The Synthesis and Physical Properties of Some Organo- and Organosiloxysilicon Phthalocyanines[1]

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A series of organo- and organosiloxysilicon phthalocyanines has been synthesized and characterized by proton nuclear magnetic resonance, infrared, powder X-ray, and differential thermal analysis techniques. The diamagnetic shielding of the protons in the substituent groups by the macrocycle has been found to be very large.

Introduction

In a previous paper it was pointed out that tetravalent metal phthalocyanines are soluble in organic solvents if the *trans* groups attached to the metal are of a suitable kind.[2] Subsequent work in this laboratory has shown that among the *trans* groups which impart solubility are methylsiloxy groups having two or more silicon atoms. In this study use has been made of this knowledge in preparing a series of symmetrical siloxysilicon phthalocyanines of sufficient solubility to be useful for physical studies requiring solutions. These compounds have then been used for a nuclear magnetic resonance investigation of silicon phthalocyanines.

In addition, work has been carried out on the synthesis of a series of silicon phthalocyanines where one, but not both, of the *trans* groups is a methyl or a phenyl group. These compounds have been used to obtain additional information on the nature of the octahedral silicon–carbon bond.

One of the methyl compounds has also been used as an intermediate in the synthesis of other nonmethyl unsymmetrical compounds, the syntheses being based on blocking procedures involving the methyl group. In these compounds the *trans*-methylsiloxy group has been chosen to be of such a type as to impart high solubility to the molecule. This has permitted the other group to be chosen without primary attention being given to its solubilizing characteristics and has made possible physical studies requiring solutions on otherwise inaccessible groups, *e.g.*, methoxy.

Experimental Section

α-PcSi(CH₃)Cl.—The satisfactory nature of the PcSiCl₂ synthesis based on 1,3-diiminoisoindoline[3] paved the way for the successful synthesis of PcSi(CH₃)Cl. In one run 31.4 g (0.216 mole) of 1,3-diiminoisoindoline, 18.0 ml (0.153 mole) of methyltrichlorosilane, and 300 ml of quinoline in a 500-ml, two-neck, round-bottom flask fitted with a water condenser and a mechanical stirrer were refluxed for 90 min. The reaction mixture was filtered immediately and the recovered product was washed and dried. Additional product was obtained upon refiltration of the reaction mixture after it had been cooled to 55°. The

total yield was 16.6 g, 52%, based on diiminoisoindoline. No method of purifying this polymorph was found.

β-PcSi(CH₃)Cl.—To obtain an analytical sample of this polymorph, 6.41 g of the α polymorph was placed in a dried, aluminum foil wrapped, Bailey–Walker extraction apparatus, filled with 220 ml of dried chlorobenzene and, under nitrogen, was extracted for 35 hr. By this procedure 822 mg of purple-reflecting, green-transmitting crystals was obtained.

Anal. Calcd for C₃₃H₁₉N₈SiCl: C, 67.05; H, 3.24; Si, 4.75; Cl, 6.00. Found: C, 66.84; H, 3.06; Si, 4.97; Cl, 5.79.

PcSi(CH₃)OH.—An 18.8-g sample of PcSi(CH₃)Cl was stirred with 300 ml of concentrated sulfuric acid until the evolution of HCl ceased. The dark brown mixture was then added, with stirring, to 2 l. of crushed ice, and the resultant green precipitate was separated and stirred with 600 ml of concentrated ammonium hydroxide. The final product, after being washed with water and dried, weighed 15.0 g, an 82% yield.

Recrystallization of this product from *o*-dichlorobenzene (care being taken to minimize exposure of the dissolved compound to light) yielded small, dichroic, purple-reflecting, green-transmitting crystals.

Anal. Calcd for C₃₃H₂₀N₈SiO: C, 69.21; H, 3.52; Si, 4.91. Found: C, 68.96; H, 3.44; Si, 5.07.

The sodium methoxide–water–ethanol[3] and pyridine–ammonium hydroxide[4] mixtures used earlier for the hydrolysis of PcSiCl₂ were found to be very ineffective for the hydrolysis of PcSi(CH₃)Cl.

PcSi(CH₃)OD.—A reaction mixture of 106 mg of pure β-PcSi(CH₃)Cl, 10 ml of dried pyridine, and 1.5 ml of D₂O was refluxed, with stirring, for 7.5 hr. This yielded 99 mg of the deuterioxide.

A product identical by both infrared and X-ray powder data was obtained from α-PcSi(CH₃)Cl.

PcSi(CH₃)F.—A mixture of 1.63 g of PcSi(CH₃)Cl and 12 ml of 48% HF was evaporated to dryness on a steam bath and oven dried at 115° for 30 min. This yielded a product weighing 1.15 g. Recrystallization of this product from *o*-dichlorobenzene twice gave purple-reflecting, green-transmitting dichroic crystals.

Anal. Calcd for C₃₃H₁₉N₈SiF: C, 68.97; H, 3.33; Si, 4.89; F, 3.31. Found: C, 69.04; H, 3.37; Si, 4.68; F, 3.45.

When treated in the same way, PcSi(CH₃)OH also yielded PcSi(CH₃)F.

β-PcSi(CH₃)OC₆H₅.—To prepare an analytical sample of the phenoxide in the β form, a mixture of 1.64 g of PcSi(CH₃)OH, 5.5 g of phenol, and 45 ml of 1,2,4-trimethylbenzene was refluxed for 70 min and filtered. The filtrate was allowed to stand overnight and, upon filtration, yielded 825 mg of the α polymorph. Digestion of 808 mg of this in 10 ml of 1,2,4-trimethylbenzene containing 387 mg of phenol gave 570 mg of purple-reflecting, green-transmitting dichloric crystals.

Anal. Calcd for C₃₉H₂₄N₈SiO: C, 72.20; H, 3.73; Si, 4.33. Found: C, 72.33; H, 3.89; Si, 4.46.

α-PcSi(CH₃)OC₆H₅.—The α polymorph was prepared by recrystallization of the phenoxide from dilute solution under

(1) This work was supported by the Office of Naval Research under Contract No. 1141(18) and by the National Science Foundation under Grant GP-1702.

(2) P. C. Krueger and M. E. Kenney, *J. Org. Chem.*, **28**, 3379 (1963).

(3) M. K. Lowery, A. J. Starshak, J. N. Esposito, P. C. Krueger, and M. E. Kenney, *Inorg. Chem.*, **4**, 128 (1965).

(4) R. D. Joyner and M. E. Kenney, *ibid.*, **1**, 236 (1962).

conditions minimizing exposure of the solution to light. A 236-mg sample of the phenoxide, previously twice recrystallized from 1,2,4-trimethylbenzene, was refluxed for 5 min with 47 ml of 1,2,4-trimethylbenzene containing 56 mg of phenol and cooled slowly. Filtration of the resultant product, after 5 hr of standing and again after overnight standing, yielded a total of 141 mg of thin, purple-reflecting, green-transmitting crystals.

Anal. Calcd for $C_{39}H_{24}N_8SiO$: C, 72.20; H, 3.73; Si, 4.33. Found: C, 72.05; H, 3.87; Si, 4.28.

Partial conversion of the α form to the β form was effected by heating the α form at 150° for 3 hr under vacuum. More substantial conversion was produced by heating the α form under vacuum for 1 hr at 190° and for 1 additional hr at 230°.

PcSi(CH₃)OC₆H₄Cl-*p*.—A reaction mixture of 1.95 g of PcSi-(CH₃)OH, 1.19 g of *p*-chlorophenol, and 50 ml of 1,2,4-trimethylbenzene was refluxed for 30 min. After 4 hr the product was recovered and found to weigh 2.00 g. Recrystallization of the product thus obtained from toluene afforded purple-reflecting, green-transmitting plates. These were dried at 110° for 1 hr and at 100° under vacuum for 45 min.

Anal. Calcd for $C_{39}H_{23}N_8SiClO$: C, 68.56; H, 3.39; Si, 4.11; Cl, 5.19. Found: C, 68.65; H, 3.46; Si, 4.26; Cl, 5.42.

Recrystallization of a similarly synthesized reaction product from 1,2,4-trimethylbenzene gave crystals which gas chromatographic data showed to be solvated with 1,2,4-trimethylbenzene. Weight loss data indicated that the solvate was probably a 1:1 solvate.

PcSi(C₆H₅)Cl.—A mixture of 20.0 g of 1,3-diiminoisoindoline, 35 ml of phenyltrichlorosilane, and 250 ml of quinoline in a two-neck, round-bottom flask, fitted with a water condenser and a mechanical stirrer, was heated for 4.8 hr in an oil bath at 180°. The reaction product, after being filtered off and washed with a copious amount of methanol, weighed 3.69 g, a 16% yield based on diiminoisoindoline.

To obtain an analytically pure sample, the reaction product was extractively recrystallized from toluene. This yielded purple-reflecting, green-transmitting crystals.

Anal. Calcd for $C_{38}H_{21}N_8SiCl$: C, 69.88; H, 3.24; Si, 4.30; Cl, 5.43; N, 17.16. Found: C, 69.72; H, 3.45; Si, 4.05; Cl, 5.12; N, 16.93.

Recrystallization of the reaction product from chlorobenzene gave a chlorobenzene solvate.

PcSi(OSi(CH₃)₂OSi(CH₃)₃)₂.—A mixture of 0.59 g of PcSi-(OH)₂, 0.4 g of (CH₃)₃SiOSi(CH₃)₂H, 0.05 g of H₂PtCl₆·6H₂O dissolved in 5 ml of acetone, and 28 ml of 1,2,4-trimethylbenzene was refluxed, with stirring, for 2 hr and filtered while hot. The resulting solution was evaporated to about 5 ml and placed on an alumina column (80–200 mesh, activity 1). Elution with petroleum ether brought through a colorless fraction (methylsiloxanes). Further elution, this time with benzene–petroleum ether, brought down a deep blue band followed by a lighter blue band. A green band was left at the top. The middle portion of the deep blue band was collected and the phthalocyanine was recovered by evaporation of the solvent. Recrystallization from cyclohexane yielded approximately 50 mg of purple-reflecting, blue-transmitting crystals; mp 291–293° subl.

Anal. Calcd for $C_{42}H_{46}N_8O_4Si_5$: C, 58.15; H, 5.35; Si, 16.20. Found: C, 58.28; H, 5.42; Si, 16.31.

Nmr spectra revealed the presence of an impurity giving a small peak at τ 12.85.

PcSi(OSi(CH₃)(OSi(CH₃)₃)₂)₂.—To prepare this compound a mixture 0.94 g of PcSi(OH)₂, 1.2 g of ((CH₃)₃SiO)₂Si(CH₃)H, 100 mg of H₂PtCl₆·6H₂O dissolved in acetone, and 18 ml of 1,2,4-trimethylbenzene was refluxed for 6 hr, filtered hot, and evaporated to dryness on a steam bath. The product was dissolved in carbon tetrachloride and chromatographed on an alumina column with petroleum ether and petroleum ether–benzene as eluants. A final recrystallization from cyclohexane yielded purple-reflecting, blue-transmitting crystals; mp 258°.

Anal. Calcd for $C_{46}H_{58}N_8O_6Si_7$: C, 54.39; H, 5.76; Si, 19.37. Found: C, 54.32; H, 5.94; Si, 19.62.

PcSi(OSi(OSi(CH₃)₃)₃)₂.—In a typical preparation a mixture of

1.05 g of PcSi(OH)₂, 0.8 g of ((CH₃)₃SiO)₃SiH, 100 mg of H₂PtCl₆·6H₂O in acetone, and 20 ml of 1,2,4-trimethylbenzene was refluxed for 7 days, filtered while hot, and evaporated to dryness. This product was chromatographed as before and recrystallized from cyclohexane. Purple-reflecting, blue-transmitting crystals were obtained, mp >325° dec.

Anal. Calcd for $C_{50}H_{70}N_8O_8Si_9$: C, 51.57; H, 6.06; Si, 21.74. Found: C, 51.86; H, 6.29; Si, 22.03.

O(PcSiOSi(OSi(CH₃)₃)₃)₂.—Further elution of the column from which the pure PcSi(OSi(OSi(CH₃)₃)₃)₂ was obtained with benzene–petroleum ether brought down an additional band. Recrystallizaton of the product from this very deep blue band yielded purple-reflecting, blue-transmitting crystals; mp >325° dec.

Anal. Calcd for $C_{82}H_{86}N_{16}O_9Si_{10}$: C, 57.25; H, 5.04; Si, 16.33. Found: C, 57.41; H, 5.20; Si, 16.15.

PcSi(CH₃)(OSi(CH₃)(OSi(CH₃)₃)₂).—A mixture of 1.07 g of PcSi(CH₃)OH, 0.8 g of ((CH₃)₃SiO)₂Si(CH₃)H, 100 mg of H₂PtCl₆·6H₂O in 5 ml of acetone, and 20 ml of 1,2,4-trimethylbenzene was refluxed for 1 hr, filtered hot, and evaporated to dryness. The product was dissolved in carbon tetrachloride and chromatographed on an alumina column wrapped with aluminum foil, petroleum ether and petroleum ether–benzene being the eluants. The green band was collected and the product was recrystallized from *n*-hexane under conditions minimizing exposure to light. This gave purple-reflecting, green-transmitting crystals; mp 251–252°.

Anal. Calcd for $C_{46}H_{46}N_8O_3Si_4$: C, 60.57; H, 5.08; Si, 14.17. Found: C, 60.38; H, 5.00; Si, 14.41.

To test the sensitivity of PcSi(CH₃)(OSi(CH₃)(OSi(CH₃)₃)₂) to various portions of the visible spectrum, a petroleum ether solution of it was exposed to radiation from a tungsten filament lamp filtered through Klett filters No. 44 (4100–4800 Å), No. 50 (4700–5300 Å), and No. 64 (6200–6800 Å). Light from the red and blue filters was found to cause its decomposition.

PcSi(OH)(OSi(CH₃)(OSi(CH₃)₃)₂).—A dilute solution of chromatographed PcSi(CH₃)(OSi(CH₃)(OSi(CH₃)₃)₂) in petroleum ether was stirred vigorously in sunlight for about 2 hr and the resulting blue precipitate recrystallized from a 1:2 toluene–methylcyclohexane solution. Purple-reflecting, blue-transmitting crystals were obtained.

Anal. Calcd for $C_{39}H_{38}N_8O_4Si_4$: C, 58.95; H, 4.77; Si, 14.15. Found: C, 59.10; H, 4.73; Si, 14.28.

PcSi(OCH₃)(OSi(CH₃)(OSi(CH₃)₃)₂).—A mixture of 0.9 g of PcSi(OH)(OSi(CH₃)(OSi(CH₃)₃)₂) and 20 ml of methanol was refluxed for 2 hr, filtered, and evaporated to dryness. A carbon tetrachloride solution of the resultant product was chromatographed on an alumina column (activity 3–4) with petroleum ether–benzene. The chromatographed product was rechromatographed and recrystallized from pentane. This gave purple-reflecting, blue-transmitting crystals; mp 279–280°.

Anal. Calcd for $C_{40}H_{40}N_8O_4Si_4$: C, 59.37; H, 4.98; Si, 13.90. Found: C, 59.47; H, 4.99; Si, 14.16.

Nmr spectra revealed an impurity giving a small peak at τ 8.75.

PcSi(OCH₂C(CH₃)₃)(OSi(CH₃)(OSi(CH₃)₃)₂).—A mixture of 0.32 g of PcSi(OH)(OSi(CH₃)(OSi(CH₃)₃)₂), 1.0 g of 2,2-dimethyl-1-propanol, 8 ml of toluene, and 16 ml of xylene was refluxed for 2 hr, filtered, and evaporated to dryness. Recrystallization of the product from pentane yielded purple-reflecting, blue-transmitting crystals; mp 268–269°.

Anal. Calcd for $C_{44}H_{48}N_8O_4Si_4$: C, 61.05; H, 5.59; Si, 12.99. Found: C, 60.91; H, 5.58; Si, 13.12.

PcSi(OCH₃)₂.—A mixture of 0.82 g of PcSiCl₂, 6 g of NaOCH₃, and 25 ml of methanol was refluxed for 16 hr, and the product was recrystallized from *o*-dichlorobenzene. Purple-reflecting, blue-transmitting crystals were obtained.

Anal. Calcd from $C_{34}H_{22}N_8O_2Si$: C, 67.85; H, 3.67; Si, 4.66. Found: C, 68.16; H, 3.65; Si, 4.53.

Nmr Spectra.—A Varian A60 spectrometer operating at approximately 40° was used to obtain spectra of a number of the compounds. Tetramethylsilane, benzene, and chloroform were used as internal standards for the spectra taken in deuterio-

TABLE I

NMR SPECTRA

Compound	Solvent	3,6 ring	4,5 ring	Outer side chain	Inner side chain	OCH$_2$ or $_3$	C(CH$_3$)$_3$	CH$_3$
PcSi(CH$_3$)F	H$_2$SO$_4$	−0.19	0.94					14.14
PcSi(CH$_3$)OH	H$_2$SO$_4$	−0.23	0.88					13.96
PcSi(OSi(CH$_3$)$_2$OSi(CH$_3$)$_3$)$_2$	CCl$_4$	0.19	1.58	11.26	12.93			
PcSi(OSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$)$_2$	CCl$_4$	0.20	1.60	11.25	12.98			
PcSi(OSi(OSi(CH$_3$)$_3$)$_3$)$_2$	CCl$_4$	0.24	1.62	11.24				
PcSi(CH$_3$)(OSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$)	CCl$_4$	0.29	1.66	11.26	13.00			16.33
PcSi(OCH$_3$)(OSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$)	CCl$_4$	0.22	1.62	11.25	12.98	11.85		
PcSi(OCH$_2$C(CH$_3$)$_3$)(OSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$)	CCl$_4$	0.21	1.59	11.26	12.99	12.60	11.66	
O(PcSiOSi(OSi(CH$_3$)$_3$)$_3$)$_2$	CDCl$_3$	0.93	1.67	11.87				

TABLE II

INFRARED SPECTRA (CM^{-1})

F	OH	OD	α-Cl	β-Cl	α-OC$_6$H$_5$	β-OC$_6$H$_5$	OC$_6$H$_4$Cl	C$_6$H$_5$Cl	Assignment
	3522 vw, b								OH
3054 vw	3050 vw	3052 vw	3054 vw	3055 vw	3054 vw	3059 vw	3056 vw	3057 vw	PcSi
		2600 vw, b							OD
1617 w	1615 w	1616 w	1613 w	1615 w	1614 w	1609 w	1605 w	1613 w	PcSi
1595 vw	1593 vw	1595 vw	1595 vw	1597 vw	1591 w	1591 m	1587 vw	1595 vw	PcSi and OPh
1516 m	1509 m	1507 m	1517 w	1522 w	1515 m	1514 m	1513 m	1515 w	PcSi
					1487 m	1487 m	1486 m		OPh
1429 m	1427 m	1427 m	1428 m	1430 m	1428 m	1425 m	1428 m	1429 m	PcSi
1334 s	1334 s	1334 s	1336 s	1336 s	1334 s	1332 s	1334 s	1336 s	PcSi
1290 m	1289 m	1288 m	1290 m	1289 m	1290 m	1287 m	1290 m	1291 m	PcSi
1273 vw	1273 vw	1272 vw	1271 w	1263 w	1269 w	1258 m	1269 m		CH$_3$
1267 vw	1267 vw	1266 vw							CH$_3$
					1249 m	1250 m	1253 m		CO
1163 m	1164 m	1164 m	1166 m	1164 m	1165 m	1163 m	1166 m	1164 m	PcSi
1120 s	1120 s	1120 s	1121 s	1122 s	1120 s	1118 s	1121 s	1122 s	PcSi
1076 s	1072 s	1073 s	1078 s	1077 s	1077 s	1076 s	1078 s	1081 s	PcSi
909 m	908 m	908 m	910 m	910 m	909 m	909 m	909 m	911 m	PcSi
					871 m	867 m	872 m		OPh
839 vw	835 vw	836 vw			830 vw	830 w	834 m		
793 m	791 m	791 m	793 vw	798 vw	797 vw	794 vw	796 vw		SiO or SiF and PcSi
777 m	777 m	777 m	782 w	782 w	780 vw	781 vw	779 vw	784 vw	PcSi
						767 m			
759 m	757 m	757 m	758 m	758 m	758 m	757 m	757 m	759 m	PcSi
			737 s						
728 s	728 s	727 s	731 s	730 s	735 s	733 s	737 s	729 s	PcSi
					697 m	702 m			OPh
		685 m		664 m				696 w	
643 w	643 w	642 w	642 vw	645 vw	642 w	645 w	642 vw	646 w	PcSi

chloroform or carbon tetrachloride while trimethylsilyl sulfate was used for those taken in concentrated sulfuric acid. The results of this work are presented in Table I.

Visible Spectra.—The spectra of cyclohexane solutions of PcSi(CH$_3$)(OSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$) and PcSi(OH)(OSi(CH$_3$)(OSi(CH$_3$)$_3$)$_2$) over a 3000–7500-A range were taken with the aid of a Cary 14 spectrophotometer equipped with matched 1.0-cm cells. The spectra are (maxima (A), $\epsilon \times 10^{-4}$): PcSi(CH$_3$)(OSi(CH$_3$)-(OSi(CH$_3$)$_3$)$_2$): 6727, 44.5; 6425, 3.9; 6155, 2.6 (shoulder); 6072, 4.5; 3529, 3.8; 3423, 4.3; 3290, 4.4; PcSi(OH)(OSi(CH$_3$)-(OSi(CH$_3$)$_3$)$_2$): 6655, 36.2; 6365, 3.7; 6100, 2.4 (shoulder); 6006, 4.1; 3535, 5.7; 3425, 5.5; 3300, 4.3.[5]
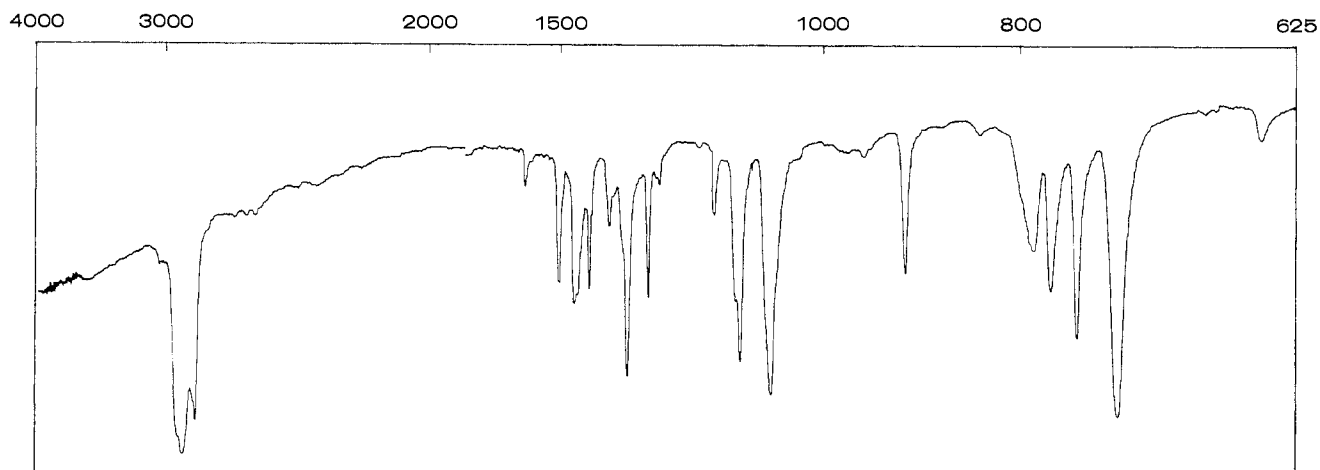
Dta Studies.—An R. L. Stone dta apparatus was used for dta studies on some of the compounds. These studies were carried out over a 30–500° range, with a 10°/min heating rate. Nitrogen was used as an atmosphere and powdered quartz as a reference. The results obtained (exotherms unless noted) are: PcSi(CH$_3$)F, 374°; α-PcSi(CH$_3$)Cl, 373°; PcSi(CH$_3$)OH, 306 (endotherm), 313, 378°; α-PcSi(CH$_3$)OC$_6$H$_5$, 230, 288 (endo-

therm), 295, 306, 377°; β-PcSi(CH$_3$)OC$_6$H$_5$, 317 (endotherm), 324, 372°.[5]

Infrared Spectra.—Infrared spectra of a number of the compounds are given in Table II. These spectra were obtained from mineral oil mulls with the aid of Beckman IR 8 and IR 5A CsBr infrared spectrophotometers. Polystyrene and 1,2,4-trichlorobenzene were used for calibration. Figure 1 shows a typical spectrum.[5]

X-Ray Powder Patterns.—Powder patterns of the simple methylsilicon phthalocyanines were obtained from samples in 0.3-mm glass capillaries with a 114.6-mm diameter Debye–Scherrer camera and vanadium-filtered Cr Kα radiation. The calculated d spacings and visually estimated intensities for the compounds, with the exception of PcSi(CH$_3$)OC$_6$H$_4$Cl-p, which gave only a diffuse pattern, are: PcSi(CH$_3$)F: 12.5 vs, 6.68 s, 6.22 w, 5.98 w, 5.36 m, 3.55 m, 3.44 s, 3.17 vw, 3.05 vw; PcSi-(CH$_3$)OH: 12.5 vs, 6.72 s, 6.24 w, 5.88 w, 5.33 m, 3.54 m, 3.44 s, 3.16 vw, 3.04 vw, 2.92 vw; PcSi(CH$_3$)OD: 12.5 vs, 6.72 s, 6.26 w, 5.88 w, 5.34 m, 3.55 m, 3.45 s, 3.13 vw, 3.04 vw, 2.93 vw; α-PcSi(CH$_3$)Cl: 12.4 vs, 6.81 m, 5.94 w, 5.22 m, 5.00 m, 4.10 vw, 3.86 s, 3.53 w, 3.40 w, 3.08 m; β-PcSi(CH$_3$)Cl: 10.5 s, 9.70 s; 8.46 w, 7.12 m, 6.34 s, 5.48 vs, 5.03 vw, 4.70 m, 4.54 m,

Figure 1.—Infrared spectrum of PcSi(CH₃)OH.

3.64 w, 3.36 w, 3.15 s; α-PcSi(CH₃)OC₆H₅: 17.0 w, 12.4 vs, 8.22 s, 7.16 m, 6.80 w, 6.21 w, 5.85 m, 5.61 vw, 5.37 s, 5.08 m, 4.57 w, 4.15 vw, 4.05 vw, 3.76 s, 3.51 w, 3.44 m, 3.17 vw, 3.05 vw, 2.92 vw, 2.71 vw, 2.54 vvw, 2.28 vvw, 2.09 vvw; β-PcSi-(CH₃)OC₆H₅: 11.7 m, 9.08 m, 8.44 vs, 7.52 vw, 7.13 s, 6.57 m, 5.54 s, 5.37 s, 5.14 w, 4.96 vw, 4.50 w, 4.23 vw, 4.01 w, 3.69 w, 3.23 s.

Discussion

Nmr Spectra and Structural Considerations.— Previous work has shown that protons on the periphery of a porphyrin[6] or a phthalocyanine[7] ring are subject to deshielding. This effect has been interpreted in terms of ring currents associated with the large conjugated rings existing in these molecules.

On the basis of this work it is reasonable to assign the lowest field multiplet observed in all the spectra, Table I, to the 3 and 6 macrocyclic ring protons in each case, and the other low-field multiplet to the 4 and 5 ring protons, Figure 2. Integrated intensity data are in accord with these assignments. The relative low-field shifts of the multiplet in the sulfuric acid spectra of PcSi(CH₃)F and PcSi(CH₃)OH are attributable to the nature of the solvent. Of particular interest is the high-field shift of the 3–6 multiplet in O(PcSiOSi(OSi(CH₃)₃)₃)₂, a compound in which two phthalocyanine rings are oxygen-bridged to each other. It seems probable that this shift is the result of shielding of the 3 and 6 protons belonging to one macrocycle by the benzene ring currents associated with the other macrocycle, Figure 3. Since the two multiplets have the same general outline as in the single macrocycle compounds, it is apparent that both the 3 and 6 protons experience equal shielding. In view of the fact that it is probably not possible to have a staggered arrangement of the two macrocycles in which the 3 and 6 protons are shielded equally and sufficiently to account for the experimental results, it appears that the macrocycles rotate with relative freedom about the Si–O–Si backbone. The unshifted position of the 4–5 multiplet shows a lack of either shielding or de-
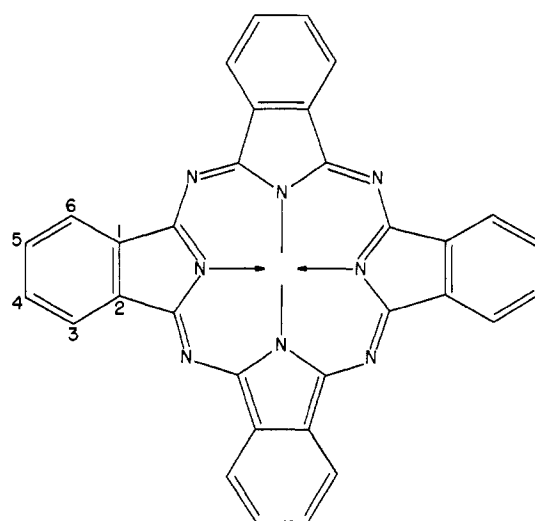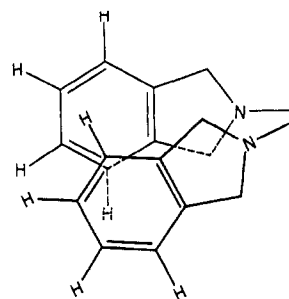

Figure 2.—The phthalocyanine ligand and the numbering system for its peripheral hydrogen atoms.

Figure 3.—Top view of the staggered arrangement of the two macrocycles in O(PcSiOSi(OSi(CH₃)₃)₃)₂ postulated to account for the observed shielding of the 3 and 6 protons.

shielding of the 4 and 5 protons of one ring by the anisotropic magnetic field associated with the other ring. Apparently the peripheral ring current effects fall off rapidly in the required direction.

Since large downfield shifts are observed for the peripheral protons of the phthalocyanine ring, it is reasonable to expect large upfield shifts for protons above and below the plane of the ring, although no phthalocyanines having such protons appear to have

(6) G. L. Closs, J. J. Katz, F. C. Pennington, M. R. Thomas, and H. H. Strain, *J. Am. Chem. Soc.*, **85**, 3809 (1963), and references therein.

(7) J. A. Elvidge, A. B. P. Lever, and M. P. Sammes, as quoted by A. B. P. Lever, *Advan. Inorg. Chem. Radiochem.*, **7**, 82 (1965).

been studied before. This is, in fact, just what is observed, Table I.

For the methyl protons attached to the inner and outer siloxy side chain silicon atoms, both integrated intensity data and the internal consistency of the values given in Table I support the assignments made. Appearance of the inner methyl protons at higher fields is attributable to their greater proximity to the macrocycle and the large ring current associated with its inner aromatic system.[8] Inspection of the data shows that the methyl protons of the two-ring compound appear at an especially high field. This shift can be assigned to a summation of the shielding effects of the ring currents associated with each of the two parallel macrocycles. Evidently the effects of these ring currents attenuate only slowly along the axis perpendicular to the rings.

The data in Table I indicate that the shielding experienced by the protons of the methyl group attached to the central silicon atom is exceptionally large, assuming, as is reasonable, that comparable un-shielded protons would give a line at about τ 10. This large shielding is easily understandable in terms of the proximity of the group to the center of the macrocycle, Figure 4.

The assignment of lines at τ 11.85–12.60 to the protons of the OCH_3 and $OCH_2C(CH_3)_3$ side chains in $PcSi(OCH_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$ and $PcSi(OCH_2C(CH_3)_3)(OSi(CH_3)(OSi(CH_3)_3)_2)$ is consistent with the other assignments and with intensities. Appearance of the lines for the methylene protons at higher field than that for the methyl protons in the $OCH_2C(CH_3)_3$ side chain (the reverse of the order of appearance of the lines in the parent alcohol) can again be attributed to the anisotropy of the magnetic field near the ring.

In view of the nmr results already obtained it would be of interest to get nmr data for $PcSi(C_6H_5)Cl$ or a related phenylsilicon phthalocyanine. So far, a compound of this type having suitable solubility characteristics has not been prepared.

On the basis of the nmr results obtained, it is clear that the magnetic field surrounding the *trans* groups of a tetravalent metal phthalocyanine is quite inhomogeneous and that the inhomogeneity extends to a considerable distance from the ring. All this suggests that certain groups which give complex patterns of lines might be investigated fruitfully by the nuclear magnetic resonance technique when bonded to the central metal atom of a phthalocyanine. Under favorable circumstances considerable simplification of the spectra could result.

As a whole the nmr data strongly support the structures assumed for the compounds reported in this paper. Of particular structural interest among these compounds are the methylsilicon phthalocyanines, for in these compounds an approximate calculation indicates that the alkyl group fits very snugly against the
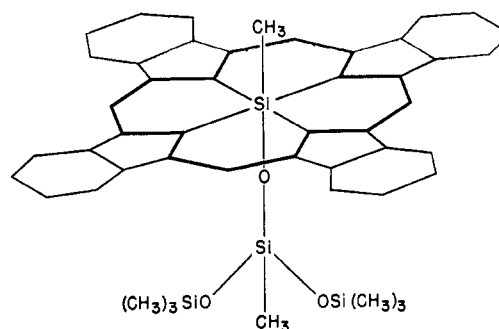

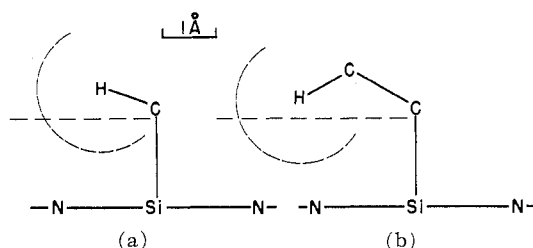Figure 4.—A perspective view of the structure of $PcSi(CH_3)-(OSi(CH_3)(OSi(CH_3)_3)_2)$.

Figure 5.—The estimated spatial relationships between (a) the methyl group and the ring and (b) the phenyl group and the ring.

macrocycle. Thus assuming, for the sake of the calculation, ordinary bond lengths, *i.e.*, Si–C and C–H as 1.90 and 1.10 A,[9] and reasonable bond angles, *i.e.*, N–Si–C and Si–C–H as 90 and 109°, respectively, the calculated distance between the plane of the ring nuclei and the methyl protons is 2.26 A. This value is appreciably less than 2.9 A, the sum of the van der Waals radius of hydrogen, 1.2 A, and half the van der Waals thickness of the phthalocyanine ring, 1.7 A,[10,11] Figure 5. Even if a somewhat longer Si–C bond length is used, because of the octahedral coordination of the silicon atom, the calculated distance is still less than the sum of the van der Waals radii.

A similar calculation for $PcSi(C_6H_5)Cl$ yields a value of 2.05 A for the distance between the *ortho* hydrogen atoms of the *trans*-phenyl group and the plane of the ring. Apparently these *ortho* hydrogen atoms are actually embedded in the π cloud of the macrocycle. In view of the required proximity of nonbonded nuclei to each other in both the methyl and phenyl compounds, it can be anticipated that detailed structural work will reveal relatively long Si–C bond lengths and somewhat distorted H–C–Si and H–C–C bond angles in these compounds.

Also of structural interest is the two-macrocycle compound. Previous evidence for the oxygen bridging of the silicon atoms of phthalocyanine rings was derived, somewhat indirectly, from chemical, infrared, and X-ray powder data.[12,13] The properties of this compound provide ample verification for the postulation of this type of bridging.

(8) The aromatic system of the analogous compound, porphin, has been discussed recently: L. E. Webb and E. B. Fleischer, *J. Am. Chem. Soc.*, **87**, 667 (1965).

(9) L. E. Sutton, "Interatomic Distances," The Chemical Society, London, 1958, pp S13–19.

(10) J. M. Robertson and I. Woodward, *J. Chem. Soc.*, 36 (1940).

(11) J. M. Robertson and I. Woodward, *ibid.*, 219 (1937).

(12) W. J. Kroenke, L. E. Sutton, R. D. Joyner, and M. E. Kenney, *Inorg. Chem.*, **2**, 1064 (1963).

(13) R. D. Joyner and M. E. Kenney, *ibid.*, **1**, 717 (1962).

Photolytic and Other Data Pertaining to the Octahedral Silicon–Methyl Bond.

—It seems reasonable to conclude that, when exposed to red light, $PcSi(CH_3)$-$(OSi(CH_3)(OSi(CH_3)_3)_2)$ is not merely activated but, rather, is actually photolyzed and that the photolytic process involves just one proton. If so, an upper limit of about 45 kcal/mole can be set for the silicon–methyl bond dissociation energy, a relatively low limit.[14] Further, it becomes likely that the reaction proceeds by a free-radical mechanism. Initial absorption of energy by the molecule is, of course, attributable to the macrocycle.

Quite consistent with the results of the photolytic experiments are the results of the dta work. As already noted, all of the methylsilicon phthalocyanines show pronounced exotherms in the 370–380° range. (The peaks corresponding to these exotherms for $PcSi(CH_3)Cl$, $PcSi(CH_3)OH$, and α- and β-$PcSi$-$(CH_3)OC_6H_5$ are all broad and quite similar in shape, while that for $PcSi(CH_3)F$ is much sharper.) In contrast $PcSiCl_2$ shows no peaks over the whole range studied; accordingly, it appears that the ~375° exotherm results from the scission of the silicon–methyl bond. (Among the remaining dta peaks the exotherm at 230° in α-$PcSi(CH_3)OC_6H_5$ can be assigned to the α to β transition, and the endotherms at 306, 288, and 317 in the hydroxide and phenoxides to condensation reactions accompanied by the loss of water or phenol.)

Contrasting with the ease with which the silicon–methyl bond is pyrolyzed and photolyzed is its resistance to chemical attack. For example, a solution of $PcSi(CH_3)OH$ in concentrated sulfuric acid is stable for more than 8 months, according to nmr measurements.

While all these data are consistent with a fairly low bond energy for the silicon–methyl bond accompanied by very complete shielding of it from chemical attack, the question as to why the bond energy is low remains unanswered. Perhaps a partial answer lies in the nature of silicon itself. Silicon in organosilicon compounds is known to have little tendency to act as an acceptor in the formation of stable complexes. If this is due, as seems probable, to the reluctance of silicon in organosilicon compounds to accept additional negative charge, then a reduction in the silicon–carbon bond strength can be anticipated when silicon is forced to coordinate.[15]

Infrared Spectra of the Methyl- and Phenylsilicon Phthalocyanines.

—The spectra of this series of compounds show, as expected, the absorptions characteristic of silicon phthalocyanines, e.g., absorptions at about

3050 w, 1615 w, 1595 w, 1520 m, 1430 m, 1335 s, 1290 m, 1165 m, 1120 s, 1075 s, 910 m, 760 m, and 730 s cm^{-1}, in the NaCl region, and 645 m, 575 m, and 530 s cm^{-1}, in the CsBr region. Not surprisingly, the positions of these absorptions in the NaCl region, Table II, and in the CsBr region show little variation for those compounds which X-ray powder data indicate to be isostructural, e.g., $PcSi(CH_3)F$, $PcSi(CH_3)OH$, and $PcSi$-$(CH_3)OD$. However, the positions of these absorptions are relatively constant, not just for these compounds, but for the whole series. This constancy suggests that the macrocycle is little influenced structurally by changes in the shape and size of the *trans* groups. This is in spite of the fact that the measurements pertain to crystalline samples where differences in packing could lead to extensive deformations of the ring.

Of some special interest among the spectral data are the data on the α and β forms of the phenoxide. Although the spectra of these two polymorphs are quite similar, certain differences stand out. The α form has a weak absorption at 1591 cm^{-1}, while the β form has a medium band at the same frequency; the α form has a band at 1269 cm^{-1}, while the comparable band in the β form is at 1258 cm^{-1}; the α form has no band to match the 767-cm^{-1} band of the β form; and the α form has a band at 697 cm^{-1}, while the β form has a considerably less intense band at 702 cm^{-1}. The bands associated with these differences all may be associated in part or completely with the *trans* groups—the 1600- and 700-cm^{-1} bands with vibrations of the phenyl group and the 1300-cm^{-1} band with methyl group. All this leads to the conclusion that the environment of the phenoxy group in the two polymorphs is different and suggests that the two polymorphs contain molecules of different configuration and not merely molecules of the same configuration packed differently.

The spectral data on the p-chlorophenoxy derivative are also of structural interest. The spectra of samples of this compound, which have been heated to a maximum of 150° and allowed to stand for varying periods of time, show readily apparent differences. In particular, the pair of bands at 1270 and 1250 cm^{-1} and the band at 834 cm^{-1} are found to be subject to marked variation in shape and intensity, and as already noted, the lines in the powder pattern of the compound are diffuse even though it appears crystalline. Using the same line of reasoning as above, these data suggest that the p-chlorophenoxy group in this compound is quite easily shifted and that the molecule has no strongly preferred configuration.

(14) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press Ltd., Oxford, 1962, p 148.

(15) This line of reasoning is similar to that used by West in his discussion of the first recognized octahedral organosilicon compounds, the methyl and phenyl acetylacetonates: R. West, *J. Am. Chem. Soc.*, **80**, 3246 (1958).