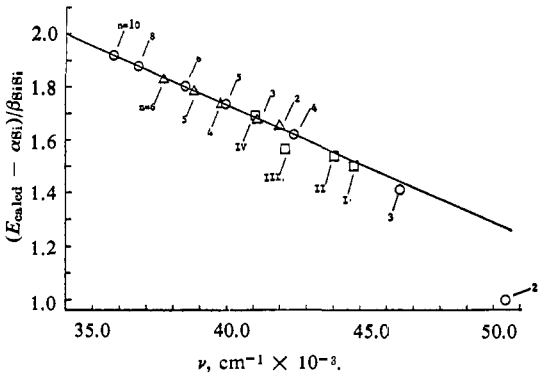

Figure 1. Plot of $(E_{calcd} - \alpha_{Si})/\beta_{SiSi}$ *vs.* ν (cm^{-1} × 10^{-3}) for the series (A) $Me(Me_2Si)_nMe$, -O-O-O-, with n = 2–6, 8, 10; (B) $(C_6H_5\text{-}(Me_2Si)_nC_6H_5$, -Δ-Δ-Δ-, with n = 2–6; (C) vinylpentamethyldisilane (I), 1,2-divinyltetramethyldisilane (II), 1-vinylheptamethyltrisilane (III), and 1,4-divinyloctamethyltetrasilane (IV), -□-□-□-.

state. Using various values for the energy of the π^* orbital relative to that of the silicon d orbital, expressed in the form $\alpha_\pi^* = \alpha_{Si} + \mu\beta_{SiSi}$, and the resonance integral between the π^* and $-Me_2Si-$ orbitals, $\beta_{Si\pi}^* = \lambda\beta_{SiSi}$, the energy of the orbital for a given compound (i) was obtained as

$$E_i = \alpha_{Si} + f_i(\lambda,\mu)\beta_{SiSi}$$

The reported[4f,5a] absorption maxima (ν_i) were plotted against the function $f_i(\lambda,\mu)$. The values of λ and μ which gave the best linear correlation (see Figure 1) are presented in Table I. Since the data for methyl-, phenyl-, and vinyl-substituted polysilanes can be fitted to the same straight line, it is implied that the lower state of the transition for each series has the same and constant energy, *i.e.*, that of the Si_σ framework.

Table I

Series	λ	μ	β_{π^*Si}, ev	$(\alpha_\pi^* - \alpha_{Si})$, ev	$(\alpha_\pi^* - E_\sigma)$, ev
$-(SiMe_2)_n-$	1	0	−2.79	0	9.79
$C_6H_5(SiMe_2)_nC_6H_5$	0.245	1.55	−0.68	−4.32	5.47
$CH_2{=}CH(SiMe_2)_n-$	0.224	1.44	−0.62	−4.02	5.77

The success of this simple treatment allows us to predict certain of the properties of polysilanes. For example, the absorption maxima of other permethylated polysilanes may be deduced: $Me(Me_2Si)_nMe$ (n, λ_{max} (mμ)) 7, 267.4; 9, 275.8; 11, 280.9; 12, 282.9; ∞, 294.

The energy of this transition also corresponds to the activation energy of electron transport along a one-dimensional chain of silicon atoms and may be used to predict the semiconductor properties of such molecules.

It is reasonable to anticipate that the simple HMO treatment may be extended to catenates of other elements which possess empty (or partially filled) d orbitals of accessible energy. However, it should be mentioned that the ultraviolet absorption maxima of branched[4d] and cyclic[4c,10] polysilanes cannot readily be correlated by the above treatment.

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Volatile Silicon Complexes of Etioporphyrin I[1]

Sir:

The presence of several homologous series of porphyrins has been demonstrated in some oil shale rocks, shale oils, and petroleums.[2] However, the application of microanalytical techniques (*i.e.*, mass spectrometry and gas chromatography[3]) to structure determination of individual porphyrin components has been limited due to their low volatility.

We wish to report the synthesis of several novel Si^{IV}–etioporphyrin I derivatives and the effects that their various additional silicon ligands have on porphyrin volatility as measured by gas chromatography at normal pressure.

The treatment of etioporphyrin I (50 mg) with silicon tetrachloride or hexachlorodisiloxane (0.5 ml)[4] and anhydrous pyridine (3.0 ml) in a sealed glass tube at 185° for 6 hr, followed by the hydrolysis of the residue in dilute (1 *N*) aqueous, ethanolic hydrochloric acid (10 ml), gave, after purification on alumina ($CHCl_3$ solvent), a 60% yield of product A. The absorption spectrum was metalloporphyrin-like with a Soret band at $\lambda_{max}^{CHCl_3}$ 405 mμ (ε 314,000) and two longer wavelength bands at $\lambda_{max}^{CHCl_3}$ 535 (ε 11,700) and 572 mμ (ε 13,800). The mass spectrum of A showed a strong molecular ion at *m/e* 538, followed by a more intense peak at *m/e* 521 corresponding to the loss of an OH ligand. Thus the structure dihydroxy-$Si^{(IV)}$-etioporphyrin I was indicated.

Silylation of A with bis(trimethylsilyl)acetamide (BSA) in pyridine gave a product B, subliming at 145° (0.05 mm).[5] Mass spectral analysis of the sublimate showed predominant ions at *m/e* 682 and 593. The fragment *m/e* 593 was the most intense peak, corresponding to loss of one ligand of 89 mass units ($OSi(CH_3)_3$). Thus B was assigned the structure bis(trimethylsiloxy)-$Si^{(IV)}$-etioporphyrin I.

(1) Work supported, in part, by the National Aeronautics and Space Administration (Grant NsG 101-61) and, in part, by the U. S. Atomic Energy Commission.

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(3) R. L. Levy, H. Gesser, E. A. Halevi, and S. Saidman, *J. Gas Chromatog.*, **2**, 254 (1964).

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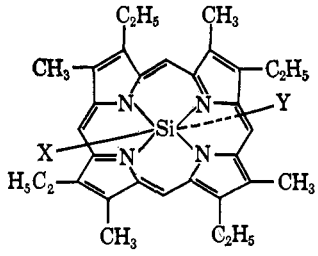
(5) Silylations were carried out by adding one part of a 50% solution of BSA (General Electric Research Laboratories, now commercially available from Applied Science Laboratories, State College, Pa.) and pyridine to three parts of a saturated benzene solution of porphyrin sample. These mixtures were heated to 60° for 15 min when prepared in quantity or simply injected directly into the gas chromatograph when gas chromatographic purification techniques were applied.

Table I. Gas Chromatographic Retention Times[a] and Predominant 70-ev Mass Spectral Ions[b] of X,Y-Si^{IV}-Etioporphyrins



Compd	X	Y	m/e M$^+$	m/e (M − (X or Y))$^+$
A	OH	Y = X	538	521
B	$OSi(CH_3)_3$	Y = X	682	593
C	OCH_2CH_3	Y = X	594	549
D	$OSi(OCH_2CH_3)_3$	OH	700	683,521
E	$OSi(OCH_2CH_3)_3$	$OSi(CH_3)_3$	772	683,593
F	$OSi(OCH_2CH_3)_3$	Y = X	862	683
G	$OSiOC(CH_3)_3(OCH_2CH_3)_2$	Y = X_H[c]	946	739,711
H	$OSi(OC(CH_3)_3)_2OCH_2CH_3$	Y = X	974	739
I	$OSi(OC(CH_3)_3)_2OH$	Y = X	918	711
J	$OSi(OC(CH_3)_3)_2OSi(CH_3)_3$	Y = X	1062	783
K	$OSi(OC(CH_3)_3)_3$	Y = X	1030	767

[a] The following gas chromatographic retention times were observed: compound B (11 min), E (14 min), F (17 min), G (21 min), H (25 min), J (>27 min), K (>27 min). [b] All mass spectra were obtained using an AEI MS-12 mass spectrometer equipped with a solid sample probe. [c] X_H = ligand X on compound H.

Compounds C, D, F, G, H, I, K (Table I) were isolated from a complex mixture of products produced when the contents of the sealed tube reaction were treated with ethyl or *t*-butyl alcohol. Trimethylsilylation of D and I gave compounds E and J, respectively. Mass spectral analysis indicated that the predominant high mass fragmentation was due to loss of one ligand. In silicon complexes where two different ligands were present, such as in compounds D, E, and G, predominant high mass fragmentation ions occurred at both mass (M − X) and (M − Y).

Preliminary gas chromatographic analysis of the silicon complex porphyrins was accomplished on an 11 ft × 0.25 in. i.d. glass column packed with 1% (OV-1) (methylsilicone phase) coated 100–120 mesh smooth glass beads. The temperature was kept isothermal at 250° and a helium carrier flow of 27 cc/min was used. Each chromatographic peak was collected and identified by mass spectrometry. Etioporphyrin I, Ni^{II}-etioporphyrin I, and diethoxy-Si^{IV}-etioporphyrin I (C) would not chromatograph under the described conditions. However, bis(trimethylsiloxy)-Si^{IV}-etioporphyrin I (B) showed a marked increase in volatility and could be chromatographed despite an increase in molecular weight of 88 mass units over the diethoxysilicon complex. The increased volatility can be attributed, at least in part, to the shielding of the aromatic porphyrin ring by the bulky trimethylsiloxy groups above and below the porphyrin plane, thus preventing the close approach and reducing the natural attraction between the planes. Consideration of the gas chromatographic retention times (Table I) indicates that additional ligand bulkiness (E to H, J, K) does not render the porphyrin nucleus more volatile than B but the volatility seems to vary directly with the molecular weight.

In the past, standard gas chromatography has had no practical use in porphyrin separations.[6] The results of our preliminary study indicate that conversion of porphyrins into volatile tetravalent silicon derivatives should provide a means by which microquantities of complex mixtures of homologous series, such as those found in ancient biogenetic deposits, can be separated and structurally studied using gas chromatography–mass spectrometry combinations. This work will also be expanded to include development of a rapid quantitative means for positive identification of porphyrins and chlorins extracted from recent biological sources.

Acknowledgment. We are grateful to Dr. G. Eglinton for useful discussions.

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Structural Analysis of Polynucleotides by Sequential Base Elimination. The Sequence of the Terminal Decanucleotide Fragment of the Ribonucleic Acid from Bacteriophage f2

Sir:

Recently we reported a method by which the terminal fragments produced by specific cleavage of ribonucleic acids could be oxidized by periodate, selectively absorbed on aminoethylcellulose, and subsequently recovered in a pure condition.[1] The application of this method to a ribonuclease T_1 digest of the ribonucleic acid from bacteriophage f2 produced a terminal fragment which was assigned the structure (3Cp,2Up,-2Ap)Cp by virtue of a preliminary base ratio analysis. In this report we show by analysis of the products formed by hydrolysis of the fragment with pancreatic ribonuclease that the composition of the oligonucleotide is, in fact, (2Cp,2Up,2ApCp)Cp. In addition, we have developed an improved method for sequence analysis of polynucleotides based on the classical periodate oxidation–β-elimination approach.[2] The application of this method to the analysis of the terminal fragment demonstrates that the terminal undecanucleotide sequence of f2 RNA is -GpUpUpApCpCpAp-CpCpCpA.

For the ribonuclease hydrolysis, the fragment (2.1 $ODU_{260m\mu}$) and the enzyme (0.05 mg) in 0.1 *M* ammonium bicarbonate buffer, pH 9 (0.2 ml), were kept at 25° for 12 hr. The products were identified by chromatography on a column (0.4 × 42 cm) of DEAE-Sephadex A25. On such a column, using ribonuclease digests of model compounds, mononucleotides were shown to be eluted separately with 0.2 *M* ammonium bicarbonate pH 9, while dinucleotides required the same buffer at 0.4 *M* concentration for separation and elution. The products obtained from the fragment were cytidine 3′-phosphate, 83 mμmoles; uridine 3′-phosphate,

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