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 $30\text{86}$ of 90° double bond twists. The calculated energy difference of $30\text{86}$ of 90° double bond twists. The calculated energy difference gives a distinct global minimum for a twisted structure starting from either cis- or trans-stilbene.

**Outlook.** The simple extension of the conjugated $\pi$-system of stilbene to a $p$-styrlylstitbene changes the mechanism for the photoinduced $Z/E$ isomerization from diabatic to mainly adiabatic processes. This together with previous findings by us and others of adiabatic singlet and triplet $Z/E$ photoisomerizations encourage us to try to explore the scope and limitations as well as applications of this conceptually new photoreaction in molecules with extended linear or cyclic $\pi$-systems.

**Acknowledgment.** Financial support from the Swedish Natural Science Research Council and the Swedish Board of Technical Development is gratefully acknowledged. We also thank Prof. K. Mullen, Mainz, for discussions and a sample of 3,5-di-tert-butylbenzyltriphenylphosphonium bromide.

### 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 $10^{-7}$ S/m. The polymer substituted with 21-crown-7 rings conducts sodium ions.

Phthalocyanines (Pcs) substituted with crown ether rings are currently receiving great interest. Recently, we reported that these molecules can be aggregated by addition of alkali-metal salts, which become complexed to the crown ether rings. 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 phthalocyanines. This method, first described by Joyner and Kenney, involves the polycondensation of a phthalocyaninato dihydroxysilane for 1–12 h at 440 °C under solid state conditions in the presence of alkali-metal salts. 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.

**Table I.** $^{13}$C Chemical Shifts of Sc in Solution and in the Solid State

<table>
<thead>
<tr>
<th></th>
<th>C$_1$C$_1'$</th>
<th>C$_2$C$_2'$</th>
<th>C$_3$C$_3'$</th>
<th>C$_4$C$_4'$</th>
<th>crown ether</th>
</tr>
</thead>
<tbody>
<tr>
<td>solution$^a$</td>
<td>151.3</td>
<td>155.0</td>
<td>132.3</td>
<td>108.1</td>
<td>72.4</td>
</tr>
<tr>
<td>solid state</td>
<td>151.8</td>
<td>151.0</td>
<td>129.5</td>
<td>102.5</td>
<td>70.9</td>
</tr>
</tbody>
</table>

$^a$In ppm relative to tetramethylsilane. $^b$Solvent CD$_3$OD.

Polysiloxanes are formed by the uncatalyzed polycondensation of phthalocyaninato dihydroxysilanes for 1–12 h at 440 °C under solid state conditions in the presence of alkali-metal salts. 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.

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$^3$University of Nijmegen.

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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 $\approx 39^\circ$). 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 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(dodecyloxymethyl)-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(dodecyloxy)-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.

Figure 1. Linear chain of "crowned" phthalocyanines.

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Results and Discussion

**Synthesis.** 4,5-Dicyanobenzocrown 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 dihydroxysilane 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. Prolonged heating (~70 h) resulted in the formation of higher weight polymers (yield 70%) which are insoluble in common 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 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

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Figure 2. NMR spectra of 5c and of its oligomer (n = 3–4) in solution: (A) 200 MHz ¹H NMR (CD₃OD) spectrum of 5c, (B) 200 MHz ¹C NMR (CD₃OD) spectrum of 5c, (C) 400 MHz ¹H NMR (CDCl₃) spectrum of oligomeric 5c, (D) 400 MHz ¹C NMR (CDCl₃) spectrum of oligomeric 5c. Signals marked X are due to solvent.

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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 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 C$_3$ and C$_4$. The crown ether signals appear at 72 ppm.$^{5,10}$ The atoms C$_3$ and C$_4$ of the Pc macrocycle have signals at 151 and 155 ppm, respectively.$^{7-10}$ Assignment was aided by measurement of a Pc (with dodecy substituents) that had been enriched with $^{13}$C at C$_1$ and C$_4$.$^{11}$ The remaining signal at 132 ppm is ascribed to C$_2$.

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$_1$ and C$_4$ 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$_3$, 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.$^{9-15}$ In these positions the carbon pairs C$_3$ and C$_4$, C$_3$ and C$_4$, become magnetically inequivalent.$^{7-9}$ The oligomers are thus expected to give a spectral pattern that is more complex than the $^{13}$C NMR spectra. In the CPMAS spectra of monomeric and dimeric 5c, the signals are broad. Attempts to separate spinning side bands from the isotropic chemical shifts failed so far. An increase in temperature did not result in any appreciable change of the spectra.

The $^{13}$C CPMAS NMR spectrum of 5c gave, as expected, one intense singlet at -110.8 ppm whereas polymers 1 gave two signals, a large multiplet at -115.1 ppm and a small singlet at -138.5 ppm. The polymer signals come from silicon in two very different environments, namely in Si-O-Si-O-Si fragments and in the end groups Si-O-Si-OF. 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 monomer 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 678 nm loses intensity and simultaneously there appears a new band at 640 nm that can be ascribed to the dimeric species of 5.$^{3b,4}$ 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 650 nm.$^{3e}$ 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 (Al$_2$O$_3$, eluent CHCl$_3$/MeOH 1:1 v/v). Monomeric and dimeric...
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 phthalocyaninate polysiloxanes between 1000 and 1130 cm\(^{-1}\), \(a\) 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, \(b\) 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, \(c\) 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 940 and 980 cm\(^{-1}\). Other notable changes upon polymerization are also seen in the bands at 1210 and 1290 cm\(^{-1}\), which are assigned to the antisymmetric 0-Si-0 stretch vibration, and the bands at 1420, 1350, 1480, and 1520 cm\(^{-1}\); the intensity of bands at 760 and 1610 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, \(\Delta G^\circ\), 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 \(\Delta G^\circ\) 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 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

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**References:**


**Figures:**

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) (A). Free energies of binding of picrate salt to 5c (●) and of picrate salt to oligomer 1c (m = 4-5) (A) (B).
Table II. Association Constants of Alkali Metal Picrate Salt–Phthalocyanine Complexes

<table>
<thead>
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<th>host</th>
<th>cation of guest</th>
<th>$K_a$, $10^{-3}$ M$^{-1}$</th>
</tr>
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<tr>
<td>1b</td>
<td>Li$^+$</td>
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<td></td>
<td>Na$^+$</td>
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<tr>
<td></td>
<td>K$^+$</td>
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<tr>
<td></td>
<td>Rb$^+$</td>
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<td></td>
<td>Cs$^+$</td>
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<td></td>
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<td></td>
<td>Cs$^+$</td>
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<td></td>
<td>K$^+$</td>
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<td></td>
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<td></td>
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<td></td>
<td>K$^+$</td>
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<tr>
<td></td>
<td>Rb$^+$</td>
<td>249</td>
</tr>
<tr>
<td></td>
<td>Cs$^+$</td>
<td>315</td>
</tr>
</tbody>
</table>

*Trimer. $n_m = 4-5.$

Figure 6. Saturation levels of polymers 1a–c for Na$^+$. The 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 $\Delta G^o$ 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 various 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 $H_2Pc$. 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$^+$) (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 for 1a–c could be fitted to the equivalent circuit $R_0Q$, where $R_0$ represents the bulk electronic resistance, and $Q$ is the constant phase element (CPE), with an impedance $Z = (k(i\omega)^\alpha)$. For all samples the CPE has a value for $\alpha$ 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 $E_a$, calculated from the In $\sigma$ 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, $\Delta E_f$, on the activation energy of intramolecular charge migration, $\Delta E_m$, and on the activation energy of intermolecular charge crossing, $\Delta E_{inter}$. 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 $\Delta E_f$ and $\Delta E_{inter}$ has values over 1 eV, and $\Delta E_m$ 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(I)/$Na$ 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 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 $\sigma_{Na^+}(II) = 0$ 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

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>$7 \times 10^{-2}$ (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>$1 \times 10^{-3}$ (100 °C)</td>
<td>0.38</td>
</tr>
</tbody>
</table>


plot, an $R_\text{oc}$ of $1.3 \times 10^5 \Omega$ was calculated. This $R_\text{oc}$ 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 ionization diameter small compared to that of the crown ether, and this is the case of sodium complexed in the 21-crown-7 polymer. The present data reveal that the crown ether rings and their size do play a distinctive role in cationic permeability.

**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 200, and Bruker AM 400 instruments. Tetramethylsilane was used as the internal standard. $^{29}$Si, $^1$H, and $^{13}$C CPMAS-NMR spectra were recorded on Bruker AM 500 and Bruker CXP 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.

Seebach measurements were performed as described previously. Impedance spectra were recorded in the temperature range of 250-500 °C and analyzed as described earlier.

Ionic conductivity experiments were performed using concentration cells of the Na-nanalagm(1)Na picrate (30 mol %)-1Hg(II). In the discharge mode, the dc resistance ($R_\text{dc}$) was determined from normalized load-circuit voltages (LCV/OCV) vs load-current densities ($i$), the relation between these parameters being:

$$\text{LCV} = \frac{R_\text{dc}}{\text{OCV} - \frac{1}{i}} + 1 \quad (1)$$

where OCV represents the open-circuit voltage of the concentration cell. The OCV is governed by the Nernst expression

$$\text{OCV} = \frac{kT}{q} \ln \left(\frac{\alpha_{\text{Na}}(I)}{\alpha_{\text{Na}}(II)}\right) \quad (2)$$

OCV and LCV were recorded with a Teletec Airtronic TE 924 electrometer. The sodium amalgam was prepared by dissolving 55 mg of sodium in 101 g 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.

1,3-Diimino-5,6-(1,4,7,10,13-pentaoxatridecamethylene)-1,3-dihydroisoindole (3a). Aqueous ammonia was bubbled through a solution of 0.03 g of acetylene 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 dark blue/black powder was isolated, washed with acetone, and dried in vacuo. The product was dried over silica gel 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%; mp 102 °C dec; FAB MS m/e 336 (M$^+$); IR (KBr) 3400 (NH), 3200 (OH), 2910-2885 (CH$_2$), 1100-1060 (COC) cm$^{-1}$; $^1$H NMR (CDCl$_3$, 60 MHz) 6 2.9-3.5 (br, 2 H, CH$_2$N), 4.3-4.5 (br, 2 H, CH$_2$), 7.0-7.8 (br, 4 H, ArH); UV/vis (pyridine) $\lambda_{\text{max}}$ 302, 680-664 (sh), 630 (sh), 444, 417 (sh), 372 (nm). 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 dark blue/black powder was isolated, washed with acetone, and dried in vacuo.

**Figure 7.** Normalized load-circuit voltages vs load currents for a concentration cell with a sodium picrate-1e complex as membrane; $T = 80^\circ$ C.
Annulation Experiments. The complex stoichiometries of Na+ in compounds 1a-c were determined by shaking the powdered solid polymers (~4mg) with picrate solutions (10M M) for 7h 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 complexes sodium (Na+comp) 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.

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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, 125541-35-5; 5a, 118342-88-8; 5b, 125541-41-5; 5c, 125541-42-6; SiCl4, 10026-04-7; Li+*, 7439-93-2; Na+, 7440-23-5; K+, 7440-09-7; Rb+, 7440-17-7; Cs+, 7440-46-2; ammonia, 7664-41-7.

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 vinylketene, 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 hyellazole 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 annulations1 which have been developed recently include methods based on Diels-Alder chemistry,2 carbonyl condensation reactions,3 and transition-metal-mediated processes. Prominent among the last class of reactions are the cobalt-mediated [2 + 2 + 2] acetylene cycloadditions investigated by Vollhardt4 and the Dötz reaction of Fischer carbene complexes.5 We have recently shown that addition of vinylketenes