configuration interactions is necessary to obtain a solution where the energies of the different geometries of the singlet excited state are stable. As the CI number was increased the energies of the perpendicular geometries were less affected (lowered) compared with the E and Z ones.

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

A prerequisite for an adiabatic mechanism is that there are no energy minima on the excited-state energy surface in the regions of 90° double bond twists. The calculated energy difference between $^1Zp^*$ and $^1ZZ^*$ (5.1 kcal mol^{-1}) and that between $^1ZE^*$ and $^1Ep^*$ (6.0 kcal mol^{-1}) are remarkably close to the experi-

mentally determined energy barriers for the adiabatic isomerizations of 1 and 2 (4.6 kcal mol^{-1} for both).

For comparison the method of calculation applied to stilbene gives a distinct global minimum for a twisted structure starting from either *cis*- or *trans*-stilbene.

Outlook. The simple extension of the conjugated π-system of stilbene to a *p*-styrylstilbene 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 π-systems.

Phthalocyaninato Polysiloxanes Substituted with Crown Ether Moieties

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Contribution from the Department of Organic Chemistry, University of Utrecht, Padualaan 8, 3584 CH Utrecht, The Netherlands, the Laboratory for Inorganic Chemistry, Delft University of Technology, Julianalaan 136, 2628 BL Delft, The Netherlands, and the Department of Organic Chemistry, University of Nijmegen, Toernooiveld, 6525 ED Nijmegen, The Netherlands. Received June 13, 1989

Abstract: We describe the synthesis and characterization of phthalocyaninato polysiloxanes substituted with 15-crown-5, 18-crown-6, and 21-crown-7 rings. The degree of polymerization of the polymer samples depends on the size of the crown ether rings and varies between 6 and 18 units. NMR spectroscopy reveals that the polysiloxanes have a rigid structure with staggered phthalocyaninato (Pc) units. The binding of alkali-metal ions to the plymers 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 (Pc's) substituted with crown ether rings are currently receiving great interest.[1,6] Recently, we reported that these molecules can be aggregated by addition of alkali-metal salts, which become complexed to the crown ether rings.[1b,c] 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.[2] This method, first described by Joyner and Kenney,[3a] involves the polycondensation of a phthalocyaninato dihydroxysilane containing four crown ether rings. In this way a stacked quasi-one-dimensional arrangement of crowned Pc's is achieved in which the central silicon atoms are bridged through O^{2-} ligands (Figure 1). These stacks are expected to transport electrons and ions in the stacking direction: electrons via the central Pc macrocycles and cations via the crown ether moieties. Such compounds when incorporated in vesicle bilayers could be used as synthetic models to mimic both electron and ion channels of natural transport systems.

Substituted and unsubstituted phthalocyaninato polysiloxanes, [PcSiO]$_m$, have been studied by many scientists.[3] Unsubstituted

Table I. ^{13}C Chemical Shifts of **5c** in Solution and in the Solid State[a]

	C$_1$,C$_1'$	C$_4$,C$_4'$	C$_2$,C$_2'$	C$_3$,C$_3'$	crown ether
solution[b]	151.3	155.0	132.3	108.1	72.4
solid state	151.8	151	129.5	102.5	70.9

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

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

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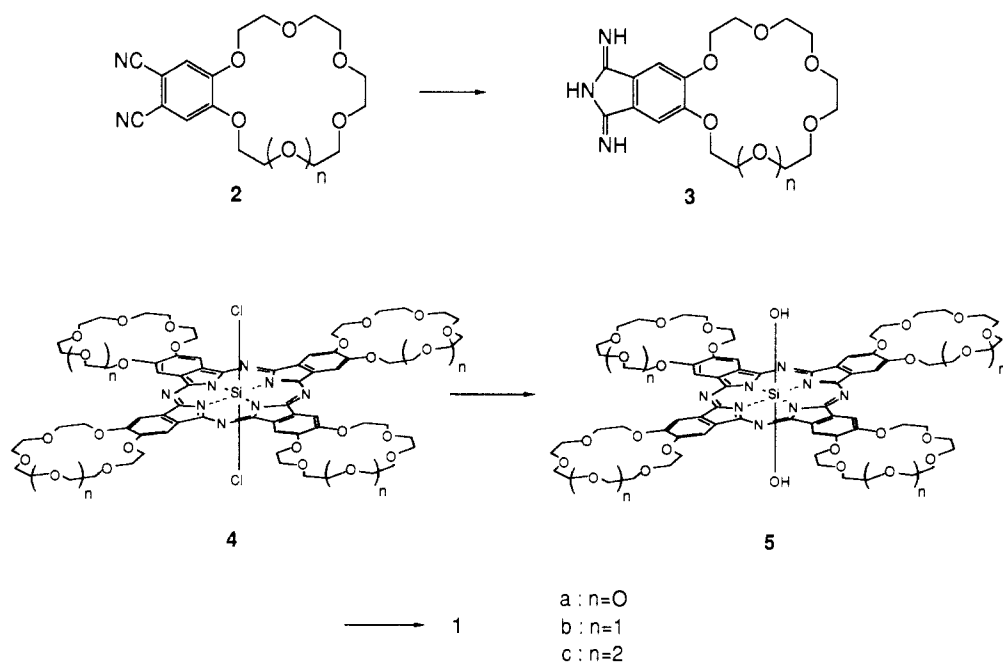(2) A preliminary communication has appeared: Sielcken, O. E.; van der Kuil, L. A.; Drenth, W.; Nolte, R. J. M. *J. Chem. Soc., Chem. Commun.* **1988**, 1232–1233. Independently, the synthesis of phthalocyaninato polysiloxanes substituted with 15-crown-5 rings was reported by Ahsen, V.; Yilmazer, E.; Gürek, A.; Gül, A.; Bekâroglu, Ö. *Helv. Chim. Acta* **1988**, *71*, 1616–1621.

Scheme I

2   3

4   5

a : n=0
b : n=1
c : n=2

———→ 1

vacuum, or in 1-chloronaphthalene at reflux.[3a] 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^{-5} S/m.[3b]

Peripherally substituted polysiloxanes cannot be synthesized under the above-mentioned conditions because of thermal degradation of the substituents. Wegner and co-workers[3j] 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.[3n] The rate of reaction is very low, and relatively low molecular weight polymers are obtained; chain lengths of tetra-*tert*-butyl-substituted[3h] and octakis(dodecoxymethyl)-substituted[3l] phthalocyaninato polysiloxanes were estimated to be between 10 and 25 Pc units.[3i,j] These polymers are soluble in common organic solvents. Very recently, Wegner and co-workers[3n] 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
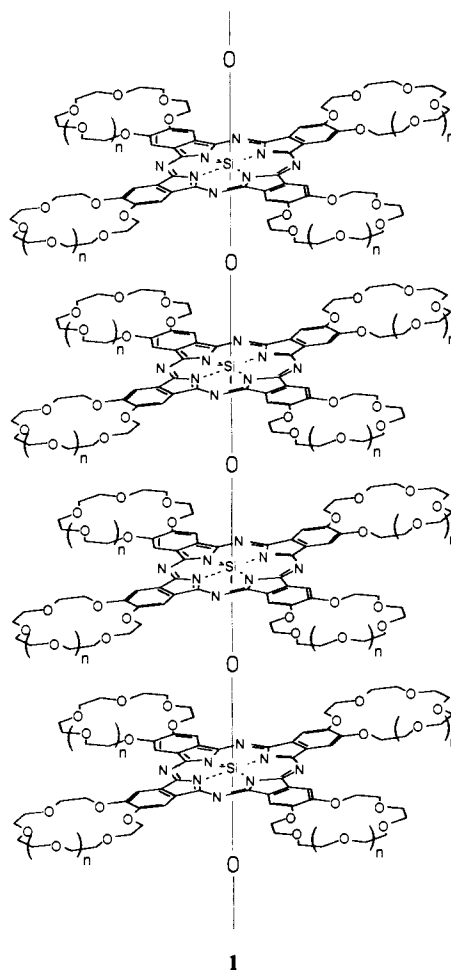
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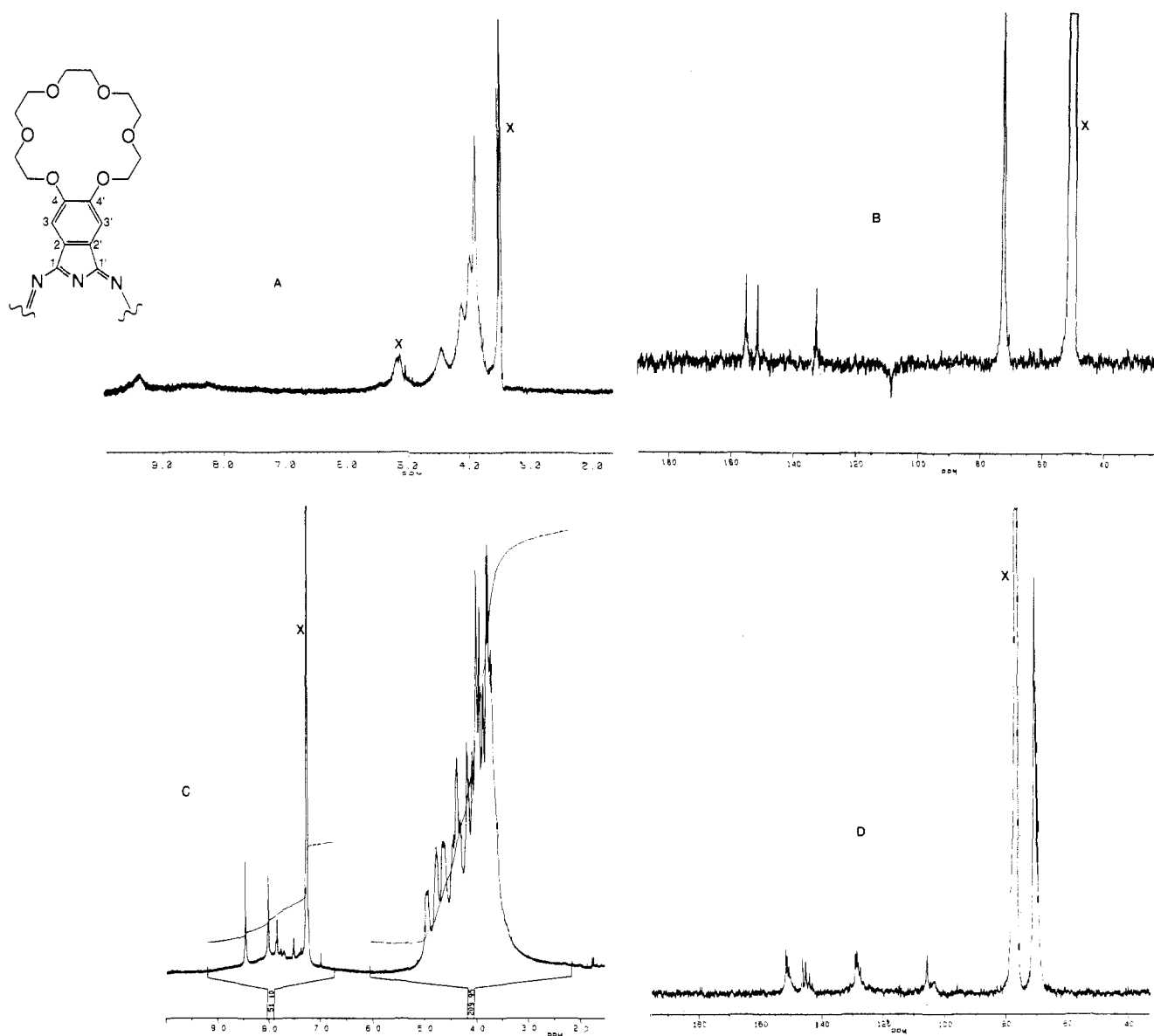

Figure 1. Linear chain of "crowned" phthalocyanines.

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 2. NMR spectra of **5c** and of its oligomer (m = 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-diimino-1,3-dihydroisoindole derivative (**3a–c**) by reaction with sodium methoxide and ammonia in methanol[4] (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 SiCl$_4$ in quinoline[3e] 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 CaCl$_2$ as catalyst.[3j] 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 ^{1}H NMR spectra of the dihydroxysilanes **5a–c** are similar to those of their free base derivatives.[6a] 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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ether signals is complex, due to the chemically inequivalent ether fragments.

The ^{13}C NMR (CD$_3$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[7a,9,10] 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$_{3'}$. The crown ether signals appear at 72 ppm.[9,10] The atoms C$_1$,C$_{1'}$ and C$_4$,C$_{4'}$ of the Pc macrocycle have signals at 151 and 155 ppm, respectively;[7a,10] assignment was aided by measurement of a Pc (with dodecoxy substituents) that had been enriched with ^{13}C at C$_1$ and C$_{1'}$.[11] The remaining signal at 132 ppm is ascribed to C$_2$,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$_1$,C$_{1'}$ and C$_4$,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$_3$,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 ($\phi \neq 45°$). In these positions the carbon pairs C$_1$,C$_{1'}$, C$_2$,C$_{2'}$, C3,C$_{3'}$, and C$_4$,C$_{4'}$ become magnetically inequivalent.[7a] 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,[7b] 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.[7b] 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;[7b] these signals disappear upon adding CD$_3$OD. 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
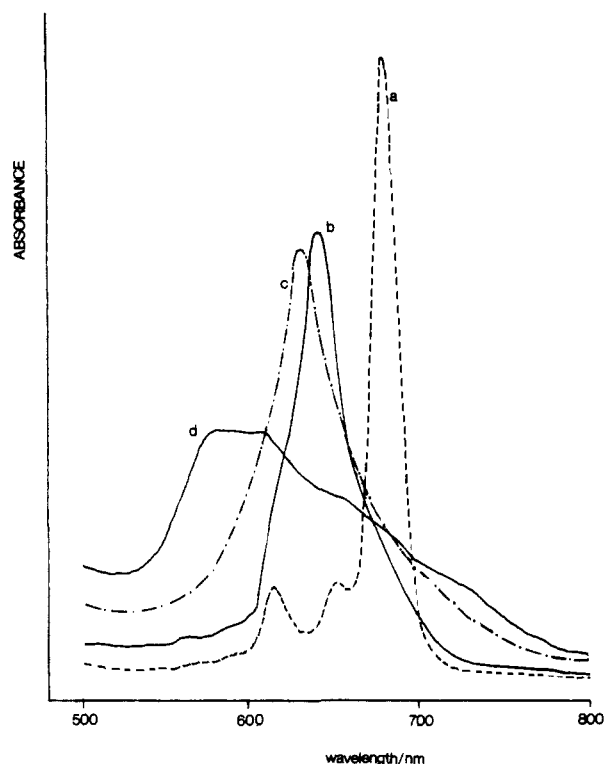
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Figure 3. Electronic absorption spectra of monomeric (a), dimeric (b), trimeric (c), and oligomeric (d) products of 5.

temperature and this fact, combined with the observed splitting of the aromatic signals, indicates that the oligomeric compounds have rigid structures. Since addition of KSCN to the oligomeric compounds resulted in a further upfield expansion of the crown ether signals without changes in the aromatic signals, it would appear that complexation of an ion does not influence the staggered conformation of the Pc macrocycles.

The ^{13}C CPMAS NMR spectra of polysiloxanes 1a–c are poorly resolved, and compared to the spectra of 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 ^{29}Si 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*–OH. From these spectra (with poor resolution) we were only able to make a rough estimate of the chain lengths of the polymer; the numbers yielded are similar to those obtained by IR spectroscopy (see below).

UV/Vis Spectroscopy. The electronic absorption spectra of monomers 5 and their polycondensation products are given in Figure 3. Monomers 5 show a Q band with maximum at 678 nm and two weaker bands at 650 and 612 nm. During the condensation process of monomeric 5 to the polycondensation products 1 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.[3h,j,e] 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.[3n] 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
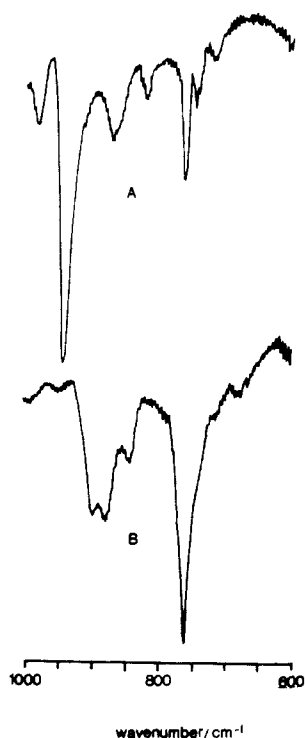
wavenumber/cm⁻¹

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

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.[3e] 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,[3e] 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,[3c] 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,[3e] 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, Δ*G*°, 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.[8] This method is not applicable to **5a** and its oligomers, because not only was **5a** too soluble in water but also there was
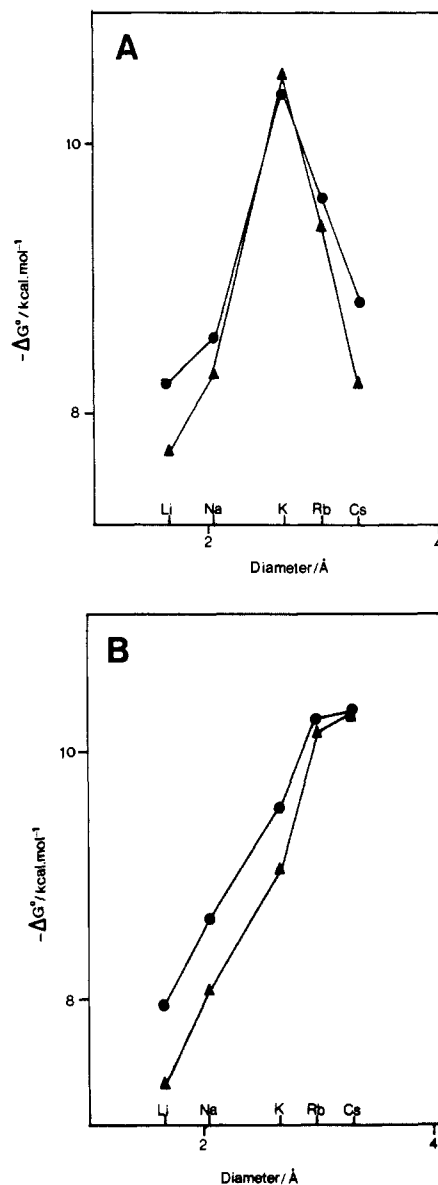

Diameter/Å

Diameter/Å

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).

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 Δ*G*° 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.[6a] 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**.[6a] 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[6a] and the 21-crown-7 rings prefer the larger Rb⁺ and Cs⁺ ions over the smaller ions. For oligomeric **5b** and **5c** a further increase in selectivity is to be expected for the higher molecular weight polymers. The reason that the oligomers show more selective binding than the monomers may be related to a difference in

Phthalocyaninato Polysiloxanes

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

host	cation of guest	K_a, 10^{-5} M^{-1}
5b	Li⁺	9.8
	Na⁺	16.3
	K⁺	367
	Rb³	104
	Cs⁺	27.2
1b[a]	Li⁺	4.1
	Na⁺	10.8
	K⁺	481
	Rb⁺	70.8
	Cs⁺	10.4
5c	Li⁺	4.5
	Na⁺	19.7
	K⁺	88.7
	Rb⁺	292
	Cs⁺	329
1c[b]	Li⁺	6.3
	Na⁺	7.9
	K⁺	39.7
	Rb⁺	249
	Cs⁺	315

[a] Trimer. [b] m = 4–5.
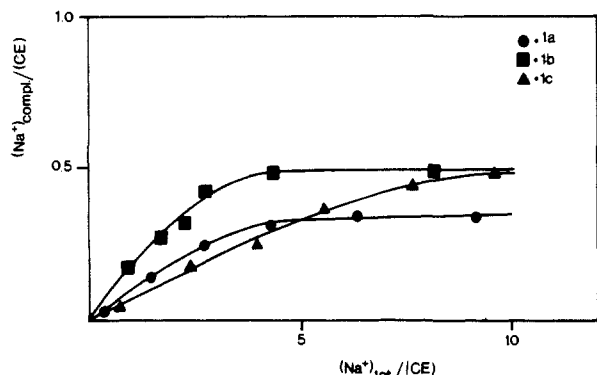
Figure 6. Saturation levels of polymers **1a–c** for Na⁺.

conformation of the crown ether rings in the two systems. An isolated crown ether has a folded conformation,[15] 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 $\Delta G°$ 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 H₂Pc. 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 complexed Na⁺ (Na⁺_compl) to crown ether (CE) ratio of 0.48 was obtained. The saturation level of **1c** is reached at a higher overall cation to crown ether ratio than that of **1b**, because Na⁺ is less 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 (Na⁺_compl)/(CE) ratio of 1.0 is not reached in our polymers because of the above-mentioned electrostatic repulsion between the com-

Table III. Electronic Conductivities (σ) and Conduction Activation Energies (E_a)

compound	σ, S m^{-1}	E_a, eV
5a–c	$<10^{-9}$	–
1a	7×10^{-7} (25 °C)	0.23
1b	3×10^{-7} (25 °C)	0.29
1c	1×10^{-8} (100 °C)	0.38

plexed cations. This is supported by results from similar measurements on rigid poly(isocyanides) with pendant crown ether moieties.[16] 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.[1b,e] 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 $R_b Q_p$, where p stands for parallel, R_b represents the bulk electronic resistance, and Q is the constant phase element (CPE), with an impedance $Z = (k(i\omega)^\alpha)^{-1}$. For all samples the CPE has a value for α 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, σ, and the conductivity activation energy, E_a, calculated from the ln σ 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 σ than the lower molecular weight polymer **1c**. The explanation for this is that charge transport will be facilitaed 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, ΔE_f, on the activation energy of intramolecular charge migration, ΔE_m^{intra}, and on the activation energy of intermolecular charge crossing, ΔE_m^{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 ΔE_f and ΔE_m^{inter} has values over 1 eV.[1c] ΔE_m^{inter} 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 $a_{Na}(II)$ = 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

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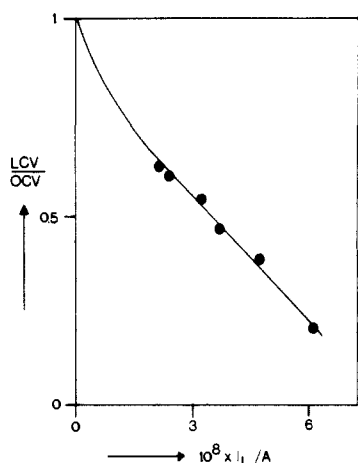
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Figure 7. Normalized load-circuit voltages vs load currents for a concentration cell with a sodium picrate–**1c** complex as membrane; $T = 80$ °C.

plot, an R_{dc} of 1.3×10^7 Ω was calculated. This R_{dc} 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 of the crown ether,[14] and this is the case of sodium complexed in the 21-crown-7 polymer **1c**. However, the R_{dc} value indicates that transport of sodium is very low. This feature can be explained by the structural difference of the two polymers. In the poly(isocyanide) the crown ether rings are stacked on top of each other and form extended channels whereas in **1c** the Pc units have a staggered arrangement. This latter arrangement could result in distortion or even the complete absence of a channel structure, and therefore, ion transport may be hindered or even prevented. Better results for cationic conductivity are to be expected for Pc polymers containing crown ether rings larger than 21-crown-7. The present data reveal that the crown ether rings and their size do play a distinctive role in cationic conductivity.

Experimental Section

Infrared spectra were measured on Perkin-Elmer 283 and Perkin-Elmer 1800 instruments. UV/vis spectra were recorded on a Perkin-Elmer 555 spectrometer. Solution ¹H NMR and ¹³C NMR spectra were recorded on Varian EM 360, Bruker WP 200, and Bruker AM 400 instruments. Tetramethylsilane was used as the internal standard. ²⁹Si, ¹H, and ¹³C 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.

Seebeck measurements were performed as described previously.[1b] Impedance spectra were recorded in the temperature range of 25–250 °C and analyzed as described earlier.[1b]

Ionic conductivity experiments were performed using concentration cells of the type Na-amalgam(I)|Na picrate (30 mol %)–1|Hg(II). In the discharge mode, the dc resistance (R_{dc}) was determined from normalized load-circuit voltages (LCV/OCV) vs load-current densities (I_L), the relation between these parameters being[5]

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

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

$$OCV = \frac{kT}{q} \ln \frac{a_{Na}(I)}{a_{Na}(II)} \quad (2)$$

OCV and LCV were recorded with a Teletec 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 under the Saturation Experiments section. The sample was washed with water and dried under vacuum.

4,5-Dicyanobenzo-15-crown-5 (2a), 4,5-dicyanobenzo-18-crown-6 (2b), and 4,5-dicyanobenzo-21-crown-7 (2c) were prepared as described previously.[6a]

1,3-Diimino-5,6-(1,4,7,10,13-pentaoxatridecamethylene)-1,3-dihydroisoindole (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 4 h at 95 °C while the addition of ammonia was continued and then cooled to room temperature. A white precipitate of sodium methoxide was filtered off, and the filtrate was evaporated to dryness. The remaining solid was extracted with dry chloroform. Remaining sodium salts, complexed in the crown ethers, were removed with an ion-exchange resin (Amberlyst 15). After recrystallization in dry chloroform, 1.3 g of a light green solid was obtained: yield 83%; mp 108 °C dec; FAB MS m/e 336 (M + H)⁺; IR (KBr) 3400 (NH), 3200 (NH), 2910–2870 (CH₂), 1630 (C–N), 1110–1040 (COC) cm⁻¹; ¹H NMR (DMSO-d_6) δ 3.6–4.4 (m, 16 H, CH₂O), 7.3 (s, 2 H, ArH), 7.7–8.2 (br s, 3 H, NH) ppm.

Dihydroxy[4,5:4′,5′:4″,5″:4‴,5‴-tetrakis(1,4,7,10,13-pentaoxatridecamethylene)phthalocyaninato]silicon(IV) (5a). To a mixture of 1.33 g (3.99 mmol) of **3a** in 10 mL of quinoline (freshly distilled from barium oxide) was added, under an atmosphere of N₂, 2 mL (17 mmol) of SiCl₄. The temperature of the mixture was quickly brought to 100 °C and kept there for 12 h. At the end of this time the reaction mixture was brown. After cooling, an excess of SiCl₄ was distilled off, 20 mL of water was added, and the mixture was stirred for 4 h. In this period the color changed from brown to green. A precipitate was filtered off, and the clear filtrate was added dropwise to ethyl acetate. The green precipitate of the product which formed was filtered off and washed with acetone. Recrystallization of **5a** was performed by slowly evaporating ether into a solution of the product in pyridine. The solid was filtered off, dried, and further purified by gel permeation chromatography (Sephadex LH 60, eluent CHCl₃/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 (OH), 2910–2885 (CH₂), 1100–1060 (COC) cm⁻¹; ¹H NMR (CDCl₃, 60 MHz) δ 0.0 (s, 2 H, SiOH), 3.3–4.5 (m, 64 H, CH₂O), 8.0–8.5 (br s, 8 H, ArH); UV/vis (CHCl₃) λ_{max} (log ε) 678 (5.3), 650 (4.6), 612 (4.6), 444 (sh), 417 (4.6), 359 (5.0) nm. Anal. Calcd for C₆₄H₇₄SiN₈O₂₂: C, 57.56; H, 5.59; N, 8.39. Found: C, 58.8; H, 5.6; N, 8.3 (different samples gave varying results with a maximum variation of about 1.5% for all elements). (**4a**: UV/vis (pyridine) λ_{max} 702, 680–664 (sh), 630 (sh), 612–604 (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 CaCl₂ was heated under an atmosphere of N₂ at 200 °C for 70 h. The resulting dark blue/black powder was isolated by filtration and washed by using a sonicator at 50 °C with subsequently H₂O (3×), DMSO, pyridine, and CHCl₃. The product was dried over P₂O₅ under reduced pressure: yield 0.2 g (80%); TGA 280 °C dec. Anal. Calcd for (C₆₄H₇₂N₈O₂₁Si)ₙ: 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-Diimino-5,6-(1,4,7,10,13,16-hexaoxahexadecamethylene)-1,3-dihydroisoindole (3b). This compound was synthesized from **2b** as described for **3a**: yield 74%; mp 95 °C dec; FAB MS m/e 380 (M + H)⁺; IR (KBr) as for **3a**; ¹H NMR (CDCl₃) δ 3.6–4.4 (m, 20 H, CH₂O), 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″:4‴,5‴-tetrakis(1,4,7,10,13,16-hexaoxahexadecamethylene)phthalocyaninato]silicon(IV) (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 (CHCl₃) and IR (KBr) as for **5a**; ¹H NMR (CDCl₃, 200 MHz) δ 3.3–4.5 (m, 80 H, CH₂O), 9.4 (br s, 8 H, ArH) ppm. Anal. Calcd for C₇₂H₉₀N₈O₂₆Si: 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 (C₇₂H₈₈N₈O₂₅Si)ₙ: C, 57.89; H, 5.95; N, 7.50. Found: C, 58.4; H, 5.7; N, 8.1.

1,3-Diimino-5,6-(heptaoxanonadecamethylene)-1,3-dihydroisoindole (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**; ¹H NMR (CDCl₃) δ 3.6–4.4 (m, 24 H, CH₂O), 7.3 (s, 2 H, ArH), 7.4–7.8 (br s, 3 H, NH) ppm.

Dihydroxy(4,5:4′,5′:4″,5″:4‴,5‴-tetrakis(1,4,7,10,13,16,19-heptaoxanonadecamethylene)phthalocyaninato)silicon(IV) (5c). This compound

was synthesized from **3c**, as described for **5a**: yield 32%; TGA 350 °C dec; UV/vis and IR (KBr) as for **5a**; ^{1}H NMR (CD$_3$OD) δ 3.7–4.5 (m, 96 H, CH$_2$O), 9.4 (br s, 8 H, ArH) ppm. Anal. Calcd for C$_{80}$H$_{106}$N$_8$O$_{30}$Si: C, 58.69; H, 6.07; 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 (C$_{86}$H$_{104}$N$_8$O$_{29}$Si)$_n$: 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 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 ^{1}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_a and $\Delta G°$ Values. The K_a values were determined by the picrate extraction technique from H$_2$O into CHCl$_3$ at 25 °C as described in the literature.[8] The $\Delta G°$ values were calculated from the K_a values by using the expression $\Delta G° = -RT \ln K_a$.

Saturation Experiments. The complex stoichiometries of Na$^+$ in compounds **1a–c** were determined by shaking the powdered solid polymers ($\sim$4 mg) with picrate solutions (10^{-3} M) for 7 h at 25 °C with a Griffin flask shaker. From the decrease of picrate concentrations, measured spectrophotometrically, the complexed cation to crown ether ratio was determined by plotting the molar ratio of the complexed sodium ions (Na$^+_{compl}$) to host (CE) vs the molar ratio of the total amount of sodium present (Na$^+_{tot}$) and host (CE). Solid H$_2$Pc was used as a reference compound to measure the adsorption of picrate salts to solid material.

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 α-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 metalation 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[1] 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 Vollhardt[4] and the Dötz reaction of Fischer carbene complexes.[5] We have recently shown that addition of vinylketenes

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