Isolation, spectroscopic properties, and electrochemical properties of two oligomeric silicon phthalocyanines


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Isolation, Spectroscopic Properties, and Electrochemical Properties of Two Oligomeric Silicon Phthalocyanines


Received June 4, 1986

A new method for synthesizing \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\) and methods for isolating \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\) and \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\) from a mixture containing these two oligomers are described. Well-resolved NMR spectra of the three oligomers and of \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\) are presented. Electrochemical studies of the series \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\) \((n=1-4)\) show a one-electron oxidation and a one-electron reduction waves and give evidence of the delocalization of charge among the cofacial phthalocyanine rings in the dimer, trimer, and tetramer.

Shortly after the first silicon phthalocyanine had been reported, several oligomeric silicon phthalocyanines with silicon–oxygen backbones were reported. Subsequently, the polymer was found to be a good conductor when fractionally oxidized with oxidants such as iodine. This has led to considerable interest in the polymer and oligomers related to it.

In a previous paper, we reported on the synthesis of the oligomer mixture \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\) and a mixture of oligomers of this type and on the synthesis of the homologous monomer, \((n-C_6H_{13})_3SiOSi(PcO)\). We also reported on the isolation of the dimer, \((n-C_6H_{13})_3SiOSi(PcO)\), and on the electrochemical and spectroscopic properties of the monomer and dimer. In the present paper, an alternative synthesis for the dimer and new information on the electrochemical and spectroscopic properties of the monomer and dimer are given. In addition, methods for the isolation of the homologous trimer and tetramer, \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\), and \((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\), and information on the electrochemical and spectroscopic properties of these oligomers are reported.

Experimental Section

Syntheses. \((n-C_6H_{13})_3SiOSi(PcO)\). A preparation and purification of the monomer have been described previously. IR (Nujol) 1250 (Si–CH2), 1040 (Si–O–Si), 1280 (Si–PcO) cm\(^{-1}\); \(\delta\) NMR (CDCl3, 190 °C) \(\delta\) 9.65 (m, 1,4-Pc), 8.32 (m, 2,3-Pc), 7.84 (m, terminal 2,3-Pc), 7.68 (m, middle 2,3-Pc), 7.96 (middle 2,3-Pc) ppm.

\((n-C_6H_{13})_3SiOSi(PcO)Si(n-C_6H_{13})\). A suspension of \(n\)-butylsilane (1.5 mL) was added to the dried suspension, and the resulting mixture was refluxed for 4 h and then purified by chromatography (alumina, activity 111; hexanes–toluene solution, 3:1) into the dimer (376 mg, 41%).

\((n-C_6H_{13})_3SiOSi(PcO)\). A solution of \(n\)-butylsilane in hexanes–toluene solution (1:1) was refluxed for 4 h and then purified by chromatography (alumina, activity 111; hexanes–toluene solution, 3:1) into the dimer (376 mg, 41%).


1 The University of Texas.
2 Case Western Reserve University.

(8) For a recent paper, see, for example: Toscana, P. J.; Marks, T. J. J. Am. Chem. Soc. 1986, 108, 437.
(10) The positions of the middle ring protons of the trimer and tetramer can be calculated with the incremental shift procedure used earlier for analogous oligomers. These calculated positions are as follows: trimer (8.87 (middle 1,4-Pc) and 8.20 (middle 2,3-Pc)) tetramer (8.87 (middle 1,4-Pc) and 7.96 (middle 2,3-Pc)). As is seen, these calculated positions support the assignments made for the observed resonances.
Oligomeric Silicon Phthalocyanines

Results and Discussion

Synthesis. While the route to the dimer through HOSiPcOSi(\(n\)-C\(_6\)H\(_4\))\(_3\) appears to hold little or no practical advantage over that through SiPcCl\(_2\) and SiPc(OH)\(_2\),\(^{11}\) the route is interesting because the dimerization reaction involved seems to be a solid-state reaction. This is not particularly surprising since the hydroxy group of one molecule of HOSiPcOSi(\(n\)-C\(_6\)H\(_4\))\(_3\) may be positioned close to that of another (the full structure of HOSiPcOSi(\(n\)-C\(_6\)H\(_4\))\(_3\) has not been determined). Further, it is known that the reaction leading to the polymerization of GePc(OH)\(_2\) can be a solid-state reaction.\(^{12}\) The cap scrambling that occurs during the dimerization reaction is also not surprising and can be attributed to the liability of siloxane linkages at elevated temperatures. The melting of the reaction product observed at higher reaction temperatures is probably due to melting of the dimer formed.

NMR Spectra. The positions of the \(^1\)H resonances of the trimer and tetramer, like those of the monomer and dimer,\(^{13}\) clearly show the presence of large ring-current effects. This is in accordance with expectations.\(^{13}\)

From Figure 1, it is seen that the resolution of the aromatic resonances of the trimer and tetramer with benzene-\(d_6\) as a solvent is excellent. Similar excellent resolution of these resonances is found with toluene-\(d_6\). However, with chloroform-\(d\) the resolution is poor. These solvent effects probably arise in part because of strong \(\pi-\pi\) interactions between the oligomers and the aromatic solvents.

The position of the \(^29\)Si resonance of the monomer's central silicon, \(-217.7 \text{ ppm}\), is substantially above the ordinary range reported for the resonance of octahedral silicon, \(-140 \text{ to } -200 \text{ ppm}\). Interpretation of this result will have to await the development of a fuller understanding of the factors influencing \(^29\)Si resonances.\(^{14}\)

Electrochemical Data. The stability limits of 0.1 M (TBA)BF\(_4\) in CH\(_2\)Cl\(_2\) are \(+1.70 \text{ to } -2.00 \text{ V vs. Ag reference electrode (+1.85 to } -1.85 \text{ V vs. SCE)}\). Within this potential window, three reductions and three oxidations of the trimer are observed, while four reductions and four oxidations are observed for the tetramer. Typical cyclic voltammograms for the silicon phthalocyanine oligomer series are shown in Figure 2. From their general shape, all waves appear to be reversible one-electron transfers and are similar in nature to the waves found in electrochemical studies of related compounds.\(^9\) Peak potentials, averaged peak potentials (\(E^p\)), peak splittings, peak currents, and peak current ratios are shown in Table I. Reversibility of all reactions and product stability is indicated by peak splittings of about 60 mV, peak current ratios of approximately 1.0, and constant \(i_{pc}/i_{ac}\) values for potential sweep rates between 20 and 1000 mV/s. Determination of \(n_{app}\) was made by bulk electrolysis. For the trimer, electrolysis at the first cathodic wave gave an \(n_{app} = 0.96,\)

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with the previous report by Armstrong et al., on similar electrolysis to encompass both cathodic waves. Thus, in agreement in the potential of the quasi-reference electrode, causing the reinvestigate the dimer.

one-electron waves for trimer and tetramer encouraged us to the first waves of the dimer. However, the finding of multiple for the previous finding, but suspect it arose because of a drift we proposed the coulometric studies showed oxidations. The time for each of these electrolyses was 40 min.

Cyclic voltammetry of the electrolyzed so-

tetramer the $D$ value decreases as the molecular size increases, as expected. Surprisingly the monomeric species deviates from this trend and shows a smaller $D$ than the dimer. Absorbance measurements at 670 nm over a monomer concentration range

Table I. Cyclic Voltammetric Data for (n-C$_6$H$_{13}$)SiO(SiPcO)$_3$Si(n-C$_6$H$_{13}$)$_3$ ($n = 3,4$)$^a$

<table>
<thead>
<tr>
<th>wave</th>
<th>$E_{pa}$</th>
<th>$E_{pc}$</th>
<th>$\Delta E_p$</th>
<th>$t_{pa}$</th>
<th>$t_{pc}$</th>
<th>$t_{pa}/t_{pc}$</th>
<th>$E^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4th oxidn</td>
<td>+1.44</td>
<td>+1.51</td>
<td>0.08</td>
<td>6.5</td>
<td>4.9</td>
<td>0.8</td>
<td>+1.47</td>
</tr>
<tr>
<td>3rd oxidn</td>
<td>+0.96</td>
<td>+1.04</td>
<td>0.08</td>
<td>5.5</td>
<td>4.8</td>
<td>0.9</td>
<td>+1.00</td>
</tr>
<tr>
<td>1st oxidn</td>
<td>+0.56</td>
<td>+0.62</td>
<td>0.06</td>
<td>5.8</td>
<td>4.3</td>
<td>0.8</td>
<td>+0.59</td>
</tr>
<tr>
<td>1st redn</td>
<td>-1.09</td>
<td>-1.02</td>
<td>0.07</td>
<td>5.1</td>
<td>5.0</td>
<td>1.0</td>
<td>-1.06</td>
</tr>
<tr>
<td>3rd redn</td>
<td>-1.44</td>
<td>-1.38</td>
<td>0.06</td>
<td>5.2</td>
<td>4.5</td>
<td>1.2</td>
<td>-1.41</td>
</tr>
</tbody>
</table>

$^a$0.1M (TBA)BF$_4$ in CH$_2$Cl$_2$ at Pt electrode. All potentials in V vs. SCE ($\pm 0.5$ mV) and currents in $\mu$A. $^b$electrode area = 3.29 x 10$^{-3}$ cm$^2$; concentration = 0.41 mM. $^c$electrode area = 2.68 x 10$^{-3}$ cm$^2$; concentration = 0.34 mM.

(where $n_{app}$ is the number of coulombs consumed per mole of electroactive substance), while electrolysis at the first anodic wave yielded $n_{app} = 0.97$. Cyclic voltammetry of the electrolyzed solutions gave voltammograms identical with those of solutions of the parent compound, and reoxidation (or rereduction) regenerated solutions matching the original solution and consumed the same number of coulombs as the original reduction (oxidation). Electrolysis times were typically 2 to 3 h, demonstrating the high stability of products. For the tetramer, bulk electrolysis was performed on the first two anodic waves, because of the overlap of the first two cathodic waves. Successive electrolysis at the first and second anodic waves gave $n_{app} = 0.90$ at each. Cyclic voltammograms taken immediately after each electrolysis were identical with those for the parent compound, and reoxidation after the second electrolysis produced a solution matching the original solution and consumed twice as many coulombs as each of the oxidations. The time for each of these electrolyses was 40 min.

In a previous paper on the electrochemistry of monomer and dimer, we proposed the coulometric studies showed $n_{app}$ of 1 for the first reduction and oxidation wave of the monomer but a value 2 for the first waves of the dimer. However, the finding of multiple one-electron waves for trimer and tetramer encouraged us to reinvestigate the dimer. Bulk coulometry of each anodic wave of the dimer yielded $n_{app} = 1.09$. We cannot completely account for the previous finding, but suspect it arose because of a drift in the potential of the quasi-reference electrode, causing the electrolysis to encompass both cathodic waves. Thus, in agreement with the previous report by Armstrong et al., on similar com-

Table II. $E^o$ and Diffusion Coefficient Values for (n-C$_6$H$_{13}$)SiO(SiPcO)$_3$Si(n-C$_6$H$_{13}$)$_3$ ($n = 1-4$)$^a$

<table>
<thead>
<tr>
<th>wave</th>
<th>monomer</th>
<th>dimer</th>
<th>trimer</th>
<th>tetramer</th>
<th>$E^o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4th oxidn</td>
<td>+1.38</td>
<td>+1.47</td>
<td>+1.15</td>
<td>+1.07</td>
<td>+1.43</td>
</tr>
<tr>
<td>3rd oxidn</td>
<td>+1.00</td>
<td>+1.20</td>
<td>+1.47</td>
<td>+1.15</td>
<td>+1.79</td>
</tr>
<tr>
<td>1st oxidn</td>
<td>-0.90</td>
<td>-0.81</td>
<td>-0.78</td>
<td>-0.84</td>
<td>-0.98</td>
</tr>
<tr>
<td>1st redn</td>
<td>-1.48</td>
<td>-1.21</td>
<td>-1.06</td>
<td>-0.98</td>
<td>-1.30</td>
</tr>
<tr>
<td>3rd redn</td>
<td>-1.41</td>
<td>-1.41</td>
<td>-1.30</td>
<td>-1.54</td>
<td>-1.54</td>
</tr>
</tbody>
</table>

$^a$All potentials in V vs. SCE; 0.1 M (TBA)BF$_4$ in CH$_2$Cl$_2$ at Pt electrode.

10$^{-3}$ cm$^2$/s

1.1  2.0  1.0  0.76
Oligomeric Silicon Phthalocyanines


Figure 3. \((n-C_6H_{13})_3SiO(SiPcO)_2Si(n-C_6H_{13})_3\) \((n = 3, 4)\) ac voltammetry in 0.1 M (TBA)BF\(_4\) in CH\(_2\)Cl\(_2\) at Pt electrode. All potentials in V vs. Ag reference electrode: (a) trimer at 0.34 mM concentration, electrode area = 3.8 \(\times\) 10\(^{-2}\) cm\(^2\), \(f\) = 100 Hz; scan rate = 5 mV/s; (b) tetramer at 0.41 mM concentration, electrode area = 3.3 \(\times\) 10\(^{-2}\) cm\(^2\), \(f\) = 200 Hz, scan rate = 5 mV/s.

Figure 4. Electronic absorption spectra of \((n-C_6H_{13})_3SiO(SiPcO)_2Si(n-C_6H_{13})_3\) \((-\)) and \((n-C_6H_{13})_3SiO(SiPcO)_2Si(n-C_6H_{13})_3\) \((-\)) in CH\(_2\)Cl\(_2\) of 0.0054–1.09 mM followed Beer’s laws, suggesting aggregation of monomer does not occur. At this time, we cannot account for this apparent anomaly in \(D\).

The ac voltammetric results (in-phase current component) for the trimer and tetramer are shown in Figure 3. Like their dc counterparts, equal peak currents, indicating equal \(n\) values for all anodic and cathodic waves, are observed. Peak widths at half-height of approximately 90 mV and the superimposition of forward and reverse scans again indicate the reversibility of all of the electrochemical processes.\(^{15}\)

UV-visible wavelength absorbance spectra are virtually identical for both the trimer and tetramer (Figure 4), and are like the spectra of the trimer and tetramer of a similar oligomer set.\(^{16}\) As with the dimer, the trimer and tetramer show no fluorescence.

Conclusions

The results reported here for the compounds \((n-C_6H_{13})_3SiO-(SiPcO)_2Si(n-C_6H_{13})_3\) \((n = 1–4)\) suggest delocalization of charge and strong interaction among the cofacial phthalocyanine rings.\(^{17,18}\) The values of \(E^\circ\), i.e. the values for the first oxidation and reduction waves, are given in Table II. For the anodic waves, the values of \(E^\circ\) become less positive with an increase in \(n\); this trend parallels that found, for example, with aromatic hydrocarbons with an increasing number of rings and extent of overlap.\(^{19}\)


The appreciable interaction between the phthalocyanine rings also results in significant (ca. 0.4 V) spacings between the successive oxidation waves; for negligible interactions, this spacing would be only about 36 mV. The shift of the first reduction wave with increasing n is much less pronounced than that for the first oxidation wave, and the two first reduction waves of the trimer and tetramer are more closely spaced than the first two oxidation waves. These results provide a basis for further calculations of orbital energies in oligomers of this type. The delocalization of charge in these cofacial phthalocyanine systems that is indicated by these results is consistent with the high conductivities observed with partially oxidized cofacial phthalocyanine polymers.7,17

**Acknowledgment.** The support of this work by the National Science Foundation (Grant CHE8402135) and the Office of Naval Research is gratefully acknowledged.

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**Oxidation of Hydrazine and Methyl-Substituted Hydrazines by the Cyano Complexes of Iron(III), Molybdenum(V), and Tungsten(V). A Kinetic Study**

C. Robert Dennis,* Abraham J. Van Wyk,* Stephen S. Basson, and Johann G. Leipoldt

*Received February 20, 1986*

Electron-transfer between the hydrazines and the cyano complexes of Fe(III), Mo(V), and W(V) in aqueous solution proceeds via an outer-sphere mechanism, and the rate data are consistent with the Marcus theory. The reactions are pH-dependent with a rate law $R = k/(1 + [H^+]_1 \cdot [M(CN)\text{--}])$.[1][2] From the kinetic data were obtained acid dissociation constants for the different hydrazines. Estimates of an upper limit of the $E^*$ values for the different hydrazine couples, as well as a one-electron-self-exchange rate constant for the hydrazines, were obtained by application of the Marcus theory.

**Introduction**

The oxidation of hydrazine by several oxidizing agents has been the subject of a considerable amount of studies.1 It was shown3 that $N_2H_4^+$ is the reactive species in acidic media. The oxidation of hydrazine by Mo(CN)$_6^{3-}$, W(CN)$_6^{3-}$, and Fe(CN)$_6^{3-}$ suggested that $N_2H_4$ is the reactive species in alkaline medium and that the rates of electron transfer are consistent with the Marcus theory.3 The oxidation of hydrazine by the hexachloroiridate(IV) ion was studied over a wide pH range (pH 1-10). The reaction rate was found to be pH-dependent and consistent with the rate law

$$R = \frac{k[\text{IrCl}_6^{2-}][N_2H_4]^+}{1 + [H^+] \cdot [N_2H_4]^+} \tag{1}$$

The hydrazinium radical, $N_2H_4^+$, as well as $N_2^+$ as reaction product has been identified, and the reaction mechanism, eq 2-4,

$$\begin{align*}
N_2H_4^+ & \rightarrow N_2H_4 + H^+ \tag{2} \\
\text{IrCl}_6^{2-} + N_2H_4 & \rightarrow N_2H_4^+ + \text{IrCl}_6^{3-} \tag{3} \\
3\text{IrCl}_6^{3-} + N_2H_4^+ & \rightarrow N_2 + \text{products} \tag{4}
\end{align*}$$

was proposed. An upper limit for the reduction potential of the $N_2H_4^+//N_2H_4$ couple has also been estimated as $E^* (N_2H_4^+//N_2H_4) \leq 0.73$ V (vs. NH$_3$) by considering electron transfer between Fe(CN)$_6^{3-}$ and $N_2H_4$. A self-exchange rate constant for the $N_2H_4^+//N_2H_4$ couple was calculated to be $\leq 3 \times 10^{-1} \text{ M}^{-1} \text{ s}^{-1}$.

The previous study and our present data yielded rate laws similar to that of the above-mentioned reaction. Since electron transfers in these reported studies are in support of an outer-sphere reaction pathway, the oxidations of the methyl-substituted hydrazines were studied for comparison with the hydrazide studies.

**Experimental Section**

C$_5$Mo(CN)$_6$·2H$_2$O and C$_5$W(CN)$_6$·2H$_2$O were prepared as described by Leipoldt et al.10,11 and were used as primary standards after recrystallization. All other reagents were of Merck "pro analysi" standard and were used as received. Hydrazinium sulfate, methylhydrazine, and

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**Table I. Kinetic, Structural, and Electrochemical Data for Reactants**

<table>
<thead>
<tr>
<th>couple</th>
<th>self-exchange rate const. $k$</th>
<th>$E^*$, V</th>
<th>$r$, Å</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo(CN)$_6^{3-}$/Mo(CN)$_6^{4-}$</td>
<td>$3 \times 10^4$</td>
<td>0.76</td>
<td>4.8</td>
<td>27, 28, 24</td>
</tr>
<tr>
<td>W(CN)$_6^{3-}$/W(CN)$_6^{4-}$</td>
<td>$7 \times 10^4$</td>
<td>0.54</td>
<td>4.8</td>
<td>27, 24</td>
</tr>
<tr>
<td>Fe(CN)$_6^{3-}$/Fe(CN)$_6^{4-}$</td>
<td>$7 \times 10^4$</td>
<td>0.36</td>
<td>4.5</td>
<td>29, 27, 24</td>
</tr>
<tr>
<td>IrCl$_6^{3-}$/IrCl$_6^{4-}$</td>
<td>$2 \times 10^4$</td>
<td>0.89</td>
<td>3.4</td>
<td>30</td>
</tr>
<tr>
<td>$N_2H_4^+/N_2H_4$</td>
<td>$\leq 1.0$</td>
<td>$\leq 0.73$</td>
<td>1.1</td>
<td>6, this work</td>
</tr>
<tr>
<td>(CH$_3$)$_2N_2H_4^+/$(CH$_3$)$_2N_2H_3$</td>
<td>$\leq 1.0$</td>
<td>$\leq 0.62$</td>
<td>1.5</td>
<td>this work</td>
</tr>
<tr>
<td>(CH$_3$)$_2N_2H_4H(CH_3)$</td>
<td>$\leq 1.0$</td>
<td>$\leq 0.56$</td>
<td>1.8</td>
<td>this work</td>
</tr>
</tbody>
</table>

1,2-dimethylhydrazinium dichloride were used as sources of the hydrazinium species. Redistilled water was used throughout.

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**Contribution from the Department of Chemistry, University of The Orange Free State, Bloemfontein 9300, Republic of South Africa**

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