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 \(n\)-alkoxymethyl derivatives, such as 1\(c\) and 2\(c\), while Cook synthesized non-peripherally octasubstituted \(n\)-alkyl and \(n\)-alkoxy derivatives, such as 1\(d,e\) and 2\(d,e\). It was found that derivatives 1\(e\) and 2\(e\) 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 \(\text{K}_2\text{CO}_3\)) to give 3\(a\) and 3\(b\), respectively. Subsequent bromination was accomplished using molecular bromine in methylene chloride. A Rosenmund–Von Braun reaction\(^9\) yielded the dicyanides 5\(a\) and 5\(b\), which were converted into the corresponding Pc's 1\(a,b\) and 2\(a,b\) by refluxing in 2-(dimethylamino)ethanol\(^10\). Heating 5\(a\) and 5\(b\) in the presence of a copper(II) salt produced the corresponding copper phthalocyanines 2\(a\) and 2\(b\). 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 (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 and are very different from the fanshaped textures of a Dhd phase, found for 1c. 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>1a</td>
<td>83[65]</td>
<td>109</td>
<td>307</td>
</tr>
<tr>
<td>2a</td>
<td>95[76]</td>
<td>108</td>
<td>295</td>
</tr>
<tr>
<td>1b</td>
<td>94[77]</td>
<td>75</td>
<td>205</td>
</tr>
<tr>
<td>2b</td>
<td>112[85]</td>
<td>83</td>
<td>216</td>
</tr>
<tr>
<td>1c</td>
<td>78[55]</td>
<td>113</td>
<td>321</td>
</tr>
</tbody>
</table>

* 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.  
  * ΔS = ΔH/T.  
  * Determined by polarizing microscopy.  
  * Decomposition took place before isotropization could be detected.  
  * See ref. 6.

Structure

We have performed powder X-ray diffraction measurements on unaligned samples as a function of temperature.
Fig. 3. Micrographs of textures observed for compound 1a; a (upper picture): at 275°C after annealing 1 h; b: at 290°C after cooling from the isotropic phase at a rate of 5°C/min.

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.
Table II  Structural parameters for the Dho phase at 125°C.

<table>
<thead>
<tr>
<th>Compound</th>
<th>D/Å</th>
<th>h/Å</th>
<th>t/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; t: average interatomic distance between the side-chains.

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 ξ, a measure of the intracolumnar order, is presented as a function of temperature. This correlation length was calculated according to the Scherrer formula:

\[ \xi = \frac{\lambda}{(2B\cos\theta)} \]

in which \(\lambda\) is the wavelength of the radiation in Å, \(B\) the half bandwidth in radians and \(\theta\) the Bragg angle of the corresponding reflection. Just after passing the solid → mesophase transition, a value of approximately 72 Å or 21 molecules is calculated for ξ. For the reflection around 4.6 Å, a value of 5 Å (1 or 2 molecules) was calculated for ξ, 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 (Allinger's Molecular Mechanics Program MM2P). 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–OCH₂ 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 alkoxymethyl derivatives is too large to give ordered columns. With the alkoxymethyl derivatives, the fixed position of the first methylene group makes it less favourable for the chains to attain a tilted conformation, thus making a Dho phase more probable. In Table III, the intercolumnar distance calculated for the case in which all bonds in the chains have a fully antiperiplanar conformation is compared with the distance observed experimentally. The theoretical distance is calculated from the equation

\[ D_{\text{calc}} = 2l \cdot \cos\alpha + D_{\text{core}} \]

in which \(l\) is the length calculated for the completely extended aliphatic chain, \(\alpha\) the angle between the chain and the plane of the aromatic nucleus (compare Fig. 5a) and \(D_{\text{core}}\) the core diameter. The latter was estimated from CPK models to be 15 Å. The observed intercolumnar distances are appreciably shorter than the calculated ones.

Table III  Structural parameters

<table>
<thead>
<tr>
<th>Compound</th>
<th>l/Å</th>
<th>(\alpha)/degree</th>
<th>(D_{\text{calc}})/Å</th>
<th>(D_{\text{obs}})/Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>16.4</td>
<td>2.6</td>
<td>47.8</td>
<td>55.6</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>

* l: 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.

Similar differences between calculated and observed intercolumnar distances have also been found by other investigators who concluded that the cause of this dif-
ference is not an interpenetration of chains in neighbouring columns, but rather a large increase in the number of syn- 
clinal 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 inter-
columnar distance of 1a and 1c is in reasonable agreement 
with the observed difference of 4.6 Å, supporting the cor-
rectness 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 
ordered mesophase is related to the coplanarity of the alkoxy 
chains and the central core, allowing a strong cohesion 
between the discs, as was also observed for truxenes and 
triphenylenes.

**Conclusion**

New octa-α-alkoxy substituted phthalocyanines have been 
synthesized and shown by optical observation and powder 
X-ray diffraction measurements to exhibit a hexagonal 
ordered mesophase. The formation of this mesophase is 
favoured by the planarity of the molecules. The electrical 
properties of the materials are currently under investigation.

**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 283 and a 
Perkin-Elmer 555 spectrometer, respectively. DSC thermograms 
were determined on a Perkin Elmer differential scanning calorimetry. 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-K\(\alpha\) radiation). Catechol was recrystallized three times from toluene 
and stored at 4°C under nitrogen. 1-Bromododecane, 1-bromo-
ocetane, 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 
CaCl\(\textsubscript{2}\) prior to use.

1.2-Bis(dodecyl)benzene (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 
of K\(\textsubscript{2}\)CO\(\textsubscript{3}\) 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 
was washed with 200 ml of water, dried over MgSO\(\textsubscript{4}\) and concentrated 
under vacuum. Excess 1-bromododecane was removed by distil-
ation 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 (α-substituted benzene), 1020 (ArOC) cm\(^{-1}\). 
\(^1^H\) NMR (CDCl\(\textsubscript{3}\)) \(\delta: 0.90\) (t, 6H, CH\(_3\)), 1.3 (s, br, 36H, CH\(_3\)), 3.90 
(t, 4H, OCH\(_2\)), 6.90 (s, 4H, ArH).

1.2-Bis(octyloxy)benzene (3b)

This compound was synthesized from catechol and 1-bromo-
ocetane 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 (α-substituted benzene), 1050 (ArOC) cm\(^{-1}\). 
\(^1^H\) NMR (CDCl\(\textsubscript{3}\)) \(\delta: 0.90\) (t, 6H, CH\(_3\)), 1.3 (s, br, 24H, CH\(_3\)), 3.90 (t, 4H, OCH\(_2\)), 6.90 (s, 4H, ArH).

1.2-Dibromo-4,3-bis(dodecyl)benzene (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 Br\(_2\) 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 (SiO\(_2\) eluent hexane/toluene 3/1 v/v). \(\delta: 0.55\); 3a \(R_f = 0.25\); monobromide \(R_f = 0.95\). The reaction 
mixture was washed with 10% aqueous NaH\(\textsubscript{2}CO\(_3\)), 10% aqueous 
NaHCO\(_3\), and twice with water. The extract was dried over MgSO\(\textsubscript{4}\) 
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 (CDCl\(\textsubscript{3}\)) \(\delta: 0.90\) (t, 6H, 
CH\(_3\)), 1.3 (s, br, 36H, CH\(_3\)), 3.93 (t, 4H, OCH\(_2\)), 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 1/1 v/v yielded 88% of pure product; m.p. 39.9°C. IR (KBr): 650 (ArBr), 1020 (ArCH2), 3.93 (t, 4H, OCH2), 7.07 (s, 2H, ArH).

2,3,9,10,16,17,23,24-Octakis(octyloxy)phthalocyanine (1b)

This compound was synthesized from 5b as described for 2a. Yield 40%; K → M: 112°C. IR (KBr): 2840/2905 (str, CH), 1272 (ArO), 750 cm⁻¹. UV/Vis (CHCl₃): λmax [logε/(dm³ mol⁻¹ cm⁻¹)]: 705 (5.20), 660 (5.17), 644 (4.45).

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References