

Supramolecular Organization of Macrocyclic Rings. Cofacial Assembly of Crown-ether-substituted Silicon Phthalocyanines

Ot E. Sielcken,^a Lucia A. van de Kuil,^a Wiendelt Drenth,^a and Roeland J. M. Nolte^{b*}

^a Department of Organic Chemistry, University at Utrecht, 3584 CH Utrecht, The Netherlands

^b Department of Organic Chemistry, University at Nijmegen, 6525 ED Nijmegen, The Netherlands

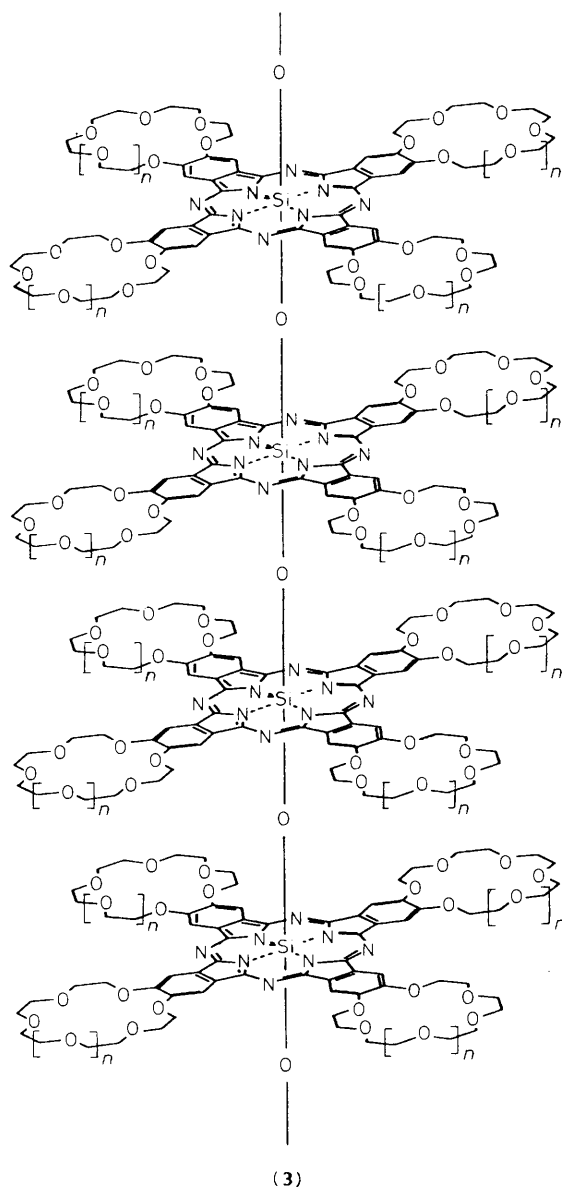
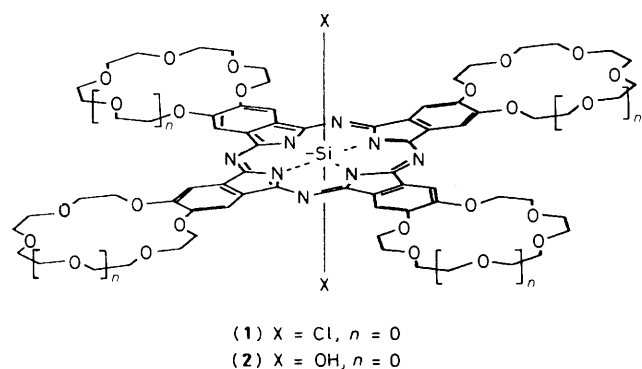
A poly(oxy silicon phthalocyanine) containing 15-crown-5 subunits has been synthesized and its electrical conductivity determined.

In nature, ion transport across membranes frequently occurs by means of ion channels.¹ The best studied example is the Gramicidin A channel.² Synthetic models of ion channels are very scarce.³ Recently, we proposed a route for constructing synthetic ion channels, *viz.* by stacking of crown ether rings.⁴ By using a rigid polymer the rings were kept at a distance of *ca.* 4 Å. When incorporated into the bilayer of synthetic vesicles, the crown ether channels were able to facilitate the translocation of cobalt ions.⁵ In this communication we report another method of constructing ion channels, namely *via* linear arrangement of phthalocyanine crowns (Figure 1).

4,5-Dicyanobenzo-15-crown-5⁶ was converted into the corresponding 1,3-di-imino-1,3-dihydroisindole derivative by reaction with sodium methoxide and ammonia in methanol.⁷ Treating the product with SiCl₄ in quinoline⁸ at elevated temperatures produced the dichlorosilicon phthalocyanine crown ether (**1**; *n* = 0). This compound was readily hydrolysed in the presence of water to give the dihydroxysilicon phthalocyanine (**2**; *n* = 0) (30% yield from the isindole derivative).[†] Compound (**2**) is soluble in common organic solvents and sparingly soluble in water and hexane.

Heating (**2**) in quinoline at 200 °C induced polycondensation. This reaction is catalysed by CaCl₂.⁹ Short reaction times (1–5 h) gave a mixture of oligomers. Prolonged heating resulted in the formation of high molecular weight polymers which were insoluble in all organic solvents but soluble in concentrated sulphuric acid. During the condensation reaction the monomer peak at 678 nm in the visible spectrum gradually disappeared and a new broad band attributed to oligomeric (**3**; *n* = 0) became visible at 637 nm. The condensation process can also be followed by recording the increase in the intensity of characteristic i.r. bands at 750

and 1610 cm⁻¹, and decrease of the band at 940 cm⁻¹. The poly(phthalocyanine) (**3**; *n* = 0) had elemental analyses and spectroscopic data consistent with its structure.[†] The polymeric nature of (**3**) also follows from its electrical properties, as measured by a.c. impedance spectroscopy.¹⁰ The values of the electrical conductivity (σ) at 25 °C and of the conductivity activation energy (E_a) amounted to 10⁻⁷ S m⁻¹ and 0.4 eV, respectively. The electrical conductivity of (**2**) was much lower



[†] Compound (**2**; *n* = 0) (Found: C, 58.8; H, 5.6; N, 8.3. C₆₄H₇₄SiN₈O₂₂ requires C, 57.55; H, 5.6; N, 8.4%); ¹H n.m.r. (CDCl₃) δ 0.0 (s, 2H, SiOH), 3.3–4.5 (m, 64H, CH₂O), and 7.5–8.5 (m, 8H, ArH); u.v.–vis. (CHCl₃) λ_{max} . (log ϵ) 680 (5.31), 650 (4.60), 612 (4.60), 417 (4.57), 359 (5.04), and 340sh nm; TGA transition 310 °C (decomp.). Compound (**3**; *n* = 0) [Found: C, 59.6; H, 4.3; N, 9.1. anal. calcd. for (C₆₄H₇₂SiN₈O₂₁)_n requires C, 58.3; H, 5.5; N, 8.5%]; no SiOH i.r. band at 820 cm⁻¹; TGA transition 280 °C (decomp.).

Figure 1. Linear chain of phthalocyanine crowns.

and could not be measured accurately by the impedance technique.

Capping an oligomer of (2) of appropriate molecular weight with R_3SiCl will produce a channel of a length comparable to the thickness of a vesicle bilayer. Such a channel could facilitate the transport of both ions and electrons across the vesicle wall. Work along these lines is in progress with channel compounds derived from 18-crown-6 (3; $n = 1$) and 21-crown-7 (3; $n = 2$). Details will be published elsewhere.

Received, 24th February 1988; Com. 8/00749G

References

- 1 S. L. Bonting and J. J. H. M. De Pont, 'Membrane Transport,' New Comprehensive Biochemistry, vol. 2, eds. A. Neuberger and L. L. M. Van Deenen, Elsevier, Amsterdam, 1981.
 - 2 D. W. Urry, *Top. Curr. Chem.*, 1985, **128**, 175; P. C. Jordan, *J. Phys. Chem.*, 1987, **91**, 6582.
 - 3 J.-H. Fuhrhop, H.-H. David, J. Mathieu, U. Liman, H.-J. Winter, and E. Boekema, *J. Am. Chem. Soc.*, 1986, **108**, 1785.
 - 4 R. J. M. Nolte, A. J. M. van Beijnen, J. G. Neevel, J. W. Zwicker, A. J. Verkley, and W. Drenth, *Isr. J. Chem.*, 1984, **24**, 297.
 - 5 U. F. Kragten, M. F. M. Roks, and R. J. M. Nolte, *J. Chem. Soc., Chem. Commun.*, 1985, 1275.
 - 6 O. E. Sielcken, M. M. van Tilborg, M. F. M. Roks, R. J. M. Nolte, and W. Drenth, *J. Am. Chem. Soc.*, 1987, **109**, 4261.
 - 7 G. Pawlowski and M. Hanack, *Synthesis*, 1980, 287.
 - 8 C. W. Dirk, T. Inabe, K. F. Schoch, Jr., and T. J. Marks, *J. Am. Chem. Soc.*, 1983, **105**, 1539.
 - 9 E. Orthmann and G. Wegner, *Makromol. Chem., Rapid Commun.*, 1986, **7**, 243.
 - 10 O. E. Sielcken, J. Schram, R. J. M. Nolte, J. Schoonman, and W. Drenth, *J. Chem. Soc., Chem. Commun.*, 1988, **108**, 108.
-