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

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A new method for synthesizing $(n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3$ and methods for isolating $(n\text{-}C_6H_{13})_3SiO(SiPcO)_3Si(n\text{-}C_6H_{13})_3$ and $(n\text{-}C_6H_{13})_3SiO(SiPcO)_4Si(n\text{-}C_6H_{13})_3$ from a mixture containing these two oligomers are described. Well-resolved NMR spectra of the three oligomers and of $(n\text{-}C_6H_{13})_3SiOSiPcOSi(n\text{-}C_6H_{13})_3$ are presented. Electrochemical studies of the series $(n\text{-}C_6H_{13})_3SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ (n = 1–4) show n one-electron oxidation and n 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,[1] several oligomeric silicon phthalocyanines with silicon–oxygen backbones,[2-5] and a polymeric silicon phthalocyanine with a silicon–oxygen backbone[6] were reported. Subsequently, the polymer was found to be a good conductor when fractionally oxidized with oxidants such as iodine.[7] This has led to considerable interest in the polymer and oligomers related to it.[8]

In a previous paper, we reported on the synthesis of the oligomer mixture $(n\text{-}C_6H_{13})_3SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ and a mixture of oligomers of this type and on the synthesis of the homologous monomer, $(n\text{-}C_6H_{13})_3SiOSiPcOSi(n\text{-}C_6H_{13})_3$. We also reported on the isolation of the dimer of this series, $(n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3$, and on the electrochemical and spectroscopic properties of the monomer and dimer.[9] 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, $(n\text{-}C_6H_{13})_3SiO(SiPcO)_3Si(n\text{-}C_6H_{13})_3$ and $(n\text{-}C_6H_{13})_3SiO(SiPcO)_4Si(n\text{-}C_6H_{13})_o$, and information on the electrochemical and spectroscopic properties of these oligomers are reported.

Experimental Section

Syntheses. $(n\text{-}C_6H_{13})_3SiOSiPcOSi(n\text{-}C_6H_{13})_3$. A preparation and purification of the monomer have been reported previously:[9] IR (Nujol) 1250 (Si–CH_2), 1040 (SiR–O–SiPc) cm^{-1}; ^1H NMR (C_6D_6, 70 °C) δ 9.70 (m, 1,4-Pc), 7.96 (m, 2,3-Pc), 0.93 (m, ϵ-CH_2), 0.77 (t, CH_3), 0.56 (m, δ-CH_2), 0.24 (m, γ-CH_2), –0.41 (m, β-CH_2), –2.10 (m, α-CH_2); ^{29}Si NMR ($CDCl_3$, 19 °C) δ –7.70 (s, $SiCH_2$), –221.7 (s, SiPc).

The crude monomer can be purified by an alternative procedure. In this, the monomer is washed with pentane and ethanol–water solutions and then recrystallized from methylcyclohexane.

$(n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3$. Likewise, a preparation and purification of the dimer have been reported previously:[9] IR (Nujol) 1252 (Si–CH_2), 1030 (SiR–O–SiPc), 979 (SiPc–O–SiPc) cm^{-1}; ^1H NMR (C_6D_6 70 °C) δ 9.20 (m, 1,4-Pc), 8.08 (m, 2,3-Pc), 0.58 (overlapping m, ϵ-CH_2 and CH_3), 0.07 (m, δ-CH_2), –0.38 (m, γ-CH_2), –1.86 (m, β-CH_2), –3.16 (m, α-CH_2).

An alternative synthesis for the dimer can be employed. This utilizes $CH_3SiPcOSi(n\text{-}C_6H_{13})_3$ and $HOSiPcOSi(n\text{-}C_6H_{13})_3$ as intermediates.

$CH_3SiPcOSi(n\text{-}C_6H_{13})_3$. A suspension of $CH_3SiPcOH_2$ (2.39 g, prepared by a NaOH–pyridine–H_2O hydrolysis of $CH_3SiPcCl_2$) and pyridine (275 mL) was dried by distillation (25 mL of distillate). Tri-*n*-hexylchlorosilane (1.5 mL) was added to the dried suspension, and the resulting mixture was refluxed for 4 h with protection from moisture and light. The product was filtered, and the residue was washed with pyridine. The filtrate and washings were combined and evaporated to dryness under vacuum. After being washed, the residue was vacuum-dried (110 °C) (950 mg, 27%): ^1H NMR ($CDCl_3$, 18 °C) δ 9.65 (m, 1,4-Pc), 8.32 (m, 2,3-Pc), 0.82 (m, ϵ-CH_2), 0.70 (t, CCH_3), 0.36 (m, δ-CH_2), 0.02 (m, γ-CH_2), –1.30 (m, β-CH_2), –2.50 (m, α-CH_2), –6.33 (s, $SiCH_3$).

$HOSiPcOSi(n\text{-}C_6H_{13})_3$. A solution of $CH_3SiPcOSi(n\text{-}C_6H_{13})_3$ (940 mg) and toluene (1 L) was irradiated with direct sunlight for 2 h while being stirred. The product was filtered, and the residue was washed with toluene. The filtrate and the washings were combined and evaporated to dryness under vacuum. After being washed, the residue was air-dried (387 mg, 41%): IR (Nujol) 3500 (OH), 1250 (Si–CH_2), 835 (Si–OH) cm^{-1}.

$(n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3$. A thin layer of $HOSiPcOSi(n\text{-}C_6H_{13})_3$ (343 mg) was heated at ~189 °C for 30 min. CH_2Cl_2 was mixed with the product, and the resulting solution was filtered. The solid was washed with CH_2Cl_2, and the filtrate and washings were combined and evaporated to dryness under vacuum. The residue was washed and vacuum-dried (110 °C) (242 mg).

A similarly prepared mixture (400 mg) was separated by chromatography (alumina, activity III; hexanes, hexanes–toluene solutions, 3:1 and 1:1) into three product fractions; monomer (i.e., $(n\text{-}C_6H_{13})_3SiOSiPcOSi(n\text{-}C_6H_{13})_3$) (82 mg, 21% of load), the desired product (140 mg, 35% of load), and trimer (25 mg, 6% of load).

A significant amount of dimer is formed when $HOSiPcOSi(n\text{-}C_6H_{13})_3$ is heated to ~171 °C even though the $HOSiPcOSi(n\text{-}C_6H_{13})_3$ does not melt. When the dimer reaction product is heated to temperatures moderately above that at which the $HOSiPcOSi(n\text{-}C_6H_{13})_3$ is used up, the relative amounts of dimer formed do not increase. At ~196 °C, the reaction product is appreciably melted.

$(n\text{-}C_6H_{13})_3SiO(SiPcO)_3Si(n\text{-}C_6H_{13})_3$. In a typical experiment, a mixture of the oligomers (1.13 g) was separated by chromatography (alumina, activity III; hexanes–toluene solution, 3:1) into the dimer (376 mg, 33% of load) and a residue (this part of the experiment has been described previously[9]). This residue was separated by additional elution (hexanes–toluene solution, 1:1) into an additional fraction (267 mg, 24% of load) and a new residue. Further similar experiments yielded more of the same fraction: IR (Nujol) 1013 (SiR–O–SiPc), 981 (SiPc–O–SiPc) cm^{-1}; ^1H NMR (C_6D_6, 70 °C) δ 8.75 (m, terminal 1,4-Pc) 8.69 (m, middle 1,4-Pc), 8.21 (m, middle 2,3-Pc), 7.84 (m, terminal 2,3-Pc), 0.36 (m, overlapping ϵ-CH_2 and CH_3), –0.23 (m, δ-CH_2), –0.71 (m, γ-CH_2), –2.30 (m, β-CH_2), –3.65 (m, α-CH_2).[10] Anal. Calcd for $C_{132}H_{126}N_{24}O_4Si_5$: C, 70.37; H, 5.64; Si, 6.23. Found: C, 70.30; H, 5.88; Si, 5.95.

$(n\text{-}C_6H_{13})_3SiO(SiPcO)_4Si(n\text{-}C_6H_{13})_3$. In a typical experiment, the trimer separation residue described above was separated by further elution (hexanes–toluene solution, 1:3) into another fraction (44 mg, 4% of

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(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.[3] These calculated positions are as follows: trimer δ 8.70 (middle 1,4-Pc) and 8.20 (middle 2,3-Pc); tetramer δ 8.25 (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.

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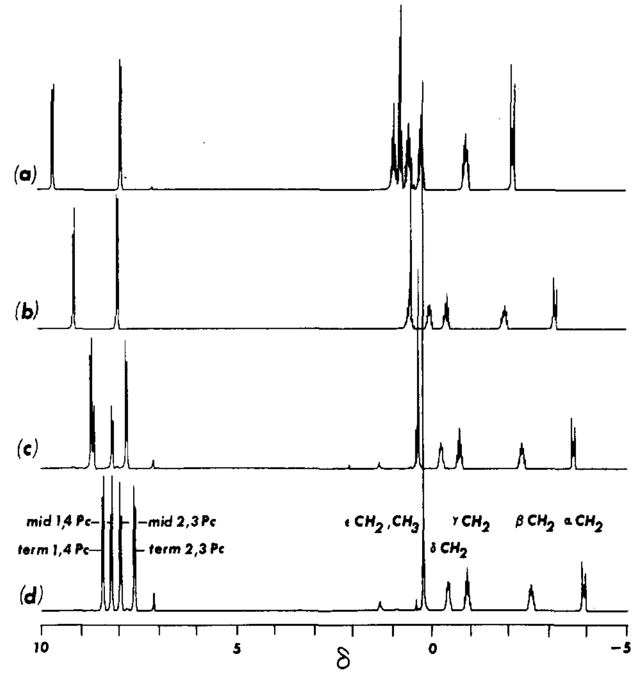

Figure 1. NMR spectra, 200 MHz: (a) $(n\text{-}C_6H_{13})_3SiOSiPcOSi(n\text{-}C_6H_{13})_3$; (b) $(n\text{-}C_6H_{13})_3SiO(SiPcO)_2Si(n\text{-}C_6H_{13})_3$; (c) $(n\text{-}C_6H_{13})_3SiO(SiPcO)_3Si(n\text{-}C_6H_{13})_3$; (d) $(n\text{-}C_6H_{13})_3SiO(SiPcO)_4Si(n\text{-}C_6H_{13})_3$.

load) and another residue. Additional similar experiments yielded more of the same fraction: IR (Nujol) 1029 (SiR–O–SiPc), 1000 (SiPc–O–SiPc) cm^{-1}; ^{1}H NMR (C_6D_6, 70 °C) δ 8.47 (m, terminal 1,4-Pc), 8.25 (m, middle 1,4-Pc), 8.01 (m, middle 2,3-Pc), 7.65 (m, terminal 2,3-Pc), 0.24 (m, overlapping ε-CH$_2$ and CH$_3$), −0.39 (m, δ-CH$_2$), −0.89 (m, γ-CH$_2$), −2.53 (m, β-CH$_2$), −3.89 (m, α-CH$_2$).[10] Anal. Calcd for $C_{164}H_{142}N_{32}O_5Si_6$: C, 70.11; H, 5.09; Si, 6.00. Found: C, 70.04; H, 5.22; Si, 5.65.

The minor resonances at 0.9 and 1.3 ppm in the samples of the trimer and tetramer that were made (Figure 1) are due to impurities.

The trimer and tetramer, like the monomer and dimer, are blue solids and are soluble in common organic solvents.

Spectral Studies. Electronic spectra were recorded with a Cary 17D spectrophotometer (Varian Associates Inc., Palo Alto, CA). Infrared spectra were obtained with a Perkin-Elmer 598 spectrophotometer (Perkin-Elmer Corp., Norwalk, CT). ^{1}H and ^{29}Si NMR spectra were recorded with Varian XL-200 spectrometers. Chromium acetylacetonate was added to the solution used for acquisition of the ^{29}Si data. The ^{29}Si data were collected with the aid of the Compton-Purcell spin-echo technique (to reduce interference from silicon in the glass of the NMR tube). The ^{1}H spectra were referenced to the signals of the residual protons in the solvents ($CDCl_3$ at 7.26 ppm and C_6D_6 at 7.15 ppm) while the ^{29}Si spectrum was referenced to tetramethylsilane.

Electrochemical Studies. Methylene chloride (Spectranalyzed grade from Fisher Scientific, Fair Lawn, NJ) was stirred over molecular sieves (Type 4A, Fisher Scientific), then vacuum distilled onto calcium hydride (95+%, −4 +40 mesh, Aldrich Chemical Co., Milwaukee, WI), and finally treated with five cycles of a freeze (liquid N_2)–pump–thaw sequence. Tetrabutylammonium fluoborate ((TBA)BF$_4$, electrometric grade, Southwestern Analytical Chemicals, Austin, TX) was recrystallized (hot filtration) three times from ethyl acetate (ACS grade, Fisher Scientific) and, prior to use, was dried under vacuum at 120 °C overnight. For the electrochemical measurements, three-compartment electrochemical cells of 25-mL capacity were employed. Pt disk electrodes were used as working electrodes. The areas of the electrodes were calculated from their chronocoulometric behavior in 10 mM $K_4Fe(CN)_6$ in 1.0 M KCl. Large-area Pt gauze electrodes were used for bulk electrolysis. A silver wire separated from the working solution by a fine porosity glass frit was employed as a quasi-reference electrode. The counter electrode was made of large-area reticulated vitreous carbon. It was separated from the main compartment by a fine-porosity glass frit and was immersed in 0.1 M (TBA)BF$_4$ in CH_2Cl_2. In a typical experiment, the electrolyte was dried in the cell. After the electrolyte and cell had been cooled to room temperature, the solvent was vacuum-distilled directly into the cell. The cell was next sealed by closing an appropriately positioned stopcock. Then the compound of interest was added from a sidearm hopper. The potential of the Ag wire quasi-reference electrode remained stable throughout the course of the experiment, since the observed peak potentials did not change with time. At the end of the experiment, the potential of the quasi-reference electrode was determined relative to an SCE that had been dipped into the working solution.

For the cyclic voltammetry, an EG&G Princeton Applied Research (PAR, Princeton, NJ) Model 173 potentiostat and Model 175 universal programmer equipped with a Houston Instruments (Austin, TX) Model 2000 X-Y recorder were used; for the bulk electrolyses and chronocoulometry, a Bioanalytical Systems (West Lafayette, IN) Model 100 electrochemical analyzer and a Houston Instruments Model DMP-40 digital plotter were used. A lock-in amplifier technique employing a PAR Model 5204 lock-in amplifier, a Hewlett-Packard (Palo Alto, CA) Model 200 CD oscillator, and a Soltec (Sun Valley, CA) Model 6432 X-Y$_1$Y$_2$ recorder was used for the ac voltammetry.[9]

Results and Discussion

Synthesis. While the route to the dimer through $HOSiPcOSi(n\text{-}C_6H_{13})_3$ appears to hold little or no practical advantage over that through $SiPcCl_2$ and $SiPc(OH)_2$,[9,11] 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 $HOSiPcOSi(n\text{-}C_6H_{13})_3$ may be positioned close to that of another (the full structure of $HOSiPcOSi(n\text{-}C_6H_{13})_3$ 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 lability 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,[9] clearly show the presence of large ring-current effects. This is in accordance with expectations.[3]

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_8. However, with chloroform-d the resolution is poor. These solvent effects probably arise in part because of strong π–π interactions between the oligomers and the aromatic solvents.

The position of the ^{29}Si resonance of the monomer's central silicon, −221.7 ppm, is substantially above the ordinary range reported for the resonance of octahedral silicon, −140 to −200 ppm.[13] 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_2Cl_2 are +1.70 to −2.00 V vs. Ag reference electrode (+1.85 to −1.85 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 ($E°$), 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 $i_{p,c}/v^{1/2}$ 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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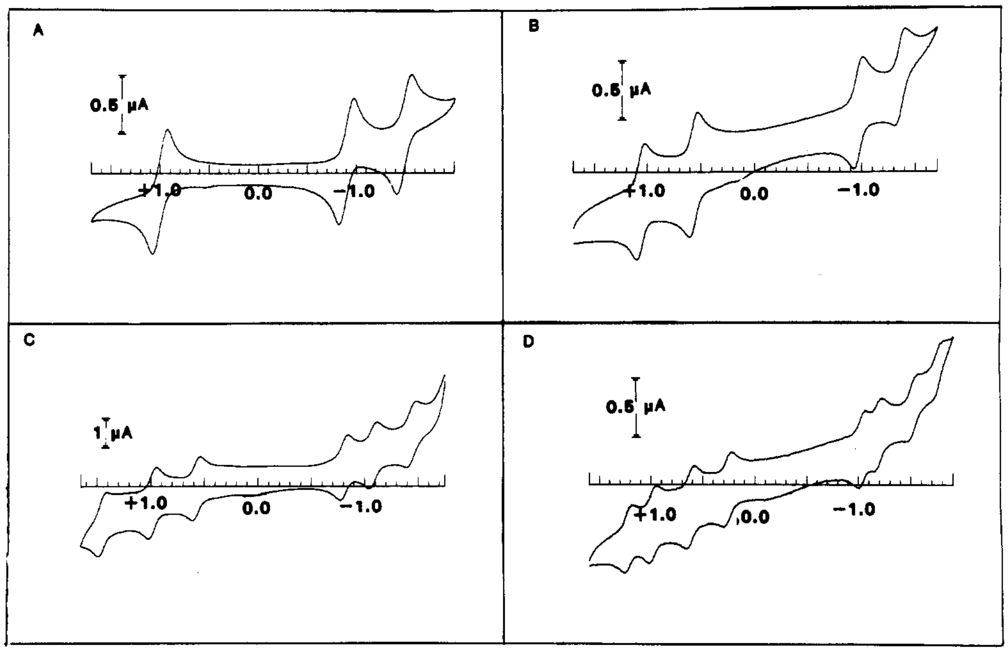

Figure 2. Cyclic voltammograms of $(n\text{-}C_6H_{13})_3SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ (n = 1–4) in 0.1 M $(TBA)BF_4$ in CH_2Cl_2 at Pt electrode. All potentials in V vs. Ag reference electrode: (A) monomer at 0.70 mM concentration, scan rate = 100 mV/s, electrode area = 2.5 × 10^{-2} cm^2; (B) dimer at 0.64 mM concentration, scan rate = 100 mV/s, electrode area = 3.3 × 10^{-3} cm^2; (C) trimer at 0.34 mM concentration, scan rate = 100 mV/s, electrode area = 2.7 × 10^{-2} cm^2; (D) tetramer at 0.41 mM concentration, scan rate 100 mV/s, electrode area = 3.3 × 10^{-3} cm^2.

Table I. Cyclic Voltammetric Data for $(n\text{-}C_6H_{13})_3SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ (n = 3,4)[a]

	trimer[b]							tetramer[c]						
wave	$E_{p,c}$	$E_{p,a}$	ΔE_p	$i_{p,c}$	$i_{p,a}$	$i_{p,c}/i_{p,a}$	$E°$	$E_{p,c}$	$E_{p,a}$	ΔE_p	$i_{p,c}$	$i_{p,a}$	$i_{p,c}/i_{p,a}$	$E°$
4th oxidn								+1.35	+1.42	0.07	0.136	0.130	1.0	+1.38
3rd oxidn	+1.43	+1.51	0.08	6.5	4.9	0.8	+1.47	+1.12	+1.18	0.06	0.135	0.140	1.0	+1.15
2nd oxidn	+0.96	+1.04	0.08	5.5	4.8	0.9	+1.00	+0.75	+0.82	0.07	0.130	0.150	0.9	+0.79
1st oxidn	+0.56	+0.62	0.06	5.8	4.3	0.8	+0.59	+0.40	+0.47	0.07	0.125	0.162	0.8	+0.43
1st redn	−0.82	−0.75	0.07	4.9	4.5	1.1	−0.78	−0.86	−0.80	0.06	0.152	0.120	1.3	−0.84
2nd redn	−1.09	−1.02	0.07	5.1	5.0	1.0	−1.06	−1.01	−0.95	0.06	0.148	0.140	1.1	−0.98
3rd redn	−1.44	−1.38	0.06	5.2	4.5	1.2	−1.41	−1.34	−1.26	0.07	0.150	0.138	1.1	−1.30
4th redn								−1.57	−1.50	0.07	0.140	0.130	1.1	−1.54

[a] 0.1M $(TBA)BF_4$ in CH_2Cl_2 at Pt electrode. All potentials in V vs. SCE (±5 mV) and currents in μA. [b] electrode area = 3.29 × 10^{-3} cm^2; concentration = 0.41 mM. [c] electrode area = 2.68 × 10^{-2}; concentration = 0.34 mM.

Table II. $E°$ and Diffusion Coefficient Values for $(n\text{-}C_6H_{13})SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ (n = 1–4)[a]

	$E°$			
wave	monomer	dimer	trimer	tetramer
4th oxidn				+1.38
3rd oxidn			+1.47	+1.15
2nd oxidn		+1.20	+1.00	+0.79
1st oxidn	+1.00	+0.71	+0.59	+0.43
1st redn	−0.90	−0.81	−0.78	−0.84
2nd redn	−1.48	−1.21	−1.06	−0.98
3rd redn			−1.41	−1.30
4th redn				−1.54
10^5D, cm^2/s	1.1	2.0	1.0	0.76

[a] All potentials in V vs. SCE; 0.1 M $(TBA)BF_4$ in CH_2Cl_2 at Pt electrode.

(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 $2^1/_2$ 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 rereduction 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 coulomety 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.,[11] on similar compounds, all waves for monomer and dimer are also attributed to one-electron-transfer reactions.

Chronocoulometry at the first anodic wave was used to determine the diffusion coefficients of all of these compounds. Plots of Q vs. $t^{1/2}$ exhibited good linearity for pulse widths of 25 to 1000 ms. The average slope of six runs was used to calculate D. The results are collected in Table II. For the dimer, trimer, and 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

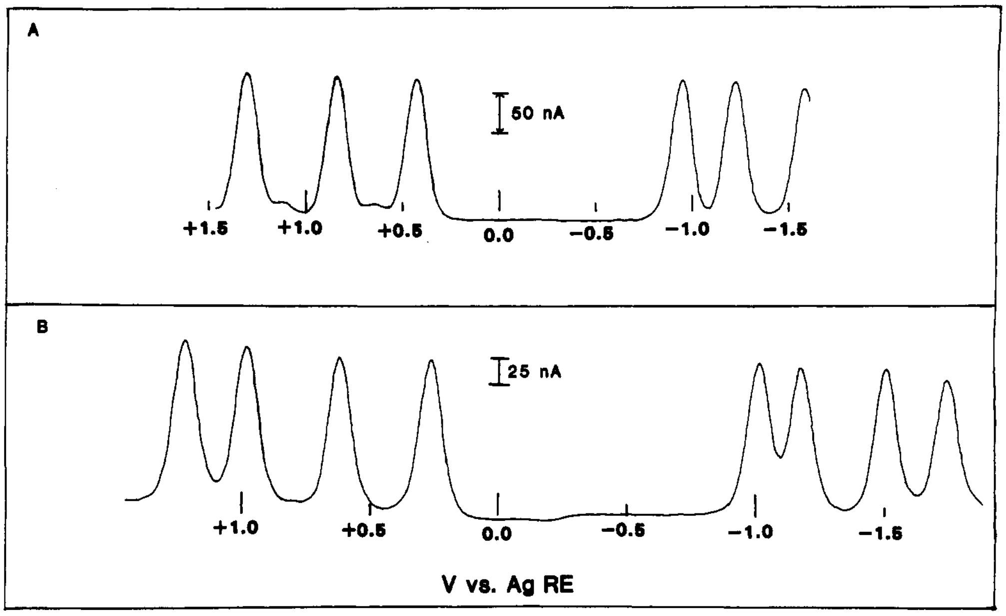

Figure 3. $(n\text{-}C_6H_{13})_3SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ (n = 3, 4) ac voltammetry in 0.1 M (TBA)BF_4 in CH_2Cl_2 at Pt electrode. All potentials in V vs. Ag reference electrode: (a) trimer at 0.34 mM concentration, electrode area = 3.8×10^{-2} cm^2, f = 100 Hz; scan rate = 5 mV/s; (b) tetramer at 0.41 mM concentration, electrode area = 3.3×10^{-2} cm^2, f = 200 Hz, scan rate = 5 mV/s.

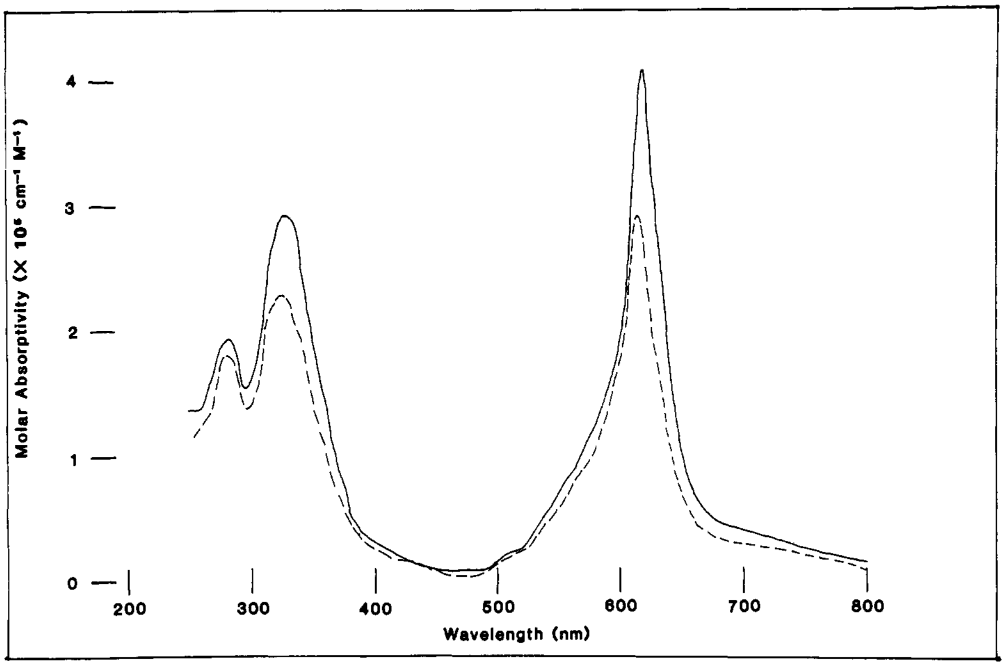

Figure 4. Electronic absorption spectra of $(n\text{-}C_6H_{13})_3SiO(SiPcO)_3Si(n\text{-}C_6H_{13})_3$ (—) and $(n\text{-}C_6H_{13})_3SiO(SiPcO)_4Si(n\text{-}C_6H_{13})_3$ (—) in CH_2Cl_2.

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 $(n\text{-}C_6H_{13})_3SiO(SiPcO)_nSi(n\text{-}C_6H_{13})_3$ (n = 1–4) suggest delocalization of charge and strong interaction among the cofacial phthalocyanine rings.[7,17,18] The values of $E^{0\prime}$, i.e. the values for the first oxidation and reduction waves, are given in Table II. For the anodic waves, the values of $E^{0\prime}$ 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]

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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.[20] The shift of the first reduction wave with increasing n is much less pronounced than that for the first oxidation wave, and the first two 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.[18] 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]

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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

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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 $R = (k/(1 + [H^+]/K_a))[M(CN)_n^{3-}]$[hydrazine]. 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 shown[2,3] that $N_2H_5^+$ is the reactive species in acidic media. The oxidation of hydrazine by $Mo(CN)_8^{3-}$, $W(CN)_8^{3-}$, and $Fe(CN)_6^{3-4}$ suggested that N_2H_4 is the reactive species in alkaline medium and that these rates of electron transfer are consistent with the Marcus theory.[5] The oxidation of hydrazine by the hexachloroiridate(IV) ion[6] 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

$$R = \frac{k[IrCl_6^{2-}][N_2H_4]_T}{1 + [H^+]/K_a} \tag{1}$$

The hydrazinium radical, $N_2H_4^+$,[7] as well as N_2,[8,9] as reaction product has been identified, and the reaction mechanism, eq 2-4,

$$N_2H_5^+ \overset{K_a}{\rightleftharpoons} N_2H_4 + H^+ \tag{2}$$

$$IrCl_6^{2-} + N_2H_4 \xrightarrow{k} N_2H_4^+ + IrCl_6^{3-} \tag{3}$$

$$3IrCl^{2-} + N_2H_4^+ \xrightarrow[\text{fast}]{} N_2 + \text{products} \tag{4}$$

was proposed. An upper limit for the reduction potential of the $N_2H_4^+/N_2H_4$ couple has also been estimated as $E°(N_2H_4^+/N_2H_4) \le 0.73$ V (vs. NHE) 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 $\le 3 \times 10^{-1}$ M^{-1} s^{-1}.

The previous study[4] 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 hydrazine studies.

Experimental Section

$Cs_3Mo(CN)_8{\cdot}2H_2O$ and $Cs_3W(CN)_8{\cdot}2H_2O$ were prepared as described by Leipoldt et al.[10,11] and were used as primary standards[12] after recrystallization. All other reagents were of Merck "pro analisi" standard and were used as received. Hydrazinium sulfate, methylhydrazine, and 1,2-dimethylhydrazinium dichloride were used as sources of the hydrazinium species. Redistilled water was used throughout.

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

couple	self-exchange rate const, M^{-1} s^{-1}	$E°$, V	r, Å	ref
$Mo(CN)_8^{3-}/Mo(CN)_8^{4-}$	3×10^4	0.76	4.8	27, 28, 24
$W(CN)_8^{3-}/W(CN)_8^{4-}$	7×10^4	0.54	4.8	27, 24
$Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	7×10^3	0.36	4.5	29, 27, 24
$IrCl_6^{2-}/IrCl_6^{3-}$	2×10^5	0.89	3.4	30
$N_2H_4^+/N_2H_4$	≤1.0	≤0.73	1.1	6, this work
$(CH_3)N_2H_3^+/(CH_3)N_2H_3$	≤1.0	≤0.62	1.5	this work
$(CH_3)HN_2H(CH_3)^+/$ $(CH_3)HN_2H(CH_3)$	≤1.0	≤0.56	1.8	this work

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