Preliminary Notes

Ultraviolet properties of compounds containing the silicon–silicon bond

This investigation is part of a general study on new types of organosilicon polymers.

Polysilanes with phenyl groups attached to silicon have been shown to have interesting ultraviolet properties. Hague and Prince[1] have suggested that the unique spectral properties of hexaphenyldisilane are due to an intense interaction between phenyl groups which is facilitated by a type of conjugation involving overlap of vacant d-orbitals on silicon. Prompted by this observation a study of the ultraviolet properties of the series of compounds, $\mathrm{Ph[SiMe_2]_nPh}$, has recently been reported[2]. With these compounds, where $n = 2$–6, the successive interposing of dimethylsilylene units between the phenyl groups should effectively diminish the interaction between the phenyl groups. However, quite the opposite was observed and the behavior noted can be considered to be analogous to the properties of the α,ω-diphenylpolyenes[3]. This implied that the polysilane chain itself might absorb ultraviolet radiation without the presence of phenyl groups.

TABLE 1

UV SPECTRAL DATA OF THE $\mathrm{Me[SiMe_2]_nMe}$ SERIES[a]

Compound n	*Band position* λ_{max}, mμ	*Molar absorptivity* ε
2	197.1–199.5[b]	8,500–7,230
3	215.0	9,020
4	235.0	14,700
5	250.0	18,400
6	260.0	21,100
	220.0 (Shoulder)	14,000
8	272.5	38,800
	240.5	18,000
	215.0 (Shoulder)	29.000

[a] Obtained with a Beckman DK2A Spectrophotometer using cyclohexane as solvent. [b] Values are somewhat imprecise because of solvent cutoff. Position and intensity vary with concentration. In the vapor phase hexamethyldisilane absorbs at 192.9 mμ.

We have investigated the ultraviolet properties of the family of permethylated straight-chain polysilanes*, $\mathrm{Me[SiMe_2]_nMe}$, and found that they in fact do possess characteristic ultraviolet spectra (Table 1). The simple disilane, hexamethyldisilane, was found to have absorption in the far ultraviolet region of the spectrum. All other homologues absorbed in the normal ultraviolet region. The position of maximum

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* Some of these compounds were graciously supplied by Professor MAKOTO KUMADA of Kyoto University, Japan. We have found his procedures[4] for the synthesis of some of them to be quite satisfactory.

TABLE 2

UV SPECTRAL DATA OF PHENYL- AND METHYL-SUBSTITUTED DISILANES[a]

Compound	*Band position* λ_{max}, *mμ*	*Molar absorptivity* ε
$Me_3SiSiMe_3$	199.5[b]	7,230
$PhMe_2SiSiMe_3$	230.5	11,200
$Ph_2MeSiSiMe_3$	230.5	16,500
$PhMe_2SiSiMe_2Ph$	236.0	18,200
$Ph_3SiSiMe_3$	234.0	19,300
$Ph_2MeSiSiMe_2Ph$	237.0	21,300
$Ph_3SiSiMe_2Ph$	239.0	23,800
$Ph_2MeSiSiMePh_2$	239.0	25,500
$Ph_3SiSiMePh_2$	242.5	28,200
$Ph_3SiSiPh_3$[1]	246.5	32,600

[a] Spectra obtained with a Beckman DK2A Spectrophotometer using cyclohexane as the solvent. [b] See Table 1.

absorption and the molar absorptivity increase quite regularly with increasing chain length, a property which is observed with other linearly conjugated systems[5].

Hexamethyldisilane and hexaphenyldisilane represent the extremes of a family of disilanes which have only phenyl and methyl groups attached to silicon. The ultraviolet properties of all of the members of this family are represented in Table 2. The most dramatic increase in the λ_{max} is observed when one methyl group of hexamethyldisilane is replaced by a phenyl group to give phenylpentamethyldisilane. The phenyl group effectively lengthens the conjugated system and would therefore be expected to cause an increase in the λ_{max}.

In general the molar absorptivity in this series of compounds increases with the increasing number of phenyl groups and with optimum conjugation across the silicon–silicon bond. The positions of absorption maxima tend to follow the same order; however, there are some discontinuities because the conjugation of vicinal phenyl groups has greater influence than the addition of phenyl groups in a geminal position.

A similar enhancement of λ_{max} and molar absorptivity is found in replacing a methyl group of octamethyltrisilane with a phenyl group. Thus, 1-phenylheptamethyltrisilane absorbs at 239.5 mμ [$\varepsilon = 11{,}130$] and 2-phenylheptamethyltrisilane

TABLE 3

UV SPECTRAL DATA OF SOME POLYSILANES[a]

Compound	*Band position* λ_{max}, *mμ*	*Molar absorptivity* ε
$Cl(SiMe_2)_2Cl$	218.5	—
$Cl(SiMe_2)_4Cl$	235.0	—
$Cl(SiMe_2)_6Cl$	259.0 222.0 (Shoulder)	22,300
$CH_2{=}CH(SiMe_2)_2CH{=}CH_2$	225.0	7,900
$CH_2{=}CH(SiMe_2)_4CH{=}CH_2$	243.5	14,000

[a] Spectra obtained with a Beckman DK2A Spectrophotometer using cyclohexane as the solvent.

absorbs at 243 mμ [ε = 11,150]. Replacing methyl groups with chlorine atoms has little effect on the ultraviolet spectra (Table 3). The only other group which has so far been found to be effective in altering the band position is the vinyl group. Thus, 1,2-divinyltetramethyldisilane and 1,4-divinyloctamethyltetrasilane possess ultraviolet spectra with maximum absorption at 225 and 243.5 mμ, respectively.

From the foregoing discussion it can be seen that the unique spectral properties of polysilanes are due to the silicon–silicon bond acting as a chromophore, probably through the use of vacant *d*-orbitals of the silicon atom. Substituents such as phenyl and vinyl with their π-electron systems are apparently able to be conjugated with polysilane chains through suitable overlap of *d*- and π-orbitals.

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Chemistry of the metal carbonyls

XXVII. The infrared spectra of organomanganese and organorhenium pentacarbonyls[*]

Recent interest in CO stretching modes in manganese[2–5], technetium[3] and rhenium[3] pentacarbonyls prompts us to report observations which appear to confirm a theoretical prediction[2]. Complexes of subgroup seven metals of type $LM(CO)_5$ should show three CO fundamental infrared bands, classified as two A_1 and one E stretching modes. The generality of this deduction has been confirmed experimentally[3,6], but it has been pointed out[2] that in addition to the normal frequencies, splitting of the intense E transition and appearance of a low intensity B_1 transition might be observed in the complexes if the ligand–metal group lacks axial symmetry.

Many manganese and rhenium complexes $LM(CO)_5$ (where L is an asymmetric fluorocarbon group) have been prepared[7]. We are currently measuring their infrared spectra under conditions of high resolution. When the organic group in the manganese pentacarbonyls is not axially symmetric, spectra in which the E band is split, such

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[*] For Part XXVI of this series, see ref. 1.