Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

POLYHALO-ORGANOMETALLIC AND -ORGANOMETALLOIDAL COMPOUNDS

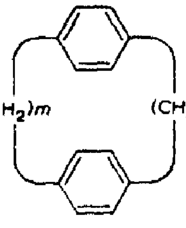
XII*. ULTRAVIOLET SPECTRA OF SOME PERHALOAROMATIC ORGANOSILICON DERIVATIVES

IONEL HAIDUC**,***, IOVANCA HAIDUC** AND HENRY GILMAN
Iowa State University, Department of Chemistry, Ames, Iowa 50010 (U.S.A.)

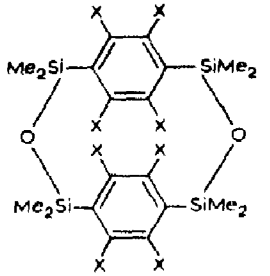
(Received August 16th, 1967)

INTRODUCTION

In connection with the investigation of polyhaloaromatic derivatives of silicon and other elements in this laboratory, we have synthesized perhalogenated analogs of paracyclophanes (I) with disiloxanyl bridges linking the aromatic rings[2]:



(I)



(IIa), X = Cl; (IIb), X = F

A non-halogenated analog of (II) (X = H) has been previously prepared by the condensation of 1,4-bis(hydroxydimethylsilyl)benzene[3] or by the depolymerization of a high polymeric *p*-phenylenetetramethyldisiloxane[4].

It was found that paracyclophanes with *m* and *n* equal or smaller than 3, exhibit abnormal ultraviolet spectra in comparison with the analogs with longer bridging chains ($m, n \geqslant 4$), due to the bending of aromatic nuclei and transannular interactions between the *p*-phenylene groups[5]. The deformation of aromatic nuclei was confirmed[6] also by X-ray diffraction studies of the paracyclophane with $m = n = 2$. A similar observation has been made[3] during the investigation of the ultraviolet spectrum of the compound (II), X = H. The "abnormality" of these ultraviolet (UV) spectra consists of a strong bathochromic shift of the B bands of the aromatic nucleus.

These interesting findings prompted us to investigate the ultraviolet absorption spectra of compounds (IIa) and (IIb), and of several perhaloaromatic compounds with related but non-cyclic structures. Previously, in this laboratory[7] several perhalophenyl-silanes and -polysilanes were investigated in a similar way.

---

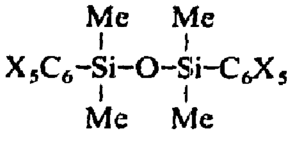
* For Part XI see ref. 1.

** Present address: Chemistry Department, Babes-Bolyai University, Cluj (Romania).

*** Postdoctoral Fulbright visiting scholar, 1966–1967.

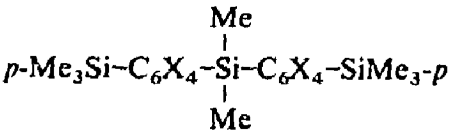
RESULTS AND DISCUSSION

The ultraviolet spectra (in cyclohexane solution) of the following compounds were investigated in this work: perchloro- and perfluoro-cyclobis(*p*-phenylenetetramethyldisiloxanes) (II), 1,3-bis(pentahalophenyl)tetramethyldisiloxanes (III), bis[*p*-(trimethylsilyl)tetrahalophenyl]dimethylsilanes (IV), 1,3-bis[*p*-(trimethylsilyl)-tetrachlorophenyl]tetramethyldisiloxane (V), (pentachlorophenyl)pentamethyldisiloxane (VI), *p*-bis(trimethylsilyl)tetrachlorobenzene (VII) and bis(pentachlorophenyl)dimethylsilane (VIIIa). The spectra quoted for bis(pentafluorophenyl)-dimethylsilane (VIIIb) and (pentachlorophenyl)trimethylsilane (IX) were previously reported[7].



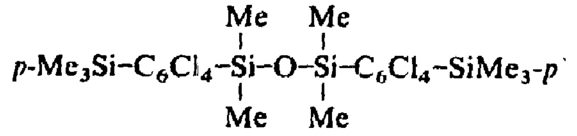
$X_5C_6-Si(Me)_2-O-Si(Me)_2-C_6X_5$

(IIIa), X = Cl
(IIIb), X = F



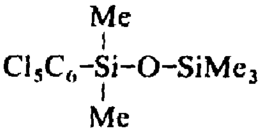
$p\text{-}Me_3Si-C_6X_4-Si(Me)_2-C_6X_4-SiMe_3\text{-}p$

(IVa), X = Cl
(IVb), X = F



$p\text{-}Me_3Si-C_6Cl_4-Si(Me)_2-O-Si(Me)_2-C_6Cl_4-SiMe_3\text{-}p$

(V)

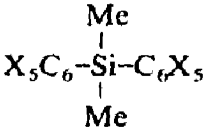


$Cl_5C_6-Si(Me)_2-O-SiMe_3$

(VI)

$p\text{-}Me_3Si-C_6Cl_4-SiMe_3$

(VII)



$X_5C_6-Si(Me)_2-C_6X_5$

(VIIIa), X = Cl
(VIIIb), X = F

The UV spectral data obtained for the compounds investigated are listed in Table 1, together with the spectra of (VIII), which were previously investigated[7].

The spectra of the perchloro derivatives exhibit a fine structure of the B bands, which consists of two peaks and a shoulder. The B band in the spectrum of the cyclic compound (IIa) exhibits however, only a broader peak, with two shoulders towards the lower wave lengths. The perfluoro compounds exhibit very broad bands without any fine structure. The B band in the spectrum of compound (IIb) is more unsymmetrical and exhibits a shoulder towards longer wave lengths.

The positions of the B bands are clearly influenced by the nature of the substituents attached to the aromatic nuclei. As expected, there is some similarity with the UV spectra of hexachloro- and pentachlorobenzene[8,9]. The introduction of either chlorine[8,9] atoms or trimethylsilyl groups[10] into the aromatic nucleus has a bathochromic effect in the UV spectrum, and therefore the B bands will be shifted towards the longer wave lengths with respect to the spectrum of the unsubstituted aromatic nucleus.

The B bands of the cyclic compounds (IIa) and (IIb) exhibit the most dramatic

TABLE 1

ULTRAVIOLET SPECTRAL DATA FOR POLYHALOAROMATIC SILICON DERIVATIVES
$\lambda_{max}\,\varepsilon\cdot 10^{-3}$.

Compound	*No.*	*E bands*			*B* bands		
$(p\text{-}C_6Cl_4\text{-}SiMe_2OSiMe_2)_2$	(IIa)	217(41.9),	237^a(7.42),	247^a(5.17)	297^a(1.10),	311^a(2.6),	318(3.07)
$(p\text{-}Me_3Si\text{-}C_6Cl_4)_2SiMe_2$	(IVa)	223(54.6),	237^a(24.1),	244^a(19.5)	292^a(1.5),	301(2.89),	310(3.17)
$(p\text{-}Me_3Si\text{-}C_6Cl_4SiMe_2)_2O$	(V)	219(89.2)		243^a(22.5)	295^a(1.7),	303(3.1),	312(3.5)
$p\text{-}Me_3Si\text{-}C_6Cl_4\text{-}SiMe_3{}^b$	(VII)	221(40),	236^a(12.8),	244^a(10.8)	293^a(0.7),	302(1.45),	311(1.6)
$Cl_5C_6\text{-}SiMe_2OSiMe_2C_6Cl_5$	(IIIa)	214(131)		242^a(19.0)	286^a(0.7),	296(0.3),	306(1.6)
$Cl_5C_6\text{-}SiMe_2OSiMe_3$	(VI)	216(102)		243^a(12.8)	288^a(0.4),	295(0.8),	306(1.0)
$Cl_5C_6\text{-}SiMe_2\text{-}C_6Cl_5{}^c$	(VIIIa)	217(154),	234^a(55.0),	244^a(26.7)	286^a(0.7),	295(1.3),	305(1.6)
$Cl_5C_6\text{-}SiMe_3{}^d$	(IX)	216(69.5),	229^a(24.2),	242^a(11.6)	282^a(1.0),	293(1.2),	303(1.1)
$(p\text{-}C_6F_4\text{-}SiMe_2OSiMe_2)_2$	(IIb)	218(28.1),	226^a(9.7)		283(5.60),	292^a(4.7)	
$(p\text{-}Me_3Si\text{-}C_6F_4)_2SiMe_2$	(IVb)	225^a(38.0),	231(46.3)		284(6.8)		
$C_6F_5\text{-}SiMe_2OSiMe_2C_6F_5$	(IIIb)	212^a(10.3)			265(1.89)		
$C_6F_5\text{-}Me_2Si\text{-}C_6F_5{}^d$	(VIIIb)	216(16.0)			266(1.99)		

[a] Shoulder. [b] Prepared by K. Shiina, unpublished data. [c] See also ref. 7. [d] From ref. 7.

bathochromic shifts, thus suggesting that the deformation of the aromatic nuclei and some transannular interaction of the two aromatic rings is a feature which persists also in the disiloxane bridged polyhaloaromatic derivatives of type (II).

Some more conclusions can be drawn from a comparison of the perhaloaromatic organosilicon derivatives with non-cyclic structures. Similarities are observed within selected groups of related compounds and differences are noticed between the different groups. Thus, all three compounds containing $-C_6Cl_5$ groups (VI, VIIIa, IIIa) either linked through a $-SiMe_2-$ or $-SiMe_2-O-SiMe_2-$ bridge, or simply attached to a terminal $-SiMe_3$ (in $C_6Cl_5SiMe_3$)[7] or $-SiMe_2-O-SiMe_3$ group, are practically identical, except in (insignificant) differences in the values of the molar absorptivities. Similarly, the spectra of the compounds containing $-C_6F_5$ groups (IIIb and VIIIb) are also practically identical. This suggests that little interaction occurs between the isolated aromatic nuclei through the dimethylsilane or tetramethyldisiloxane bridge, and that the presence of the oxygen in the bridge does not essentially affect the ultraviolet absorption spectrum.

Another group of very similar spectra is that involving compounds containing the $-C_6Cl_4-SiMe_3$ moiety (IVa, V, and VII). These compounds, differing only in the nature of the bridging ($-SiMe_2-$ or $-SiMe_2-O-SiMe_2-$) or terminal ($-SiMe_3$) groups, exhibit practically identical spectra, thus suggesting again that the interaction between the aromatic groups isolated by such bridges is negligible.

If compounds containing $-C_6Cl_5$ and $-C_6Cl_4-SiMe_3$ groups are compared, it becomes clear that the replacement of a chlorine atom for a $-SiMe_3$ group in a *para*-position, has a definite bathochromic effect on the spectrum, shifting the B bands about 5–6 mμ. This may be due to an interaction of the trimethylsilyl groups in the *para*-position with the aromatic nucleus. It seems to us currently that there is no contradiction between the ability of the silicon atom to interact with the aromatic nucleus attached to it and the inability of the silicon atom to transmit any electronic effect when it acts as a bridge between two such nuclei.

The replacement of chlorine for fluorine atoms in the aromatic nuclei has also a pronounced effect upon the ultraviolet absorption spectrum, resulting in a broadening of the B band, disappearance of the fine structure and a strong hypsochromic effect upon this band.

Apparently, similar conclusions apply to the E bands in the discussed spectra. An interesting feature of these bands is the high molar absorptivities associated with them, observed in the case of chloro compounds, as noted earlier for several pentachlorophenyl-substituted polysilanes[7].

ACKNOWLEDGEMENTS

One of us (I. H.) acknowledges receipt of a U.S. Department of State Grant within the scientific and cultural exchange program between U.S.A. and Romania (under the sponsorship of the Committee on International Exchange of Persons and National Academy of Sciences, Washington, D.C.) and is grateful to Babes-Bolyai University, Cluj (Romania) for his selection as a participant in this program.

SUMMARY

The ultraviolet spectra of several perchloro- and perfluoro-aromatic organosilicon derivatives are presented and discussed. The data suggest that the aromatic ring in cyclobis(*p*-phenylenedisiloxanes) suffers a deformation, due to the strain in these systems.

REFERENCES

1 I. Haiduc and H. Gilman, *J. Organometal. Chem.*, 11 (1968) 55.
2 I. Haiduc and H. Gilman, unpublished studies (communicated at *3rd Intern. Symp. Organometal. Chem.*, Münich, September, 1967).
3 F. P. McKay, Ph.D. Thesis, Pennsylvania State University, 1956; *Dissertation Abstr.*, 17 (1957) 225.
4 R. L. Merker and M. J. Scott, *J. Polym. Sci., Part A-2*, (1964) 15.
5 D. J. Cram and H. Steinberg, *J. Amer. Chem. Soc.*, 73 (1951) 5691; D. J. Cram, N. L. Allinger and H. Steinberg, *J. Amer. Chem. Soc.*, 76 (1954) 6132; see also D. J. Cram, R. C. Helgeson, D. Lock and L. A. Singer, *J. Amer. Chem. Soc.*, 88 (1966) 1325, and references cited therein.
6 C. J. Brown, *J. Chem. Soc.*, (1953) 3265.
7 H. Gilman and P. J. Morris, *J. Organometal. Chem.*, 6 (1966) 102.
8 H. Conrad-Billroth, *Z. Phys. Chem.*, B19 (1932) 76.
9 M. Ballester and J. Castaner, *J. Amer. Chem. Soc.*, 82 (1960) 4259.
10 C. Eaborn, *Organosilicon Compounds*, Academic Press, New York, 1960, 484.