The following full text is a publisher's version.

For additional information about this publication click this link.
http://hdl.handle.net/2066/16294

Please be advised that this information was generated on 2018-11-26 and may be subject to change.
configuration interactions is necessary to obtain a solution where the energies of the different geometries of the singlet excited state are stable. As the CI number was increased the energies of the perpendicular geometries were less affected (lowered) compared with the E and Z ones.

The results are summarized in Figure 4. As regards the Franck-Condon transition energies the agreement with experimental data is fair. The structureless absorption and emission spectra of 1 and 2 make the energy evaluations somewhat ambiguous. The longest wavelength absorption maxima at 153 K (where the vibronic structures in the spectra of 3 are resolved) correspond to the energies 86, 83, and 75 kcal mol\(^{-1}\) for 1, 2, and 3, respectively. The Franck-Condon energies similarly estimated from the emission spectra are 64, 66, and 72 kcal mol\(^{-1}\).

A prerequisite for an adiabatic mechanism is that there are no energy minima on the excited-state energy surface in the regions of 90\(^\circ\) double bond twists. The calculated energy difference of the nonaggregated ones.

Such compounds when incorporated in vesicle bilayers could be achieved in which the central silicon atoms are bridged through

Kenne\(^{\text{a},*}\) involves the polycondensation of a phthalocyaninato \[\text{PcSiO}\] \(_\text{n}\), have been studied by many scientist\(^{\text{a}}\). Unsubstituted phthalocyaninato polysiloxanes substituted with 15-crown-5, 18-crown-6, and 21-crown-7 rings. The degree of polymerization of the polymer samples depends on the size of the crown moieties (Figure 1). These stacks are expected to transport electrons and ions in the stacking direction: electrons via the phthalocyanines.\(^{2}\) This method, first described by Joyner and Kenney,\(^{14}\) involves the polycondensation of a phthalocyaninato dihydroxysilane for 1-12 h at 440 °C under solid state solution butylbenzyltriphenylphosphonium bromide.

### Phthalocyaninato Polysiloxanes Substituted with Crown Ether Moieties

O. E. Sielcken,\(^1\) L. A. van de Kuil,\(^2\) W. Drent,\(^1\) J. Schoonman,\(^4\) and R. J. M. Nolte*\(^{1,2}\)

**Contribution from the Department of Organic Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands, the Laboratory for Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands, and the Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands.**

**Received June 13, 1989**

**Abstract:** We describe the synthesis and characterization of phthalocyaninato polysiloxanes substituted with 15-crown-5, 18-crown-6, and 21-crown-7 rings. The degree of polymerization of the polymer samples depends on the size of the crown ether rings and varies between 6 and 18 units. NMR spectroscopy reveals that the polysiloxanes have a rigid structure with staggered phthalocyaninato (Pc) units. The binding of alkali-metal ions to the polymers and their monomers is reported and discussed. Upon polymerization of the phthalocyaninato dihydroxysilanes the electronic conductivity increases from 10\(^{-9}\) to 10\(^{-7}\) S/m. The polymer substituted with 21-crown-7 rings conducts sodium ions.

Phthalocyaninates (Pc's) substituted with crown ether rings are currently receiving great interest.\(^{1,14}\) Recently, we reported that these molecules can be aggregated by addition of alkali-metal salts, which become complexed to the crown ether rings.\(^{1,2}\) Electrical measurements of the aggregated species revealed an increase in electrical conductivity that is 2-3 powers of 10 higher than that of the nonaggregated ones.

In this paper we report another method of aggregating phthalocyaninates.\(^{2}\) This method, first described by Joyner and Kenney,\(^{14}\) involves the polycondensation of a phthalocyaninato dihydroxysilane containing four crown ether rings. In this way a stacked quasi-one-dimensional arrangement of crowned Pc's is achieved in which the central silicon atoms are bridged through O\(^2\) ligands (Figure 1). These stacks are expected to transport electrons and ions in the stacking direction: electrons via the central Pc macrocycles and cations via the crown ether moieties. Such compounds when incorporated in vesicle bilayers could be used as synthetic models to mimic both electron and ion channels of natural transport systems.

Substituted and unsubstituted phthalocyaninato polysiloxanes, \[\text{[PcSiO]}_n\] have been studied by many scientists.\(^3\) Unsubstituted polysiloxanes are formed by the uncatalyzed polycondensation of phthalocyaninato dihydroxysilane for 1-12 h at 440 °C under solid state solution butylbenzyltriphenylphosphonium bromide.

**Table I.** \(^{13}\)C Chemical Shifts of Se in Solution and in the Solid State

<table>
<thead>
<tr>
<th></th>
<th>C1</th>
<th>C2</th>
<th>C3</th>
<th>C4</th>
<th>C5</th>
<th>C6</th>
<th>C7</th>
<th>C8</th>
<th>crown ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution</td>
<td>151.3</td>
<td>155.0</td>
<td>132.3</td>
<td>108.1</td>
<td>72.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>solid state</td>
<td>151.8</td>
<td>151</td>
<td>129.5</td>
<td>102.5</td>
<td>70.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*In ppm relative to tetramethylsilane.  \(^{a}\)Solvent CD\(_2\)OD.

polyoxides are formed by the uncatalyzed polycondensation of phthalocyaninato dihydroxysilane for 1–12 h at 440 °C under solid state solution butylbenzyltriphenylphosphonium bromide.

\(^{1}\)University of Utrecht.  
\(^{2}\)Delft University of Technology.  
\(^{3}\)University of Nijmegen.
These polymers, for which a degree of polymerization, \( m \), of 70–140 can be reached, exhibit high thermal and chemical stabilities. Structural information, obtained by X-ray powder diffraction, has shown these polymers to have an orthorhombic structure with an interplanar \( \text{Pc} \) distance of 3.33 Å and a staggered arrangement of the \( \text{Pc} \) macrocycles (staggering angle = 39°). Polycrystalline samples are reported to exhibit a room temperature conductivity of \( 10^{-4} - 10^{-3} \) S/m.

Peripherally substituted polysiloxanes cannot be synthesized under the above-mentioned conditions because of thermal degradation of the substituents. Wegner and co-workers have developed a milder procedure for the polycondensation of substituted \( \text{Pc} \)’s by using metal salt catalysts, though little is known about the operative reaction mechanism. The rate of reaction is very low, and relatively low molecular weight polymers are obtained; chain lengths of tetra-tert-butyl-substituted and octakis(dodecoxy)-substituted phthalocyaninato polysiloxanes were estimated to be between 10 and 25 \( \text{Pc} \) units. These polymers are soluble in common organic solvents. Very recently, Wegner and co-workers developed a route to higher molecular weight polymers. This route involves the polycondensation of octakis(dodecoxy)-substituted phthalocyaninato silanols in which the hydroxyl functions have first been converted with trifluoroacetic acid anhydride into good leaving groups. They proved the polymers to have a rigid rodlike structure with an interplanar \( \text{Pc} \) spacing of 3.4 Å and a Si–O–Si bond angle of 180°.

Figure 1. Linear chain of “crowned” phthalocyanines.
Results and Discussion

**Synthesis.** 4,5-Dicyanobenzo-crown ether (2a–c, Scheme I, Figure 1) was converted into the corresponding 1,3-dimino-1,3-dihydroisoindole derivative (3a–c) by reaction with sodium methoxide and ammonia in methanol (yield 83%). Sodium salts, complexed in the crown ethers of 3a–c, were removed by treatment with an ion exchange resin. Reaction of 3a–c with SiC14 in quinoline at elevated temperatures (130 °C) produced the phthalocyaninato dichlorosilanes 4a–c. These dichloro compounds are extremely air- and moisture-sensitive. Hydrolysis is rapid if the solvent is not rigorously anhydrous or when a sample is kept open to the air. Compounds 4a–c were readily hydrolyzed by water to give the dihydroxysilanes 5a–c (30% yield from the isoindole derivative). Polycondensation of 5a–c was induced by heating in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ethers is destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.

**NMR Spectroscopy.** The 1H NMR spectra of the dihydroxysilanes 5a–c are similar to those of their free base derivatives. The proton spectrum of 5c (CD3OD, 200 MHz) is presented in Figure 2A. Signals for the crown ether protons appear between 3.7 and 4.8 ppm, while the aromatic protons afford a broad singlet at 9.4 ppm. The Si–OH protons are present in the TMS region at 0 ppm (not shown). The pattern of the crown ether moieties are destroyed. Calcium chloride, complexed to the polymers, was removed by repeated sonication with water. Polycondensation of 5a–c in quinoline without the catalyst, resulted in high molecular weight polymers as well, but much longer reaction times were required (~350 h). Under the reaction conditions employed, the 15-crown-5 derivative 5a gave higher molecular weight polysiloxanes than the 18-crown-6 5b and the 21-crown-7 5c derivatives (vide infra). The rate of polycondensation apparently depends on the size of the crown ether ring. Compounds 1a–c were obtained as dark blue/black powders which were stable up to 280 °C but which decomposed at higher temperatures.
Phthalocyaninato Polysiloxanes

The 13C NMR (CD3OD) spectrum of 5c is given in Figure 2B. It shows four different aromatic carbon atoms and the carbon atoms of the crown ether rings. This spectrum is the result of an attached proton test (APT) experiment, which was used to assign the signals. In this APT experiment, carbon atoms of CH groups provide negative signals and the signal at 108 ppm can therefore be attributed to carbon atoms C3 and C3. The crown ether signals appear at 72 ppm.2,10

The atomic C3 and C3, atoms C3, and C3, of the Pc macrocycle have signals at 151 and 155 ppm, respectively.2,10 Assignment was aided by measurement of a Pc (with dodecyloxy substituents) that had been enriched with 13C at Cl and C1.1 The remaining signal at 132 ppm is ascribed to C2, C2.

The 13C CPMAS spectra of 5c (not shown) were complicated by spinning side bands and chemical shift data were extracted from several spectra recorded at varying spinning frequencies. As can be seen from Table I, the 13C CPMAS spectra show close analogies to the 13C solution NMR spectra. In the CPMAS spectra, C1, C2, and C3 are almost coincident.

The 1H NMR and 13C NMR spectra of oligomeric 5c (m = 3, 4) are shown in Figure 2C.D. The 13C spectrum is analogous to that of the monomer, though all signals, except that of C3, C3, are split into four and are shifted to higher field. The reason for these phenomena could be that the phthalocyaninato macrocycles are arranged in staggered positions (Φ ~ 45°). In these positions the carbon pairs C1, C1, C2, C2, C3, C3, and C4, C4 become magnetically inequivalent.2,10 The oligomers are thus expected to give a spectral pattern that is more complex than the D4h MPc monomers. The 1H NMR spectrum of monomeric 5c changes dramatically when it is polymerized (Figure 2A,C). The broad aromatic singlet at 9.4 ppm changes into a very complex pattern of sharp, upfield-shifted signals. The large number of these signals can be explained by the inequivalence of all aromatic protons in the trimer and tetramer. Kenney and co-workers, working with dimeric, trimeric, and tetramer SiPc compounds,2,10 observed a similar increasing upfield shift of the aromatic protons with increasing oligomer length, and they found that signals of the inner protons in the stack are shifted more upfield than those of the outer protons due to the shielding effect of the Pc macrocycles.7

In our spectra of 5c we find that the axially coordinated OH groups Si-0-Si-OH. From these spectra (with poor resolution) we were only able to make a rough estimate of the chain lengths of the polymer; the numbers yielded are similar to those obtained by IR spectroscopy (see below).

UV/Vis Spectroscopy. The electronic absorption spectra of monomers 5a and their polycondensation products are given in Figure 3. Monomers 5 show a Q band with maximum at 678 nm and two weaker bands at 650 and 612 nm. During the condensation process of monomeric 5 to the polycondensation products the degree of conversion can be estimated by following the changes of the bands in the absorption spectra; the monomeric band at 578 nm loses intensity and simultaneously there appears a new band at 640 nm that can be ascribed to the dimeric species of 5.3,4 After 3 h the band at 678 nm had almost disappeared. Prolonged reaction times resulted in the appearance of a new band at 634 nm which we attribute to a trimeric species. For 5a and 5b further condensation resulted in a precipitate of higher oligomers that is not soluble in organic solvents. Only for 5c did we obtain a soluble oligomer (m > 3), and this gave a broad maximum between 610 and 560 nm.3,6 Apparently, the solubility of these oligomeric compounds increases with increasing size of their crown ether subunits.

The polycondensation process can be followed by TLC as well (A1203, eluent CHCl3/MeOH 1:1 (v/v)).

Figure 3. Electronic absorption spectra of monomers 5a, 5b, 5c, and oligomers (d) of 5.


species can be separated over Sephadex LH 60.

Infrared Spectroscopy. The polycondensation process of 5 to 1 can be readily followed by IR spectroscopy. The spectra of compounds 5 differ considerably from those of the unsubstituted silicon phthalocyanines. Unfortunately, most Pc skeleton and Si–OH vibrations, which are often used to estimate the chain length by end group analysis, are masked by the vibrations of the crown ether rings. In our condensed compounds the antisymmetric Si–O–Si stretch vibration, which is visible in unsubstituted phthalocyaninato polysiloxanes between 1000 and 1130 cm⁻¹, is dominated by the aliphatic ether bands. This IR method is therefore not expected to give accurate results for the degree of polymerization of our condensed materials.

Figure 4 shows the IR spectra of monomer 5a and its polymer 1a. The intensity of the absorption band at 870 cm⁻¹, ascribed to the Si–OH stretch vibration, decreases during the polycondensation process and, simultaneously, a complex band between 900 and 840 cm⁻¹ appears. The weak absorption at 820 cm⁻¹, assigned to the antisymmetric O–Si–O stretch vibration, and the bands at 940 and 980 cm⁻¹ disappear as well. Other notable changes upon polymerization are the increase in intensity of the bands at 1520 cm⁻¹; the intensity of bands at 1480, 1420, 1350, 1290, and 1210 cm⁻¹ remain constant. An indication of the chain length of polymers 5b–c was obtained with use of relative intensities and intensity changes of the IR bands mentioned. The IR spectra of isolated mono-, di-, and trimeric derivatives of 5 were used as references, and for these derivatives the ratio of the absorbances were plotted versus molecular weight. The molecular weights of the polymers were subsequently derived by linear extrapolation. This method can only be applied to polymers with relatively short chain lengths.

Alkali-Metal Binding. The association constants, Kᵣ, and the free energies of complexation, ΔGᵣ, of 5b and 5c and their corresponding soluble oligomers (m = 3–5) with various alkali-metal ions were determined by the picrate extraction method developed by Cram. This method is not applicable to 5a and its oligomers, because not only was 5a too soluble in water but also there was strong emulsion formation on addition of picrate. In Table II are presented the association constants (Kᵣ) which were calculated assuming a 1:1 complex formation between crowns and cations. In Figure 5 the ΔGᵣ values of the various complexes (calculated from Kᵣ) are presented graphically.

For all alkali-metal ions except Cs⁺, compound 5b shows a binding profile similar to that of its copper derivative. Compound 5b is a good complexing agent for K⁺, because the 18-crown-6 ethers have a diameter that matches the diameter of this ion. The Rb⁺ and Cs⁺ ions are too large to be encapsulated in these crown ethers and they may, therefore, induce dimer formation of the phthalocyanines as was observed for the copper derivative of 5b. UV/vis spectra, however, show that such dimer formation does not occur, probably because of steric hindrance by the axial OH groups. We can not exclude, however, the formation of a non-cofacial dimer.

Oligomeric 5c like 5b show a somewhat more selective binding profile toward alkali-metal ions than the monomer. The binding profile of 5c is similar to that of its copper derivative and the 21-crown-7 rings prefer the larger Rb⁺ and Cs⁺ ions over the smaller ions. For oligomeric 5b and 5c a further increase in selectivity is to be expected for the higher molecular weight polymers. The reason that the oligomers show more selective binding than the monomers may be related to a difference in
Phthalocyaninato Polysiloxanes

Table II. Association Constants of Alkali Metal Picrate Salt-Phthalocyanine Complexes

<table>
<thead>
<tr>
<th>host</th>
<th>cation of guest</th>
<th>$K_a$, $10^{-4}$ M$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>5b</td>
<td>Li$^+$</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
<td>Na$^+$</td>
<td>16.3</td>
</tr>
<tr>
<td></td>
<td>K$^+$</td>
<td>367</td>
</tr>
<tr>
<td></td>
<td>Rb$^+$</td>
<td>104</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>27.2</td>
</tr>
<tr>
<td>1b$^+$</td>
<td>Li$^+$</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>Na$^+$</td>
<td>10.8</td>
</tr>
<tr>
<td></td>
<td>K$^+$</td>
<td>481</td>
</tr>
<tr>
<td></td>
<td>Rb$^+$</td>
<td>70.8</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>104.9</td>
</tr>
<tr>
<td>5c</td>
<td>Li$^+$</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Na$^+$</td>
<td>19.7</td>
</tr>
<tr>
<td></td>
<td>K$^+$</td>
<td>88.7</td>
</tr>
<tr>
<td></td>
<td>Rb$^+$</td>
<td>292.9</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>329.9</td>
</tr>
<tr>
<td>1c$^+$</td>
<td>Li$^+$</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>Na$^+$</td>
<td>7.9</td>
</tr>
<tr>
<td></td>
<td>K$^+$</td>
<td>39.7</td>
</tr>
<tr>
<td></td>
<td>Rb$^+$</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>315</td>
</tr>
</tbody>
</table>

$^4$Trimer. $^b m = 4-5.$

Figure 6. Saturation levels of polymers 1a–c for Na$^+$.

Table III. Electronic Conductivities ($\sigma$) and Conduction Activation Energies ($E_a$)

<table>
<thead>
<tr>
<th>compound</th>
<th>$\sigma$, S m$^{-1}$</th>
<th>$E_a$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a–c</td>
<td>$&lt;10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>1a</td>
<td>$7 \times 10^{-2}$</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>($25 \degree C$)</td>
<td></td>
</tr>
<tr>
<td>1b</td>
<td>$3 \times 10^{-2}$</td>
<td>0.29</td>
</tr>
<tr>
<td></td>
<td>($25 \degree C$)</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>$1 \times 10^{-8}$</td>
<td>0.38</td>
</tr>
<tr>
<td></td>
<td>($100 \degree C$)</td>
<td></td>
</tr>
</tbody>
</table>

conplexed cations. This is supported by results from similar measurements on rigid poly(isocyanides) with pendant crown ether moieties. For these polymers also a cation to crown ether ratio lower than 1 was found even for ions with diameters that match the size of the crown ethers.

**Electronic Conductivity.** The electrical properties of phthalocyanines 5 and 1 were studied in the solid state by ac impedance spectroscopy. All spectra revealed one semicircular arc, indicating that the materials behave as a dielectric with a minor contribution of electronic conductivity. Seebeck measurements showed that compounds 1a-c are $p$-type electronic conductors. The impedance spectra of 1a-c could be fitted to the equivalent circuit $R_Q$, where $p$ stands for parallel, $R_Q$ represents the bulk electronic resistance, and $Q$ is the constant phase element (CPE), with an impedance $Z = (KQ)^{1/2}$. For all samples the CPE has a value for $\alpha$ of about 0.9, and therefore, the character of a capacitance. Compounds 5a–c and their dimeric and trimeric derivatives could not be measured accurately by ac impedance spectroscopy, because these compounds had bulk resistances that were too high.

The electronic conductivity, $\sigma$, and the conductivity activation energy, $E_a$, calculated from the ln $\sigma$ vs $1/T$ plots are presented in Table III. As can be seen from this table, the electronic conductivity increases upon polymerization of the monomeric compounds 5. The higher molecular weight polymers 1a and 1b show larger values for $\sigma$ than the lower molecular weight polymer 1c. The explanation for this is that charge transport will be facilitated in longer chains of Pc units because the number of intermolecular barriers that the charge carriers have to cross, is reduced. The conduction activation energies of 1a–c differ only slightly in magnitude. The $E_a$ values may be dependent on the intrinsic charge formation activation energy, $\Delta G^*$, on the activation energy of intramolecular charge migration, $\Delta G_m$, and on the activation energy of intermolecular charge crossing, $\Delta G_m$. In our case we are inclined to believe that the $E_a$ values are to be correlated with migration only. Previously, we showed that the sum of $\Delta G_1$ and $\Delta G_m$ has values over 1 eV. $\Delta G_m$ is dependent on the distance between the stacks, which in turn is determined by the size of the crown ether rings. Indeed, Table III shows that the $E_a$ value decreases in the series 1c $>$ 1b $>$ 1a.

**Ionic Conductivity.** The occurrence of ionic conduction in compounds 1a–c was tested by using these polymers as a membrane in the concentration cell Na-amalgam(1)Na picrate (30 mol %)-polymer complex[Hg(II)]. The open-circuit voltage (OCV) of this cell was measured at various times intervals of utilization in the discharge mode at 80 °C. For the 15-crown-5 polysiloxane 1a and the 18-crown-6 polysiloxane 1b, no decrease of the OCV was observed during a period of 72 h. This result indicates that compounds 1a and 1b are not able to transport sodium ions, the rationale being the strong complexation of sodium ions by these polymers. For the 21-crown-7 polymer 1c, the OCV decreased with time from a starting value of approximately 1.5 V. This initial value is not well defined because $\Delta G_m(II) = 0$ at $t = 0$. After 24 h, the OCV was 1.28 V and in the following period of 95 h, the OCV decreased to 0.73 V. Subsequent replacement of the Na-amalgam(I) electrode for Hg resulted in an OCV of ~0.22 V. These data reveal that the 21-crown-7 polymer 1c does conduct sodium ions. From the open-circuit-voltage (OCV), load-circuit-voltages (LCV), and load-current ($I_L$) data for the concentration cell in the discharge mode, a discharge curve LCV/OCV vs $I_L$ was constructed (Figure 7). From the linear part of this


plot, an $R_0$ of $1.3 \times 10^4 \ \Omega$ was calculated. This $R_0$ value is very high compared to that found for K$^+$ transport through a polymer of poly(isocyanide) containing 18-crown-6 rings. An appreciable cation transport is only expected for ions having low free energies of complexation, i.e., for ions having an ionic diameter small compared to that of the crown ether, and this is the case of sodium complexed in the 21-crown-7 polymer. However, the $R_0$ value indicates that transport of sodium is very low. This feature can be explained by the structural difference of the two polymers. In the poly(isocyanide) the crown ether rings are stacked on top of each other and form extended channels whereas in 1e the Pc units have a staggered arrangement. This latter arrangement could result in distortion or even the complete absence of a channel structure, and therefore, ion transport may be hindered or even prevented. Better results for cationic conductivity are to be expected for Pc polymers containing crown ether rings larger than 21-crown-7. The present data reveal that the crown ether rings and their size do play a distinctive role in cationic conductivity.

Experimental Section

Infrared spectra were measured on Perkin-Elmer 283 and Perkin-Elmer 1800 instruments. UV/vis spectra were recorded on a Perkin-Elmer 555 spectrometer. Solution $^1$H NMR and $^{13}$C NMR spectra were recorded on Varian EM 360, Bruker WP 200, and Bruker AM 400 instruments. Tetramethylsilane was used as the internal standard. $^1$H, $^13$C, and $^{15}$N spectra were recorded on Bruker WP 2000 spectrometers. Abbreviations used are as follows: singlet, d = doublet, t = triplet, q = quartet, b = broad, and sh = shoulder. FAB mass spectra were recorded on a VG ZAB 2F spectrometer. Elemental analyses were performed by the Elemental Analytical Section of the Institute for Applied Chemistry, TNO, Zeist, The Netherlands.

Seebeck measurements were performed as described previously. Impedance spectra were recorded in the temperature range of 250–250 °C and analyzed as described earlier.

Ionic conductivity experiments were performed using concentration cells with a sodium picrate-lc complex as membrane; Figure 1 compared to that of the crown ether, and this is the case of complexation, i.e., for ions having an ionic diameter small compared to that of the solution turned from colorless to green. The solution was heated for 4 h at 95 °C while the addition of ammonia was continued and then cooled to room temperature. A white precipitate of sodium methoxide was filtered off, and the filtrate was evaporated to dryness. The remaining solid was extracted with dry chloroform. Remaining sodium salts, complexed in the crown ethers, were removed with an ion-exchange resin (Amberlyst 15). After recrystallization in dry chloroform, 1.3 g of a light green solid was obtained: yield 83%; mp 108 °C; FAB MS m/z 336 (M + H)$^+$; IR (KBr) 3400 (OH), 2910–2885 (CH$_3$), 1100–1060 (COC) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) $\delta$ 3.6–4.4 (m, 16 H, CH$_3$O), 7.3 (s, 2 H, ArH), 7.7–7.8 (br s, 3 H, NH) ppm.

Dihydroxy[4,5,4',5'4''.5''-tetrakis(1,7,10,13-pentaazadecamethine)phthalocyaninato]silicon(IV) (5a). To a mixture of 1.33 g (3.99 mmol) of 3a in 10 mL of quinoline (freshly distilled from barium oxide) was added, under an atmosphere of N$_2$, 2 mL (17 mmol) of KHCO$_3$. The temperature of the mixture was quickly brought to 100 °C and held there for 12 h. At the end of this time the reaction mixture was brown. After cooling, an excess of SiCl$_4$ was distilled off, 20 mL of water was added, and the mixture was stirred for 4 h. In this period the color changed from brown to green. A precipitate was filtered off, and the clear filtrate was added dropwise to ethyl acetate. The green precipitate of the product which formed was filtered off and washed with acetone. Recrystallization of 5a was performed by slowly evaporating ether into a solution of the product in pyridine. The solid was filtered off, dried, and further purified by gel permeation chromatography (Sephadex LH-60, eluent CHCl$_3$/MeOH 1:1). An amount of 395 mg of a dark green solid was obtained: yield 30%; TGA 310 °C; FAB MS m/z 1335 (M + H)$^+$; IR (KBr) 3400 (OH), 2910–2885 (CH$_3$), 1100–1060 (COC) cm$^{-1}$; $^1$H NMR (CDCl$_3$, 60 MHz) $\delta$ 0.0 (2 H, CH$_2$OH), 2.0–2.6 (br s, 8 H, ArH), 4.0–4.5 (br s, 3 H, SiOH), 3.3–4.5 (m, 64 H, CH$_2$O), 7.3–7.7 (s, 2 H, ArH), 8.0–8.4 (br s, 8 H, ArH); UV/vis (CHCl$_3$) $\lambda_{max}$ 560 (5.3), 650 (4.6), 612 (4.6), 444 (sh), 417 (4.6), 359 (5.0) nm. Anal. Calcd for C$_{60}$H$_{72}$SiN$_4$: C, 58.3; H, 5.5; N, 8.5. Found: C, 59.6; H, 5.7; N, 8.1.

Polycondensation of 5a To Give 1a. A solution of 0.25 g (0.19 mmol) of 5a in 20 mL of quinoline (freshly distilled) from barium oxide and a catalytic amount of CaCl$_2$ was heated under an atmosphere of N$_2$ at 200 °C for 1 h. The resulting blue/black powder was isolated by filtration and washed with using a sonicator at 50 °C with subsequently H$_2$O (3X), DMF, pyridine, and CHCl$_3$. The product was dried over P$_2$O$_5$ under reduced pressure: yield 0.2 g (80%); TGA 280 °C dec. Anal. Calcd for C$_{60}$H$_{72}$SiN$_4$: C, 58.3; H, 5.5; N, 8.5. Found: C, 59.6; H, 5.7; N, 8.1. Different samples gave varying results with a maximum variation of about 1.5% for all elements). (4a: UV/vis (pyridine) $\lambda_{max}$ 702, 680–664 (sh), 630 (sh), 642, 444, 417 (sh), 372 nm.)

Polycondensation of 5b To Give 1b. Compound 1b was synthesized as described for 3a: yield 74%; mp 95 °C dec; FAB MS m/z 380 (M + H)$^+$; IR (KBr) as for 3a; $^1$H NMR (CDCl$_3$) $\delta$ 3.6–4.4 (m, 20 H, CH$_3$O), 5.4 (s, 1 H, NH), 7.4 (s, 2 H, ArH), 7.6 (br s, 2 H, NH) ppm.

Dihydroxy[4,5,4',5'4''.5''-tetrakis(1,7,10,13-pentaazadecamethine)phthalocyaninato]silicon(IV) (5b). This compound was synthesized from 3b as described for 5a: yield 25%; TGA 310 °C dec; FAB MS m/z 151 (M + H)$^+$; UV/vis (CHCl$_3$) and IR (KBr) as for 5a; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 3.3–4.5 (m, 80 H, CH$_3$O), 9.4 (br s, 8 H, ArH) ppm. Anal. Calcd for C$_{60}$H$_{72}$SiN$_4$O$_2$: C, 57.2; H, 6.0; N, 7.5. Found: C, 56.5; H, 5.9; N, 7.5. (Different samples gave varying results with a maximum variation of about 1.5% for all elements). For other physical properties, see text.

1,3-Dimino-5,6-(1,4,7,10,13,16-hexaoxaheptadecamethine)-1,3-dihydroxidoindole (3b). This compound was synthesized from 2b as described for 3a: yield 74%; mp 95 °C dec; FAB MS m/z 380 (M + H)$^+$; IR (KBr) as for 3a; $^1$H NMR (CDCl$_3$) $\delta$ 3.6–4.4 (m, 20 H, CH$_3$O), 5.4 (s, 1 H, NH), 7.4 (s, 2 H, ArH), 7.6 (br s, 2 H, NH) ppm.

Dihydroxy[4,5,4',5'4''.5''-tetrakis(1,4,7,10,13,16-hexaoxaheptadecamethine)phthalocyaninato]silicon(IV) (5b). This compound was synthesized from 3b as described for 5a: yield 69%; TGA 280 °C dec. Anal. Calcd for C$_{60}$H$_{72}$SiN$_4$O$_2$: C, 57.9; H, 5.9; N, 7.5. Found: C, 58.4; H, 5.7; N, 8.1.

1,3-Dimino-5,6-(heptaoxanonadecamethine)-1,3-dihydroxidoindole (3c). This compound was synthesized from 2c as described for 3a: yield 56%; mp 102 °C dec; FAB MS m/z 424 (M + H)$^+$; IR (KBr) as for 3a; $^1$H NMR (CDCl$_3$) $\delta$ 3.6–4.4 (m, 24 H, CH$_3$O), 7.3 (s, 2 H, ArH), 7.4–7.8 (br s, 3 H, NH) ppm.

Dihydroxy[4,5,4',5'4''.5''-tetrakis(1,4,7,10,13,16,19-heptaoxanonadecamethine)phthalocyaninato]silicon(IV) (5e). This compound...
An Annulation Method for the Synthesis of Highly Substituted Polycyclic Aromatic and Heteroaromatic Compounds

Rick L. Danheiser, Ronald G. Brisbois, James J. Kowalczky, and Raymond F. Miller

Contribution from the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139. Received September 27, 1989

Abstract: A general strategy for the synthesis of highly substituted polycyclic aromatic and heteroaromatic compounds has been developed. The new aromatic annulation is achieved simply by the irradiation of a dichloroethane solution of an acetylene derivative and a vinyl or aryl diazo ketone. Mechanistically, the reaction proceeds via the photochemical Wolff rearrangement of the diazo ketone to generate an aryl- or vinylketene, followed by a cascade of three pericyclic reactions. A variety of substituted phenols, naphthalenes, benzo-furans, benzothiophenes, indoles, and carbazoles can be prepared by using the method. The application of the aromatic annulation to the total synthesis of the marine alkaloid hydrazelline demonstrates the synthetic utility of the method.

The invention of efficient methods for the synthesis of substituted aromatic compounds has commanded the interest of chemists since the time of the earliest synthetic organic investigations in the 19th century. Classical approaches to aromatic compounds exploited readily available benzene derivatives and relied heavily on electrophilic and nucleophilic substitution reactions. In recent years, directed metalation reactions have joined classical linear substitution strategies, especially when applied to the introduction of substituents onto preexisting aromatic rings. A second approach to highly substituted aromatic compounds involves the application of annulation methods: convergent strategies in which the aromatic system is assembled from acyclic precursors in a single step, with all (or most) substituents already in place. Annulation strategies enjoy several advantages over the more conventional routes. The intrinsic convergent nature of annulation strategies facilitates the efficient assembly of highly substituted aromatics that would require long, multistep routes using classical substitution methodology.