TABLE II

MASS SPECTRUM OF "SeF_5OSeF_5"

Fragment	m/e	Rel[a] abund	Fragment	m/e	Rel[a] abund
$^{80}Se^+$	80	10	$^{80}SeOF_2{}^+$	134	99
$^{80}SeO^+$	96	19	$^{80}SeF_3{}^+$	137	92
$^{80}SeF^+$	99	12	$^{80}SeOF_3{}^+$	153	28
$^{80}SeOF^+$	115	100	$^{80}SeF_5{}^+$	175	50
$^{80}SeF_2{}^+$	118	26	$^{80}SeF_5O^{80}SeF_4{}^+$	347	<1

[a] Relative to $^{80}SeOF^+$.

The mass spectrum was obtained at an accelerating voltage of 40 eV and the fragments identified are shown in Table II. The elenium isotope ratios for all ions corresponded to those expected. There was no evidence for an ion containing two atoms of oxygen.

Other Reactions of SeF_5OF.—Several unsuccessful attempts were made to prepare compounds containing the SeF_5O group by reactions analogous to some used successfully with SF_5OF. For the following reactants, when contacted with SeF_5OF, no products containing the SeF_5O group were identified: N_2F_4, SO_2, C_2H_4, C_2F_4, C_3F_6. Explosions occurred with C_2H_4. In all other cases much of the SeF_5OF was converted to SeF_6. For the latter two reactants there was some evidence for low yields of products containing the SeF_5O group.

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The Nuclear Magnetic Resonance Spectra and the Electronic Spectra of Some Silicon and Germanium Phthalocyanines[1,2]

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The nmr spectra of the phthalocyanines $PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$, $PcSi(CH_3)(OSi(C_3H_7)_3)$, $PcSi(OSi(C_3H_7)_3)_2$, $PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$, $PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$, and $PcSi(CH_3)(OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2)$ have been examined. For the first four compounds particular attention has been given to the simplification of the spectra of the side groups caused by the ring current of the phthalocyanine ring. For the last two compounds attention has been given to a determination of the ^{29}Si–C–H coupling constants of the side groups. Also examined have been the electronic spectra of the first four members of the series of compounds $(((CH_3)_3SiO)_2(CH_3)SiO)(PcSiO)_n(Si(CH_3)(OSi(CH_3)_3)_2)$ and the first two members of the analogous series of germanium compounds.

Introduction

In previous papers on the nmr spectra of the group IV phthalocyanines, the spectra of various groups attached to the *trans* positions of the central metal atom have been studied.[3–7] The present paper describes additional work of this same type. Here attention is given to an examination of the spectra of the triphenylsiloxy, tripropylsiloxy, propyl, and $-OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2$ groups and to a reexamination of the spectra of the methyl and $-OSi(CH_3)(OSi(CH_3)_3)_2$ groups. For the phenyl and propyl groups the main emphasis is on the simplification of the spectra caused by the ring current of the phthalocyanine ring, while for the methyl and methylsiloxy groups the emphasis is on the ^{29}Si–C–H coupling constants.

In addition to these nmr studies, work on the electronic spectra of the oligomers $(((CH_3)_3SiO)_2(CH_3)SiO)(PcSiO)_{1-4}(Si(CH_3)(OSi(CH_3)_3)_2)$ and $(((CH_3)_3SiO)_2(CH_3)SiO)(PcGeO)_{1-2}(Si(CH_3)(OSi(CH_3)_3)_2)$ is presented. The nmr spectra of these compounds have been described and analyzed in detail earlier[3] but their electronic spectra, although of interest because of their unusual ring-upon-ring structures, have not been taken up before.

Experimental Section

$PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$.—A mixture of $PcSi(OH)(OSi(CH_3)(OSi(CH_3)_3)_2$ (0.39 g),[7] triphenylsilanol (0.55 g), and chlorobenzene (25 ml) was refluxed for 1.5 hr and evaporated to dryness. The product was chromatographed on Woelm alumina (activity II–III). This gave red-reflecting, blue-transmitting crystals (0.12 g). These were crushed and vacuum dried at 100°. *Anal.* Calcd for $C_{57}H_{52}N_8O_4Si_5$: C, 64.98; H, 4.98; Si, 13.33. Found: C, 64.77; H, 4.91; Si, 13.63.

$PcSi(CH_3)(OSi(C_3H_7)_3)$.—A mixture of $PcSi(CH_3)(OH)$ (0.57 g),[7] tri-*n*-propylchlorosilane (0.50 ml), chlorobenzene (20 ml), and pyridine (5 ml) was refluxed for 45 min, filtered, and evaporated to dryness on a steam bath. The product was chromatographed on Woelm alumina (activity II) and recrystallized from a methylcyclohexane–toluene solution (3:1). The resultant red-reflecting, green-transmitting crystals (0.19 g) were crushed and vacuum dried at 100°. *Anal.* Calcd for $C_{42}H_{40}N_8OSi_2$: C, 69.20; H, 5.53; Si, 7.71. Found: C, 68.74; H, 5.26, Si, 8.06.

$PcSi(OSi(C_3H_7)_3)_2$.—A mixture of $PcSiCl_2$ (2.1 g),[8] tri-*n*-propylsilanol (4.0 ml), xylene (50 ml), and pyridine (20 ml) was

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[1] This paper is based in part on the Ph.D. thesis of A. R. Kane, University Microfilms No. 70-5101. The work was supported by the National Science Foundation under Grants GP 1702 and GP 8368 and under the RPCT Program, by the National Aeronautics and Space Administration under its fellowship program, and by the Office of Naval Research.

[2] The abbreviation Pc is used for the phthalocyanine ligand, $C_{32}H_{16}N_8$.

[3] T. R. Janson, A. R. Kane, J. F. Sullivan, K. Knox, and M. E. Kenney, *J. Am. Chem. Soc.*, **91**, 5210 (1969).

[4] A. R. Kane, R. G. Yalman, and M. E. Kenney, *Inorg. Chem.*, **7**, 2588 (1968).

[5] L. E. Sutton and M. E. Kenney, *ibid.*, **6**, 1869 (1967).

[6] J. N. Esposito, L. E. Sutton, and M. E. Kenney, *ibid.*, **6**, 1116 (1967).

[7] J. N. Esposito, J. E. Lloyd, and M. E. Kenney, *ibid.*, **5**, 1979 (1966).

[8] M. K. Lowery, A. J. Starshak, J. N. Esposito, P. C. Krueger, and M. E. Kenney, *ibid.*, **4**, 128 (1965).

TABLE I
NMR DATA[a,b]

	Ligand protons		Phenyl protons			Propyl protons				Siloxy methyl protons			Central methyl protons
	3,6	4,5	4	3,5	2,6	γ	β	α	$J_{CH_2CH_3}$	Outer	Middle	Inner	
$PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$[c]	0.49	1.79	3.37	3.77	5.23[d]						11.24	12.92	
$PcSi(CH_3)(OSi(C_3H_7)_3)$[c]	0.40	1.74				10.32	11.23	12.55	6.9				16.35
$PcSi(OSi(C_3H_7)_3)_2$[c]	0.36	1.72				10.26	11.14	12.44	6.8				
$PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$[c]	0.39	1.74				11.54	13.97	16.20	7.1		11.21	13.00	
$PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$[e]	0.40	1.73									11.26	12.99	16.31
$PcSi(CH_3)(OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2)$[e]	0.41	1.74								10.66	11.60	12.94	16.32

[a] Chemical shifts, τ. [b] Coupling constants, Hz. [c] A-60A spectra. [d] Experimental values. [e] HA-100 spectra.

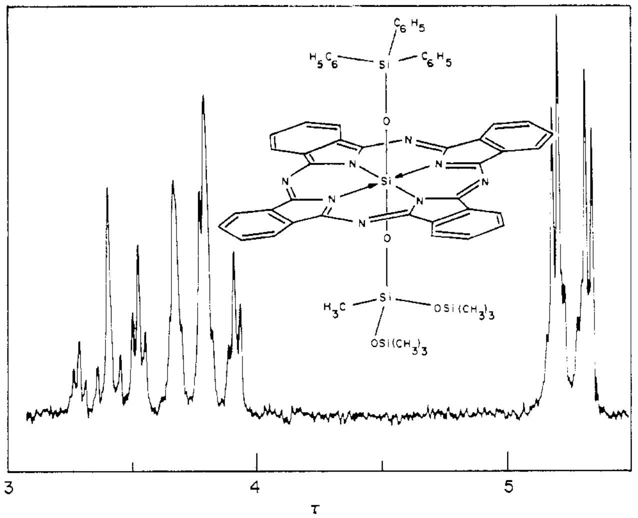

Figure 1.—The phenyl region of the 60-MHz spectrum of $PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$.

refluxed for 24 hr, filtered, and evaporated to dryness on a steam bath (2.5 g). The product was chromatographed on Woelm alumina (activity II), recrystallized from methylcyclohexane (0.27 g), and vacuum dried at 100°. The crystals thus obtained were red reflecting and blue transmitting. *Anal.* Calcd for $C_{50}H_{58}N_8O_2Si_3$: C, 67.68; H, 6.59; Si, 9.50. Found: C, 66.76; H, 6.71; Si, 9.34.

$PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$.—A mixture of 1,3-diiminoisoindoline[8] (20 g), *n*-propyltrichlorosilane (30 ml), and quinoline (150 ml) was heated to 150° over a 6-hr period, and then maintained at 150–160° for 36 hr. The product was recovered by filtration and washed (3.2 g). A slurry of this product (2.1 g) and concentrated sulfuric acid (20 ml) was allowed to stand 1 hr and then poured onto ice (200 g). The resultant product was recovered, washed with concentrated ammonium hydroxide and water, and dried (1.9 g). A mixture of this (0.72 g), 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ol[4] (1.0 ml), and chlorobenzene (50 ml) was refluxed for 1.2 hr, filtered, and evaporated to dryness on a steam bath (0.56 g). The product was chromatographed on Woelm alumina (activity II). This gave crystals which were red reflecting and green transmitting (0.17 g). These were vacuum dried at 100°.

The nmr spectrum of these crystals showed a small impurity resonance at τ 8.7. This was probably associated with an aliphatic decomposition product or with petroleum ether (from the chromatography). The crystals decomposed to a yellow product on standing.

$PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$.—This compound was synthesized from $PcSi(CH_3)(OH)$ and 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ol in chlorobenzene in a manner analogous to that used for the preceding compound. It was found that this synthetic procedure was superior to the one reported earlier,[7] both in terms of yield and in terms of product purity.

The resistance of the central methyl group in this compound to cleavage by base was checked by refluxing a sample of it (0.23 g) with 0.5 *M* methanolic sodium hydroxide (30 ml) in the dark for 2.5 hr. The product obtained was $PcSi(CH_3)(OH)$. Previously such a methyl group had been shown to be highly resistant to acid cleavage.[7,9]

$PcSi(CH_3)(OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2)$.—A mixture of 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ol (28 ml) and N,O-bis(dimethylsilyl)acetamide (24 ml) in chloroform–ether solution was stirred for 3 hr and the product isolated by vacuum distillation. Over a 10-min period a portion of this product (30 ml) was added to a stirred mixture of dioxane (105 ml), neutralized 5% palladium-on-carbon catalyst (0.25 g), and an aqueous buffer solution containing 0.65 g of $NaH_2PO_4 \cdot H_2O$ and 4.0 g of NaOH/l. (9 ml).[10] After 3 hr of stirring, the mixture was filtered and the resultant silanol was isolated by vacuum distillation.

A mixture of some of this silanol (0.84 g), $PcSi(CH_3)(OH)$ (0.49 g), and chlorobenzene (29 ml) was refluxed for 1.5 hr, filtered, and evaporated to dryness on a steam bath (0.44 g). The product was purified by column chromatography on Woelm alumina (activity II), combined with several like products, and recrystallized from a methylcyclohexane–ethanol solution (5:3). The crystals thus obtained (0.31 g) were vacuum dried at 100°. They were red reflecting and green transmitting. *Anal.* Calcd for $C_{42}H_{46}N_8O_4Si_5$: C, 58.16; H, 5.35; Si, 16.19. Found: C, 58.04; H, 5.52; Si, 15.77.

Instrumentation.—For the nmr work Varian A-60A and HA-100 spectrometers were used. Carbon tetrachloride was used as a solvent and tetramethylsilane as an internal standard.

For the electronic spectra work a Cary Model 14 recording spectrophotometer was used. Cyclohexane was used as a solvent for the silicon compounds and *n*-hexane as a solvent for the germanium compounds.

Discussion

Spectral Simplification.—Earlier work has drawn attention to the fact that groups located above the center of the ring in porphyrin-type compounds are subject to an amount of shielding which increases as the proximity of the group to the ring center increases and that for groups quite near the ring center the shielding provided is substantial.[3,4,11,12] Because of this shielding, groups bonded to the ring center of porphyrin-type compounds tend to have widely separated multiplets for their different types of protons and tend to give simplified and sometimes approximately first-order spectra.

For example, it has been shown that the methyl and methylene protons of the ethyl groups in the two compounds N-ethyletioporphyrin II[11] and ethyltriethyl-

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(9) The ability of this type of Si–CH_3 grouping to withstand both electrophilic and nucleophilic attack is probably partly due to the fact that the silicon atom and the Si–C bond are both highly protected and thus that any mechanisms involving direct attack on the silicon atom or the Si–C bond as essential steps are strongly hindered.

(10) G. H. Barnes, Jr., and N. E. Daughenbaugh, *J. Org. Chem.*, **31**, 885 (1966).

(11) W. S. Caughey and P. K. Iber, *ibid.*, **28**, 269 (1963).

(12) C. B. Storm and A. H. Corwin, *ibid.*, **29**, 3700 (1964).

siloxysilicon phthalocyanine[4] give widely separated triplets and quartets. Similarly, it has been shown that the 2,6, the 3,5, and the 4 protons in the pyridine groups in magnesium tetraphenylporphin pyridinate and magnesium etioporphyrin II pyridinate give three distinct multiplets.[12]

The ability of porphyrin-type rings to spread and simplify the spectra of groups under their influence is also illustrated by the phenyl region of the 60-MHz spectrum of the compound $PcSi(OSi(C_6H_5)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$, Figure 1 and Table I. Here the resonances associated with the 2,6 protons are well separated from those of the 3,5 and 4 protons and even the resonances of the latter two sets of protons are reasonably well separated from each other. At 100 MHz the separation is even greater and the multiplets have even more the appearance of two triplets and a doublet split by further interactions. In neither case, however, is the spectrum approximately first order, nor can it become so at still higher field because of the presence of magnetically nonequivalent protons.[13]

The chemical shifts of the 2,6, the 3,5, and the 4 protons as determined from the line positions in the 60-MHz spectrum and the computer procedure LAOCN3 are, respectively, τ 5.23, 3.73, and 3.40. These values are very close to those obtained by taking the centers of the multiplets, Table I, as the chemical shifts of the three types of protons, *i.e.*, by assuming full separation of the multiplets.

The coupling constants obtained from the computer matching procedure are 7.4, 1.3, 0.7, 1.4, 7.4, and 1.1 Hz for $J_{2,3}$, $J_{2,4}$, $J_{2,5}$, $J_{2,6}$, $J_{3,4}$, and $J_{3,5}$, respectively. These are, of course, in accord with expectations.[14]

The spectra of the three *n*-propyl compounds, $PcSi(CH_3)(OSi(C_3H_7)_3)$, $PcSi(OSi(C_3H_7)_3)_2$, and $PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$, Table I and Figure 2, also illustrate the spreading and simplifying power of the phthalocyanine ring. The greater upfield shift of the propyl multiplets in $PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$ is due, of course, to the greater proximity of the propyl group in this compound to the center of the ring.

An interesting aspect of these spectra is the shape of the propyl multiplets. In all three spectra the α multiplets are complex but similar, the β multiplets are complex but similar, and the γ multiplets are triplets. To try to gain more information about these multiplets both temperature-variation and spin-decoupling experiments were carried out on the compound $PcSi(OSi(C_3H_7)_3)_2$. The temperature variation work, using chlorobenzene and chloronaphthalene as solvents and temperatures of up to 170°, showed that the shapes of the multiplets are quite temperature insensitive, only slight narrowing of the α multiplet being observed. The decoupling work showed that irradiation of the α protons leads to a quartet and a triplet, irradiation of the β protons to a pair of singlets, and irradiation of the γ protons to a pair of AA′BB′ multiplets.

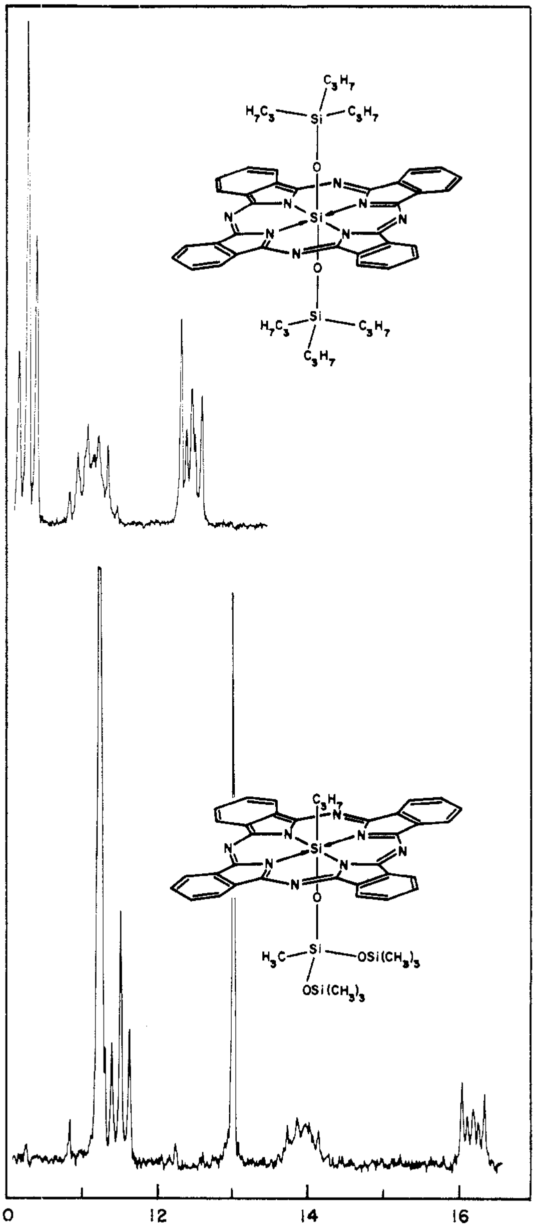

Figure 2.—The propyl region of the 60-MHz spectra of $PcSi(OSi(C_3H_7)_3)_2$ and $PcSi(C_3H_7)(OSi(CH_3)(OSi(CH_3)_3)_2)$.

All of these results are consistent with strongly preferred *trans* conformers at the α-carbon–β-carbon bonds in these propyl groups. Consideration of the size of the groups attached to the pairs of carbon atoms indicates that this is reasonable.

^{29}Si–C–H Coupling Constants.—The structures of the phthalocyanines $PcSi(CH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$ and $PcSi(CH_3)(OSi(CH_3)_2OSi(CH_3)(OSi(CH_3)_3)_2)$ are unusual in that they contain methyl groups bonded to octahedrally coordinated silicon atoms and in addition methyl groups bonded to tetrahedrally coordinated silicon atoms carrying, respectively, one and three oxygen atoms and one, two, and three oxygen atoms. Because of these unusual structural features, the ^{29}Si–

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[13] E. O. Bishop in "Nuclear Magnetic Resonance for Organic Chemists," D. W. Mathieson, Ed., Academic Press Inc., New York, N. Y., 1967, p 108.

[14] F. A. Bovey, "Nuclear Magnetic Resonance Spectroscopy," Academic Press Inc., New York, N. Y., 1969, p 368.

C–H coupling constants of these two compounds, Table II, are of interest.

Table II

^{29}Si–C–H Coupling Constants (Hz)

Coordination of silicon	No. of methyls attached	PcSi(CH$_3$)(OSi-(CH$_3$)(OSi-(CH$_3$)$_3$)$_2$)	PcSi(CH$_3$)(OSi-(CH$_3$)$_2$OSi(CH$_3$)-(OSi(CH$_3$)$_3$)$_2$)
Tetrahedral	1	8.6	8.7
Tetrahedral	2		7.1
Tetrahedral	3	6.6	6.7
Octahedral	1	7.7	7.6

As is seen, the ^{29}Si–C–H coupling constants for the tetrahedral methyl groups have values of the expected magnitude.[15] Those for the octahedral methyl groups have values of this same magnitude, but little comment can be offered on this fact since data on comparable methyl groups are lacking.

Electronic Spectra.—The unusual ring-upon-ring arrangement of the rings in the silicon and germanium oligomers (((CH$_3$)$_3$SiO)$_2$(CH$_3$)SiO)(PcSiO)$_{1-4}$(Si(CH$_3$)-(OSi(CH$_3$)$_3$)$_2$) and (((CH$_3$)$_3$SiO)$_2$(CH$_3$)SiO)(PcGeO)$_{1-2}$-(Si(CH$_3$)(OSi(CH$_3$)$_3$)$_2$) has been established by previous nmr work.[3] As expected the electronic spectra of these compounds are quite sensitive to the number of rings per molecule, Table III and Figure 3. Particularly striking are the blue shifts of the Q and B bands of these compounds with increasing chain length.

Table III

Electronic Spectra [$\tilde{\nu}_{max}$, cm^{-1} (ϵ, M^{-1} cm^{-1} × 10^{-4})]

Central element	No. of rings	Q transitions	B transitions
Si	1	15,040 (46)	28,470 (7.8) 29,310 (7.6) 30,180 sh (6.5)
Si	2	15,880 (27)	30,380 (12)
Si	3	16,180 (16)	30,550 (15)
Si	4	16,270 (17)	30,710 (18)
Ge	1	14,970 (48)	28,330 (7.8) 29,150 (6.5) 30,300 sh (5.3)
Ge	2	15,840 (28)	30,210 (8.9)

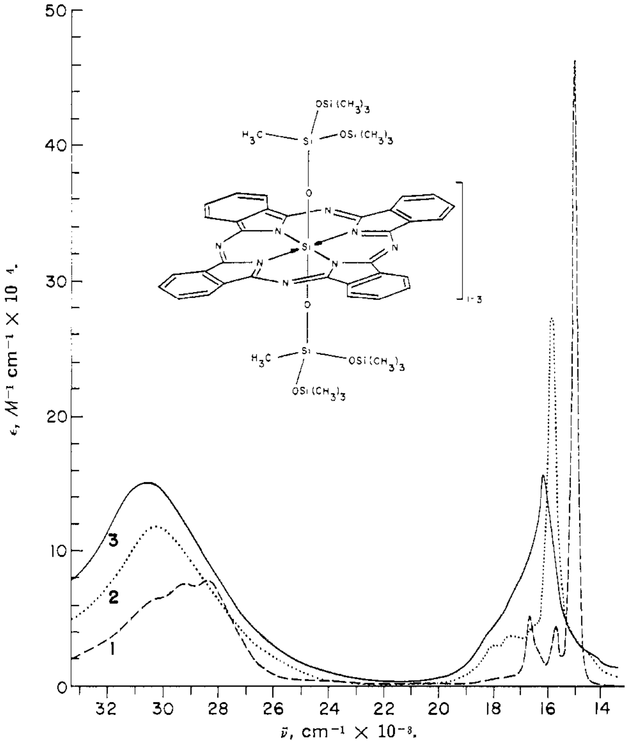

Figure 3.—The electronic spectra of the silicon phthalocyanine oligomers containing one ring (1), two rings (2), and three rings (3).

These can be rationalized if it is assumed that the π–π* transitions corresponding to these bands[16] have their electronic transition dipoles in the planes of the rings. The transition dipoles must then be parallel and theory predicts blue shifts.[17]

Also of interest with regard to the spectra are the changes in extinction coefficients of the Q and B bands with increasing chain length and the loss of fine structure in the band envelopes of the Q and B bands with increasing chain length (the germanium compounds show the same trend in envelope shape as do the silicon compounds). The loss of fine structure is obviously attributable to alterations in the electronic energy levels of the rings caused by ring–ring interactions.

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(15) E. A. V. Ebsworth in "Organometallic Compounds of the Group IV Elements," Vol. 1, Part I, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., New York, N. Y., 1968, p 73.

(16) A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, **7**, 74 (1965).

(17) M. Kasha, *Radiation Res.*, **20**, 55 (1963).