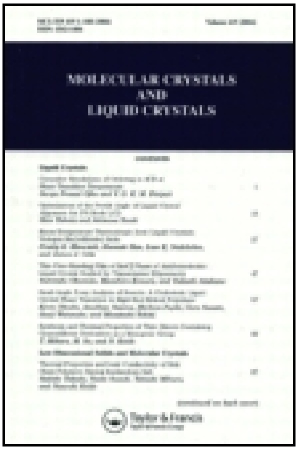

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Columnar Mesophases From Metal and Metal-Free Derivatives of Phthalocyanine

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Columnar Mesophases From Metal and Metal-Free Derivatives of Phthalocyanine

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A series of phthalocyanine octasubstituted derivatives were studied using optical microscopy and X-ray diffraction. Some of them were metal-free; the rest contained various metal atoms such as copper, zinc or manganese in the center of the aromatic cores. For most of the derivatives, the substituents consisted of eight peripheral dodecyloxymethyl chains; for one there were six of these plus two cyano groups attached to the same benzene ring; for another, there were short "polyethylene oxide" chains. All the samples considered in this work exhibited columnar mesophases with hexagonal packing of the columns, stable in a wide range of temperatures.

INTRODUCTION

Columnar mesophases were recently observed for the copper[1] and the metal-free[2] derivatives of octa(dodecyloxymethyl) phthalocyanine. The transition from the crystal to the liquid crystal was found to occur at about 53°C and 79°C, respectively. The transition from the liquid crystal to the isotropic liquid was detected only for the metal-free derivative, at about 260°C; no such transition could be detected for the copper derivative up to 300°C, where decomposition began. The structure of the columnar mesophase was determined using X-ray diffraction. It was described as corresponding to the stacking of the flat aromatic cores of the phthalocyanine molecules in columns, surrounded by the aliphatic chains in a disordered state and laterally assembled in a two-dimensional hexagonal lattice.

In the present paper we report on further observations indicating that columnar mesophases can actually be obtained with a variety of phthalocyanine derivatives.

EXPERIMENTAL AND RESULTS

The mesogenic phthalocyanine derivatives considered in this paper (Table I, Figure 1) were synthesized and purified following a method described elsewhere.[3,4] Four of them are octa(dodecyloxymethyl)-substituted phthalocyanine molecules in which the central hole of the aromatic core contains two hydrogen, a copper, a zinc and a manganese atom, respectively. The fifth compound is a metal-free phthalocyanine molecule substituted with six dodecyloxymethyl peripheral chains and two highly dipolar cyano groups attached to the same benzene ring. The last one is a metal-free phthalocyanine molecule carrying eight trioxa-2,5,8-nonyl peripheral chains.

Observations of microscopic textures and verifications of transition temperatures (Table I) were carried out using a Leitz polarizing microscope equipped with a Mettler FP 52 hot stage. Upon heating above a certain temperature ($T_{K \rightarrow D} < 100°C$), the solid phase present at room temperature was transformed into a highly viscous and spon-

TABLE I

Transition temperatures $C_{12} = CH_3(CH_2)_{11}OCH_2-$; $O_3 = CH_3(OCH)_2 - CH_2)_2OCH_2-$; Pc = phthalocyanine (Figure 1)

Product	T (°C) K → D	T (°C) D → I
$(C_{12})_8PcH_2$	79	~260
$(C_{12})_8PcCu$	53	>300
$(C_{12})_8PcZn$	78	>300
$(C_{12})_8PcMn$	44	280
$(C_{12})_6(CN)_2PcH_2$	~40	>300
$(O_3)_8PcH_2$	<25	>300

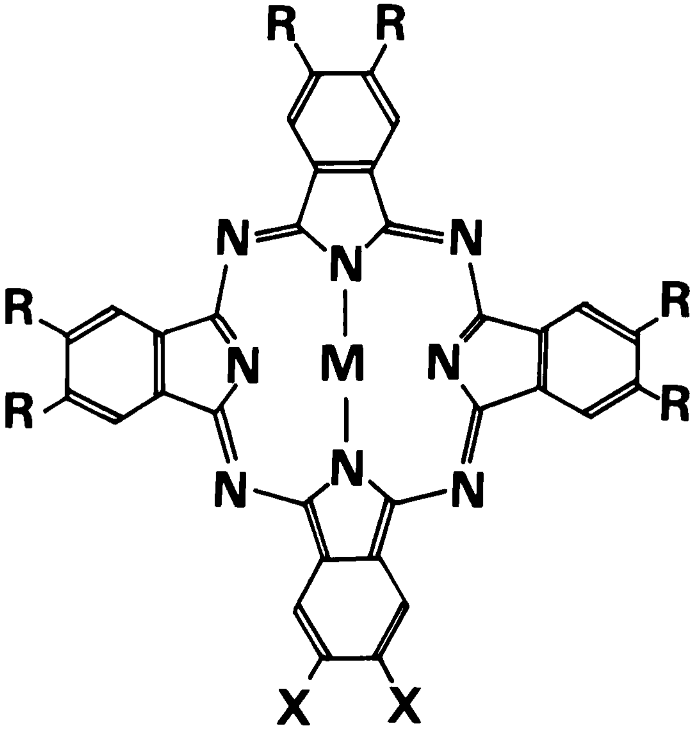

FIGURE 1 Chemical structure of phthalocyanine derivatives (R = C_{12} or O_3; X = CN or R; M = metal or two hydrogen atoms; see Table I)

taneously birefringent mass, which turned out to be a columnar mesophase. Examples of the characteristic texture observed are shown in Figure 2. On further heating, some of the products studied suddenly became optically isotropic at a temperature ($T_{D \rightarrow I}$) lying in the range from 200 to 260°C; others remained stable to above 300°C where they started to decompose.

Powder small-angle X-ray diffraction patterns of the columnar mesophases were recorded using a Guinier focusing camera equipped with a bent-quartz monochromator ($K_{\alpha 1}$ copper radiation). Corresponding wide-angle patterns were recorded with the aid of a Searle camera, equipped with Elliott toroidal mirror optics using Ni-filtered copper radiation (35 kV). All samples were studied at 120°C, except for $(O_3)_8PcH_2$ which was examined at 50°C; heating was achieved using home-made electric furnaces or Mettler PF 52 hot stages.

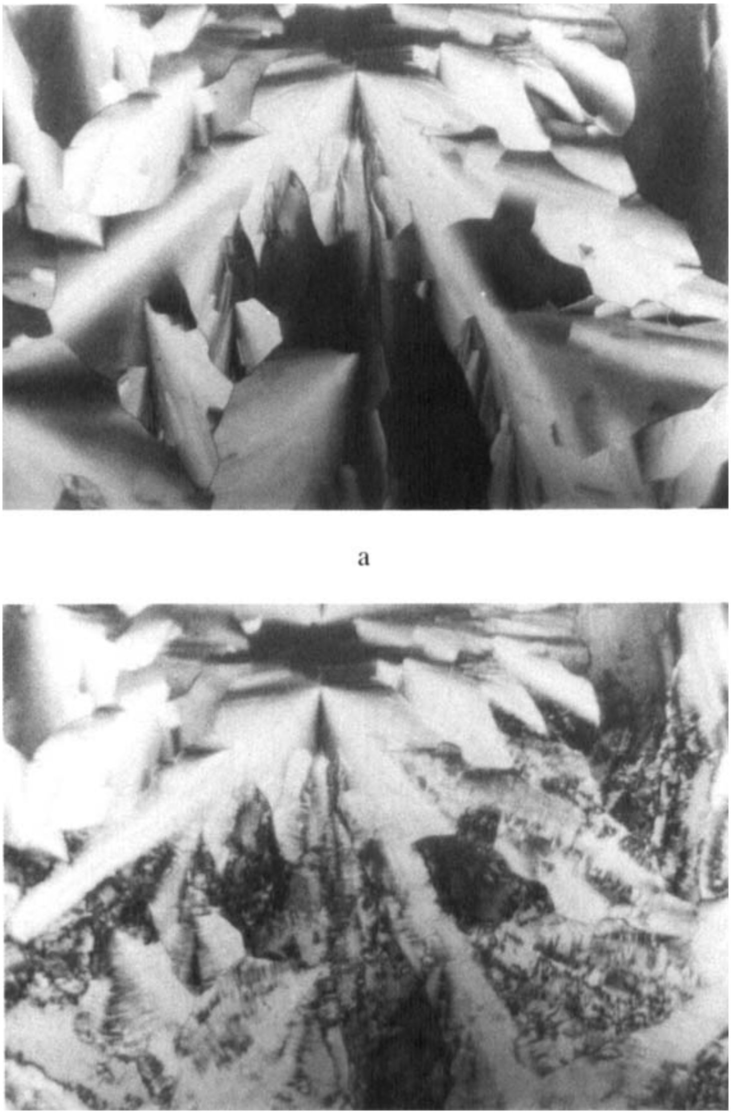

FIGURE 2 Characteristic textures of columnar mesophases

Small-angle X-ray patterns consisted of a series of at least four or five sharp Bragg reflections whose reciprocal spacings were in the ratio 1: $\sqrt{3}$: $\sqrt{4}$: $\sqrt{7}$: $\sqrt{9}$, indicative of the classical two-dimensional

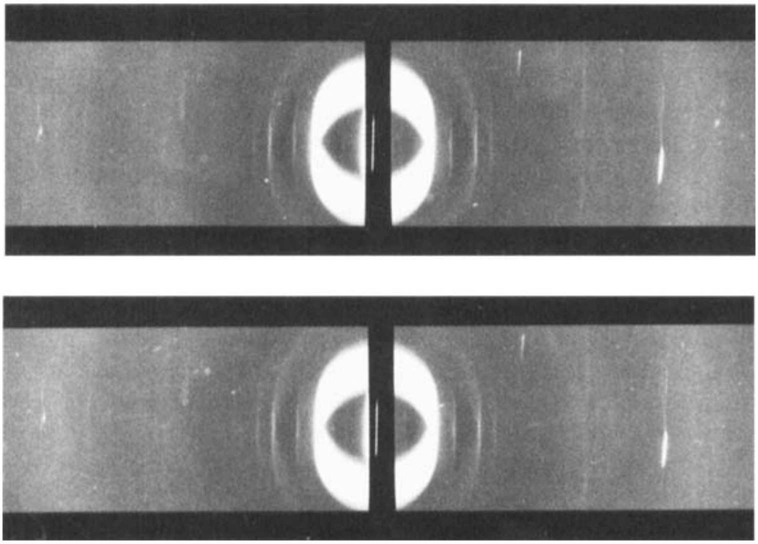

FIGURE 3 Small-angle X-ray diffraction pattern of $(C_{12})PcZn$ at 120°C

hexagonal packing of the columns (Figure 3). The distance D between the axes of neighbouring columns (Table II) was found to be almost the same (D ~ 31 Å) for all the samples considered in this work, except $(O_3)_8PcH_2$ where D was found to be only 25 Å. This difference is due to the shortness of the O_3 side chains as compared to the C_{12} ones. It should be noted in addition, that in the case of $(O_3)_8PcH_2$, the diffraction lines are rather weak and not very sharp; and quite

TABLE II

X-ray diffraction data. D: distance between the axes of neighbouring columns; Λ: period of the modulation along the columns; h: stacking period of molecules within the columns; L: correlation length of disordered side chains

Product	D (Å)	Λ (Å)	h (Å)	L (Å)
$(C_{12})_8PcH_2$	31	20.5	-	4.6
$(C_{12})_8PcCu$	31[a]	-	3.4[a]	4.7
$(C_{12})_8PcZn$	31	21.6	3.6	4.7
$(C_{12})_8PcMn$	31	18.9	-	4.6
$(C_{12})_6(CN)_2PcH_2$	32	-	3.4[b]	4.7
$(O_3)_8PcH_2$	25	-	3.5	4.7

[a] more accurate values than those quoted in ref. 1
[b] rather sharp diffraction peak

unexpectedly, that the (200) and (300) Bragg reflections are absent while the (210) one was clearly present.

For three of the samples, the X-ray patterns contained one extra sharp peak, unrelated to the hexagonal lattice and located in the small-angle region at a Bragg spacing of about 20 Å (Table II, Figure 3). This has been interpreted as indicative of a periodic modulation of the electron density along the columns,[2] probably connected with "a periodic sequence of . . . . pinched regions...." rising from the fact "the optimal spacing of the . . ." aromatic cores" is assumed to be smaller than the optimal spacing of the chains."[5]

In the wide-angle region, the X-ray patterns usually contain a diffuse ring, located at about 4.7 Å (Table II), which is due to the disordered configuration of the flexible peripheral chains. There is an additional band, which is more or less wide, in the X-ray patterns of $(C_{12})_8PcCu$, $(C_{12})_8PcZn$ and $(O_3)_8PcH_2$, and a rather sharp band in that of $(C_{12})_6(CN)_2PcH_2$. Located around 3.5 Å (Table II), these bands correspond to the stacking periodicity of the molecules within the columns.

DISCUSSION

As pointed out in a previous paper,[2] one of the interesting properties of phthalocyanines is their ability to form stable complexes with a wide variety of metal ions. From the observations reported in the present work, it is clear that this property can induce columnar mesophases with various metal atoms incorporated in the columns. It is possible that these will behave as novel one-dimensional conductors.

It is of interest to add in this connection that apparently one is free to modify the chemical nature of the peripheral substituents of the phthalocyanine ligand without destroying the columnar mesophase. In particular, it is perfectly permissible to replace two of the aliphatic side chains by two highly dipolar cyano groups, or even to replace all of them by short polyethylene oxide chains. This offers a further means to control the detailed structure of the mesophase, more specifically the polarity of the intercolumnar regions, making it possible to envisage the production of specialized mesophases containing salts or dopants dissolved between the columns.

It is useful to conclude this paper with a comment on the special case of the dicyano derivative. It is indeed surprising that this compound yields a columnar mesophase, and more specifically a columnar mesophase with a two-dimensional hexagonal lattice, when the symmetry of its molecules is low† and when the transverse dipole moment induced by the cyano group is high. But in fact, what is important with respect to the formation of the hexagonal columnar mesophase is the symmetry of the columns themselves, on the scale of a few molecules. Thus, it turns out that the in-place rotation of the phthalocyanine moieties stacked one above the other within the columns—in particular through an angle of 135° for adjacent molecules, as depicted in Figure 3A, reference 4—is sufficient to smooth out the density irregularity arising from the non-uniform distribution of the side chains and to ensure the weakest possible dipole interactions among the cyano groups.

Further experiments on the subject are, of course, necessary to deal with all of the specific points raised in the present work. Specific volume measurements, combined with the X-ray measurements of D, will allow the accurate determination of the stacking period h. The preparation of oriented samples will no doubt be useful to analyze in better detail the internal structure of the columns. Finally, a study of the temperature dependence of the modulation along the columns would be of interest in order to estimate the thermal stability of the modulation.

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† The absence of a symmetry axis normal to the plane of the molecules is due to the non-uniform distribution of the flexible side chains around the aromatic core.