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NOVEL AMPHIPHILIC PHTHALOCYANINE MESOGENS

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Abstract A number of novel amphiphilic phthalocyanines (Pcs) have been prepared containing long alkyl ($-C_{16}H_{33}$) and oligo(ethyleneoxy) chains ($-O(C_2H_4O)_3CH_3$) in the peripheral positions. All the Pcs prepared showed liquid crystalline behaviour, with most compounds giving two mesophases. Optical microscopy suggests that the lower temperature mesophase (M1) is a discotic rectangular mesophase, and that the higher temperature mesophase (M2) is a discotic hexagonal phase.

INTRODUCTION

Phthalocyanines (Pcs) have been much studied materials in recent years due to their interesting electro-optical properties, such as electronic conductivity and electrochromism.[1] In addition, attachment of appropriate substituents (e.g. alkyl,[2] alkyloxy,[3] oligo(ethyleneoxy),[4] etc.) can lead to columnar liquid crystalline behaviour.[5] Oligo(ethyleneoxy) substituents are of particular interest due to their polar and hydrophilic nature. For example, recent work in our laboratory has shown that tetra-[oligo(ethyleneoxy)]phthalocyanines exhibit columnar lyotropic mesophases in water in addition to thermotropic columnar mesogenicity.[6]

In this paper we describe the initial studies of the thermotropic mesophase properties of some novel Pc derivatives which contain both hexadecyl and methoxy-tri(ethyleneoxy) (EO_3) side-chains in the 2,3,9,10,16,17,23,24 positions, the so called peripheral sites of substitution. Such Pcs allow investigations into the effects of unsymmetrical substitution patterns on Pc mesogenicity, in addition to providing materials which may also produce ordered assemblies of molecules, such as Langmuir-Blodgett film or micelles, due to their amphiphilic character.[7]

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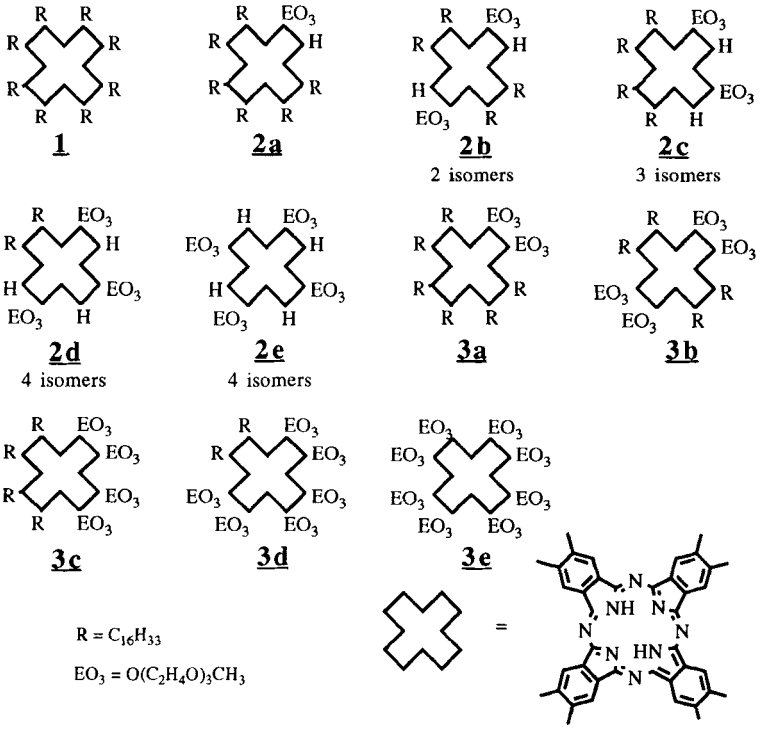
EXPERIMENTAL

Pc preparation

Metal-free Pcs are conveniently prepared by the lithium pentyloxide catalysed reaction of phthalonitrile precursors in refluxing pentanol. Thus, Pcs **2a-e** were synthesised by the reaction between a 1:1 molar mixture of 4,5-dihexadecylphthalonitrile[3] and 4-[methoxy-tri(ethyleneoxy)]phthalonitrile followed by chromatographic separation of the resultant mixture of Pcs (silica, THF/toluene eluent). Similarly, Pcs **3a-e** were prepared by the mixed reaction between 4,5-dihexadecylphthalonitrile and 4,5-di[methoxy-tri(ethyleneoxy)]-phthalonitrile and were also separated by column chromatography (silica, THF/toluene eluent). Pcs **1**, **2a**, **3a-e** are all single compounds; however Pcs **2b**, **c**, **d**, **e** were obtained as mixtures of 2, 3, 4 and 4 inseparable positional isomers, respectively. Each compound gave a Fast Atom Bombardment mass spectrum, ^{1}H nmr (500 M Hz) spectrum and elemental analysis consistent with the proposed structure. A more detailed account of the Pc synthesis will be given in a subsequent paper.[8]



Mesophase Characterisation

The mesophase properties were investigated by using a Nikon Optiphot-2 Optical Microscope with a Mettler FP80 HT Hot Stage. Differential Scanning Calorimetry

(DSC) measurements were carried out using a Seiko 220 DSC machine at a heating rate of 10 °C/min.

RESULTS AND DISCUSSION

Two distinct mesophase textures were observed by optical microscopy, designated M1 and M2. M2, which is displayed by all the Pcs with the exception of **3b**, has a 'fan-like' texture (Fig. 1) characteristic of a columnar mesophase in which the columns are arranged with hexagonal symmetry. The mesophase M1 is exhibited by Pcs **1**, **2a**,**b**,**c** and **3a**,**b**,**c**,**d** and has a 'finger-print' texture (Fig. 2) in which radial striations are superimposed on the fan structures on cooling the appropriate samples below the M2-M1 transition temperatures. This texture is associated with rectangular columnar symmetry, previously denoted as a $D_{rd(P2_1/a)}$ mesophase.[9] Final confirmation of the structures of M1 and M2 await detailed X-ray diffraction studies.

A number of trends are apparent from a consideration of the transition temperatures given in Tables 1 and 2 and depicted graphically in Fig. 3. For example, the Pc clearing temperatures increase with a greater degree of EO_3 substitution. It is likely that this effect is due to the shorter length of the EO_3 moiety in comparison to the hexadecyl chain. A similar relationship between chain length and clearing temperature has been observed previously in a homologous series of octa-alkyl Pcs.[2a] In contrast, for series **3** a greater degree of EO_3 substitution decreases the solid to mesophase transition temperatures to such an extent that the symmetrical octa-EO_3-Pc displays room temperature liquid crystallinity.

FIGURE 1. Photomicrograph (x100) of M2 - **1** at 190°C

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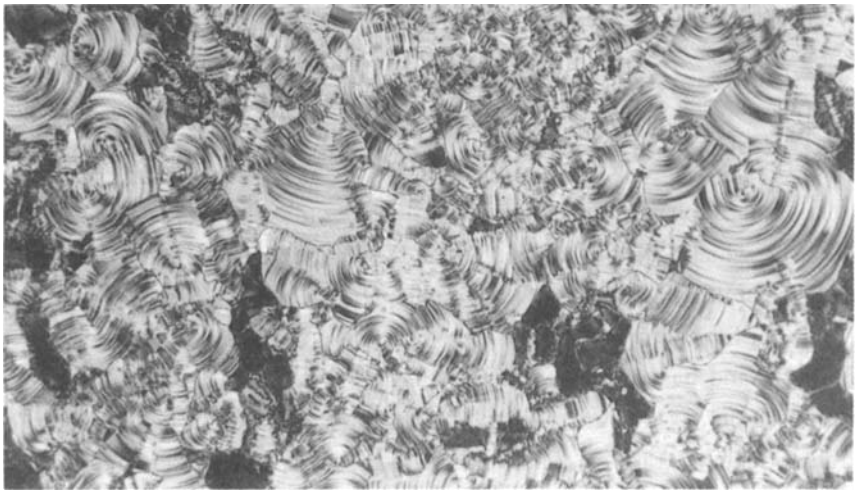

FIGURE 2. Photomicrograph (x100) of M1 - 1 at 160°C

Cpd.	K	T/°C(ΔH/Jg^{-1})	M1	T/°C(ΔH/Jg^{-1})	M2	T/°C(ΔH/Jg^{-1})	I
1	•*	108 (41.9)	•	170 (<1)	•	196 (2.6)	•
2a	•	81 (55.4)	•	86†	•	206 (1.3)	•
2b	•	43 (55.1)	•	142 (23.1)	•	243 (1.0)	•
2c	•	81 (53.4)	•	92 (1.2)	•	243 (1.1)	•
2d	•‡	102 (20.8)			•	302 (1.2)	•
2e	•	78 (24.7)			•	>330	

TABLE 1. Phase Transition Data of 1 and Series 2 from Differential Scanning Calorimetry and Optical Microscopy. * K-K transition at 98 °C. † Transition not seen by DSC, value is from optical microscopy. ‡ K-K transition at 52 °C.

Cpd.	K	T/°C(ΔH/Jg^{-1})	M1	T/°C(ΔH/Jg^{-1})	M2	T/°C(ΔH/Jg^{-1})	I
3a	•	85 (59.5)	•	94 (<1)	•	208 (2.5)	•
3b	•*	78 (32.5)	•			240 (4.3)	•
3c	•	78 (44.0)	•	178†	•	211 (2.1)	•
3d	•	43 (23.1)	•	175 (0.6)	•	229 (1.9)	•
3e	•	19 (12.7)			•	293 (3.5)	•

TABLE 2. Phase Transition Data of Series 3 from Differential Scanning Calorimetry and Optical Microscopy. * K-K transition at 59 °C. † Transition not seen by DSC, value is from optical microscopy.

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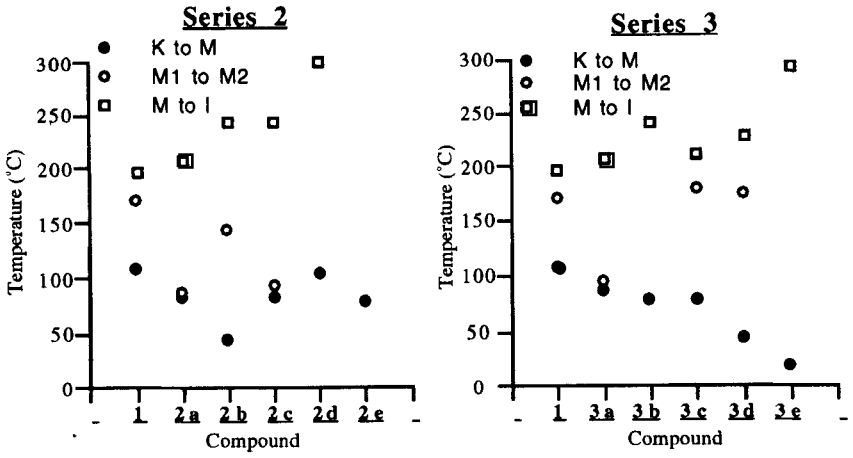

FIGURE 3. Transition temperatures of the Pc derivatives.

Of particular interest is the difference in melting behaviour shown by those Pcs which do not differ in the number of EO/alkyl side-chains but only in their pattern of substitution. Thus, **2b** and **3b** in which the EO_3 side-chains are placed on opposite benzo-subunits on the Pc ring possess the rectangular columnar mesophase over a much wider temperature range compared to the isomers, **2c** and **3c**, in which the EO3 moieties are on neighbouring benzo-subunits. Pc **3b** is a highly unusual Pc mesogen in that it possesses no hexagonal columnar mesophase but only the rectangular columnar mesophase. Detailed X-ray diffraction analysis of the structure within the mesophases should help to explain these interesting results.

CONCLUSION

A number of novel phthalocyanines have been prepared containing differing proportions of alkyl and oligo(ethyleneoxy) chains. The Pcs are easily separated by chromatography and all exhibit one or more columnar mesophase. The lower temperature phase seems to be rectangular in symmetry whereas the higher temperature phase is hexagonal.

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