2,3,7,8,12,13,17,18-Octakis(β-hydroxyethyl)porphyrin (octaethanolporphyrin) and its liquid crystalline derivatives: synthesis and characterization

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Porphyridin thin films have been received considerable attention be-
cause of their interesting excited-state chemistry and catalytic
behavior and because of Nature's ubiquitous use of porphyrins
in electron-transfer processes. Their photoactivity, high visible
extinction coefficients, and low processing costs make them at-
tractive candidates for electrophotographic, photovoltaic, and
photoelectrochemical applications. Especially intriguing is the
ability to adjust the porphyrin's structural and electrical properties
by synthetic means, thus making them ideal model compounds
for the study of semiconduction in the organic solid state.
A great deal of current research is being devoted to the un-
derstanding of systems, biomimetic and otherwise, that self-as-
semble into organized structures. Liquid crystals represent
one of the best known classes of self-organizing materials, ex-
hibiting properties that range from surfactants that can form
micelles, monolayers, and membranes, to the rodlike molecules
used in liquid crystal displays, to the recently discovered disklike
crystalline and amorphous silicon.10 However, the attainment of
large-area single crystals of semiconductors is difficult and ex-
ensive. Hence, for example, there has been a great deal of effort
expended on the growth of crystalline silicon ribbon and an even
larger effort on improving the semiconductor properties of poly-
crystalline and amorphous silicon.11,12
Given the inherent tendency of liquid crystals (LCs) to self-
order, it is tempting to speculate about the possibility of liquid
crystalline electronic devices. LC displays are known in which
a single (liquid crystal) film, 5 μm thick, covering an area of ca.
500 cm², is formed by simple capillary-filling of the isotropic material
between two sheets of conducting glass (coated with the appro-
riate aligning agents) and cooling into the liquid crystalline phase.
These inexpensive, thin, large-area crystals are precisely what is
needed in some applications such as in the matrix addressing of
flat panel displays14 and in the conversion of solar energy.15 Of
course, the above-mentioned LCs are electronic insulators; what
is needed is a liquid crystalline semiconductor.
Because of their symmetry (spherical), no elemental semi-
ciconductor can be a liquid crystal. In fact, it would appear that,
without a substantial organic (or silicone?) component to provide
the necessary asymmetry, no inorganic semiconductor can be a
liquid crystal. Therefore, LC semiconductors should be sought in
the realm of organic semiconductors,5,10 in which the porphyrins
and the phthalocyanines are among the best known.
To our knowledge, the first LC semiconductor was synthesized by
Goodby et al.17 by esterifying the acetic and propionic acid
esters of the phthalocyanines, (β-hydroxyethyl)porphyrin (octaethanolporphyrin) and Its Liquid Crystalline Derivatives: Synthesis and Characterization

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Abstract: A synthesis is reported for 2,3,7,8,12,13,17,18-Octakis(β-hydroxyethyl)porphyrin
(Octaethanolporphyrin) and Its Liquid Crystalline Derivatives: Synthesis and Characterization

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side chains of uroporphyrin I with dodecanol. The resulting octaester had an LC phase over a range of 0.1 °C only on cooling. Apparently no other derivatives were synthesized, and no attempt was made to measure its electrical or optical properties.

Two years later, in 1982, Piechocki et al.13 published the synthesis of an LC phthalocyanine (Pc). This compound, copper octa- 

decylphosphoribocyanine, was made to measure its electrical or photophysical properties. No attempt was made to capillary-fill it into a device. Also, without an isotropic phase or a fluid mesophase, it would be extremely difficult to align (order) this material.

In an attempt to solve these problems, we decided to synthesize a porphyrin analogue of the LC phthalocyanine. A porphyrin, having a smaller central core and 16 fewer π electrons than a phthalocyanine, should inherently be much less viscous than the Pc. Also, it should require shorter alkyl side chains to induce mesophase formation, further decreasing the viscosity. One final consideration: the replacement of the meso nitrogens in the Pc for carbons in the porphyrin allows the possibility of derivatizing the semiconductor (at the meso positions) with electron-donating or -withdrawing groups. Thus, the redox potential, dielectric constant, and polarizability of the porphyrin could be adjusted without (greatly) affecting crystal packing.

We recently reported the synthesis of a series of LC porphyrin octaesters25 based on (octacetyl acid)porphyrin.26 We now describe a much improved synthetic procedure that leads to a new series of LC porphyrin octaethers. The parent compound of this series is the hitherto unreported octaethanolporphyrin. We show that the appearance and the temperature range of a liquid crystalline phase depend markedly on the presence of a central metal and on the length of the ether side chains. These compounds melt to isotropic liquids well below their decomposition points and exhibit a relatively low viscosity, columnar discotic mesophase.

Experimental Section

Instrumentation. High-resolution carbon and proton NMR spectra were measured on either a General Electric GN-500 (500 MHz) or a General Electric QE-300 (300 MHz) spectrometer, while the low-resolution proton NMR spectra were measured on a Varian EM-390 (90 MHz) instrument. High-resolution mass spectra were obtained with a Consolidated Electrodynamics Corp. 110-21C mass spectrometer equipped with an electron impact ionization source. Fast atom bombardment mass spectra were performed on a Finnigan TSQ 70 instrument with the sample in a 3-nitrobenzyl alcohol matrix. Differential scanning calorimetry27 was performed with a Perkin-Elmer DSC 2. UV-visible spectra were taken on a Hewlett-Packard 8451A spectrophotometer. The optical
textures were observed as a function of temperature between crossed polarizers in a Leitz polarizing microscope, equipped with a hot stage, at 100X magnification.

Synthesis. The synthesis is outlined in Figure 1. The resulting family of octaethers is shown in Figure 2.

Methyl 3-acytethyl-5-(methoxy-carbonyl)-2-methylpyrrole-4-acytate (2) was prepared in 54% yield from 2,4-pentanediome and dimethyl 1,3-acetoacetic-carboxylate (1) in almost quantitative yield. The solution was concentrated to 800 mL before being washed 4 times with a total of 20 mL, taken up in ether, washed with MgSO4, and evaporated. Methanol (100 mL) was added and the solution was neutralized with triethylamine, the solids were filtered and twice chromatographed and recrystallized as described in method a.

5-(Methoxy-carbonyl)-3,4-bis-(β-hydroxyethyl)-2-methylpyrrole (5). Finely powdered 4 (15 g, 0.059 mol) was dispersed in 1600 mL of dry THF under N2 and 110 mL of 1 M BH3 in THF was added. After 2 h at room temperature, 30 mL of methanol was added and the solution was stirred until a white precipitate formed. The solution was filtered, washed with ether, and acidified to pH = 5 with concentrated HCl. After standing at 5 °C for several hours, the precipitate was filtered, washed with H2O and cold acetone, and dried in vacuo. The yield of light yellow solid was 64 g (86%).

The precipitate was slowly cooled to -78 °C. The precipitate was filtered (cold) and the cold solution was concentrated to 800 mL before being washed 4 times with a total of 20 mL, taken up in ether, washed with MgSO4, and evaporated. Methanol (100 mL) was added and the solution was neutralized with triethylamine, the solids were filtered and twice chromatographed and recrystallized as described in method a.

The resulting solution was concentrated under vacuum to ca. 200 mL, taken under nitrogen, washed with 10 mL of NaOH and H2O, dried over MgSO4, and evaporated. Methanol (100 mL) was added and the solution was neutralized with triethylamine, the precipitate was filtered (cold) and the cold solution was filtered, washed with a small amount of 1 M NaOH and H2O, dried over MgSO4, and evaporated. The resulting solution was concentrated under vacuum to ca. 200 mL, taken under nitrogen, washed with 10 mL of NaOH and H2O, dried over MgSO4, and evaporated. Methanol (100 mL) was added and the solution was neutralized with triethylamine, the precipitate was filtered (cold) and the cold solution was washed with cold water, filtered, and twice chromatographed and recrystallized as described in method a.

The yield was 22 mg (9%).

5-(Methoxy-carbonyl)-3,4-bis-(β-acetoxyethyl)-2-methylpyrrole (7, R = o-acetyl). (9.5 g, 0.0177 mol) was dissolved in 30 mL of toluene, 70 mL of octanol was added, and the solution was heated under reflux overnight. The resulting solution was concentrated under vacuum to ca. 200 mL, taken under nitrogen, washed with 10 mL of NaOH and H2O, dried over MgSO4, and evaporated. Methanol (100 mL) was added and the solution was neutralized with triethylamine, the precipitate was filtered (cold) and the cold solution was heated under reflux overnight to ca. 70 °C. The precipitate was filtered (cold) and the resulting dark oil was filtered through a small silica gel column in CHCl3 to remove colored impurities. The precipitate was then recrystallized from methanol to 5 °C. The yield of light yellow oil was 7.6 g (79%).

The yield of light yellow oil was 7.6 g (79%).

5-(Methylene)carboxy-3,4-bis-(β-octyloxy)ethyl)-2-acetoxy-methylpyrrole (8) was made by a standard procedure32 in 95% yield.
mixture of 3 mL of DMF and 3 mL of triethylamine (21.5 mmol). n-Hexanoyl chloride (2 mL, 14.3 mmol) was then added and the solution was stirred at room temperature for 1 h. Dry THF (25 mL) was added followed by an additional 3 mL of triethylamine and 2 mL of acid chloride. This was stirred at room temperature for 2 days, extracted with CHCl3, washed with dilute HCl and NaOH, dried over MgSO4, and evaporated. The crude material was chromatographed in the dark on SiO2 (elution: 0.8% MeOH in CHCl3), metalated in the usual fashion, and rechromatographed as before. The product was recrystallized from CHCl3/Methanol. The yield was 43% (5%). FAB m/z caled for Cu6H12N8O2Zn 1509, m/e found 1509. 1H NMR (300 MHz, CDCl3) δ 0.74 (t, J = 7 Hz, 24 H), 1.20 (m, 32 H), 1.56 (m, 16 H), 2.35 (t, J = 7 Hz, 16 H), 4.50 (t, J = 7 Hz, 16 H), 4.99 (t, J = 7 Hz, 16 H), 10.44 (s, 4 H).

Cu(EOoct)Por (14c) was prepared by heating H2(EOoct)Por (14a) to reflux under N2 for 20 min in DMF containing excess Cu(OAc)2.

Cd(EOoct)Por (14d) was prepared by heating 14a to reflux for 1 h under N2 in phenol containing a tenfold excess of Pd(OAc)2.

Metal insertion for all the metalloporphyrins was verified by visible absorption spectroscopy, and all products were purified by chromatography on SiO2 (elution with CHCl3/methanol) and recrystallization from CHCl3/methanol. Yields were >90%.

Discussion

Synthesis. The pyrrole trimethyl ester 3 can be selectively hydrolyzed in high yield to the diacid monostearate 4 with NaOH in methanol followed by an acidic workup. The crude product was quite pure and was not noticeably improved by recrystallization from ethanol/H2O.

Diacid 4 is efficiently reduced by BH3 in THF to diol 5. The diacid has a limited solubility in THF and so was reduced as a 1:1 molar mixture. kSee text or ref 25 for the structure.

Attempts to alkylate diol 5 directly through a Williamson ether synthesis failed, so disotylose 6 was prepared in pyridine at 0 °C. Crude 6 is a waxy semisolid at room temperature that is ca. 95% pure by NMR. Attempts to purify it by recrystallization from hexane led to no further improvement.

In the presence of even weak bases, the disotylose 6 undergoes elimination and subsequent polymerization rather than the desired substitution. Therefore the substitution was carried out in the appropriate alcohol with just enough toluene to dissolve the starting material, and no attempt was made to neutralize the toxic acid byproduct. These conditions also led to the transesterification of the pyrrolic α-ester. This product, 7, was rigorously purified (see Experimental Section) before proceeding, as it is difficult to purify the following product.

Compound 7 was oxidized to 8 almost quantitatively with a 5% excess of Pb(OAc)4 in acetic acid/acetic anhydride.

Table I. Calorimetric Data for Compounds 12-19

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<th>Compd</th>
<th>R</th>
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<tbody>
<tr>
<td>19a</td>
<td>Zn</td>
<td>H</td>
<td>K</td>
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- Heating rate 10 °C/min.
- See Figure 2 for the structures of the compounds.
- Bu = n-butyl.
- Hex = n-hexyl.
- Oct = n-octyl.
- Dec = n-decyl.
- K = crystal.
- I = isotropic liquid.
- D = discotic mesophase.
- 1:1 (molar) mixture.
- See text or ref 25 for the structure.

20 °C. After a brief reflux, the solution was again cooled to ca. 20 °C before the addition of the oxidizing agent; any oxidation occurring at higher temperature resulted in lower yields.

The resulting product, H2(ETOAc)Por or M(ETOAc)Por, is identical with the corresponding octaethyloporphyrin (OEP) as far as its photophysical and electrochemical properties are concerned; only its solubility and solid-state thermal behavior are different. We employed method b (direct alkylation of Zn(ETOAc)Por) for the synthesis of the original set of octakis(alkoxyethy1)-porphyrins. This method allowed us to relatively quickly screen a number of different side chain lengths and determine which products possessed liquid crystalline phases. However, the yield from method b is quite low. Method a was subsequently developed to synthesize larger quantities of a specific derivative, in our case, the (octoloxylethyl) compound, in higher yields. Thus, the butyl, hexyl, and decyl derivaties have been prepared only by method b while the octyl derivative has been prepared by both methods.

Octaethanoloporphyrin (H2(ETOAc)Por) (11a) was prepared from diol 5 by first protecting the alcohol functionalities as the acetates, 9, and then oxidizing as before with Pb(OAc)4 to give 10. H2(ETOAc)Por was prepared in an analogous manner to H2(ETOAc)Por, although the final oxidation was done with O3 rather than p-chloranil. The product is insoluble in H2O and THF, very slightly soluble in ethanol, and quite soluble in DMF, DMSO, and pyridine.

Characterization of Porphyrin OctaalkylEthyl Ethers. The transition temperatures and enthalpies of the various porphyrin octaalkyl ethyl ethers are given in Table I. Figure 3 shows a differential scanning calorimetry (DSC) trace of Zn(EtOOCt)8Por. Two major differences between the octaethers and the previously reported octaesters are apparent from the DSC results. First, the liquid crystalline octaethers have only a single discotic LC phase, while four of the six octaesters had two discotic LC phases. Second, the free base (M = 2H) octaethers have very little tendency to form liquid crystalline phases; only one of the four derivatives has an LC phase, and that only over a temperature range of 5 °C. Apparently, the metal plays an important role in the formation of these mesophases. This is in contrast to the octaesters, where the presence or absence of a metal had only subtle effects on the thermal transitions.

Table I shows that the clearing (melting to isotropic) points of the free bases decrease, as expected, with increasing chain length. The butyl derivative melts directly to an isotropic liquid at 154 °C. The hexyl derivative shows a broad peak at 111 °C, which could not be resolved into two peaks even at the slowest scan rate employed, 1.25 °C/min. The octyl derivative of the free base shows a very narrow mesophase from 84 to 89 °C that has an optical texture similar to that of the corresponding zinc derivative (Figure 4). When the chain length is increased to decyl, the free base again melts directly to an isotropic liquid (69 °C). The zinc derivative of the butyl ether has a very narrow mesophase from 159 to 164 °C. The corresponding hexyl, octyl, and decyl ethers each have a single broad mesophase ranging over 67, 55, and 56 °C, respectively, with the clearing point decreasing by ca. 20 °C with each two-carbon increase in chain length.

Mixtures of liquid crystals are commonly employed to expand the LC temperature range relative to the individual components. To test if this behavior extended to the LC porphyrins, a 1:1 (molar) mixture of the zinc octyl and the zinc decyl ethers was prepared. This mixture had a K → D (crystal to discotic LC) transition that was 25 °C lower than that of the decyl ether and 46 °C below that of the octyl ether. Its clearing point was intermediate between that of its two constituents, giving it an LC range of 86 °C. Thus, it is possible to greatly extend the LC range of the porphyrins by making mixtures of homologous compounds.

The central metal has a dramatic effect on mesophase formation in the porphyrin octaethers (Table I), which was absent in the corresponding octaesters. Although it is often difficult to predict mesophase stability (even among the better known rodlike liquid crystals), one obvious mechanism for this effect of the central metal had to be considered: this is an analogue to the well-known tendency of porphyrins to aggregate in organic solvents. As described by Caughey et al., the participation of the porphyrin π system in donor-acceptor type interactions can lead to aggregation. They showed that the tendency of porphyrins to aggregate in solution increased in proportion to the electron-withdrawing character of the meso substituent. More recently, Abraham et al. have demonstrated a correlation between the porphyrin oxidation potential and its dimerization constant. In their model, the central cavity of the porphyrin ring (containing the metal or 2H) is considered a center of negative charge (the π system). The porphyrins have a tendency to stack up with the π cloud of one ring attracted to the central metal of the next. Thus, porphyrins containing electropositive metals such as Cd, which donate substantial electron density to the ring (and are correspondingly easily oxidized), aggregate quite readily. The Pd or free base derivatives, which are harder to oxidize, have a much lower tendency to aggregate. If this mechanism is also operative in mesophase formation, the predicted order of mesophase stability is Cd > Zn > Cu > Pd ≈ 2H. That is, the liquid crystalline temperature range should decrease in this order. When the metallo derivatives of the octyl ether were compared, the order (with the temperature range in parentheses) was Zn(55 °C) > Cu(48 °C) > Pd(34 °C) > Cd(33 °C) > 2H (5 °C). Clearly, no direct correlation exists between mesophase stability and the oxidation potential of the ring. Neither is there any obvious correlation with the size of the central ion. As yet we have no explanation for this order of mesophase stability.

One of the advantages of using porphyrins is that the meso carbons can be derivatized with electron donors or acceptors without drastically changing the crystal packing. Two preliminary attempts in this direction, the meso nitro and the meso cyano derivatives of Zn(EtOOCt)8Por, are shown also in Table I. In the cyano derivative (16b) both transition temperatures are reduced by 22 °C, leaving the LC range at 55 °C. (Note that this is further

Figure 3. Differential scanning calorimogram of Zn(EtOOCt)8Por (14b). Endothermic transitions are plotted upward.

Figure 4. Optical texture of Zn(EtOOCt)8Por (14b) in a capillary-filled cell (thickness ca. 2.5 μm, crossed polarizers, area of view 3.7 × 2.6 mm²): (a) in the liquid crystal phase, 140 °C; (b) in the solid phase at room temperature.
evidence against the dipole-dipole attraction mechanism for mesophase formation; vide supra.) The nitro derivative (17b) has a much reduced LC range of only 25 °C, presumably associated with the buckling of the porphyrin ring caused by the bulky nitro group in the meso position.66

Finally, we wished to compare the mesomorphic properties of an ester of octaethanolporphyrin (Me(EOH)8Por) to that of an ester of octaacetic acid porphyrin, Mc(AcoH)8Por.25 The last two entries in Table I are isomers; they are the octa-n-hexanolate of Zn(EOH)8Por and the octa-n-hexyl ester of Zn(AcoH)8Por, respectively. That is, they differ only in the directionality of the ester linkage. Quite surprisingly, their mesomorphic properties are completely different. The ester of Zn(EOH)8Por (18b) is not a liquid crystal at all, melting to an isotropic liquid at 169 °C. The ester of Zn(AcoH)8Por (19b) shows two broad LC phases extending over a range of 171 °C before melting to an isotropic liquid at 232 °C.25 Clearly, there is still much art contained in the science of liquid crystals.40

**Phase Behavior of Zinc Octakis(β-octyloxyl)ethylporphyrin.**

Zn(EOct)8Por (14b) is a waxy solid at room temperature that crystallizes in long threads that are unsuitable for single-crystal X-ray analysis. When crystals are placed between microscope cover slips and heated, one observes by microscopy between crossed polarizers a definite decrease in viscosity at the crystalline to liquid crystalline phase transition (107 °C). The compound becomes translucent, allowing observation of the optical texture (without polarizers) a definite decrease in viscosity at the crystalline to liquid crystalline phase transition (107 °C). On further heating, there is some minor rearrangement of the compound and the cover slips but the LC does not begin to flow. The optical texture (Figure 4) resembles that of a columnar discotic phase.42 The disclinations are more curved than was the case with the octaesters,22 and the viscosity of the mesophase is substantially lower. If the temperature is held at 5–10 °C below the clearing point (e.g., 155 °C), the LC will flow slightly under the weight of the cover slips.

**Conclusion**

An efficient synthesis has been described for a new series of liquid crystalline porphyrins based on the hitherto unreported octaethylporphyrin. The thermotropic behavior of these compounds has been investigated as a function of the length of the ether side chains and of the central metal. The LC phase is fluid enough to permit some short-range ordering of the material, and the isotropic phase permits capillary-filling and longer range ordering.

**Acknowledgment.** We are grateful to the National Science Foundation for support of the Materials Research Group at the University of Texas under whose aegis this work was performed. We are also grateful to Professor Donald Paul and Dr. Pamela S. Tucker for use of the differential scanning calorimeter.

**Glucosamine-6-phosphate Synthase from Escherichia coli: Mechanism of the Reaction at the Fructose 6-Phosphate Binding Site**

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*Contribution from the Laboratoire de Bioorganique et Biotechnologies, ENSCP, 11, rue Pierre et Marie Curie, 75 231 Paris Cédex 05, France. Received May 26, 1988

**Abstract.** A mechanistic study on the pure glucosamine-6-phosphate synthase from *Escherichia coli* has been undertaken. The stereochemistry of the reaction and the existence of a small intramolecular hydrogen transfer allow us to propose a mechanism consistent with its classification in the 2R aldose/ketose isomerase class. The fate of solvent tritium in substrate and product shows that proton transfer is followed by a slower step and that formation of a fructosimine 6-phosphate intermediate is rate limiting.

The first step in amino sugar metabolism is the interconversion of fructose 6-phosphate and glucosamine 6-phosphate catalyzed by glucosamine-6-phosphate isomerase1 (glucosamine-6-phosphate deaminase, EC 5.3.1.10) and by L-glutamine:fructose-6-phosphate amidotransferase2 (glucosamine-6P synthase, EC 2.6.1.16). The nagB- (deaminase) and glms- (synthase) encoded proteins, mapping respectively at minutes 15 and 84 on *Escherichia coli* chromosome,3 are able to synthesize glucosamine-6P, but only the

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