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13. ABSTRACT (Maximum 200 words) Several new compounds of divalent silicon and germanium, and of multiply bonded silicon and germanium have been prepared and characterized in matrix isolation. Photophysical and photochemical behavior of several oligosilanes was examined and provided clues to the properties of the industrially interesting polysilanes. The experimental work was combined with quantum chemical calculations and resulted in an improved understanding of the electronic structure of compounds with silicon-silicon bonds, particularly of the nature of sigma bond delocalization as a function of conformation.					
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FINAL REPORT

**STRUCTURE AND PROPERTIES OF NOVEL COMPOUNDS
OF SILICON, GERMANIUM AND TIN**

The Air Force Office of Scientific Research
Air Force Systems Command

Contract No. 91-0032

Principal Investigator

Josef Michl
Department of Chemistry
University of Colorado
Boulder CO 80309-0215

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Structure & Properties of Novel Compounds of
Silicon, Germanium & Tin

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FINAL REPORT

Report Period October 1, 1990 - September 30, 1992.

TECHNICAL REPORT

Our work on the organic chemistry of silicon, germanium, and tin containing compounds concentrated on the investigation of novel structures and bonding situations, particularly compounds of multiply bonded and divalent atoms of these elements. In the recent years, our interest gradually gravitated towards an interrogation of the electronic structure and bonding in saturated compounds of these elements, most of all, silicon. We believe that an understanding of this subject will have quite general consequences for the understanding of the nature of delocalized chemical bonding in saturated compounds of all main-group elements. After all, the fact that bonding in saturated compounds is not strictly a matter of entirely localized single bonds is responsible for many theoretically and practically important properties of these compounds: σ delocalization plays an essential role in phenomena as diverse as charge transfer through "inert" spacers, propagation of substituent effects, propagation of spin density in saturated radicals, nuclear-nuclear coupling in NMR of saturated molecules, their optical activity, far UV absorption, ionization, etc. Saturated silicon compounds are particularly suitable for an investigation of this type in that they display "bond delocalization" phenomena especially clearly, and in that they offer intriguing similarities and contrasts to the compounds of carbon.

1. Preparation and characterization of compounds with unusual bonding environments.

Several new organic compounds of divalent silicon and germanium have been characterized in matrix isolation: di-*t*-butylsilylene,¹ 1-silacyclopent-3-ene-1,1-diyl,¹⁶ and dimethylgermylene.³ The first of these is of interest because the bulkiness of the *t*-butyl substituents opens up the valence angle at silicon, reducing the singlet-triplet gap. We found that the ground state still is a singlet. The second is of interest because of its surprisingly low lying second excited singlet state and because of its isomerization to silacyclopentadienes. The third was the first organogermylene to be characterized by IR spectroscopy.

Several new compounds of multiply bonded silicon and germanium have also been characterized in matrix isolation: two of the three isomeric cyclopenta-1,3-dienes are in this category,¹⁶ as are dimethylgermanethione⁵ and a silanediimine derivative with cumulated double bonds.¹ The novelty of these structures made them particularly worthy of investigation.

A comprehensive review of the chemistry of multiply bonded silicon has been written.² Work with species isolated in rare gas matrices requires special spectroscopic facilities and we have invested some effort in developing these: an FT Raman spectrometer⁷ and a matrix ENDOR unit.¹⁰ Unfortunately and unexpectedly, we were not able to transfer the first of these with us when the research group moved to Colorado, since it contained parts that had been purchased with Texas money, and these we were not permitted to buy out, so this work was discontinued. We were permitted to buy the ENDOR unit and it is being installed here now.

2. Photophysics and Photochemistry of Polysilanes and Oligosilanes.

The photophysical¹¹ and photochemical behavior of polysilanes has been investigated, the latter with particular emphasis on the mechanism of radical production during irradiation¹² and on photolithography.⁴ The structure of the persistent radicals formed during the irradiation, long a subject of puzzlement, has been elucidated in this work, and a third, previously unknown, primary photochemical step was uncovered. A comprehensive review article of the subject has been written,⁶ as well as two other shorter surveys of certain aspects of polysilane research.^{17,18} The former⁶ was repeatedly listed as among the ten most quoted papers in Chemistry by *Science Watch* (Vol. 7, nos. 7 and 9, 1991).

The work on polysilanes made us realize that their understanding will be impossible without an understanding of the shorter silicon chain model compounds, the oligosilanes. We have selected three compounds of this series, with 6, 10, and 16 silicon atoms in the chain, and have characterized their singlet photophysics quite thoroughly. The quenching of their fluorescence with CCl_4 has been compared with that of a high molecular weight polysilane¹⁵ and was found to be quite unusual. Static quenching dominates the process, and the results provide evidence that in room-temperature solution the description provided by the segment model is superior to that offered by the continuous disorder model. The fluorescence itself changes dramatically as one proceeds from the longer to the shorter chains, and it is clear that the nature of the lowest excited singlet changes along the series.^{19,20}

The 16-silicon chain¹⁹ is strikingly similar to the high polymer in almost all properties. It even undergoes thermochromic changes upon cooling. These turned out to be quite complicated to unravel, and we finally determined that the material aggregates in several stages upon the cooling of its solutions to 77 K, already at concentrations as low as 10^{-6} M. In the most dilute solutions, individual conformers were discerned spectroscopically at 77 K, where their interconversion is suppressed. Evidence was also obtained for adiabatic interconversion of excited conformers in fluid solutions.

The absorption of the 6-silicon chain still looks very much like the absorption of a high polymer, but the emission is totally different.²⁰

In the case of a 4-silicon chain, there are only two distinct conformers, and we have succeeded in characterizing their IR and UV spectra individually.²¹ The results are striking in that the extension of σ conjugation upon going from a 3-bond segment to a four-bond segment causes a large red shift of the first transition if it adds a trans link, and none if it adds a gauche link. This has important consequences for the theories of σ bond delocalization in general.

We have also investigated the photochemistry of oligosilanes and found all three primary processes previously identified in the high polymers.¹⁴

3. Electronic structure of oligosilanes and polysilanes.

The photophysical and photochemical observations on these materials naturally lead to

The photophysical and photochemical observations on these materials naturally lead to questions concerning their electronic structure.⁸ We have performed a series of ab initio calculations aimed at elucidating this and have made considerable progress. Plausible photochemical paths have been proposed for all three primary processes⁹ and the nature of the excited states of various kinds has been clarified.¹³ The distinctly different spectral properties of different conformers show clearly that the standard Sandorfy C model is inadequate. We have proposed a qualitative "ladder" model of σ conjugation.²¹

4. Impact

The results appear to have been well received by silicon and polymer chemists and physicists. The work on polysilanes and oligosilanes appears to have been of particular interest as judged by invitations to give plenary lectures on the subject of polysilanes at four international conferences in 1991 (July, "15th International Conference on Photochemistry", Paris, France; August, U.S.-Australia Workshop "Radiation Effects on Polymeric Materials", Stanford, CA; August, Conference on "Optical Probes of Conjugated Polymers", Snowbird, UT; October, "2nd Symposium on Organosilicon and Related Materials", Tsukuba, Japan). In 1992, I have presented initial on oligosilanes at three international conferences (April, "25th Organosilicon Symposium", Los Angeles, CA; July, "14th IUPAC Symposium on Photochemistry", Leuven, Belgium; September, "Experimental and Theoretical Aspects of Excited State Electron Transfer and Related Phenomena", Pultusk, Poland). I have six plenary lecture conference invitations to present results on oligosilane and polysilane electronic structure, photooptics, and photochemistry in 1993. Unfortunately, the funding of this project has been discontinued.

LIST OF PUBLICATIONS

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5. Miller, R. D.; Michl, J. "Polysilane High Polymers", *Chem. Rev.* 1989, 89, 1359.
6. Michl, J.; Balaji, V. "Calculations of Photochemical Reactivity. Oligosilanes as an Illustration" in *Computational Advances in Organic Chemistry*; Ögretir, C., Csizmadia, I. G., Eds.; Kluwer: Dordrecht, The Netherlands, 1991; 323.
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14. Michl, J. "Solution Photophysics and Electronic Structure of Polysilanes", *Synth. Met.*, 1992, 50, 367.
15. Michl, J.; Sun, Y.-P. "Electronic Structure, Photophysics and Photochemistry of Polysilanes", ACS Symposium Series Book, US/Australia Workshop on Radiation Effects on Polymeric Materials, in press (expected publication date, March, 1993).
16. Sun, Y.-P.; Hamada, Y.; Huang, L. H.; Hsiao, J.-S.; West, R.; Michl, J. "Models for Polysilane High Polymers. I. Singlet Photophysics of Linear Permethylhexadecasilane ($\text{Si}_{16}\text{Me}_{34}$)", *J. Am. Chem. Soc.* 1992, 114, 6301.
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INDIVIDUALS PARTICIPATING

Karel Baše
Donald E. David
John W. Downing
Steven J. Hamrock
Valery Khabashesku
Astrid Koch
Shu Shi
Balaji Veeraraghavan

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