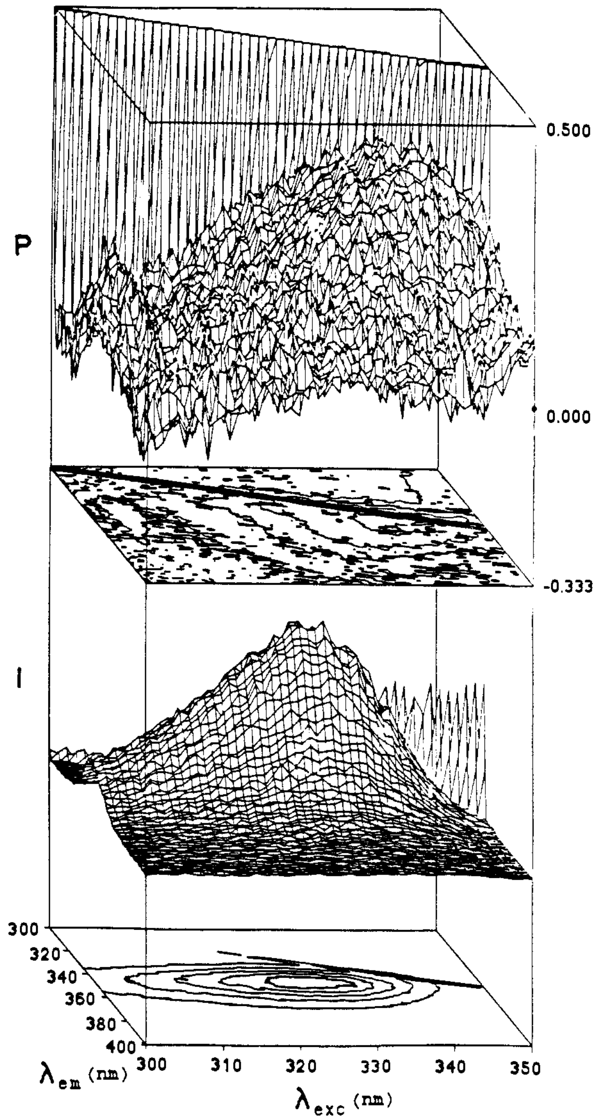

Figure 1. Fluorescence emission–excitation spectrum (bottom) and the polarization degree P (top) for **1** (3-methylpentane, flow cell, 25 °C).

The nature of the chain segments that support localized singlet excitation was explored by INDO/S[5a] calculations for $[(CH_3)_2Si]_n$ and $(H_2Si)_m$ ($n \le 20$, $m \le 40$), using molecular mechanics[5b] geometries. For interpretation, the results were transformed from the original AO basis to a basis of maximally orthogonal sp^k hybrids oriented along bond directions ($k \simeq 3$).

As in prior work by simpler methods,[6] the first transition at any conformation corresponds predominantly to σ(HOMO) →

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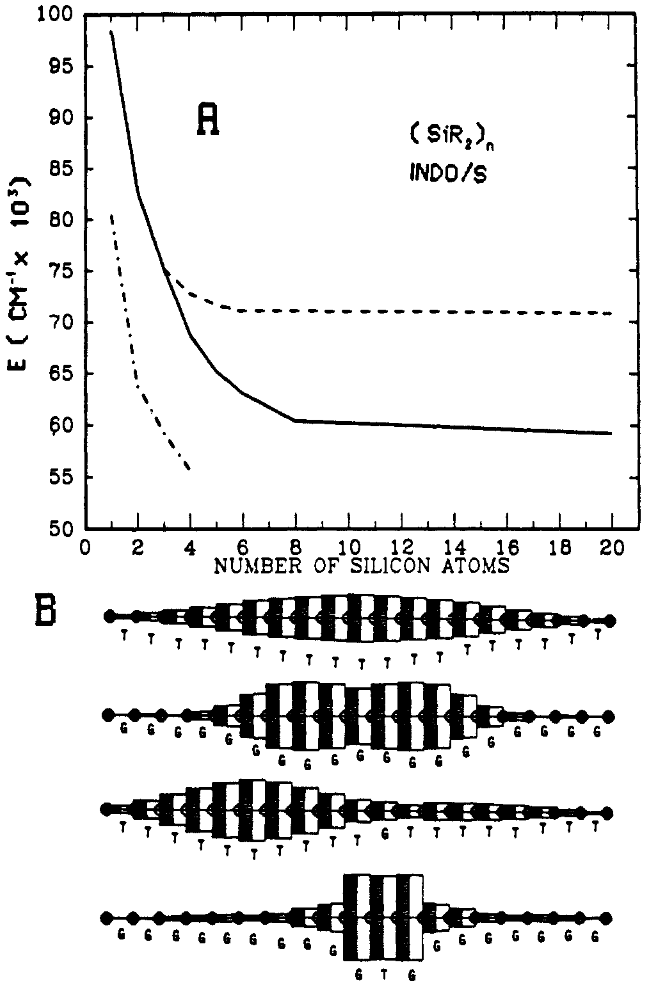

Figure 2. (A) Calculated (INDO/S) first singlet excitation energy: all-trans $[(CH_3)_2Si]_n$ (dash-dot); all-trans $[H_2Si]_n$ (full); all-gauche $[H_2Si]_n$ (dashed); (B) corresponding transition densities for the $Si_{20}H_{42}$ chain, using the notation of Figure 3.

σ^*(LUMO);[7] both orbitals have Si–Si and virtually no Si–H or Si–C character. Methyl substitution red-shifts the transition (Figure 2A) but has no other significant effect, and we concentrate on the results for $(H_2Si)_m$. As proposed previously,[8] the computed excitation energy is lower for all-trans than all-gauche backbones of equal m (Figure 2A). We attribute this to the 1–4 interaction[9] between hybrid orbitals, strong in their antiperiplanar trans and weak in the *gauche* orientation (Figure 3A). The relative phases of the hybrids (Figure 3B) make antiperiplanar 1–4 interactions (positive resonance integrals β_{14}) destabilizing in the HOMO and weakly stabilizing in the LUMO.

In chains containing trans and gauche links, the latter represent barriers in the potential for a "hole" located in the chain, so that the HOMO localizes in the longest all-trans chain present. The LUMO remains largely delocalized (Figure 3B). The lowest singlet transition density therefore localizes in the longest all-trans segments (Figure 2B) and the transition moment lies along the segment chain. The all-trans segment need not be long: an all-gauche chain containing one trans link localizes the excitation on the latter to a considerable degree (Figure 2B).

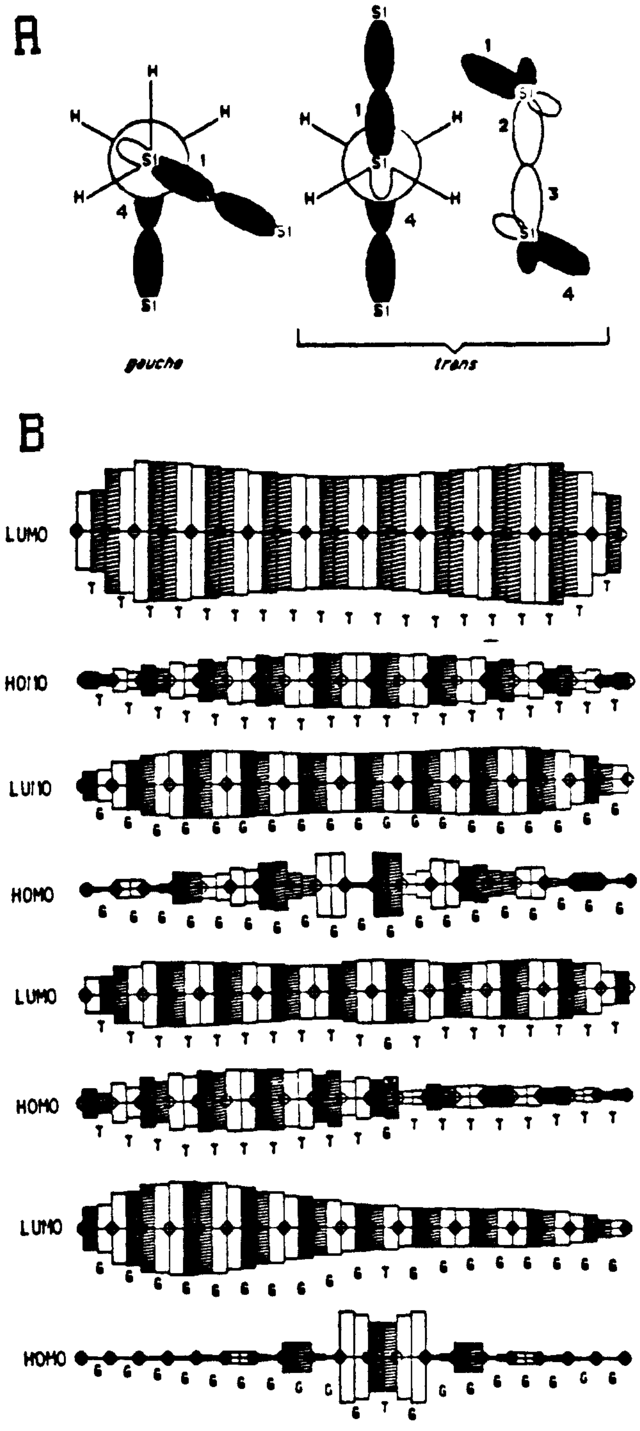

Figure 3. (A) 1–4 interactions between hybrid orbitals on neighboring Si atoms. (B) HOMO and LUMO of $Si_{20}H_{42}$ (G = gauche, T = trans) in terms of the hybrid orbital basis set (contributions from Si–H bonds are negligible). Coefficient sign (bar color) and magnitude (length) are shown for both hybrids on each Si atom (circle).

In summary, our experiments suggest that the polysilane chain is effectively separated into a series of chromophores communicating by rapid energy transfer. Our calculations suggest that these chromophores are all-trans chain segments separated by gauche links. The localization occurs already on quite short segments. It will be further enhanced by geometrical relaxation in the excited state, neglected here.

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(7) This assignment is supported by the observed positive UV dichroism of a stretched sheet of **1**.

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