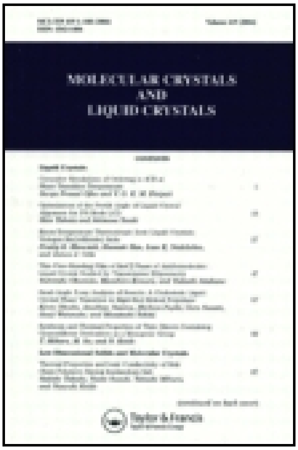

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Mesogenic Behaviour of some 1,4,8,11,15,18,22,25-Octa-alkylphthalocyanines

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Mesogenic Behaviour of some 1,4,8,11,15,18,22,25-Octa-alkylphthalocyanines

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Discotic columnar mesophase behaviour exhibited by ten metal-free and copper 1,4,8,11,15,18,22,25-octa-alkylphthalocyanines has been characterised by optical microscopy, differential scanning calorimetry, x-ray diffraction and electronic absorption spectroscopy. Compounds with side-chains as short as hexyl exhibit one or more mesophases, and a total of three *different* mesophases are apparent for the series as a whole. The highest temperature mesophase is assigned as D_{hd}. At lower temperatures, some compounds develop a second mesophase of hexagonal symmetry, whereas others form a mesophase of rectangular symmetry. One example shows all three mesophases.

INTRODUCTION

Thermotropic mesophases incorporating disc like molecules were first prepared by Chandrasekhar and co-workers in 1977.[1] The original examples, hexa-alkanoyloxy-

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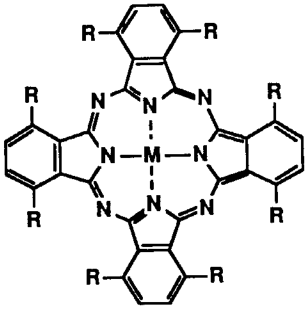
benzenes, were shown to form stacks (the discotic columnar mesophase) with the columns arranged in a hexagonal lattice.[2] Subsequently, other discotic mesogens have been identified and some of these form non-columnar discotic nematic mesophases. The rich variety of structural types which form discotic mesophases has been reviewed recently by Chandrasekhar and Ranganath,[3] a common feature being an aromatic or alicycic nucleus bearing a number of multi-atom side chains.

The first phthalocyanine derivatives to form the columnar mesophase were prepared by Simon and co-workers. Eight long chain alkyloxymethyl groups were located at the peripheral (2,3,9,10,16,17,23,24) positions and various metal ions introduced.[4,5] Mesophase behaviour is retained within lutetium sandwich complexes of this system,[6] polymer analogues[7] and when two of the side chains are replaced by nitrile groups.[8] Further mesogenic phthalocyanines have been described with alternative side chains at the peripheral sites.[5,9] In this paper we present our study of novel discogenic phthalocyanines of type (1).[10] They are distinguished from the previous examples in that the substituent groups R are alkyl chains as short as hexyl and by the substitution pattern which is 1,4,8,11,15,18,22,25.



(1) M = H,H [CnPcH$_2$]

M = Cu [CnPcCu]

n = number of carbon atoms in the (straight) alkyl chains, R.

RESULTS AND DISCUSSION

The synthesis of the metal-free and copper octa-alkylphthalocyanines discussed in this paper has been described elsewhere.[11] Each compound is symmetricallly substituted with eight equivalent unbranched alkyl groups, the chain length varying from four to ten carbon atoms. For convenience we shall refer to the compounds as CnPcH$_2$ or CnPcCu where n is the number of carbon atoms in each of the eight side chains. Mesomorphic behaviour was first suspected when it was observed that some of the compounds underwent a change in shade of colour when gently heated. Further investigation was undertaken using polarising optical microscopy, differential scanning calorimetry (DSC), x-ray diffraction, and uv-vis spectroscopy.

Polarising Optical Microscopy

Each of the compounds was observed to form an isotropic liquid state, I. The temperature for transition to I varied from 133 to 230°C for the metal-free derivatives and from 198 to 265°C for the copper analogues. Transition temperature decreased as the chain length increased. Compounds with C4 and C5 chains melted directly into the liquid state, whereas the C6-C10 derivatives exhibited a total of four different mobile birefringent mesophases, which we have tentatively labelled D1-D4. Transitions are reversible with very little supercooling. During heating the optical textures were masked by that of the crystal state, and so detailed examination was undertaken during cooling from the isotropic liquid.

The mesophase D1 was exhibited by each of the C6-C10 compounds in both the metal-free and copper sub-series and is the first phase to develop from the isotropic liquid. It is characterised by a fan texture and a tendency to homeotropy, the latter suggesting that the columns are aligned orthogonal to the surface of the slide. On further cooling, these derivatives behaved in different ways. $C6PcH_2$ and $C10PcH_2$ merely crystallised. In contrast four compounds, $C7PcH_2$, C6PcCu, C7PcCu, and C8PcCu exhibited the mesophase D2 prior to crystallisation. This has a very distinctive needle-like texture which forms within the fan texture of D1 (Fig. 1). Further diversity within the series was manifested by $C8PcH_2$, $C9PcH_2$, C9PcCu and C10PcCu. These did not go through the D2 mesophase and instead formed another type, characterised by a mosaic texture. This we have denoted as D3.

$C8PcH_2$ differs from all the other compounds investigated in that it displays a total of three mesophases. Its third mesophase, which we first denoted as D4, has a mosaic texture which is very similar to that of D3 from which it develops as the latter is cooled (Fig. 1).

Differential Scanning Calorimetry, DSC

The thermograms obtained by DSC for compounds with C4 and C5 chains showed the expected single endothermic peak which we assign to melting of the crystal into the isotropic liquid. The remaining compounds showed endothermic peaks for each of the transitions referred to above. Three of the four observed transitions from D1 into D3 and the transition from D3 into D4 occur for supercooled material. The transition temperatures and the associated enthalpy changes are summarised in Table I. Trends among the former set of data become clearer when plotted out as in Figure 2.

In both the $CnPcH_2$ and CnPcCu sub-series, there is a striking linear relationship between the D1 → I transition temperature and the number of carbons in the side-chains, the temperature decreasing as the length of the chain is increased. The presence of copper in the centre of the macrocycle also has an effect on the D1 → I transition temperature. The increase in the transition temperature relative to the metal-free analogue is between 65 and 71°C, a trend qualitatively similar to that observed in Simon's system.[5] However, in contrast to the latter, the copper ion in the present series also raises the temperature of transition from the crystal into a mesophase albeit by a fairly small amount. Overall, the role of the copper ion is to enhance the temperature range over which mesophase behaviour occurs by about 55°C.

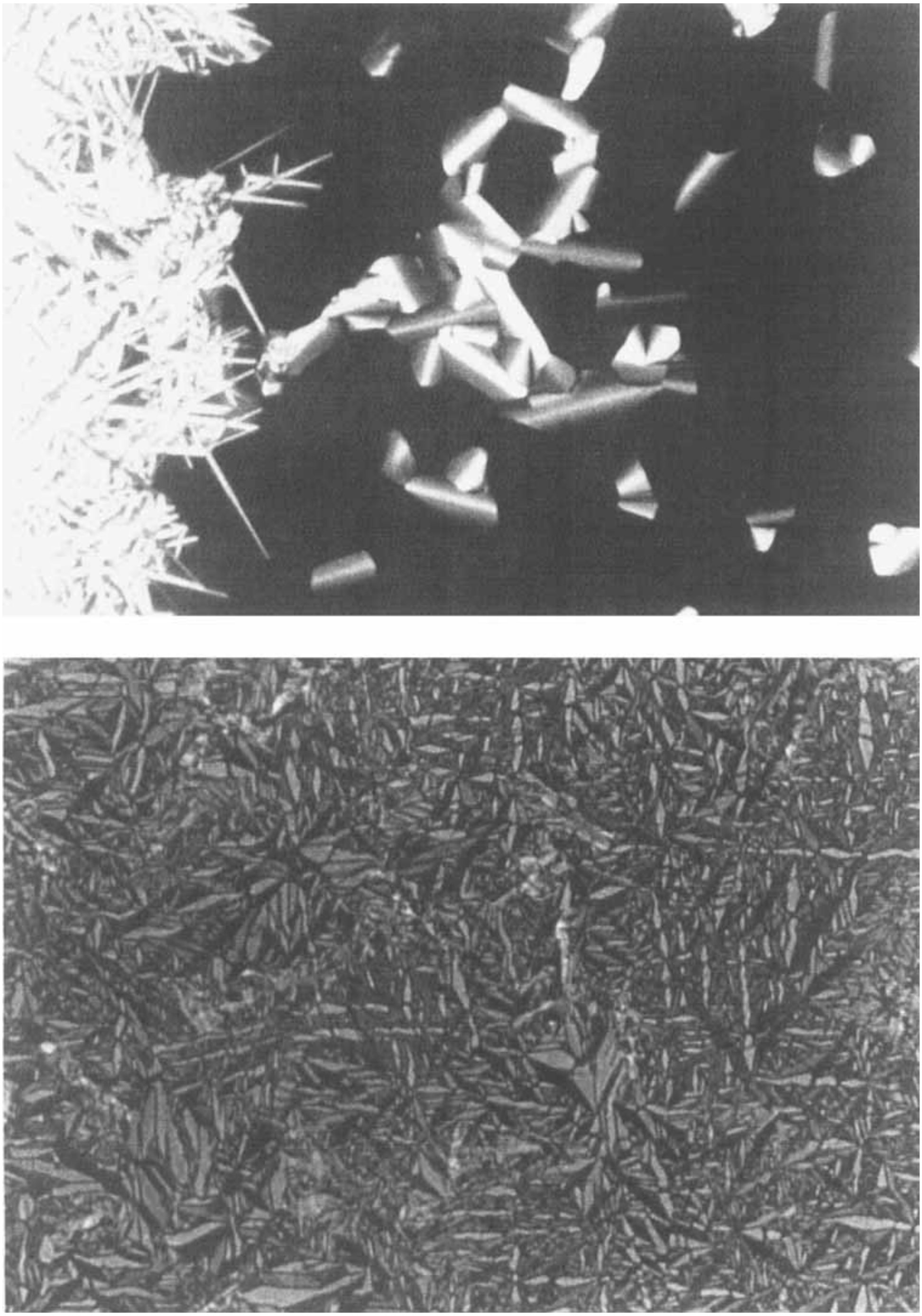
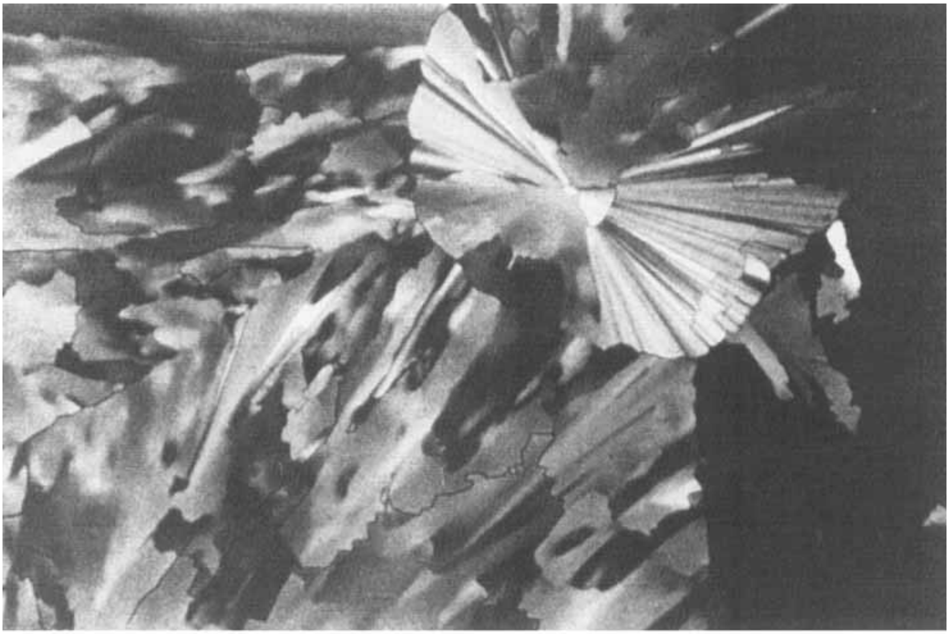


FIGURE 1 Optical textures observed during cooling from the isotropic liquid. Top; C8PcCu at 150°C. The needle texture of D2 (D_{hd}) forming in the fan texture of D1 (also D_{hd}). Bottom; C8PcCu at 140°C showing the fully developed needle texture of D2. See Color Plate III.



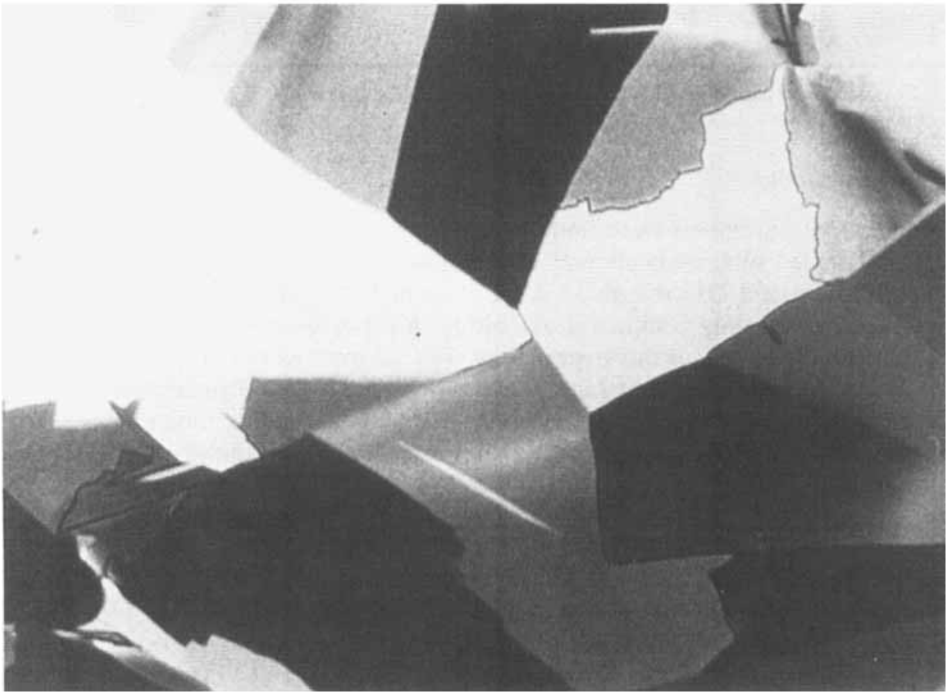


FIGURE 1 (*Continued*) Top; $C8PcH_2$ at 97°C. The mosaic texture of D3 [tentatively assigned as D_{rd}] developing within D1. Bottom; $C8PcH_2$ at 62°C. The mosaic texture of D4 [D_{hd}: see later] developing within D3. See Color Plate IV.

TABLE I

Transition temperatures, T (°C), and enthalpies, ΔH (kcal. mol^{-1}), for metal-free and copper 1,4,8,11,15,18,22,25-octa-alkylphthalocyanines

		K → I	K → D1	K → D2	K → D3	D2 → D1	D3 → D1[a]	D3 → D4[a]	D1 → I
$C4PcH_2$	T	230							
$C5PcH_2$	T	218							
$C6PcH_2$	T		161						171
	ΔH		4.4						3.8
$C7PcH_2$	T			113		145			163
	ΔH			11.0		0.25			3.0
$C8PcH_2$	T				84.5		101	(73.5)	152
	ΔH				10.0		0.05	*b*	3.5
$C9PcH_2$	T		103				(73.5)		142
	ΔH		11.8				*b*		2.0
$C10PcH_2$	T		77.5						133
	ΔH		19.0						2.1
C4PcCu	T	265							
C5PcCu	T	261							
C6PcCu	T			184		235.5			242
	ΔH			4.3		0.4			2.8
C7PcCu	T			144.5		205			235.5
	ΔH			6.8		*b*			4.2
C8PcCu	T			95.5		156			220
	ΔH			9.7		0.2			4.0
C9PcCu	T		108				(98.5)		208
	ΔH		14.4				*b*		4.1
C10PcCu	T		88				(69)		198
	ΔH		16.8				*b*		3.7

[a] Transitions in parenthesis ( ) indicate a monotropic mesophase.
[b] ΔH is very low

X-Ray Diffraction

Initially, measurements were undertaken using a simple flat plate apparatus on a 1 kwatt sealed tube x-ray source. Three examples of the D1 mesophase and one each of a D2 and D3 mesophase were examined. No data could be obtained for D4 because the only compound exhibiting this mesophase, $C8PcH_2$, crystallised within the time scale of this experiment. The samples were not aligned and were contained in 1 mm diameter Lindemann tubes. The x-ray diffraction peaks for D1 correspond to Miller indices of 200/110, and 310/020 (using indices based on a rectangular cell). The absence of a peak corresponding to the 210 plane suggests the lattice is '*c*' centered. This and the fact that the 200 and 110 peaks are coincident, which implies that $a = 3^{1/2} \times b$, indicates that D1 comprises columnar stacks of co-facial molecules arranged within a classical two dimensional hexagonal lattice symmetry, Figure 3. The observed fan texture is also consistent with this conclusion.[12] Data for the unit cell dimensions for the D1 mesophase of $C8PcH_2$, $C9PcH_2$ and C8PcCu appear in Table II. The distance between the axes of neighbouring columns increases from 22.6 to 23.6 Å on changing from $C8PcH_2$ to $C9PcH_2$. An additional band corresponding to a distance of 4.4 Å is also observed which we assign to the spacing between the faces of adjacent molecules. However, it is diffuse which indicates that there is no long range translational ordering of the molecules along

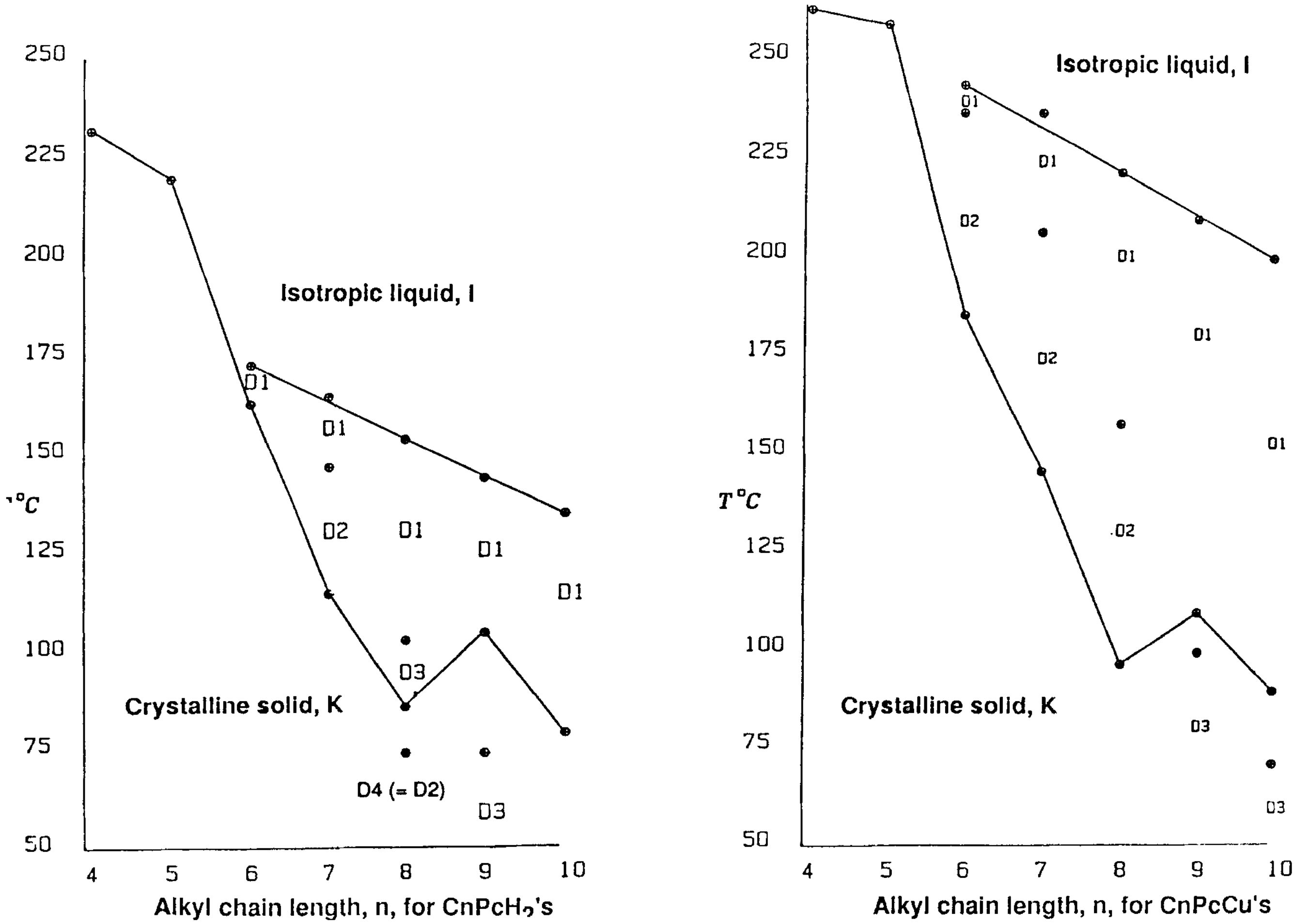


FIGURE 2 Plot of the transition temperatures, *T*, against the number of carbon atoms, n, of the alkyl chain for the series CnPcH_2 (left hand side) and their copper analogues CnPcCu (right hand side).

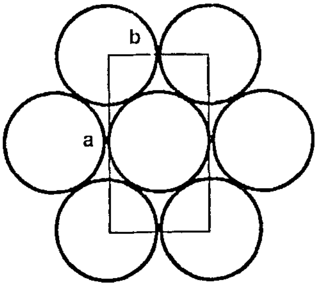


FIGURE 3 Schematic representation showing the "*c*" face within a unit cell and lattice parameters for a D_{hd} mesophase.

TABLE II

Proposed mesophase assignments and lattice parameters from x-ray diffraction patterns

Compound	*T* (°C)	mesophase	lattice parameters *a* (Å)	 *b* (Å)
$C8PcH_2$	115	D1; D_{hd}	39.3 ± 0.2	22.6 ± 0.1
$C9PcH_2$	122	D1; D_{hd}	40.9 ± 0.2	23.6 ± 0.1
C8PcCu	190	D1; D_{hd}	39.9 ± 0.5	23.0 ± 0.3
C8PcCu	125	D2; D_{hd}	39.9 ± 0.9	23.1 ± 0.5
$C8PcH_2$	90	D3; D_{rd}	39.1 ± 0.9	22.6 ± 0.6

the axis of the stack. We therefore denote the structure of D1 as discotic disorderd hexagonal (D_{hd}) after Destrade *et al.*[13] This assignment corresponds to that made by Simon's group for the fan texture observed for their octa-dodecyloxymethylphthalocyanines.[4,5] The distance between the axes of neighboring columns in the latter, *circa* 31 Å, is somewhat greater than for the present compounds, as would be expected on the basis of the longer chains and the different sites of substitution.

The diffraction photographs of the D2 mesophase (needle texture) of C8PcCu were almost identical to those obtained for D1, differing only in having an additional band corresponding to planes with Miller indices 420/510/130. We repeated diffraction measurements on the D1 and D2 mesophases of C8PcCu, using a two dimensional position sensitive x-ray detector. This confirmed that the change in the diffraction pattern on changing from D1 and D2 was the appearance of an extra diffraction ring which indexed quite satisfactorily as the 420/510/130 reflection from the two dimensional hexagonal net. There was apparently no extra peak in the D2 mesophase in the *d* spacing range 3.5 Å to 5 Å which would have been expected if the arrangement of molecules within the columns was becoming ordered. This suggests that the structures of D1 and D2 are closely related, both having disordered columns arranged on hexagonal nets. The observation of the 420/510/130 peak in D2 implies that there is some improvement in the ordering of the net, but no apparent difference in the symmetry of D1 and D2 has been observed. For the present, D2 must also be assigned as D_{hd}. Lattice data are reported in Table II. The situation appears different from that reported for metal-free octadodecycloxymethylphthalocyanine for which a second texture, termed 'striated', could only be differentiated from the fan texture by the appearance of an extra diffraction band not related to the hexagonal net.[4]

The D1 mesophase (mosaic texture) exhibited by C8PcH$_2$ shows diffraction bands corresponding to 200/110, 210, and 310/020. Diffraction arising from the 210 planes indicate that the lattice is not '*c*' centered and that the symmetry of the columns is therefore likely to be rectangular. However, the expected splitting of 200/110 or 310/020 (because $a \neq 3^{1/2} \times b$) was not apparent, possibly because of the finite resolution of the diffractometer. Lattice parameters appear in Table II. Three types of rectangular lattice have been identified hitherto[13] in columnar mesophase systems, *viz* D_{rd} (*C*2/*m*), D_{rd}(*P*2/*a*) and D_{rd}(*P*2$_1$/*a*), where *r* denotes rectangular and *d* disordered, and *C*2/*m*, *P*2/*a* and *P*2$_1$/*a* are the planar space groups. Two factors argue against assigning D3 as D_{rd}(*C*2/*m*). First, the *C*2/*m* space group normally has a larger specific area per molecule than the hexagonal lattice in the same discotic compound; the lattice paramters for the D1 and D3 mesophases of C8PcH$_2$ are the same within experimental error—see Table II. Second, *C*2/*m* should give a significant 200/110 and 400/220 splitting which is not observed. Thus diffraction data for D3 appear to preclude this space group. However, we are unable to distinguish between the likely alternative possibilities, the *P*2$_1$/*a* and *P*2/*a* space groups.

As mentioned earlier the D4 mesophase, formed on cooling the D3 mesophase of C8PcCH$_2$, was not amenable to conventional x-ray diffraction because it crystallised within a few minutes. We therefore applied a technique recently developed to measure simultaneously x-ray diffraction and DSC using synchotron radiation.[14] The measurements were performed while cooling a sample at 5°C per minute, and runs were performed at 2°C intervals. Figure 4 shows the resulting x-ray diffraction patterns. The simultaneously recorded DSC data have allowed us to distinguish the x-ray data for the different phases (D1, D3, D4 and crystal). The data for D1 and D3 agree with the results obtained photographically. In the D4 mesophase the 210 peak disappears and all the observed Bragg peaks can be indexed as a hexagonal net. The 310 peak is present in all three mesophases but grows much stronger in D4, suggesting an improvement in the hexagonal ordering. This leads us to conclude that the structure of D4 at the molecular level is, in fact, the same as that of the D2 mesophase exhibited by some of the other members of the series. The different optical textures observed for D2 and D4 are presumably the result of D2 forming on cooling D1, whereas D4 has only been observed by cooling the D3 mesophase.

Electronic Absorption Spectroscopy

The characteristic colour of phthalocyanines arises from the intense 'Q-band' absorption in the visible region of the spectrum. The observed band shape is known to be very sensitive to the environment of individual molecules. Characteristic spectra, arising from the different crystal forms of phthalocyanine,[15] are themselves very different from those of the monomer in solution. Figure 5 shows the visible region spectra obtained from C8PcH$_2$ (on a silica slide) at various temperatures during cooling from the isotropic liquid phase, through the mesophases D1 and D3, to the crystalline solid. The λ_{max} data are reported in the legend. Each phase/mesophase has characteristic absorption maxima and band shape which provides the origin of the observed change in colour shade when samples are heated. Lines

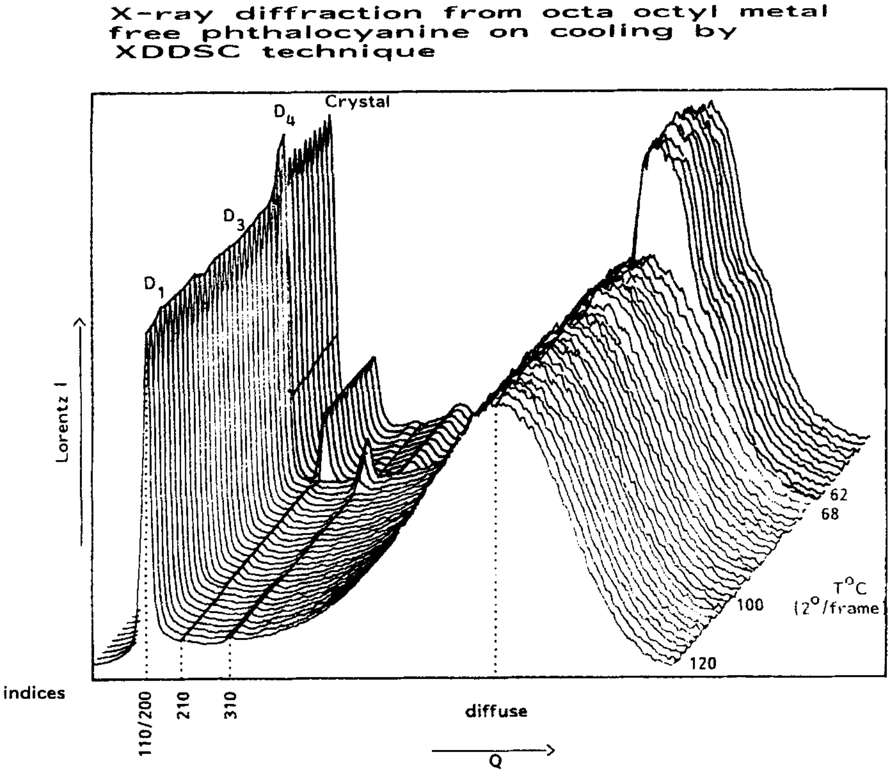


FIGURE 4 X-Ray diffraction from $C8PcH_2$ on cooling the sample, measured by the XDDSC technique. The position of the 110/200, 210 and 310 Bragg peaks and the diffuse peak at 4.8 Å are marked. It can be seen that the 210 peak (indicating a lack of '*c*' centering) is only present in the D_3 mesophase and, more strongly, in the crystal phase. The 310 peak is present in all three mesophases, but grows stronger in the D_4 (= D_2) mesophase, suggesting an improvement in the hexagonal ordering.

2 and 3, which correspond to D_1, but at different temperatures, show small differences in the bandshape. These may reflect minor changes in the organisation of the molecules in the disordered regions of the columns as the temperature is varied.

CONCLUSION

The present series of novel phthalocyanine mesogens is unusual in a number of ways. It exhibits the first examples of discotic liquid crystal behaviour observed for phthalocyanines having substituents at the 1,4,8,11,15,18,22,25 positions; indeed the system is rare among polyaromatic discotic mesogens generally in having the substituents at 'non-peripheral' sites on the ring system. Whereas similarly substituted 1,4,8,11,15,18,22,25-octa-alkoxyphthalocyanines exhibit only crystal to isotropic liquid transitions,[16] the compounds studied here show a rich diversity of mesophase behaviour which is dependent upon chain length and the ion in the

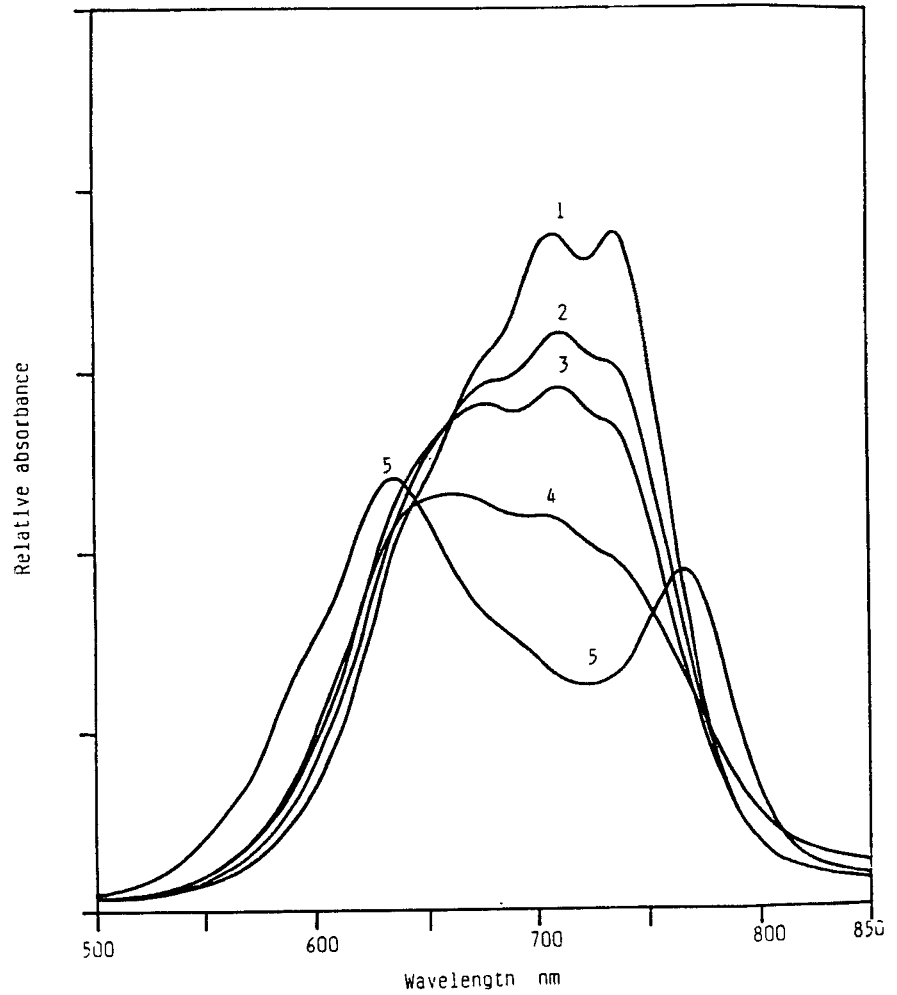


FIGURE 5 Visible region spectra of $C8PcH_2$ on a silica slide. Line 1 at 155°C isotropic liquid, λ_{max} 706, 734 nm; line 2 at 147°C, D1, λ_{max} (674), 710 nm; line 3 at 105°C, also D1, λ_{max} 674, 710 nm; line 4 at 92°C, D3, λ_{max} 662, 702 nm; line 5 at 40°C, crystallised material, λ_{max} 634, 766 nm.

centre of the macrocycle. A total of three distinct mesophases is exhibited by the series. Further x-ray diffraction experiments are needed to elucidate the details of the D2 (D4) and D3 mesophases.

EXPERIMENTAL

The preparation and routine characterisation of the compounds have been described elsewhere.[11]

Microscopy was undertaken using a Vickers polarising microscope in conjunction with a Mettler FP52 hot stage. Optical textures were viewed during cooling from the isotropic liquid phase.

Differential scanning calorimetry was performed using a Mettler TA3000 thermal analyser with a Mettler DSC 30 cell.

X-Ray diffraction measurements were performed using a conventional flat rate plate camera with copper K_α radiation. In some instances, see text, a 2-dimensional position sensitive x-ray detector was used.[17] The x-ray diffraction technique used in conjunction with DSC (XDDSC) and applied here for the study of C8PcH$_2$ has been described elsewhere.[14]

Visible region spectra of C8PcH$_2$ were measured using a Perkin-Elmer Lambda 9 spectrophotometer. The sample, on a silica slide, was heated by a Mettler FP82 hot stage located in the chamber of the spectrometer.

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