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Evidence of an ordered columnar mesophase in peripherally octa-\(n\)-alkoxy-substituted phthalocyanines

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Abstract. Liquid crystalline phthalocyanines with eight \(n\)-alkoxy chains have been synthesized and their mesophase structures determined by X-ray diffraction. The mesophases appear to be of the \(D_{ho}\) type. Reasons for the preference of ordered columns are discussed.

Introduction

Phthalocyanines (Pc's) are well known for their semi-conducting properties\(^1\), which are related to the extended \(\pi\)-electron system in these molecules\(^2\). It has been suggested that the electrical conductivity can be extended into the conducting range by increasing the \(\pi-\pi\) overlap between different Pc units\(^3\). One way of increasing this overlap may be forming extended stacks of Pc rings\(^4\). Such stacks have been synthesized by the groups of Hanack\(^5\), Simon\(^4,6\) and Cook\(^7\) starting from phthalocyanine molecules which contain at least six long aliphatic chains. It was established that these materials exhibit liquid crystalline properties, the mesomorphic temperature range being located in the region between 70 and 300 °C. Hanack and Simon used peripherally octasubstituted \(\pi\)-alkoxymethyl derivatives, such as 1c and 2c, while Cook synthesized non-peripherally octa-substituted \(\pi\)-alkyl and \(\pi\)-alkoxy derivatives, such as 1d,e and 2d,e. It was found that derivatives 1e and 2e do not exhibit liquid crystalline behaviour. Apparently, minor changes in the connection of the chains to the central core can appreciably affect the mesomorphic properties.

Synthesis and properties

The synthetic route we followed is shown in Scheme 1. Catechol (1,2-benzenediol) was alkylated with 1-bromododecane and 1-bromoctane in DMSO in the presence of a base (KOH or \(K_2CO_3\)) to give 3a and 3b, respectively. Subsequent bromination was accomplished using molecular bromine in methylene chloride. A Rosenmund–Von Braun reaction\(^9\) yielded the dicyanides 5a and 5b, which were converted into the corresponding Pc's 1a and 1b by refluxing in 2-(dimethylamino)ethanol\(^10\). Heating 5a and 5b in the presence of a copper(II) salt produced the corresponding copper phthalocyanines 2a and 2b. All the synthesized products showed spectroscopic properties (NMR, IR, UV, FAB–MS) in accordance with the proposed structures.
TGA and DSC thermograms of 1a are shown in Fig. 2. These thermograms indicate that in all cases decomposition begins at 290 °C. TGA of the other compounds gave similar results. The peaks in the DSC thermograms are very sharp, indicating that the compounds are of a high purity. DSC data of all compounds are given in Table I. Unfortunately, samples measured by DSC decomposed before the transition to the isotropic liquid could be detected. From microscopic observation it appeared that only compound 1a becomes isotropic before decomposition in the bulk takes place. Decomposition was visible only at the edges of the sample, indicating an oxidative process.

Textures, observed just before isotropization and after slow cooling from the isotropic liquid, are shown in Fig. 3. Upon heating from room temperature to 275 °C, mosaic textures appeared as observed previously for hexagonal discotic liquid crystalline phases \(^1\) (Fig. 3a). Upon cooling a sample of 1a from the isotropic liquid, needle-like defects appear. Such textures are characteristic of hexagonal ordered columnar mesophases \(^1\) and are very different from the fanshaped textures of a Dadm phase, found for 1c\(^6,8\). It is apparent from Fig. 3b that there is a very strong tendency to homeotropic alignment, except at the birefringent defects, where a deviation from homeotropy is present.

**Table I** Phase-transition temperatures and thermodynamic parameters．

<table>
<thead>
<tr>
<th>Compound</th>
<th>Transition temperature/°C</th>
<th>ΔH(kJ/mol)</th>
<th>ΔS(J/K mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>K</td>
<td>M</td>
<td>I</td>
</tr>
<tr>
<td>1a</td>
<td>83[65]</td>
<td>309[303](^c)</td>
<td>109</td>
</tr>
<tr>
<td>2a</td>
<td>95[76]</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>1b</td>
<td>94[77]</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>2b</td>
<td>112[85]</td>
<td>d</td>
<td>d</td>
</tr>
<tr>
<td>1c(^e)</td>
<td>78[55]</td>
<td>260</td>
<td>113</td>
</tr>
</tbody>
</table>

\(^a\) Cited transition temperatures and enthalpies are observed during second and subsequent heating runs. Transition temperatures measured during cooling are given in square brackets. K is crystalline phase, M discotic mesophase and I isotropic phase. \(^b\) \(\Delta S = \Delta H/T\). \(^c\) Determined by polarizing microscopy. \(^d\) Decomposition took place before isotropization could be detected. \(^e\) See ref. 6.

**Structure**

We have performed powder X-ray diffraction measurements on unaligned samples as a function of temperature.
From room temperature up to the phase-transition temperature, a series of reflections are present, characteristic of a rectangular crystalline lattice. At the transition temperature (Table I), a sharp change occurs. Most of the observed lines disappear and, at small angles, at least four new lines appear, in all cases corresponding to reciprocal spacings in the ratio $1/\sqrt{3}/\sqrt{4}/\sqrt{7}$, characteristic of a well developed two-dimensional hexagonal lattice. The structural parameters of the various compounds are summarized in Table II and compared to those of compound 1c.
At wide angles, one very broad and diffuse reflection with an average spacing of 4.6 Å, characteristic of disordered aliphatic chains, is present. A much sharper and relatively very intense reflection, which becomes broader as the temperature rises, is observed at a spacing of approximately 3.4 Å. This is the stacking period of the disc-like cores within one column. For the latter reflection, the distance derived from the observed line is plotted against temperature in Fig. 4a. In Fig. 4b, the correlation length $\xi$, a measure of the intracolumnar order, is presented as a function of temperature. This correlation length was calculated according to the Scherrer formula:

$$\xi = \lambda/(2 \cdot \text{FWHM} \cdot \cos \theta),$$

in which $\lambda$ is the wavelength of the radiation in Å, $w_{1/2}$ the half bandwidth in radians and $\theta$ the Bragg angle of the corresponding reflection. Just after passing the solid $\rightarrow$ mesophase transition, a value of approximately 72 Å or 21 molecules is calculated for $\xi$. For the reflection around 4.6 Å, a value of 5 Å (1 or 2 molecules) was calculated for $\xi$, indicating that the side-chains do have liquid-like order.

### Discussion

The intermolecular distance found for compounds 1a and 2a is larger than that observed for 1c, although the length of a completely extended chain of 1a and 2a is smaller. This discrepancy can be explained by combining the results of X-ray studies published for $o$-dimethoxybenzene derivatives with those of the theoretical calculations we performed on $o$-dipropoxybenzene and $o$-bis(propoxymethyl)benzene.

The X-ray studies indicate the ether linkage to be essentially coplanar with the aromatic ring. Within 2.6°, this coplanarity was confirmed by our calculations on $o$-dipropoxybenzene. The planarity of the Ar$\rightarrow$OCH$_2$ part causes the whole chain to be coplanar with the aromatic ring, provided that all the bonds in the chains are in their most stable antiperiplanar conformation (Fig. 5a). Totally different results were calculated for $o$-bis(propoxymethyl)benzene. In this case, the chains make an angle of 35.1° with the plane of the aromatic nucleus (Fig. 5b). This difference accounts not only for the smaller observed intercolumnar distance, but also for the disorder in the columns of 1c. The steric hindrance of the tilted chains in the alkoxyethyl derivatives is too large to give ordered columns. With the alkoxy derivatives, the fixed position of the first methylene group makes it less favourable for the chains to attain a tilted conformation, thus making a D$_{ho}$ phase more probable.

Table III Structural parameters for the D$_{ho}$ phase at 125°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$D$/Å</th>
<th>$h$/Å</th>
<th>$\ell$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>35.6</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td>2a</td>
<td>35.6</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td>1b</td>
<td>31.2</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td>2b</td>
<td>31.2</td>
<td>3.4</td>
<td>4.6</td>
</tr>
<tr>
<td>1c</td>
<td>31</td>
<td>–</td>
<td>4.6</td>
</tr>
</tbody>
</table>

* $D$: distance between the axes of neighbouring columns; $h$: stacking period; $\ell$: average interatomic distance between the side-chains.

Similar differences between calculated and observed intercolumnar distances have also been found by other investigators, who concluded that the cause of this diff-

### Table III Structural parameters.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\ell$/Å</th>
<th>$\alpha$/degree</th>
<th>$D_{calc}$/Å</th>
<th>$D_{core}$/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>16.4</td>
<td>2.6</td>
<td>47.8</td>
<td>35.6</td>
</tr>
<tr>
<td>1c</td>
<td>17.6</td>
<td>35.1</td>
<td>43.8</td>
<td>31.0</td>
</tr>
</tbody>
</table>

* $\ell$: length calculated for a completely extended chain, $\alpha$: calculated angle between the alkyl chain and the plane of the aromatic nucleus and $D$: intercolumnar distance.
ordered mesophase. The formation of this mesophase is not an interpenetration of chains in neighbouring columns, but rather a large increase in the number of synclinal conformations on going from crystal to mesophase, as indicated by several theoretical and spectroscopic studies on alkyl-chain flexibility. The decrease in effective alkyl-chain length is roughly the same in both compounds (37% for 1a and 44% for 1c), indicating an equal proportion of synclinal conformations. However, for these compounds, some interpenetration of the alkyl chains cannot be excluded. We hope to clarify this point by FTIR and NMR studies. The calculated difference of 4.0 Å between the intercolumnar distance of 1a and 1c is in reasonable agreement with the observed difference of 4.6 Å, supporting the correctness of our steric considerations.

We may therefore conclude that the presence of an ordered or a disordered columnar structure is largely determined by the type of linkage of the side-chains to the disc-like nucleus. This study supports the idea that the existence of a $D_{2d}$ phase is related to the coplanarity of the alkoxyl chains and the central core, allowing a strong cohesion between the discs, as was also observed for truxenes and triphenylenes.

**Conclusion**

New octa-alkoxy substituted phthalocyanines have been synthesized and shown by optical observation and powder X-ray diffraction measurements to exhibit a hexagonal columnar structure. 1-Bromododecane, 1-bromo-octane, bromine and CuCN were commercial products and used as received. DMSO and DMF were stored over molecular sieve prior to use.

**Experimental**

$^1$H NMR spectra were recorded on Varian EM-360 and Bruker WP-200 instruments. Chemical shifts are given in ppm relative to TMS. Abbreviations used are: s, singlet; t, triplet; br, broad; v br, very broad; sh, shoulder; str, strong; w, weak. Infrared and UV/Vis spectra were determined on a Perkin Elmer differential scanning calorimeter. FAB mass spectra were recorded on a VG ZAB 2F spectrometer. X-ray diffraction measurements were performed using a variable temperature Guinier-Lenne camera (Nickel filtered Cu-Kα radiation). Catechol was recrystallized three times from toluene and stored at 4°C under nitrogen. 1-Bromododecane, 1-bromo-octane, bromine and CuCN were commercial products and used as received. DMSO and DMF were stored over molecular sieve (4 Å). Methylene chloride and chloroform were distilled from NaH and stored at 4°C under nitrogen. 1-Bromododecane (210 g, 0.84 mol) was added and the two-phase system again deoxygenized. 125 g (0.9 mol) of K₂CO₃ was then added and the mixture heated at 100°C in a dry nitrogen atmosphere with mechanical stirring. After 8 h, 500 ml of water and 200 ml of methylene chloride were added. The organic layer was separated and the aqueous layer extracted with 3 x 50 ml of chloroform. The combined organic extracts were washed with 200 ml of water, dried over MgSO₄ and concentrated under vacuum. Excess 1-bromododecane was removed by distillation under reduced pressure (134–135°C, 6 Torr). The remaining light-brown solid was recrystallized from acetone (4–7°C). Yield 134 g (75%), of a white solid; m.p. 51°C. FAB-MS $m/z$: 447 (M+). IR (KBr): 750 (o-substituted benzene), 1020 (ArOC) cm$^{-1}$. $^1$H NMR (CDCl₃) δ: 0.90 (t, 6H, CH₃), 1.3 (s, br, 36H, CH₂), 3.90 (t, 4H, OCH₂), 6.90 (s, 4H, ArH).

**1,2-Bis(dodecylbenzene) (3a)**

From a solution of 44 g (0.40 mol) catechol in 150 ml of DMSO dissolved oxygen was removed by repeated evacuation followed by admission of nitrogen. 1-Bromododecane (210 g, 0.84 mol) was added and the two-phase system again deoxygenized. 125 g (0.9 mol) of K₂CO₃ was then added and the mixture heated at 100°C in a dry nitrogen atmosphere with mechanical stirring. After 8 h, 500 ml of water and 200 ml of methylene chloride were added. The organic layer was separated and the aqueous layer extracted with 3 x 50 ml of chloroform. The combined organic extracts were washed with 200 ml of water, dried over MgSO₄ and concentrated under vacuum. Excess 1-bromododecane was removed by distillation under reduced pressure (134–135°C, 6 Torr). The remaining light-brown solid was recrystallized from acetone (4–7°C). Yield 134 g (75%), of a white solid; m.p. 51°C. FAB-MS $m/z$: 447 (M+). IR (KBr): 750 (o-substituted benzene), 1020 (ArOC) cm$^{-1}$. $^1$H NMR (CDCl₃) δ: 0.90 (t, 6H, CH₃), 1.3 (s, br, 36H, CH₂), 3.90 (t, 4H, OCH₂), 6.90 (s, 4H, ArH).

**1,2-Bis(octyloxy)benzene (3b)**

This compound was synthesized from catechol and 1-bromooctane as described for 3a. Distillation of the crude product over a 30-cm Vigreux column (202°C, 2 Torr) yielded 63% of a colourless viscous oil. IR (NaCl): 750 (o-substituted benzene), 1050 (ArOC) cm$^{-1}$. $^1$H NMR (CDCl₃) δ: 0.90 (t, 6H, CH₃), 1.3 (s, br, 24H, CH₂), 3.90 (t, 4H, OCH₂), 6.90 (s, 4H, ArH).

**1,2-Dibromo-4,5-bis(dodecylbenzene) (4a)**

Compound 3a (102 g, 0.23 mol) was dissolved in 500 ml of methylene chloride. To this solution 26 ml (0.50 mol) of Br₂ in 50 ml of methylene chloride was added over ca. 1 h, the first half at 0°C, the second half at room temperature. The mixture was stirred for 2 h at 25°C to complete the reaction, which was checked by TLC (SiO₂: eluent hexane/toluene (3/1 v/v); 4a $R_f=0.55$; 3a $R_f=0.25$; monobromide $R_f=0.95$). The reaction mixture was washed with 10% aqueous NaHCO₃, 10% aqueous NaSO₃, and twice with water. The extract was dried over MgSO₄ and evaporated to dryness. Recrystallization from acetone yielded a white powder. Yield 131 g (94%); m.p. 53.8°C. IR (KBr): 650 (ArBr), 1020 (ArOC) cm$^{-1}$. $^1$H NMR (CDCl₃) δ: 0.90 (t, 6H, CH₃), 1.3 (s, br, 36H, CH₂), 3.93 (t, 4H, OCH₂), 7.07 (s, 2H, ArH).
1.2-Dicromo-4,5-bis(octyloxy)benzene (4b)

This compound was synthesized from 3b as described for 4a. Recrystallization from acetone/MeOH 10/1 v/v yielded 88% of pure product; mp. 39.9°C. IR (KBr): 630 (ArBr), 1020 (ArOC) cm⁻¹. ¹H NMR (CDCl₃) δ: 0.90 (t, 6H, CH₃), 1.3 (s, br, 24H, CH₂), 3.93 (t, 4H, OCH₂), 7.17 (s, 2H, ArH).

1.2-Dicyano-4,5-bis(octyloxy)benzene (5a)

A mixture of 116 g (0.19 mol) 1,2-dicromo-4,5-bis(dodecyloxy)benzene (4a) and 51.6 g (0.58 mol) CuCN was refluxed in 750 ml of DMF for 6 h under an atmosphere of dry nitrogen. After being cooled, the reaction mixture was poured into 2.5 l of concentrated ammonium hydroxide and air was led through the solution for 18 h. The remaining solid was suction-filtered over sintered glass. The residue was washed with 10% aqueous ammonia until the filtrate was colourless. Subsequently, the solid was washed with water until the washings were neutral. The dry, crude product was extracted with ether for two days using a Soxhlet apparatus. The extract was evaporated to dryness and the product recrystallized from hexane. Yield 51 g (53%); m.p. 107°C. FAB-MS m/z: 509 (M⁺), 423 (M-CH₃), 337 (M-CH₂), 251 (M-CH₃CH₂), 37 (CH₃).

2.3.9,10,16,17,23,24-Octakis(octyloxy)phthalocyanine (1a)

A solution of 8.0 g 1,2-dicromo-4,5-bis(dodecyloxy)benzene (5a), (16 mmol) in 8 ml of 2-(dimethylamino)ethanol was refluxed for 78 h in a dry nitrogen atmosphere. After being cooled to room temperature, the mixture was diluted with 30 ml of chloroform and then poured into 200 ml of acetone. The precipitate was filtered over a sintered glass grid. The residue was subsequently extracted in a Soxhlet apparatus with acetone (24 h), methanol (48 h) and ether (24 h). The product was recrystallized from hexane. Its purity was checked with TLC (SiO₂; eluent CHCl₃/acetone 10/1 v/v). When the product was not entirely pure, it was further purified by column chromatography over SiO₂ (eluent: chloroform) under slightly elevated pressure. Yield 2.4 g (30%), K → M: 83°C, M → I: 309°C. IR (KBr): 3290 (w, N-H), 1120-1130 (ArO), 1585 (C=N), 1095 (ArOC), 750 cm⁻¹. IR (KBr): 3290 (w, NH), 2840/2905 (str, CH), 11-19 (144H, CCH₃), 2.17 (br, t, 16H, OCH₂CH₃), 4.51 (br, t, 16H, OCH₂), 8.34 (br, s, 16H, ArH). UV/Vis (CHCl₃) λ_{max}/nm [logε/(dm³·mol⁻¹·cm⁻¹)]: 700 (5.23), 660 (5.19), 644 (4.60), 600 (4.46).

1.2-Dicyano-4,5-bis(octyloxy)benzene (5b)

This compound was synthesized from 1,2-dicromo-4,5-bis(dodecyloxy)benzene (4b) as described for 5a. The crude product obtained after Soxhlet extraction was recrystallized from hexane. Yield 66%; mp. 107°C. FAB-MS m/z: 385 (M⁺). IR (KBr): 2240 /2250 (v, CH), 1272 (ArO), 1095 (ArOC), 750 cm⁻¹. 'H NMR 200 MHz (CDCl₃): δ: -4.1 (v, br, 2H, NH), 0.93 (t, 6H, CH₃), 1.5 (s, br, 24H, CH₂), 4.02 (t, 4H, OCH₂), 7.17 (t, 2H, ArH).

2.3,9,10,16,17,23,24-Octakis(octyloxy)phthalocyanine-copper(II) (2a)

A mixture of 5a (8.0 g, 16 mmol) and 575 mg (4.28 mmol) of anhydrous CuCl₂ in 8 ml of 2-(dimethylamino)ethanol was refluxed for 78 h under a dry nitrogen atmosphere. The work-up procedure was identical to that described for 1a. Yield 3.4 g (40%); K → M: 95°C. IR (KBr): 2840/2905 (str, CH), 1272 (ArO), 1095 (ArOC), 750 cm⁻¹. UV/Vis (CHCl₃) λ_{max}/nm [logε/(dm³·mol⁻¹·cm⁻¹)]: 675 (5.66), 644-652 (sh), 610 (4.77).

References