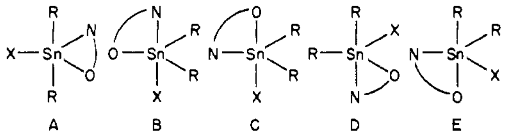

Figure 2.—Possible configurations for $R_2SnX(Ox)$.

2 are 8.2, 9.5, 4.8, 6, and 8.5 D for X = NCS and 7.2, 7.9, 4.2, 5.1, and 7 D for X = Cl. The experimental values of 6.20 and 4.79 D are indicative of a configuration similar to D in benzene solution.

Absorption at 2065 cm^{-1} by $(C_4H_9)_2Sn(NCS)(Ox)$ in a KBr disk compared to 2035 cm^{-1} in benzene solution strongly suggests –NCS– bridging in the solid (probable dimer formation) resulting in 6-coordination for tin. The quadrupole splitting, 3.25 mm/sec, suggests a *trans* arrangement for the butyl groups. The molecular weight obtained for this compound in benzene solution is 454, compared to 435 for the monomer, indicating that these bridges are broken in solution; the lack of a shoulder on the high-frequency side of the 2035 cm^{-1} absorption indicates a negligible percentage of dimers in solution. Dimerization rather than polymerization in the solid is indicated by the greater solubility and lower melting point than observed for $(C_4H_9)_2Sn(NCS)_2$. The dipole moment of $(C_4H_9)_2Sn(NCS)(Ox)$, 7.8 D, suggests a configuration similar to E (A is ruled out because of the required 120° NSnO angle) in benzene solution.

The N→Sn dative bonding in $R_2Sn(Ox)_2$ is expected to be similar to that in $R_2Sn(NCS)_2$(*o*-phen) and $R_2Sn(NCS)_2$(dipy). The more negative isomer shifts obtained for compound **10** than for **4** and **6** and for compound **11** than for **3** and **5** (Table II) indicate that the Sn–O bond is more polar than the Sn–NCS bond. The small quadrupole splittings obtained for the $R_2Sn(Ox)_2$ compounds indicate that the phenyl and butyl groups are not in *trans* positions, in line with the 111° CSnC bond angle found by Schlemper[21] in $(CH_3)_2Sn(Ox)_2$. The electric moments obtained for $(C_4H_9)_2Sn(Ox)_2$ and $(C_6H_5)_2Sn(Ox)_2$ indicate a *cis* arrangement of phenyl and butyl groups in these compounds in solution.

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A Study of Some Germanium Porphins and Some Silicon and Germanium Phthalocyanines[1]

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The nuclear magnetic resonance spectra of two unsymmetrically substituted silicon phthalocyanines have been studied. The results indicate that the shielding furnished by the ring drops off without major reversals in the region above its surface and near its fourfold axis. In addition, the spectra of two germanium porphins and two analogous germanium phthalocyanines have been compared. The results from this work show that the porphin ring offers more shielding than the phthalocyanine ring. An attempt to interpret this in terms of aromaticity is made.

In a number of recent papers describing nmr work on porphyrins and porphyrin-like compounds, the shielding region above the ring surface has figured prominently. This is true, for example, of the work done by Abraham and coworkers[2] on the π–π association of coproporphyrin I, II, III, and IV tetramethyl esters and the work done by Katz and colleagues[3] on the coordination association of chlorophylls and chlorophyll-like substances. It is also true of the work of Storm and Corwin[4] on the pyridine and methanol complexes of magnesium etioporphyrin II and magnesium *meso*-tetraphenylporphin and the work of Caughey and Iber[5] on N-methyletioporphyrin II and N-ethyletioporphyrin II. The shielded region has also figured prominently in the alkyl-, aryl-, and acylcobalt(III) etioporphyrin I work of Johnson and coworkers,[6] the methylcobalt(III) phthalocyanine work of Day, Hill, and Price,[7] and the siloxysilicon, -germanium, and -tin phthalocyanine work of this laboratory.[8]

Because of the importance of this shielded region in porphyrin-like compounds there is a need for a more detailed understanding of the region for various typical ring systems. The present paper deals with two aspects of this need, one part of it being concerned with the way in which the shielding falls off with distance from

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[1] Based on a part of the Ph.D. thesis of A. R. Kane. This work was supported in part by the National Science Foundation under Grant GP-1702. Additional support was provided by a NASA fellowship to A. R. K.

[2] R. J. Abraham, P. A. Burbidge, A. H. Jackson, and D. M. Macdonald, *J. Chem. Soc., B*, 620, (1966).

[3] J. J. Katz, H. H. Strain, D. L. Leussing, and R. C. Dougherty, *J. Am. Chem. Soc.*, **90**, 784 (1968).

[4] C. B. Storm and A. H. Corwin, *J. Org. Chem.*, **29**, 3700 (1964).

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

[6] D. A. Clarke, D. Dolphin, R. Grigg, A. W. Johnson, and H. A. Pinnack, *J. Chem. Soc., C*, 881 (1968).

[7] P. Day, H. O. A. Hill, and M. G. Price, *ibid.*, *A*, 90 (1968).

[8] L. E. Sutton and M. E. Kenney, *Inorg. Chem.*, **6**, 1869 (1967).

the ring center in the case of the phthalocyanine ring and another part of it with a comparison of the relative shielding abilities of the porphin and phthalocyanine rings.

For the work on the shielding drop off, data obtained from two siloxysilicon phthalocyanines have been used, while for the work on the relative shielding abilities of the porphin and phthalocyanine rings, data on analogous siloxygermanium phthalocyanines and siloxygermanium porphins have been used. Fortunately the necessary data for one of the phthalocyanines had already been collected in an earlier study.[9]

Presumably siloxysilicon or siloxytin analogs could have been used for the relative shielding work; however, the silicon compounds probably would have presented more synthetic difficulties than the germanium compounds and the tin compounds probably would have afforded less stability. In any event, the pairs of germanium compounds which were used to obtain the data do offer a desirable set of properties. They are exactly analogous except for the rings themselves and have probe protons which are in suitable positions and which are uninfluenced by inductive and resonance effects from the rings. The compounds also are stable, soluble in suitable solvents, and unaggregated in these solvents.

A useful by-product of this study has been the working out of a set of infrared assignments for some simple germanium porphins.

Experimental Section

The preparations of the germanium porphins described in what follows were modeled on the preparations used for the analogous germanium phthalocyanines and hemiporphyrazines.[9,10]

$PGeCl_2$.[11]—A mixture of metal-free porphin[12] (107 mg), germanium tetrachloride (0.20 ml), and quinoline (2.5 ml) was heated with stirring in a 230° oil bath for 1 hr, cooled, and centrifuged. After being washed and dried, the resultant (80 mg) was recrystallized from 1-chloronaphthalene. The product consisted of small violet-reflecting, red-brown-transmitting crystals.

$PGe(OH)_2$.—A suspension of recrystallized dichlorogermanium porphin (45 mg) and 6 *N* NaOH (2.5 ml) was refluxed for 1.8 hr, cooled, and centrifuged. The product was washed with distilled water until the washings were neutral. Initially the washings were colorless but became pink as the residual sodium hydroxide was removed. The product, after vacuum drying at 110° (29 mg), consisted of particles that reflected violet light and transmitted red light.

Vigorous conditions, such as those described, were found to be necessary for the hydrolysis of the dichloride. Thus, for example, the product recovered from the intensely red solution formed by refluxing the dichloride (25 mg) with a pyridine–water solution (1:1, 2.0 ml) for 1.3 hr was the dichloride.

$PGe(OD)_2$.—A suspension of the dichloride (25 mg) and 6 *N* NaOD in D_2O (2.0 ml) was refluxed for 4 hr, cooled, and centrifuged. The product after being washed with D_2O and vacuum dried at 100° (15 mg) was found to be violet reflecting and red transmitting. Infrared spectra indicated that it had a substantial OH content.

$PGe(OSi(C_2H_5)_3)_2$.—A mixture of dihydroxygermanium porphin (5.0 mg), triethylsilanol (0.25 ml), and chlorobenzene (1.0 ml) was refluxed for 5 min and evaporated to dryness on a steam bath. The red-transmitting product was purified by vacuum sublimation at 150° (4.5 mg).

$PGe[OSi(CH_3)(OSi(CH_3)_3)_2]_2$.—To obtain the 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ol used as an intermediate in this synthesis, the corresponding silane was hydrolyzed by the procedure of Barnes and Daughenbaugh.[13] Over a 10-min period 54 ml of 1,1,1,3,5,5,5-heptamethyltrisiloxane was added to a stirred mixture of 210 ml of dioxane, 0.50 g of neutralized 5% palladium on carbon, and 18 ml of a solution containing 0.65 g of $NaH_2PO_4 \cdot H_2O$ and 4.0 g of NaOH per liter. After 3 hr of additional stirring, the mixture was filtered and the resultant silanol was isolated by vacuum distillation. Portions of this were allowed to react with dihydroxygermanium porphin under conditions similar to those used for the synthesis of bis(triethylsiloxy)-germanium porphin. All of the products thus obtained contained difficult to remove by-products. Purification of a combined sample of these products was achieved by column chromatography on a 3:1 Celite 545–Sea Sorb 43[14] column with petroleum ether–benzene elution. The red-transmitting resultant after recovery and vacuum sublimation at 120° was nearly free of nmr-detectable contaminants, the only foreign peak in its nmr spectrum being a small one at τ 10.57.

$PcGe[OSi(CH_3)(OSi(CH_3)_3)_2]_2$.—A mixture of dihydroxygermanium phthalocyanine (1.2 g), 1,1,1,3,5,5,5-heptamethyltrisiloxan-3-ol (1.0 ml), and chlorobenzene (50 ml) was refluxed for 1.8 hr, cooled, filtered, and evaporated to dryness on a steam bath (1.8 g). The product was recrystallized three times from methylcyclohexane–toluene solutions (7:5), chromatographed on Woelm alumina (activity III), and recrystallized once again. The resulting crystals were red reflecting and blue transmitting and melted at 282°. *Anal.* Calcd for $C_{46}H_{58}N_8GeSi_6O_6$: C, 52.12; H, 5.52. Found: C, 52.11; H, 5.63.

$PcSi(CH_3)(OSi(C_2H_5)_3)$.—To prepare this compound a slurry of $PcSi(CH_3)(Cl)$[15] (0.48 g), triethylsilanol (0.50 ml), chlorobenzene (150 ml), and pyridine (25 ml) was refluxed for 20 min, filtered, and evaporated to dryness on a steam bath (0.58 g). The product was chromatographed on Woelm alumina (activity III) with petroleum ether–benzene elution and recrystallized from a toluene–cyclohexane solution (2:1). The resultant red-reflecting, green-transmitting crystals were crushed and vacuum dried at 110° to free them of cyclohexane. *Anal.* Calcd for $C_{39}H_{34}N_8Si_2O$: C, 68.19; H, 4.99; Si, 8.18. Found: C, 68.30; H, 5.11; Si, 8.33.

$PcSi(C_2H_5)(OSi(C_2H_5)_3)$.—The $PcSi(C_2H_5)(Cl)$ used as an intermediate in this synthesis was prepared in a manner similar to that used for the analogous methyl compound.[15] A mixture of 1,3-diiminoisoindoline (10 g), ethyltrichlorosilane (15 ml), and quinoline (250 ml) was heated at 165–175° by means of an oil bath for 10 hr, filtered, cooled, and refiltered (2.13 g). A mixture of a portion of the resultant $PcSi(C_2H_5)(Cl)$ (0.44 g), triethylsilanol (0.50 ml), chlorobenzene (175 ml), and pyridine (25 ml) then was refluxed for 20 min, filtered, and evaporated to dryness. The product was chromatographed on Woelm alumina (activity II) using petroleum ether and benzene as eluents and was then recrystallized from a toluene–cyclohexane solution. The red-reflecting, green-transmitting crystals thus obtained were crushed and vacuum dried at 115° to free them of cyclohexane.

Analytical values in satisfactory agreement with theory were not obtained for the compound. This was attributed, in part, to the relatively low stability of the compound (over a protracted period parts of a sample underwent complete decomposition, turning yellow).

Nmr Spectra.—Varian A-60A and HA-100 spectrometers operating at approximately 38 and 30°, respectively, were used

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

[10] R. D. Joyner, R. G. Linck, J. N. Esposito, and M. E. Kenney, *J. Inorg. Nucl. Chem.*, **24**, 299 (1962).

[11] P is used for the porphin ligand, $C_{20}H_{12}N_4$, Pc is used for the phthalocyanine ligand, $C_{32}H_{16}N_8$, and hp is used for the hemiporphyrazine ligand, $C_{26}H_{14}N_8$.

[12] Mad River Chemical Co., Antioch, Ohio.

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

[14] Fisher Scientific Co., Pittsburgh, Pa.

[15] J. N. Esposito, J. E. Lloyd, M. E. Kenney, *Inorg. Chem.*, **5**, 1979 (1966).

to obtain the nmr spectra. Carbon tetrachloride was used as a solvent, except for metal-free porphin in which case deuteriochloroform was used. Tetramethylsilane was used as an internal standard.

Infrared Spectra.—Infrared spectra were obtained from mineral oil mulls with a Beckman IR-12 infrared spectrophotometer. Polystyrene, 1,2,4-trichlorobenzene, and water vapor were used for calibration.

Mass Spectra.—Because of the limited amount of metal-free porphin available for this work, mass spectroscopy was resorted to for verification of the compositions of the porphins. Varian M66-type instruments equipped with heated sample probes and operating at 70 eV were used. PFA was used for calibration.

For all five porphins, singly charged parent ions and both singly and doubly charged parent minus two side group ions, $(P - 2Cl)^+$, $(P - 2Cl)^{2+}$, etc., were observed. Each of these ions yielded as expected a complex pattern of peaks (natural germanium has five abundant isotopes). In Table I the calculated and observed masses for the parent ions are given.

Table I

Mass Spectra

	m/e	
	Obsd	Calcd
$PGeCl_2$	452	452
$PGe(OH)_2$	417	416
$PGe(OD)_2$	419	418
$PGe(OSi(C_2H_5)_3)_2$	644	644
$PGe[OSi(CH_3)(OSi(CH_3)_3)_2]_2$	857	856

Discussion

Nmr Studies.—Convincing evidence that the shielding provided by the phthalocyanine ring drops off without major reversals in the region above the surface of the ring and near its fourfold axis is provided by the nmr data on $PcSi(C_2H_5)(OSi(C_2H_5)_3)$, Table II and Figure 1. Further support for this conclusion is found in the other data listed in Table II, the data in Table III, and the data in earlier papers on various siloxy phthalocyanines.[8,9,15]

Table II

Nmr Spectra[a,b]

	Ligand		Siloxy ethyl			Central alkyl		
	3,6	4,5	CH_3	CH_2	*J*	CH_3	CH_2	*J*
$PcSi(CH_3)(OSi(C_2H_5)_3)$[c]	0.38	1.74	11.24	12.52	7.7	16.38		
$PcSi(C_2H_5)(OSi(C_2H_5)_3)$[c]	0.32	1.66	11.25	12.54	7.6	13.77	16.27	7.5
$PcSi(OSi(C_2H_5)_3)_2$[d]	0.32	1.65	11.25	12.48	7.6			

[a] Positions, τ. [b] Coupling constants, Hz. [c] A-60A spectra. [d] Reference 8.

It seems probable that a similar relatively steady drop-off in shielding near the fourfold axis occurs also for the porphyrins. Certainly the data of Caughey and Iber[5] on N-ethyletioporphyrin II and the data of Storm and Corwin[4] on the pyridine complexes of magnesium etioporphyrin II and magnesium *meso*-tetraphenylporphin are in accord with this conclusion. It is true that the data of Johnson and coworkers[6] on alkylcobalt(III) etioporphyrin I compounds have been viewed differently but interpretation of these data has been rendered complicated by the apparently poor resolution of the spectra obtained.

In Table III the data on the siloxygermanium porphins and phthalocyanines which are pertinent to the comparative shielding abilities of the porphin and phthalocyanine rings are summarized. The data for $PcGe(OSi(C_2H_5)_3)_2$ are from the work of Sutton and Esposito.[9] The spectrum of one of the porphins, $PGe(OSi(C_2H_5)_3)_2$, is shown in Figure 2. These data clearly show that the porphin ring offers more shielding to its siloxy group protons than does the phthalocyanine ring. That this comparison is not complicated by significant special effects introduced by the germanium is indicated by the data on a dilute solution of metal-free porphin, Table III. As is seen, the positions of the *meso* and β protons in porphin are not much different from those of the germanium porphins. (No resonances attributable to the central protons of the porphin ring were observed, presumably because of quadrupole broadening.)

The bearing of this comparison and an earlier one on the aromaticities of the two rings is of some interest. Previously on the basis of data obtained from a methylcobalt porphyrin and a methylcobalt phthalocyanine (methylcobalt(III) etioporphyrin I and the tetrasodium salt of methylcobalt(III) 4,4′,4″,4‴-tetrasulfonatophthalocyanine, respectively) it was concluded that the phthalocyanine ring offers more shielding and sustains a greater ring current.[7] However, the two compounds used as a basis for this conclusion are not fully comparable (one being a salt) and are probably associated in solution to varying but important and difficult to evaluate degrees (since one side of the ring in each compound is not protected by a group projecting from the cobalt).

Even accepting the present results, *i.e.*, that a freely rotating germanium porphin ring offers more average shielding to points near its fourfold axis than does a freely rotating germanium phthalocyanine ring, the relative aromaticities of the two rings are not immediately apparent because both macrocycles are made up of complex systems of fused rings. However, if the assumption is made that the phthalocyanine ring can be approximated roughly by an inner "porphin-type" ring and four "benzene" rings, an approach to the problem can be made based on the work of Johnson and Bovey on benzene.[16]

Placing four benzene rings in space in the positions required by the phthalocyanine ring[17] and allowing them to rotate freely about the fourfold axis, it is calculated that points moderately above the plane of the rings are shielded, Figure 3. At points 3.80 Å above the plane of the rings and 2.25 Å off the fourfold axis a shielding of 0.14 ppm is calculated. Since it is estimated that the methylene protons of $PcGe(OSi(C_2H_5)_3)_2$ occupy an analogous position relative to their benzene rings and since the methylene protons of $PcGe(OSi(C_2H_5)_3)_2$ are less shielded than those of the analogous porphin, it is concluded (using shielding as a measure of aromaticity[18]) that the "porphin-type"

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[16] C. E. Johnson, Jr., and F. A. Bovey, *J. Chem. Phys.*, **29**, 1012 (1958).

[17] L. H. Vogt, Jr., A. Zalkin, and D. H. Templeton, *Inorg. Chem.*, **6**, 1725 (1967).

[18] L. M. Jackman, F. Sondheimer, Y. Amiel, D. A. Ben-Efraim, Y. Gaoni, R. Wolovsky, and A. A. Bothner-By, *J. Am. Chem. Soc.*, **84**, 4307 (1962).

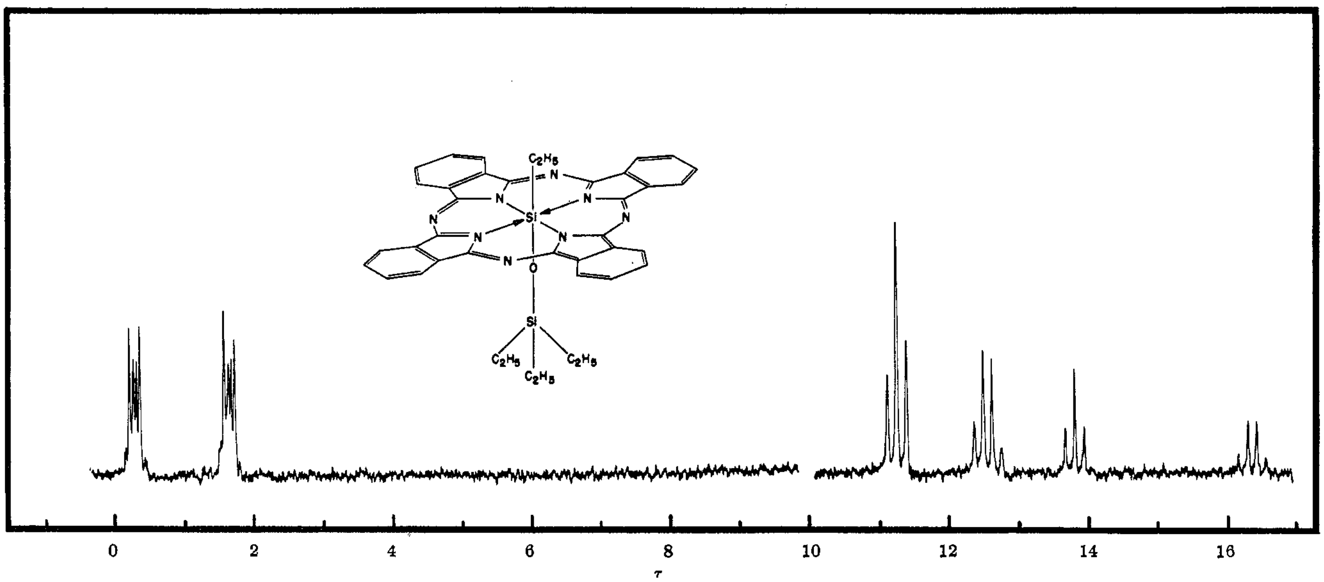

Figure 1.—The 60-MHz nmr spectrum of $PcSi(C_2H_5)(OSi(C_2H_5)_3)$.

TABLE III

NMR SPECTRA[a,b]

	Ligand				C_2H_5			$OSi(CH_3)(OSi(CH_3)_3)_2$	
	meso	β	3,6	4,5	CH_3	CH_2	J	$Si(CH_3)_3$	$Si(CH_3)_3$
$PGe(OSi(C_2H_5)_3)_2$[c]	−0.44	0.44			11.73	13.24	8.0		
$PcGe(OSi(C_2H_5)_3)_2$[d]			0.30	1.62	11.24	12.42	7.6		
$PGe[OSi(CH_3)(OSi(CH_3)_3)_2]_2$[c]	−0.48	0.41						11.47	13.88
$PcGe[OSi(CH_3)(OSi(CH_3)_3)_2]_2$[c]			0.36	1.68				11.23	12.85
$HOSi(C_2H_5)_3$[c]					9.05[e]	9.46[e]			
$HOSi(CH_3)(OSi(CH_3)_3)_2$[c]								9.97	9.89
PH_2[c]	−0.38	0.48							

[a] Positions, τ. [b] Coupling constants, J, Hz. [c] HA-100 spectra. [d] Reference 9. [e] As determined from positions of ν_A, ν_1, and ν_2.: P. T. Narasimhan and M. T. Rogers, *J. Am. Chem. Soc.*, **82,** 5983 (1960).

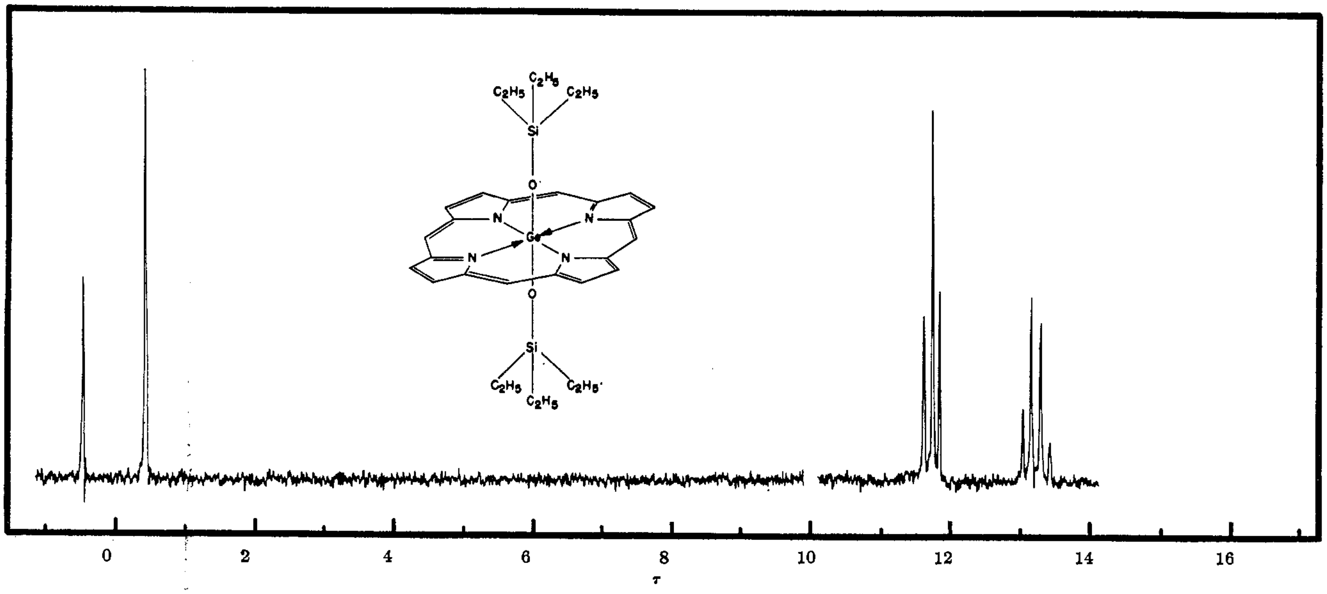

Figure 2.—The 60-MHz nmr spectrum of $PGe(OSi(C_2H_5)_3)_2$.

ring of phthalocyanine is less aromatic than the porphin ring of porphin itself. This is attributed mainly to the presence of four extra nitrogen atoms in the phthalocyanine ring which act as localizing influences.

A feature of the spectrum of $PcSi(C_2H_5)(OSi(C_2H_5)_3)$ not already mentioned is the relative position of the methylene resonance of the inner ethyl group. If the difference between the position of the methylene resonance of tetraethylsilane[19] and that in this compound, 6.93 ppm, is compared with the difference of the position of the methyl resonance of tetramethylsilane and that in $PcSi(CH_3)(OSi(C_2H_5)_3)$, 6.38 ppm, it is seen that the difference for the ethyl compounds is appreciably

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[19] T. Ostdick and P. A. McCusker, *Inorg. Chem.*, **6,** 98 (1967).

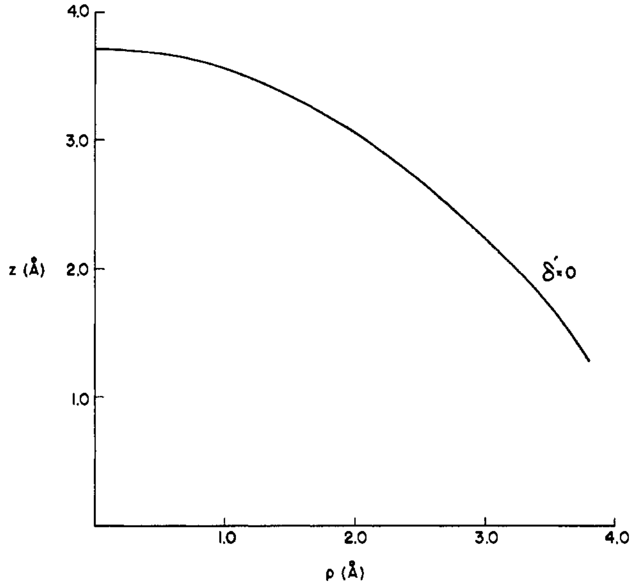

Figure 3.—The $\delta' = 0$ isoshielding line for four benzene rings placed as are the benzene rings of a phthalocyanine ring. The distance z is the height above the rings and the distance ρ the length along a perpendicular to the fourfold axis. Points above the line are shielded.

larger. This suggests that the methylene protons of the ethyl side chain are closer to the ring, probably because of steric factors associated with the bulk of the end methyl. The lower shelf stability of the ethyl compound is in accord with this interpretation, since such a structural shift could easily result in a strain on the central Si–C bond.

The spectrum of $PcSi(C_2H_5)(OSi(C_2H_5)_3)$ also illustrates the great efficiency of aromatic macrocycles such as the phthalocyanine ring in spreading out the lines associated with groups above their surfaces.[9,15] The methylene and methyl resonances of the outer ethyl groups of this compound are, as is seen, spread by 77 Hz at 60 MHz. To separate the methylene and methyl resonances of the ethyl groups of triethylsilanol (Table III) the same number of cycles would require about a 190-MHz instrument.

Infrared Studies.—In Table IV assignments are given for some of the *trans*-group vibrations of $PGe(OH)_2$, $PGe(OD)_2$, and $PGeCl_2$ and, for comparison, the corresponding set of assignments for the analogous phthalocyanines and hemiporphyrazines made by Esposito and Sutton.[9] As is seen, the three sets of assignments are all quite consistent with each other.

A significant pair of trends is apparent in the data, the Ge–Cl and Ge–O stretching vibrations substantially increasing in energy for the ligand series porphin, phthalocyanine, and hemiporphyrazine and the O–H and O–D stretching vibrations substantially decreasing for the same series. Extending suggestions made earlier,[8,9] these trends indicate that the nitrogen atoms of the porphin ring interact more strongly with the germanium atom than those of the phthalocyanine ring and still more strongly than those of the hemiporphyrazine ring. Perhaps the increase in the Ge–N interaction in the porphin ring over that in the phthalocyanine ring is associated with electronic rearrangements (which could have a variety of sources) or perhaps with a substantial shortening of the Ge–N bonds caused by the structural differences between the rings (mainly the substitution of the N bridges of the phthalocyanine ring by CH bridges).

Table IV

Infrared Spectra[a]

	P	Pc[b]	hp[b]
Ge–OH asym str	627 s	644 m	676 m
Ge–OD asym str	624 s	633 m	666 m
Ge–Cl asym str	300 s	312 s	347 s
GeO–H str	3618 m	3493 m	3403 m
GeO–D str	2665 m	2585 m	2524 m
GeO–H bend	973 m	988 m	1050 m
GeO–D bend	726 m	742 m	779 m

[a] In cm^{-1}. [b] Reference 9.

Volatility.—As stated in the Experimental Section, both of the siloxygermanium porphins sublime easily under vacuum. Apparently $PGe(OSi(CH_3)(OSi(CH_3)_3)_2$ is the more volatile of the two, presumably because it is more globular in shape.

Worth noting in connection with this volatility is the recent successful use of gas chromatography in the separation of individual porphyrins from complex mixtures.[20] In the reported work the porphyrins were converted to siloxysilicon derivatives and these were then chromatographed. Perhaps the use of siloxygermanium derivatives for this purpose would prove even better. On the basis of the present work it is clear that germanium derivatives with R_3SiO groups could be prepared easily and would be stable and volatile if the R_3SiO groups were properly chosen.

Acknowledgment.—The help of Russell Carr of Varian Associates in obtaining some of the mass spectra and of Kerro Knox and Thomas R. Janson in carrying out the four-benzene ring calculation is gratefully acknowledged. The generous gifts of chemicals from the Union Carbide Corp. and the Du Pont Corp. are also acknowledged.

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(20) D. B. Boylan and M. Calvin, *J. Am. Chem. Soc.*, **89**, 5472 (1967).