# 1,4,8,11,15,18,22,25-Octa-alkyl Phthalocyanines: New Discotic Liquid Crystal Materials

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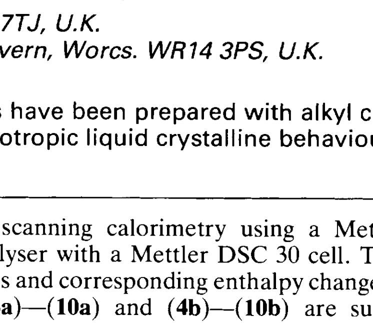
Metal-free and copper(II) 1,4,8,11,15,18,22,25-octa-alkyl phthalocyanines have been prepared with alkyl chain lengths between $C_4$ and $C_{10}$; all except those with $C_4$ and $C_5$ chains show thermotropic liquid crystalline behaviour with one or more mesophases.

Thermotropic liquid crystalline behaviour has been observed in several classes of hexa- and octa-substituted polyaromatic systems[1] such as triphenylene, truxene, and phthalocyanine. These disc-like molecules may either stack cofacially to form columns, the so-called columnar mesophase, or show orientational order in a nematic or lenticular mesophase. Polymorphism has also been observed in these materials which have been given the name 'discotic'.

To date, phthalocyanines (Pcs) reported to exhibit thermotropic liquid crystalline behaviour have been substituted only with long chain alkoxyalkyl groups at some or all of the 'peripheral' (2,3,9,10,16,17,23,24) positions *e.g.* (**1**)—(**3**).[2] We describe here two new series of metal free and copper(II) phthalocyanine derivative (**4**)—(**10**), bearing n-alkyl groups at non-peripheral sites. Both exhibit mesomorphic behaviour. The occurrence of the columnar mesophases in these compounds is unexpected in view of the position and nature of the substituents. The series appear particularly remarkable in that mesomorphic behaviour is observed in derivatives with chain lengths as short as $C_6$. Furthermore, their behaviour contrasts with that of the alkoxy analogues (**11**) and (**12**) which show no liquid crystal phases.[3] The present communication reports the effect upon the mesomorphic properties of (**4**)—(**10**) of varying the alkyl chain length.

The compounds were prepared according to the route depicted in Scheme 1. The 2,5-dialkylfurans were converted into 3,6-dialkylphthalonitriles in a one-pot reaction. Progress of the initial Diels–Alder reaction was monitored by n.m.r. spectroscopy. Once the mixture had reached equilibrium, the reaction was cooled and base was added. Quoted yields in Scheme 1 refer to materials recovered following purification procedures.† The thermal behaviour of the Pcs has been studied both optically, using a Vickers polarising microscope in conjunction with a Mettler FP52 hot stage, and by differential scanning calorimetry using a Mettler TA3000 thermal analyser with a Mettler DSC 30 cell. The transition temperatures and corresponding enthalpy changes for the two subseries (**4a**)—(**10a**) and (**4b**)—(**10b**) are summarised in Figures 1(a) and 1(b) respectively.

Four distinct mobile birefringent mesophases, labelled $D_{1-4}$ were observed with reversible transitions between them and the isotropic liquid, I, accompanied by very little supercooling. On heating, the optical textures were masked by that of the crystal. Therefore examination was carried out by cooling from the isotropic liquid. The mesophase $D_1$ was exhibited by all the compounds with chain length $C_6$—$C_{10}$. It has a characteristic fan texture and a tendency to homeotropy.‡ On further cooling compounds (**7a**), (**6b**), (**7b**), and



(**1**) R = R′ = $-CH_2O[CH_2]_{11}Me$
(**2**) R = R′ = $-CH_2OCH_2CH_2OCH_2CH_2OMe$
(**3**) R = $-CH_2O[CH_2]_{11}Me$, R′ = CN

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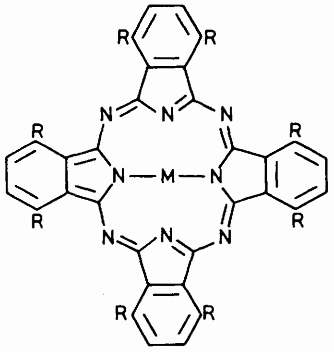
† The Pcs all gave satisfactory elemental analysis data. They were further characterised by u.v.–visible spectroscopy and, in the case of the metal-free derivatives, by $^1H$ n.m.r. spectroscopy.

‡ Homeotropy arises when the columns are orthogonal to the slide surfaces. The material is then viewed along the optical axis and there is no birefringence. Birefringence is observed when the thin layer is disturbed.



(4) **a**; M = H, H, R = n-$C_4H_9$
**b**; M = Cu, R = n-$C_4H_9$

(5) **a**; M = H, H, R = n-$C_5H_{11}$
**b**; M = Cu, R = n-$C_5H_{11}$

(6) **a**; M = H, H, R = n-$C_6H_{13}$
**b**; M = Cu, R = n-$C_6H_{13}$

(7) **a**; M = H, H, R = n-$C_7H_{15}$
**b**; M = Cu, R = n-$C_7H_{15}$

(8) **a**; M = H, H, R = n-$C_8H_{17}$
**b**; M = Cu, R = n-$C_8H_{17}$

(9) **a**; M = H, H, R = n-$C_9H_{19}$
**b**; M = Cu, R = n-$C_9H_{19}$

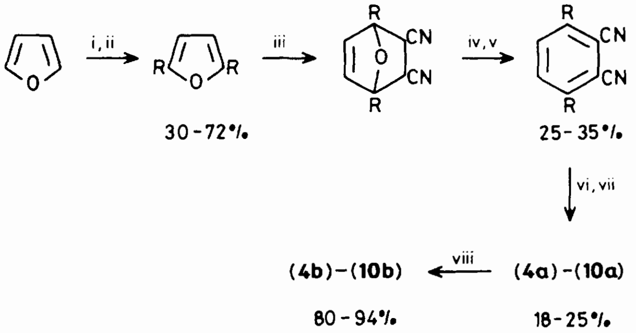
(10) **a**; M = H, H, R = n-$C_{10}H_{21}$
**b**; M = Cu, R = n-$C_{10}H_{21}$

(11) M = H, H, R = n-$OC_5H_{11}$
(12) M = H, H, R = n-$OC_8H_{17}$

(**8b**) showed a second mesophase $D_2$ with a characteristic texture comprising a geometric pattern of needle-like birefringent areas which coalesced. Compound (**6a**) supercooled to 134 °C where crystallisation of mesophase $D_1$ occurred. A second but different mesophase, characterised by a mosaic texture, was observed for (**8a**), (**9a**), (**9b**), and (**10b**). We denote this as $D_3$.

Compound (**8a**) is unique within the present series in exhibiting a total of three mesophases, the third of which, a monotropic mesophase $D_4$, also shows a mosaic texture.

Increasing the length of the alkyl chains reduces all the transition temperatures, and in a remarkably linear way for the $D_1 \rightarrow I$ phase change. Replacement of the central



**Scheme 1.** *Reagents and conditions:* i, BuLi–RBr; ii, BuLi–RBr; iii, (*E*)-NCCH=CHCN; iv, $LiN(SiMe_3)_2$, tetrahydrofuran, −78 °C; v, $H_2O$; vi, $LiOC_5H_{11}$–$C_5H_{11}OH$; vii, AcOH; viii, $(AcO)_2Cu$–$C_5H_{11}OH$.

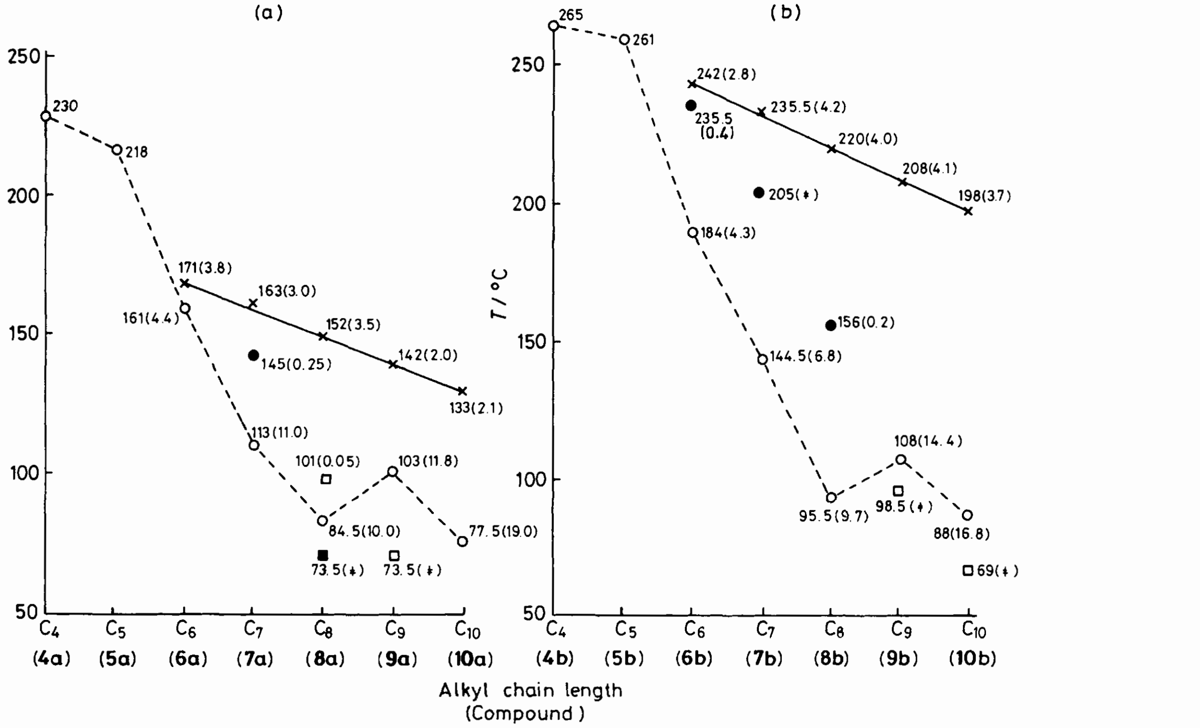


**Figure 1.** Transition temperatures and Δ*H* values (kcal $mol^{-1}$, in parentheses), of the phase changes for (a) metal free octa-alkylphthalocyanines and (b) copper(II) octa-alkylphthalocyanines. ○ = K (crystal) → mesophase ($D_1$ or $D_2$); ● = $D_2 \rightarrow D_1$; □ = $D_3 \rightarrow D_1$; ■ = $D_4 \rightarrow D_3$; × = $D_1 \rightarrow$ I. The mesophases have been provisionally identified by means of their characteristic optical textures under the polarising microscope as follows: $D_1$, fan texture; $D_2$, needle texture; $D_3$, mosaic texture; $D_4$, second mosaic texture. ‡ Indicates a very low value for Δ*H*.

hydrogens by copper(II) has the effect of increasing the thermal stability of the mesophase $D_1$.

The fan texture of mesophase $D_1$ is characteristic of hexagonal packing of the columns.[4] The homeotropic tendency strongly suggests that the columns are orthogonal to the disc-like molecules. The optical texture of mesophase $D_2$ is characteristic of a rectangular column packing and has been observed below the hexagonal mesophase in other systems.[5] It is accompanied by a very small transition enthalpy. The large enthalpy for the $D_1 \rightarrow I$ transition is usual for a disordered mesophase to isotropic transition, a more typical value being 0.3—0.5 kcal $mol^{-1}$ (1 kcal = 4.184 kJ). Unambiguous classification of the mesophases in this class of compounds awaits completion of *X*-ray studies.

The results of this study extend significantly the range of substituents and substitution patterns which give rise to columnar mesophase behaviour in phthalocyanines and promises to offer insight into the way factors such as chain length and central ion control the mesophase parameters.

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