

Ultraviolet spectra of some pentahalophenyl-substituted silanes

Although ultraviolet data on some α,ω -diphenyl-permethylated polysilanes have been published¹ (see Table 1), no reports of the ultraviolet spectral properties of comparable compounds containing perhalo-substituted phenyl groups have appeared. Substitution of polar groups into the benzene ring of the phenylpolysilane should alter the conjugation existing in the molecule, and would therefore be expected to markedly affect the ultraviolet spectrum.

TABLE 1

ULTRAVIOLET SPECTRAL DATA FOR THE SERIES $\text{Ph}(\text{SiMe}_2)_n\text{Ph}^a$

Compound <i>n</i>	Band position λ_{max} (m μ)	Molar absorptivity ϵ
2	236.0	18,200
3	243.0	18,900
4	250.5	21,500
5	257.5	24,900
6	265.0	30,500

^a The solvent used for these and all other spectral data presently reported was cyclohexane.

We now wish to report the ultraviolet properties of a series of novel, permethylated silanes containing pentahalophenyl groups. Table 2 lists the spectral properties observed for the series of pentachlorophenyl derivatives.

Thus, in contrast to the diphenyl compounds listed in Table 1, the pentachlorophenyl-substituted permethylated silanes show little variance in the wavelength of maximum absorption with increasing silicon chain length. The molar absorptivities do vary with chain length, however, and are abnormally high.

TABLE 2

ULTRAVIOLET SPECTRAL DATA FOR THE SERIES $\text{N}(\text{SiMe}_2)_n\text{Y}$

Compound <i>n</i>	Band position λ_{max} (m μ) ^a	Molar absorptivity ϵ
1 X = Me, Y = C ₆ Cl ₅	216.5	69,500
1 X = Y = C ₆ Cl ₅	217	84,500
2 X = Y = C ₆ Cl ₅	216	90,700
3 X = Y = C ₆ Cl ₅	213	105,000
4 X = Y = C ₆ Cl ₅	217	106,000
5 X = Y = C ₆ Cl ₅	219.5	108,000
6 X = Y = C ₆ Cl ₅	216	110,000

^a In addition to the major absorption, possessing weak shoulders, each spectrum showed a weak multiplet at *ca.* 280–305 m μ ($\epsilon = ca.$ 1200) which corresponded to absorptions of the pentachlorophenyl group².

It has been observed that only the low intensity benzenoid B-bands³ are exhibited by phenyl-containing monosilanes¹. In the present study, however, even the pentachlorophenyl-substituted monosilanes are seen to possess the strong ultraviolet

absorption in the region of 217 $m\mu$, showing that the absorption does not originate from a silicon-silicon bond.

An unexpectedly high molar absorptivity has also been reported for the ultraviolet spectrum of tris(pentafluorophenyl)phosphine⁴. It was therefore considered of interest to examine the ultraviolet properties of two hitherto unreported pentafluorophenyl-permethylated silanes, namely, $C_6F_5(SiMe_2)_n C_6F_5$ where $n = 1$ and 3. The spectrum of the monosilane showed an absorption at 207 $m\mu$ ($\epsilon = 19,800$) possessing a shoulder at 216 $m\mu$ ($\epsilon = 16,900$), together with a single absorption at 266 $m\mu$ ($\epsilon = 1,990$). A similar spectrum was shown by the trisilane, with the major absorption occurring at 208 $m\mu$ ($\epsilon = 21,300$) and the shoulder at 221 $m\mu$ ($\epsilon = 15,700$), although the minor absorption was shifted to 239 $m\mu$ ($\epsilon = 14,700$). Thus it would appear that only the absorption at longest wavelength is a function of the length of the silicon chain, and in fact the absorption at 239 $m\mu$ might be expected for a trisilane of this structure (see Table 1). The absorption at 266 $m\mu$ for the monosilane, possibly masked in the case of the trisilane, is associated with the Si-C₆F₅ bond*.

Since the increase of the electronegativity of the substituent in the benzene rings so drastically affected the spectra, it was considered of interest to examine the ultraviolet properties of the series of compounds $XC_6H_4(SiMe_2)_2C_6H_4X$ (Ref. 5), where $X = p\text{-Cl}^{**}$, $p\text{-Br}$, $p\text{-SiMe}_3$ and $p\text{-NMe}_2$. The results are given in Table 3.

TABLE 3

ULTRAVIOLET SPECTRAL DATA FOR THE SERIES $XC_6H_4(SiMe_2)_2C_6H_4X$

Compound <i>X</i>	Band position λ_{max} ($m\mu$)	Molar absorptivity ϵ
<i>p</i> -Cl	241.5	28,300
<i>p</i> -Br	244	32,300
<i>p</i> -SiMe ₃	245	30,300
<i>p</i> -NMe ₂	274	50,600

The position of the absorption attributed to the Si-Si bond chromophore⁶ (see Table 1) has shifted to longer wavelengths for this series of substituted diphenyldisilanes, and a considerable increase in all four molar absorptivities has occurred. Thus the conjugation existing in the unsubstituted diphenyldisilane has been increased due to the substituents in the benzene rings, the least change occurring with the most electronegative substituent. This latter fact could well be anticipated by comparison of the spectra of corresponding pentachlorophenyl- and pentafluorophenyl-permethylated silanes.

Work is being continued to examine these phenomena more fully, and to examine the extent to which silicon atoms participate in the conjugation of Si-Ph compounds.

* A sample of tetrakis(pentafluorophenyl)silane, generously provided by Dr. C. Tamborski, showed λ_{max} 270 $m\mu$.

** During the course of the present work the ultraviolet spectrum of this compound was reported by Kumada and coworkers in a highly useful study of 1,2-diphenyltetramethyldisilanes⁷. Our spectrum agrees well with that reported.

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Acetylenic complexes of palladium*

Complexes of transition metals in which an acetylene monomer is coordinated to the metal have been reported for vanadium¹, chromium², molybdenum^{3,4,5}, tungsten^{5,6}, manganese^{7,8}, rhenium⁹, iron^{10,11}, cobalt^{12,13}, rhodium¹⁴, iridium¹⁵, nickel^{11,13,16,17}, platinum^{8,18,19} as well as copper²⁰ and silver²⁰. We now report the synthesis of some palladium-acetylene complexes.

Platinum forms two types of complexes with acetylenes, one of the type $RC_2R'Pt^{II}Cl_2X$ (I, X = Cl⁻, amine, etc.) where R and R' are bulky groups such as tert-butyl¹⁹. In addition, complexes of the type (II, M = Pt) are obtained on reduction of dichlorobis(triphenylphosphine)platinum in the presence of the appropriate acetylene^{8,19}. Nickel complexes of this type (II, M = Ni) have also been reported¹⁶. The infra-red spectra of complexes (I) usually show a band at around 2000 cm⁻¹, assigned to the acetylenic C≡C stretching frequency, which has been reduced by about 250 cm⁻¹ by comparison with that in the uncomplexed acetylene¹⁸. By contrast the platinum complexes (II, M = Pt) show this band at still lower frequencies; here the change in $\nu_{C\equiv C}$ on coordination is 400-575 cm⁻¹ (Ref. 8, 19). This has been interpreted to mean that in (II) the acetylenic triple bond has been reduced nearly to a double bond and that the acetylene is now bonded to the metal by two σ -bonds, and is therefore assumed to be square planar and formally in the +2 oxidation state⁸.

It has not been possible to prepare palladium complexes of type (I) as most acetylenes are very rapidly polymerized by palladium(II) compounds. It was there-

* Part V of "Reactions of noble metal halides with acetylenes"; Part IV, P. M. MAITLIS AND A. EFRATY, *J. Organometal. Chem.*, 4 (1965) 254.