

Molar absorptivities of some polysilanes

The chromophoric, and particularly the ultraviolet, properties of polysilanes provide a useful means of identification and characterization in the field of organosilicon chemistry¹⁻³. As reported earlier in a study of fully permethylated straight-chain polysilanes, the position of maximum absorption and the molar absorptivity increase regularly with increasing chain length². The conjugated system is also lengthened by replacement of a methyl group with substituents such as phenyl or vinyl which increase the λ_{\max} and molar absorptivity². This apparently occurs through overlap with their π -electron system and the d -orbitals of the polysilane. However, it was previously reported that replacing the methyl groups with chlorine atoms had little effect on the ultraviolet spectra².

In our continued investigation on new types of organosilicon polymers our studies indicate that little or no change is observed in the λ_{\max} of permethylated polysilanes containing various substituents in the terminal positions. However, differences of an apparently regular nature are observed in the molar absorptivity. We have determined the ultraviolet spectra of several compounds in the homologous series $X-[Si(CH_3)_2]_n-X$, where $X = Cl$ or H and $n = 2$ to 6 (Ref. 4). The α,ω -disubstituted octamethyltetrasilanes in Table 1 are presented to illustrate this phenomenon. The effect of the terminal substituent was found to be consistent in its behavior with varying chain lengths of 2 to 6 atoms. This is demonstrated for the $X-[Si(CH_3)_2]_n-X$ series, where $X = H$ or Cl and $n = 2$ to 6 , in Tables 2, 3, and 4. An exception is noted in hexamethyldisilane ($\epsilon = 8,500-7,230$)² and octamethyltrisilane ($\epsilon = 9020$)² whose reported molar absorptivities are the only ones greater than the corresponding dichloro- homologs, 1,2-dichlorotetramethyldisilane ($\epsilon = 3,228$) and 1,3-dichlorohexamethyltrisilane ($\epsilon = 8,610$).

The observed effects might well be expected because differences in polarity of each of these compounds, due to the inductive effects of the terminal atom or group, could effect electron transitions throughout the chain. A question arises concerning the direction of the inductive effect of the α,ω -substituents. Possible positive inductive effects caused by hyperconjugation of hydrogen or methyl groups, participation of non-bonding electrons of chlorine or negative inductive effects based on electronegativity differences may all contribute to transitions involving empty d -orbitals of the silane chain. All of the substituents or groups attached to silicon in this study have an electronegativity value greater than that of silicon ($H, 2.1$; $C, 2.5$; $Cl, 3.0$; $Si, 1.8$ on the Pauling scale)⁵. Comparison of the molar absorptivity values reported shows that replacement of terminal methyl groups with hydrogen decreases the molar absorptivity. The replacement of terminal methyl groups with chlorine increases the molar absorptivity. Based on the assigned electronegative values of the atoms, it appears that the molar absorptivity of the polysilane increases with increasing electronegativity of the terminal substituent.

However, we cannot relate inductive effects, which are referred to as electrostatic action transmitted through chains of atoms⁶, directly to electronegativity values of the atoms. A methyl group may be a greater electron donor than a hydrogen atom regardless of the electronegativity values. A recent study on the measure of the electron-releasing power of the trimethylsilyl group has been reported⁷. The electron-

TABLE 1

UV SPECTRAL DATA OF Y-[Si(CH₃)₂]₄-X POLYSILANES^a

Compound		Band position	Molar absorptivity
Y	X	λ_{max} , $m\mu$	ϵ
H	H	235.5	12,250
H	Cl	235.0	13,340
Cl	Cl	235.0	17,426
CH ₃ ^b	CH ₃	235.0	14,700

^a Obtained with a Beckman DK-2A Spectrophotometer using cyclohexane as solvent.^b Reported in ref. 2.

TABLE 2

UV SPECTRAL DATA OF THE H-[Si(CH₃)₂]_n-H SERIES^a

Compound	Band position	Molar absorptivity	Concentration
n	λ_{max} , $m\mu$	ϵ	$M \times 10^5$
2	198.0 ^b	2,033	13.28
3	218.0	6,841	9.94
4	235.5	12,250	6.00
5	249.0, 214.0	13,590, 9,440	4.29
6	257.5, 225.0	19,456, 11,150	2.92

^a Obtained with a Beckman DK-2A spectrophotometer using cyclohexane as solvent.^b Values are somewhat imprecise because of solvent cutoff.

TABLE 3

UV SPECTRAL DATA OF THE H-[Si(CH₃)₂]_n-Cl SERIES^a

Compound	Band position	Molar absorptivity	Concentration
n	λ_{max} , $m\mu$	ϵ	$M \times 10^5$
2	194.0 ^b	2,770	12.00
3	217.5	7,150	7.55
4	235.0	13,340	4.46
5	249.5, 215.0	16,380, 8,770	3.26
6	258.0, 225.0	21,807, 11,900	3.21

^a Obtained with a Beckman DK-2A spectrophotometer using cyclohexane as solvent.^b Values are somewhat imprecise because of solvent cutoff.

TABLE 4

UV SPECTRAL DATA OF THE Cl-[Si(CH₃)₂]_n-Cl SERIES^a

Compound	Band position	Molar absorptivity	Concentration
n	λ_{max} , $m\mu$	ϵ	$M \times 10^5$
2	204.0 ^b	3,228	28.0
3	219.0	8,610	4.31
4	235.0	17,426	3.68
5	250.0, 214.0	19,532, 9,906	4.27
6	259.0, 225.0	23,250, 11,091	3.20

^a Obtained with a Beckman DK-2A spectrophotometer using cyclohexane as solvent.^b Values are somewhat imprecise because of solvent cutoff.

donor properties of highly electronegative atoms adjacent to silicon, such as oxygen or chlorine, have also been previously suggested^{8,9}.

By convention, groups which are more powerful electron attractors than the hydrogen atoms are said to exhibit negative ($-I$) effects, whereas those which are poorer electron attractors than hydrogen display positive inductive ($+I$) effects⁶. However, most polysilanes are substituted with organic groups rather than hydrogen as in carbon chemistry. The present series studied consists of an increasing number of dimethylsilylene units in which the polarity of the silicon-methyl bonds in the fully permethylated series are symmetrical or equivalent. Using this series for a relative value a $+I$ effect would be exhibited by a terminal hydrogen attached to silicon while a $-I$ effect would be displayed by chlorine. This observation would be based on the assumption that the molar absorptivity decreases with an increasing positive inductive effect of the substituent relative to a methyl group and increases with increasing negative inductive values relative to a methyl group. It would appear that further data from a variety of substituents precludes any formal assignment of the directive effects of the terminal substituents and their influence on the electron transitions involved in the ultraviolet excitations of the polysilane molecule. Further investigations are being made in this direction.

This research was supported in part by the United States Air Force under Contract AF 33(616)-6463, monitored by Materials Laboratory, Directorate of Laboratories, Wright Air Development Center, Wright-Patterson AFB, Ohio.

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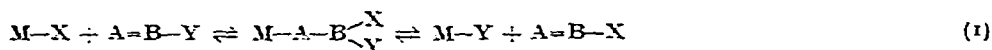
- 1 H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *Chem. Ind. (London)*, (1964) 1063.
- 2 H. GILMAN, W. H. ATWELL AND G. L. SCHWEBKE, *J. Organometal. Chem.*, 2 (1964) 369.
- 3 H. SAKURAI AND M. KUMADA, *Bull. Chem. Soc. Japan*, 37 (1964) 1894.
- 4 H. GILMAN AND D. R. CHAPMAN, *Chem. Ind. (London)*, (1965) 1788.
- 5 C. EABORN, *Organosilicon Compounds*, Butterworth, London, 1960, p. 88.
- 6 E. S. GOULD, *Mechanism and Structure in Organic Chemistry*, H. Holt, New York, 1959, p. 200.
- 7 D. R. M. WALTON, *J. Organometal. Chem.*, 3 (1965) 438.
- 8 A. G. BROOK, *J. Am. Chem. Soc.*, 82 (1960) 5102.
- 9 O. M. STEWARD AND O. R. PIERCE, *J. Am. Chem. Soc.*, 83 (1961) 4932.

Received January 8th, 1966

J. Organometal. Chem., 5 (1966) 392-394

A new route to trihalogenomethylmetallic compounds: tributyltrichloromethyltin.

The exchange of groups X and Y between a metallic compound M-X and an acceptor molecule A=B-Y can be brought about by the addition-elimination process shown in equation 1.



J. Organometal. Chem., 5 (1966) 394-395