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–Condor 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–Condor 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 3, respectively. The Franck-Condon energies similarly estimated from the emission spectra are 64, 66, and 72 kcal mol$^{-1}$.

The results are summarized in Figure 4. As regards the Franck–Condor 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–Condor 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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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.

Phthalocyaninato polysiloxanes have been studied by many scientists. Unsubstituted

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

<table>
<thead>
<tr>
<th></th>
<th>C$_1$C$_3$</th>
<th>C$_2$C$_4$</th>
<th>C$_3$C$_5$</th>
<th>C$_4$C$_6$</th>
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</thead>
<tbody>
<tr>
<td>solid state</td>
<td>151.8</td>
<td>151.0</td>
<td>129.5</td>
<td>102.5</td>
</tr>
<tr>
<td>solution$^a$</td>
<td>151.3</td>
<td>155.0</td>
<td>132.3</td>
<td>108.1</td>
</tr>
</tbody>
</table>

$^a$In ppm relative to tetramethylsilane. $^b$Solvent CD$_2$OD.

Polysiloxanes are formed by the uncatalyzed polycondensation of phthalocyaninato dihydroxysilanes for 1–12 h at 440 °C under


Phthalocyaninato Polysiloxanes

Scheme 1

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 $10^{-4}$–$10^{-5}$ 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 $n$-tert-butyl-substituted and octakis(dodecoxy)-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 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.

\[ \text{Figure 1. Linear chain of "crowned" phthalocyanines.} \]

Figure 2. NMR spectra of 5c and of its oligomer (n = 3-4) in solution: (A) 200 MHz $^1$H NMR (CD$_3$OD) spectrum of 5c, (B) 200 MHz $^{13}$C NMR (CD$_3$OD) spectrum of 5c, (C) 400 MHz $^1$H NMR (CDCl$_3$) spectrum of oligomeric 5c, (D) 400 MHz $^{13}$C NMR (CDCl$_3$) spectrum of oligomeric 5c. Signals marked X are due to solvent.

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$^6$ (yield 83%). Sodium salts, complexed in the crown ethers of 3a-q were removed by treatment with an ion exchange resin. Reaction of 3a-c with SiCl$_4$ 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 without the catalyst, resulting 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.

The $^1$H NMR spectra of the dihydroxysilanes 5a-c are similar to those of their free base derivatives.$^6$ The proton spectrum of 5c (CD$_3$OD, 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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Phthalocyaninato Polysiloxanes

...fragments.

...atoms of the crown ether rings. This spectrum is the result of and the signal at 108 ppm can therefore be attributed to carbon atoms C1,5 and C5. The crown ether signals appear at 72 ppm. The atoms C1,5, C2,5, and C3,6 of the Pc macrocycle have signals at 151 and 155 ppm, respectively assignment was aided by measurement of a Pc (with dodecyl substituents) that had been enriched with \(^{13}C\) at C1 and C5. The remaining signal at 132 ppm is ascribed to C4,5.

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 1, the \(^{13}C\) CPMAS spectra show close analogies to the \(^{13}C\) solution NMR spectra. In the CPMAS spectra, C1,5, C2,5, and C3,6 are almost coincident.

The \(^1H\) 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 C3,5, 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 (\(\phi = 45^\circ\)). In these positions the carbon pairs C1,5, C2,5, C3,5, and C4,6 become magnetically inequivalent.

The oligomers are thus expected to give a spectral pattern that is more complex than the \(^{13}C\) spectrum of the monomer, though all signals, except that of C3,5, 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 macrocycles.

In our spectra of 5c we find that the axially coordinated OH protons in the oligomer are also shifted upfield and that there are two signals present at -3.5 and -4.0 ppm, for the trimer and tetramer, respectively: these signals disappear upon adding CDOD. A remarkable feature of the spectrum of oligomeric 5c is the very broad region between 3.4 and 5.2 ppm in which the multiplets of crown ether units occur. Compared to the spectrum of monomeric 5c the signals are well-separated and spread out, especially in downfield direction: This spectral dispersion could indicate that in the stack the crown ethers have a flattened, more preorganized conformation than in the monomer. The spectrum of the oligomer does not significantly change with increasing...
specifies 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 940 and 980 cm⁻¹ and the disappearance of the band 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.

Oligomeric 5c like 5b show a somewhat more selective 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, as 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 5e like 5b show a somewhat more selective binding profile toward alkali-metal ions than the monomer. The binding profile of 5e 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 5e 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
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>
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<tbody>
<tr>
<td>5b</td>
<td>Li⁺</td>
<td>9.8</td>
</tr>
<tr>
<td></td>
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<tr>
<td></td>
<td>K⁺</td>
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<td></td>
<td>Rb⁺</td>
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<td></td>
<td>Cs⁺</td>
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<td>1b</td>
<td>Li⁺</td>
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<td></td>
<td>Na⁺</td>
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</tr>
<tr>
<td></td>
<td>Cs⁺</td>
<td>315</td>
</tr>
</tbody>
</table>

*Trimers. \( \gamma_m = 4-5. \)

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 10⁻⁵ (25^°C)</td>
<td>0.23</td>
</tr>
<tr>
<td>1b</td>
<td>8 \times 10⁻⁵ (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>

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 \( R_Q \) represents the bulk electronic resistance, and \( Q \) is the constant phase element (CPE), with an impedance \( Z = (k(Q))^{1/2} \). 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 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, \( \Delta E_f \), on the activation energy of intramolecular charge migration, \( \Delta E_m^{\text{int}} \), and on the activation energy of intermolecular charge crossing, \( \Delta E_m^{\text{int}} \). 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 \( \Delta E_{\text{f}} \) and \( \Delta E_m^{\text{int}} \) has values over 1 eV. \( \Delta E_m^{\text{int}} \) 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 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 \( \sigma \) is effectively bound in the 21-crown-7 rings. For the 15-crown-5 polymer 1a, a saturation level of 0.34 was measured. The maximum (\( \sigma_{\text{max}} \))/\( \text{CE} \) ratio of 1.0 is not reached in our polymers because of the above-mentioned electrostatic repulsion between the components.


plot, an $R_{eq}$ of $1.3 \times 10^{10}$ $\Omega$ was calculated. This $R_{eq}$ value is very high compared to that found for $K^{+}$ transport through a polymer of poly(isocyanate) containing 18-crown-6 rings.\textsuperscript{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 $K^{+}$ transport,\textsuperscript{12} and this is the case of sodium complexed in the 21-crown-7 polymer.\textsuperscript{13} However, the $R_{eq}$ 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(isocyanate) 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 $K^{+}$ polymers containing 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 a Varian EM 360, Bruker WP 200, and Bruker AM 400 instruments. Tetramethylsilane was used as the internal standard. $^1$H, $^13$C CPMAS-NMR spectra were recorded on a Bruker AM 500 spectrometer. Elemental analyses were performed by the Elemental Analytical Section of the Institute for Applied Chemistry TNO, Zeist, The Netherlands. The sample was washed with water and dried under vacuum. Impedance spectra were recorded in the temperature range of 25–250 °C.

**Results and Discussion**

**Concentration cell with a sodium picrate-lc complex as membrane:**

**Figure 7:** Normalized load-circuit voltages vs load currents for a concentration cell with a sodium picrate-lc complex as membrane; $T = 80^\circ$C.

\[ \text{OCV} = \frac{kT}{q} \ln \frac{\alpha(Na)}{\alpha(I)} + 1 \]

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

\[ \text{OCV} = \frac{kT}{q} \ln \frac{\alpha(Na)}{\alpha(I)} \]

OCV and LCV were recorded with a Teletac Airtronic TE 924 electrometer. The sodium amalgam was prepared by dissolving 57 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.

**1,4-Dicyanobenzene-15-crown-5 (2a), 4,5-dicyanobenzene-18-crown-6 (2b), and 4,5-dicyanobenzene-21-crown-7 (2c) were prepared as described previously.**

3a: $^1$H NMR (CDCl$_3$, 200 MHz) $\delta$ 3.6–4.4 (m, 16 H, CH$_2$O); 7.6 (br s, 2 H, ArH). FAB MS m/e $= 336$ (M $+$ H$^+$); IR (KBr) 3400 (OH), 3200 (NH), 2910–2870 (CH$_3$), 1630 (CN), 1100–1040 (COO) cm$^{-1}$; $^1$H NMR (DMSO-$d_6$) $\delta$ 3.7–4.4 (m, 16 H, CH$_2$O), 7.6 (br s, 2 H, ArH), 7.7–8.8 (br s, 3 H, NH) ppm.

**Dihydroxy[4,5,4',5',4''-5''-tetraakis(1,4,7,10,13-pentaoxa-15-crown-5)phthalocyanino]silicon(IV) (5a):** To a mixture of 1.3 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 HCl. The temperature of the mixture was quickly brought to 100 °C and maintained 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 this 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 in 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/e 1335 (M $+$ H$^+$); IR (KBr) 3400, 2910–2885 (CH$_3$), 1100–1060 (COO) cm$^{-1}$; $^1$H NMR (CDCl$_3$, 60 MHz) $\delta$ 0.0 (s, 2 H, SiOH), 3.3–4.5 (m, 64 H, CH$_2$O), 8.0–8.5 (br s, 8 H, ArH); UV (CHCl$_3$) $\lambda_{max}$ 673 (5.3), 650 (4.6), 612 (4.6), 447 (4.6), 359 (5.0) nm. Anal. Calcd for C$_{64}$H$_{72}$NB$_2$O$_{21}$Si$_n$: C, 58.3; H, 5.5; N, 8.5. Found: C, 59.6; H, 5.7; N, 8.1.

**Conclusion:** The present data reveal that the crown ether rings and their size do play a distinctive role in cationic conductivity.
was synthesized from \(3e\) as described for \(5a\): yield 32%; TGA 350 °C dec; UV/vis and IR (KBr) as for \(5a\); \(^1\)H NMR (CDCl\(_3\)) \(6 3.7-4.5 (m, 96 \text{ H}, 3.74, 9.4 (s, 8 H, ArH) ppm.\) Analyzed for \(C_{80}H_{1w}NB_{03}\): C, 96.88; H, 6.2; N, 6.5 (different samples gave varying results with a maximum variation of about 1.5% for all elements).

Polycorrelation of \(5c\) To Give \(1c\). This compound was synthesized from \(5c\) as described for \(1a\): yield 71%; TGA 285 °C dec. Analyzed for \(C_{86}H_{104}NB_{02}\): C, 95.4; 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 CaCl\(_2\) under an atmosphere of N\(_2\), 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 CHCl\(_3\)/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 \(K_c\) and \(\Delta G^\circ\) Values. The \(K_c\) values were determined by the picrate extraction technique from H\(_2\)O into CHCl\(_3\) at 30 °C. The AGO values were determined by the decrease of picrate concentrations, ratio was determined by plotting the molar ratio of the complexed sodium reference compound to measure the adsorption of picrate salts to solid material. From the decrease of picrate concentrations, 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.

**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 diolefin monoaddition of an acetylene derivative and a vinyl or aryl- or diazoc ketone. Mechanically, 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 hydellazine 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 replaced 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 which have been developed recently include methods based on Diels--Alder chemistry,1 carbonyl condensation reactions,2 and transition-metal-mediated processes. Prominent among the last class of reactions are the cobalt-mediated [2 + 2 + 2] acetylene cycloadditions investigated by Vollhardt3 and the Dönitz reaction of Fischer carbene complexes.4 We have recently shown that addition of vinylketenes

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