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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 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 the metal data is fair. The structureless absorption and emission bigamous. The longest wavelength absorption maxima at 153 K 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 between $1$, $2$, and $3$, respectively. The Franck–Condon energies similarly estimated from the emission spectra are 64, 66, and 72 kcal mol$^{-1}$.

Phthalocyaninato Polysiloxanes Substituted with Crown Ether Moieties


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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 $10^{-2}$ 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.\(^1\)\(^,\)\(^6\)\(^,\)\(^7\) Recently, we reported that these molecules can be aggregated by addition of alkali-metal salts, which become complexed to the crown ether rings.\(^5\)\(^,\)\(^6\) 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,\(^3\) involves the polycrystallization 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$^-$ 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.

Substituted and unsubstituted phthalocyaninato polysiloxanes, [PcSiO]$^{10}$, have been studied by many scientists.\(^3\) Unsubstituted...
vacuum, or in 1-chloronaphthalene at reflux. 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 Pc distance of 3.33 Å and a staggered arrangement of the Pc macrocycles (staggering angle = 39°). Polycrystalline samples are reported to exhibit a room temperature conductivity of \( 10^{-4} - 10^{-3} \) S/m.

Peripheral substitution on 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 Pcs 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)methyl-substituted phthalocyaninato polysiloxanes were estimated to be between 10 and 25 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 Pc spacing of 3.4 Å and a Si-O-Si bond angle of 180°.

This paper deals with the synthesis of phthalocyaninato silanols containing 15-crown-5, 18-crown-6, and 21-crown-7 rings and of their polycondensation products prepared by a metal salt catalyzed polycondensation. Spectroscopic characterization, alkali-metal binding data, and electrical properties of the prepared compounds are reported.
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 SiCl4 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 dihydroxy silane compounds 5a-c (30% yield from the isoindole derivative). Polycondensation of 5a-c was induced by heating in quinoline at 200 °C in the presence of CaCl2 as catalyst. Reaction times of 2–5 h gave a mixture of dimeric and trimeric compounds which are soluble in organic solvents. These polymers are soluble in concentrated sulfuric acid, but under these conditions 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 dihydroxy silanes 5a-c are similar to those of their free base derivatives.6a 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

Phthalocyaninato Polysiloxanes

...ether signals is complex, due to the chemically inequivalent ether fragments.

The $^{13}$C NMR (CD$_2$OD) 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 together with literature data to assign the signals. In this APT experiment, carbon atoms of CH$_2$ groups provide negative signals and the signal at 108 ppm can therefore be attributed to carbon atoms C$_3$ and C$_3'$. The crown ether signals appear at 72 ppm. The atoms C$_1$, C$_1'$, C$_2$, and C$_2'$ of the Pc macrocycle have signals at 151 and 155 ppm, respectively. Assignment was aided by measurement of a Pc (with docecoxy substituents) that had been enriched with $^{13}$C at C$_1$ and C$_1'$. The remaining signal at 132 ppm is ascribed to C$_3$, C$_3'$.

The $^{13}$C 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 $^{13}$C CPMAS spectra show close analogies to the $^{13}$C solution NMR spectra. In the CPMAS spectra, C$_1$, C$_1'$, and C$_3$, C$_3'$ are almost coincident.

The $^1$H NMR and $^{13}$C NMR spectra of oligomeric 5c ($m = 3$, 4) are shown in Figure 2C,D. The $^{13}$C spectrum is analogous to that of the monomer, though all signals, except that of C$_3$, C$_3'$, are split into four and are shifted to higher field. The reason for these phenomena could be that the phthalocyanine macrocycles are arranged in staggered positions ($\phi \approx 45^\circ$). In these positions the carbon pairs C$_1$, C$_1'$, C$_2$, C$_2'$, C$_3$, C$_3'$, and C$_4$, C$_4'$ become magnetically inequivalent. The oligomers are thus expected to give a spectral pattern that is more complex than the $D_{4h}$ Mpc monomers. The $^1$H 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 tetrameric SiPc compounds, 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 macrocycle.

The $^{13}$C CPMAS NMR spectra of polysiloxanes 5a-c and their polycondensation products are given in Figure 3. Monomers 5a show a Q band with maximum at 678 nm and two weaker bands at 650 and 612 nm. During the condensation process of monomeric 5a to the polycondensation products the degree of conversion can be estimated by following the changes of the bands in the absorption spectra; the monomer 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 5a. 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. 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. The absorbance at 366 nm is shown in Figure 3. The electronic absorption spectra of monomers 5 and their polycondensation products are given in Figure 3. Monomers 5a 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 monomer 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 5a. 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. Apparently, the solubility of these oligomeric compounds increases with increasing size of their crown ether subunits.

Figure 3. Electronic absorption spectra of monomers (a), dimeric (b), trimeric (c), and oligomeric (d) products of 5.

References:
(11) van der Pol, J.; Markies, B.; Nolte, R. J. M.; Drenth, W., to be published.
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 760 and 1610 cm⁻¹ and the disappearance of the band 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 1a–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. For samples prepared by heating for 70 h at 200 °C the degree of polymerization was calculated to be \( m = 14-18 \) for 1a, \( m = 10-15 \) for 1b, and \( m = 6-8 \) for 1c. These results reveal that the length of the polymers depends on the size of the substituent. The formation of relatively high molecular weight polymers is favored when the substituent is small.

**Alkali-Metal Binding.** The association constants, \( K_a \), and the free energies of complexation, \( \Delta G^o \), 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 \( (K_a) \) which were calculated assuming a 1:1 complex formation between crowns and cations. In Figure 5 the \( \Delta G^o \) values of the various complexes (calculated from \( K_a \) ) 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 noncofacial 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

**Figure 4.** Infrared spectra of 5a (A) and 1a (B).

**Figure 5.** Free energies of binding picrate salt to 5b (○) and of picrate salt to 1b \( (m = 3) \) (△) (A). Free energies of binding of picrate salt to 5c (●) and of picrate salt to oligomer 1c \( (m = 4-5) \) (△) (B).
conformation of the crown ether rings in the two systems. An isolated crown ether has a folded conformation, and this conformation becomes more planar upon binding a cation. Because of the packed structure of the oligomers, the crown ethers are already forced into a more planar conformation. Upon complexing an ion with a small diameter, the most favorable conformation for binding cannot be attained. This results in a lower $\Delta G^\circ$ value for the oligomers than for the free crown ether. Another aspect that may play a role in complexing ions in the oligomers is electrostatic repulsion. Preorganization of the crown ethers in the oligomers will facilitate complexation of $K^+$ to $1b$ and of $Rb^+$ and $Cs^+$ to $1c$. However, because of the packed structure of the oligomers, electrostatic repulsion between the complexed ions may prevent complete saturation of the crown ethers.

Information on the saturation level of cations in the phthalocyaninato polysiloxanes $1a-c$ was derived from extraction experiments on the solid polymers using varying amounts of aqueous sodium picrate solutions. The results obtained were corrected for adsorption of the picrate salts to solid samples. To this end similar experiments were performed with solid $H_Pc$. The results are presented in Figure 6. For both the 18-crown-6 and 21-crown-7 polymers, $1b$ and $1c$, a saturation level of 0.34 was measured. The maximum $(Na^+/complex)/(CE)$ ratio of 1.0 is not reached in our polymers because of the above-mentioned electrostatic repulsion between the complexed 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 $Z = (k(i\omega)^\mu)^{-1}$. For all samples the CPE has a value for $\mu$ of about 0.9, and has, 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, $E_\sigma$, 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 $E_\sigma$ values may be dependent on the intrinsic charge formation activation energy, $\Delta E_f$, on the activation energy of intramolecular charge migration, $\Delta E_m^\ast$, and on the activation energy of intermolecular charge crossing, $\Delta E_{inter}$. In our case we are inclined to believe that the $E_\sigma$ values are to be correlated with migration only. Previously, we showed that the sum of $\Delta E_f$ and $\Delta E_{inter}^\ast$ has values over 1 eV. $\Delta E_{inter}^\ast$ 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 $E_\sigma$ 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 time intervals of utilization in the discharge mode, a discharge curve LCV/OCV vs $t$. The initial value is not well defined because $\Delta E_f(II) = 0$ 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(1) 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

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

<table>
<thead>
<tr>
<th>Host</th>
<th>Cation of Guest</th>
<th>$K_a$, $10^{-2}$ 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>10.4</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</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>329</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>

$^a$Trimer. $h_m = 4-5.$

Table III. Electronic Conductivities ($\sigma$) and Conduction Activation Energies ($E_\sigma$) for the Polymers

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\sigma$, S m$^{-1}$</th>
<th>$E_\sigma$, eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>$5a-c$</td>
<td>$&lt;10^{-9}$</td>
<td></td>
</tr>
<tr>
<td>$1a$</td>
<td>$7 \times 10^{-2}$ (25°C)</td>
<td>0.23</td>
</tr>
<tr>
<td>$1b$</td>
<td>$3 \times 10^{-2}$ (25°C)</td>
<td>0.29</td>
</tr>
<tr>
<td>$1c$</td>
<td>$1 \times 10^{-4}$ (100°C)</td>
<td>0.38</td>
</tr>
</tbody>
</table>

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plot, an $R_{eq}$ of $1.3 \times 10^3 \, \Omega$ was calculated. This $R_{eq}$ value is very high compared to that found for K$^+$ transport through a polymer of poly(isocyanide) containing 18-crown-6 rings.12 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 found for sodium complexed in the 21-crown-7 polymer stacked $R_{dc}$ polymers.

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 a 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 400, and Bruker AM 400 instruments. Tetramethylsilane was used as the internal standard. $^1$Si, $^1$H, and $^{13}$C NMR spectra were recorded on Bruker AM 500 and Bruker EXP 300 spectrometers. Abbreviations used are as follows: $s$ = 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.

Impedance measurements were performed as described previously.16 Impedance spectra were recorded in the temperature range of 250-25°C and analyzed as described earlier.16

Ionic conductivity experiments were performed using concentration cells of the type Na-namalg(I)/Na nitrate (30 mol %)-HgI(II). In the discharge mode, the dc resistance $R_{eq}$ was determined from normalized load-circuit voltages (LCV/OCV) vs load-current densities ($i$), the relation between these parameters being

$$
\text{LCV} = \frac{R_{eq}}{\text{OCV}} (1 + \frac{kT}{q} \ln \frac{\alpha_{Na}(I)}{\alpha_{Na}(II)})
$$

where $R_{eq}$ represents the open-circuit voltage of the concentration cell. The OCV is governed by the Nernst expression

$$
\text{OCV} = \frac{kT}{q} \ln \frac{\alpha_{Na}(I)}{\alpha_{Na}(II)}
$$

OCV and LCV were recorded with a Teletie Airtronic TE 924 electron-timer.

The sodium amalgam was prepared by dissolving 57 mg of Na in 1 mL of Hg under an atmosphere of dry nitrogen. The mixture was subsequently heated at 300°C for 1 h. The polymer $^1$Na picrate complex was prepared as described under the Saturation Experiments section. The sample was washed with water and dried under vacuum.

4,5-Dicyano-15-crown-5 (2a), 4,5-dicyano-18-crown-6 (2b), and 4,5-dicyano-21-crown-7 (2c) were prepared as described previously.6a

1,3-Dimino-5,6-(1,4,7,10,13-pentaazadodecamethylene)-1,5-dihydroindolino (3a). Anhydrous ammonia was bubbled through a solution of 1.75 g (5.5 mmol) of 2a and 0.51 g (9.4 mmol) of sodium methoxide in 50 mL of absolute methanol at room temperature for 30 min during which time the color of the solution turned from colorless to green. The solution was heated for 6 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 dec; FAB MS $m/e$ 336 (M + H)+; IR (KBr) 3400 (NH), 3200 (NH), 2910-2870 (CH$_2$), 1630 (C-N), 1110-1040 (COC) cm$^{-1}$; $^1$H NMR (DMSO-d$_6$) 0.6-3.4 (m, 16 H, CH$_2$), 7.3 (2 s, 2 H, ArH), 7.7-8.2 (br s, 3 H, NH) ppm.

Dihydroxy(4,5,4',5',4'',5'':6,9,9',6',9':4',5',4'',5'':9,9',6',9':4,5,4',5',4'',5'')tetraakis(1,4,7,10,13-pentaazadodecachloro)benz[a]phthaloxyanilinocyclohexatrillicyclonitroso(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 $^1$H NMR (CDCl$_3$, 60 MHz) 0.0-6.0 (0 s, 2 H, SiOH), 3.3-4.5 (m, 64 H, CH$_2$), 8.0-8.5 (br s, 8 H, ArH); UV/vis (CHCl$_3$) $\lambda_{max}$ 678 (5.3), 650 (4.6), 612 (4.6), 446 (4.4), 417 (4.6), 359 (5.9) nm. Anal. Calcd for C$_{64}$H$_{74}$SiNB$_2$O$_{22}$: C, 57.56; H, 5.59; N, 8.39. Found: C, 58.8; H, 4.3; N, 9.1 (different samples gave varying results with a maximum variation of about 1.5% for all elements).

Polycondensation of 5a To Give 1a. A mixture 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 70 h. The resulting deep blue/black precipitate was isolated by filtration and washed with using a sonicator at 50°C with subsequently H$_2$O (3X), DMSO, pyridine, and CHCl$_3$. The precipitate was dried over P$_2$O$_5$ under reduced pressure: yield 0.8 g (80%); TGA 280°C dec. Anal. Calcd for C$_{64}$H$_{74}$SiNB$_2$O$_{22}$: C, 58.3; H, 5.5; N, 8.5. Found: C, 59.6; H, 4.3; N, 9.1. (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-bexaoxaheptadecamethylene)-1,3-dihydroindolino (3b). This compound was synthesized from 2a as described for 3a: yield 74%; mp 95°C dec; FAB MS $m/e$ 330 (M + H)+; IR (KBr) for as 3a; $^1$H NMR (CDCl$_3$) $\delta$ 3.6-4.4 (m, 20 H, CH$_2$), 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'':6,9,9',6',9':4',5',4'',5'':9,9',6',9':4,5,4',5',4'',5'')tetraakis(1,4,7,10,13,16-bexaoxaheptadecachloro)benz[a]phthaloxyanilinocyclohexatrillicyclonitroso(5b). This compound was synthesized from 3b as described for 5a: yield 25%; TGA 310°C dec; FAB MS $m/e$ 1511 (M + H)+; UV/vis (CHCl$_3$) and IR (KBr) for as 3a; $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 3.3-4.5 (m, 80 H, CH$_2$), 9.4 (br s, 8 H, ArH) ppm. Anal. Calcd for C$_{64}$H$_{74}$SiNB$_2$O$_{22}$: C, 57.21; H, 6.00; N, 7.41. Found: C, 56.2; H, 5.9; N, 7.5 (different samples gave varying results with a maximum variation of about 1.5% for all elements).

Polycondensation of 5b To Give 1b. Compound 1b was synthesized from 5b as described for 1a: yield 69%; TGA 280°C dec. Anal. Calcd for C$_{64}$H$_{74}$SiNB$_2$O$_{22}$: C, 57.89; H, 5.95; N, 7.50. Found: C, 58.4; H, 5.7; N, 8.1.

1,3-Dimino-5,6-(heptaoxasqualenocyanine)-1,3-dihydroindolino (3c). This compound was synthesized from 2c as described for 3a: yield 56%; mp 102°C dec; FAB MS $m/e$ 424 (M + H)+; IR (KBr) as for 3a; $^1$H NMR (CDCl$_3$) $\delta$ 3.6-4.4 (m, 24 H, CH$_2$), 7.3 (2 s, 2 H, ArH), 7.4-7.8 (br s, 3 H, NH) ppm.

Dihydroxy(4,5,4',5',4'',5'':6,9,9',6',9':4',5',4'',5'':9,9',6',9':4,5,4',5',4'',5'')tetraakis(1,4,7,10,13,16,19-heptaoxasqualenocyanine)phthaloxyanilinocyclohexatrillicyclonitroso(5e) (5e). This compound...
was synthesized from 3c, as described for 5a: yield 32%; TGA 350 °C dec. UV/vis and IR (KBr) as for 5a; 'H NMR (CDCl₃) δ 3.7-4.5 (m, 96 H, CH₂O), 9.4 (br s, 8 H, ArH) ppm. Anal. Calcd for C₅₉H₆₀N₂O₂Si: C, 58.69; H, 6.02; N, 6.37. Found: C, 57.9; H, 6.2; N, 6.5 (different samples gave varying results with a maximum variation of about 1.5% for all elements).

Polycondensation of 5c To Give 1c. This compound was synthesized from 5c as described for 1a: yield 71%; TGA 285 °C dec. Anal. Calcd for C₅₉H₅₀N₂O₂Si: C, 59.30; H, 6.02; N, 6.43. Found: C, 60.4; H, 6.2; N, 6.3 (different samples gave varying results with a maximum variation of about 1.5% for all elements). Dimeric, Trimeric, and Oligomeric Products of 5a- c. Soluble dimeric and trimeric compounds of 5a- c were obtained by heating the monomers in freshly distilled quinoline at 200 °C with a catalytic amount of CaCl₂ under an atmosphere of N₂, for 2 and 5 h, respectively. The reaction mixture was filtered, and the solid product was obtained as a black precipitate by slowly evaporating ether into the reaction mixture. The solid was filtered off, dissolved in chloroform, and washed with water. The products were separated by gel permeation chromatography (Sephadex LH 60, eluent CHCl₃/MeOH 1:1). Their molecular weights were estimated by 'H NMR by using the integral ratio ArH/SiOH. Soluble oligomeric 5c was prepared in a similar way but with a reaction time of 30 h.

Determination of Kₜ and ΔG° Values. The Kₜ values were determined by the picrate extraction technique from H₂O into CHCl₃ at 25 °C as described in the literature. The ΔG° values were calculated from the Kₜ values by using the expression ΔG° = -RT ln Kₜ.

**Saturation Experiments.** The complex stoichiometries of Na⁺ in compounds 1a-c were determined by shaking the powdered solid polymers (~4 mg) with picrate solutions (10⁻⁶ M) for 7 h at 25 °C with a Griffin flask shaker. From the decrease of picrate concentrations, measured spectrophotometrically, the complexed cation to crown ether ratio was determined by plotting the molar ratio of the complexed species (Na⁺amph) to host (CE) vs the molar ratio of the total amount of sodium present (Na⁺tot) and host (CE). Solid H₂Pc was used as a reference compound to measure the adsorption of picrate salts to solid material.

**Acknowledgment.** We thank Prof. J. H. van der Maas for recording and discussing the infrared spectra, Prof. C. Versluis for recording the FAB Mass spectra, Mrs. G. Nagtegaal, and Mr. A. Kentgens for helping recording and discussing the CPMAS spectra, and Mr. A. Swolfs for running the -400-MHz NMR spectra. Part of this work was supported by the Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Foundation for Scientific Research (NWO).

**Registry No.** 1a (homopolymer), 118443-49-5; 1b (homopolymer), 125541-37-9; 1c (homopolymer), 125541-39-1; 2a, 110682-73-0; 2b, 108695-56-3; 2c, 108695-57-4; 3a, 116285-46-2; 3b, 125541-32-4; 3c, 125541-33-5; 5a, 11342-88-8; 5b, 125541-41-5; 5c, 125541-42-6; 1SIC₄, 10026-04-7; 1Li⁺, 7439-93-2; 1Na⁺, 7440-23-5; 1K⁺, 7440-09-7; 1Rb⁺, 7440-17-7; 1Ca⁺, 7440-46-2; ammonia, 7664-61-7.

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**An Annulation Method for the Synthesis of Highly Substituted Polycyclic Aromatic and Heteroaromatic Compounds**

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**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 vinyl-alkylidene, followed by a cascade of three pericyclic reactions. A variety of substituted phenols, naphthalenes, benzofurans, 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 hydellazolene 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 metathesis reactions have joined the classical substitution methods as another vehicle for 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 classical linear substitution strategies, especially when applied to the preparation of highly substituted target molecules. For example, annulation routes frequently avoid the regiochemical ambiguities associated with aromatic substitution reactions and provide access to substitution patterns that cannot be obtained via 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.

Particularly noteworthy aromatic annulations have been developed recently include methods based on Diels-Alder chemistry, carbonyl condensation reactions, and transition-metal-mediated processes. Prominent among the last class of reactions are the cobalt-mediated [2 + 2 + 2] acetylene cycloadditions investigated by Vollhardt and the Dötz reaction of Fischer carbene complexes. We have recently shown that addition of vinylketenes...