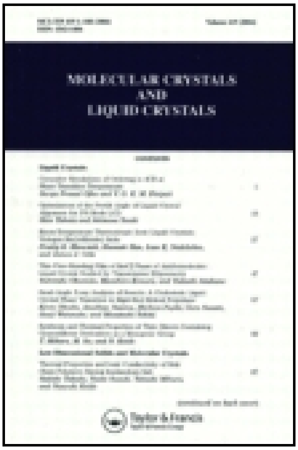

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Discotic Mesophases of the Metal-Free Derivative of Octa (Dodecyloxymethyl) Phthalocyanine

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The mesomorphic behavior of octa (dodecyloxymethyl) phthalocyanine was studied with DSC, optical microscopy, and X-ray diffraction. Two discotic mesophases were observed as a function of temperature. Their structure corresponds to the piling up of the flat molecules in columns which are laterally assembled according to a two-dimensional hexagonal lattice ($D = 31.2$ Å). The repeat distance of the molecules along the columns was found to be of about 4.5 Å. The low-temperature discotic phase showed an extra sharp reflection at 20.5 Å, indicating a further ordering of the molecules.

INTRODUCTION

The discotic mesophases were discovered in 1977 when Chandrasekhar and coworkers first studied the thermal behavior of benzene-hexa-*n*-alkanoates.[1] Quite a few disc-like molecules giving discotic mesophases have since been studied, and their structure investigated with X-ray diffraction.[1–4] It is now clear that discotic mesophases can be observed with organic compounds whose molecules are made up of a central, flat, aromatic core, surrounded by flexible aliphatic chains. Above the *melting* temperature of the chains, within the domain of stability of the discotic mesophase, the molecules pile up in parallel

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columns assembled according to a hexagonal, a rectangular, or an oblique two-dimensional crystal lattice.

The typical features of the discotic mesophases led us to consider the possibility of producing a new class of one-dimensional conductors. The conducting chains would be formed by the spine of the columns which contain the polar, flat, aromatic cores, and which are separated from one another by the neutral, molten, paraffin tails. Phthalocyanines seemed to us particularly suitable for that purpose as their electrical properties have already been investigated to a large extent, and as their aptitude for giving stable complexes with a variety of metal ions has been established.[5] As a first example of such one-dimensional liquid-crystalline conductor, we reported recently the case of the copper octa (dodecyloxymethyl) phthalocyanine.[6]

In the present paper we will be concerned with the thermotropic mesomorphic behavior of the metal-free derivative of the octa (dodecyloxymethyl) phthalocyanine, [hereafter abbreviated to $(C_{12})_8PcH_2$] which might probably be considered as the simplest possible example of discotic phthalocyanine. In a series of papers to be published soon, our intention is to further describe the discotic behavior of phthalocyanines, specifically of those containing metal ions and surrounded by various types of flexible chain.

EXPERIMENTAL

The mesogemic compound $(C_{12})_8PcH_2$ considered in this paper was synthesized and carefully purified following a method described elsewhere.[7] Its molecular weight is $M = 2{,}101.35$, and its chemical formula is represented in Figure 1. The specific gravity was measured at room temperature by means of flotation in binary mixtures carbon tetrachloride/*n*-heptane $\rho_{25} = 1.08 \pm 0.02 \ \mathrm{g \cdot cm^{-3}}$. Finally, using CPK molecular models, the diameter of the aromatic core was estimated at about 15 Å, and the length of the side-chains in the extended conformation at 18 Å.

Detection of phase transitions and measurement of temperatures and enthalpies of transition were made using a Perkin Elmer DSC 2 differential scanning calorimeter, with a heating or cooling rate of 2.5 °C/min. Observations of microscopic textures and checks on transition temperatures were carried out using a Leitz polarizing microscope equipped with a Mettler FP 52 hot stage. The X-ray diffraction experiments were performed using a Guinier focusing camera equipped with a bent-quartz monochromator. The powder

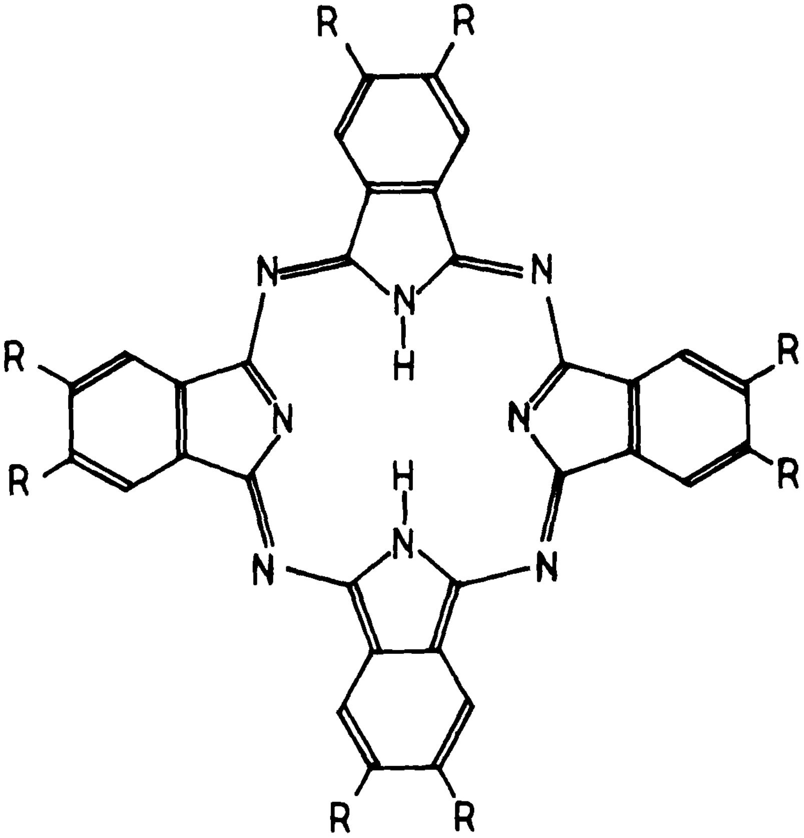

FIGURE 1 Metal-free derivative of $(C_{12})_8PcH_2$ of octa(dodecyloxymethyl) phthalocyanine: $R = CH_2O(CH_2)_{11}CH_3$.

patterns were recorded photographically with a monochromatic copper $K\alpha_1$ radiation.

RESULTS AND DISCUSSION

1. Differential scanning calorimetry

The thermograms recorded with increasing temperature showed very clearly two endothermic peaks. The first one, located at 78 °C, corresponds to an enthalpy of 27.5 kcal/mole. As we shall see later, this peak is related to the transition from the crystal into a discotic mesophase. The second peak, located at 264 °C, corresponds to an enthalpy of only 1.1 kcal/mole. It is related to the transition between a discotic mesophase and the isotropic liquid. Upon cooling from the melt, the thermograms showed two exothermic peaks at 260 °C and 55 °C with the same values of enthalpy as previously. It should be noted that the chemical stability of the product seems to fail at high temperature.

Taking into account the important amount (~ 70%) of aliphatic material in the product, the heat of transition between the crystals and the discotic mesophase can be interpreted to correspond essentially to the melting of the flexible chains alone. That fixes an upper limit for the enthalpy of *fusion* of the aliphatic tails at about 18 cal/g. In good agreement with the value deduced from the data on discotics presented in the literature,[1-4] this value is significantly lower than that (65 cal/g) found for smectics,[8] indicating either that the aliphatic chains are possibly not so disordered in the discotic mesophases as they are in the other liquid crystalline phases, or else that they are not so ordered in the crystalline state as they usually do in the crystals of simple linear aliphatic compounds.

2. Optical microscopy

Upon heating the product above 80 °C, that is above the temperature corresponding to the first transition detected by DSC, one observes the crystals to melt into a highly visquous and spontaneously birefringent mass. On further heating above 260 °C, the sample suddenly becomes very fluid and optically isotropic. This last transition is reversible. On cooling below 265 °C, the anisotropic phase reappears, showing textures (Figure 2) identical to those described previously by Chandrasekhar for a discotic mesophase.[1] However, in a rather wide temperature range (ΔT ~ 10 °C) below 185 °C, the texture gradually changes, generally becoming striated (Figure 3). This transformation is also reversible, but it shades off after a few cycles of heating and cooling the sample. It is worth stressing that in this temperature range no transition could be detected by DSC.

3. X-ray diffraction

Powder X-ray diffraction patterns were recorded at different temperatures. At 25 °C, they consist of a series of sharp Bragg reflections both in the small and in the wide angle regions. They are clearly indicative of the crystalline state of the substance.

At 225 °C, not very far below the clearing point, the X-ray patterns consist of a series of at least four to five sharp Bragg reflections

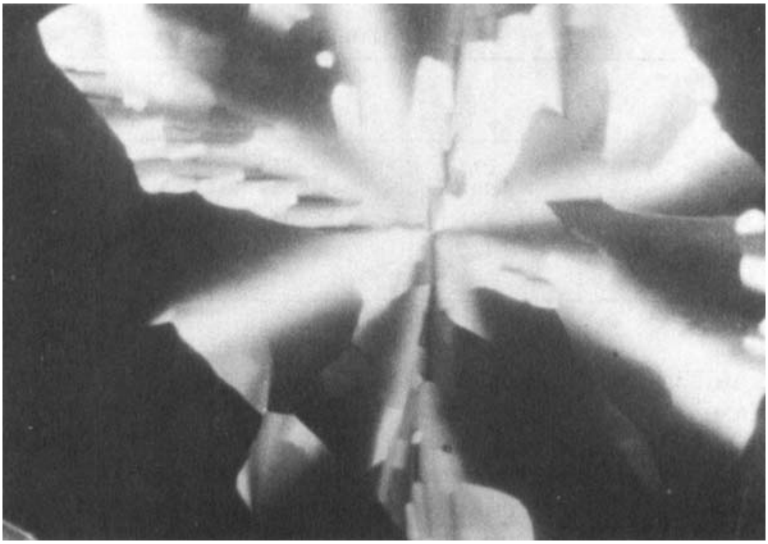

FIGURE 2 Flower-like texture at 190 °C. Crossed polarizers, ×250.

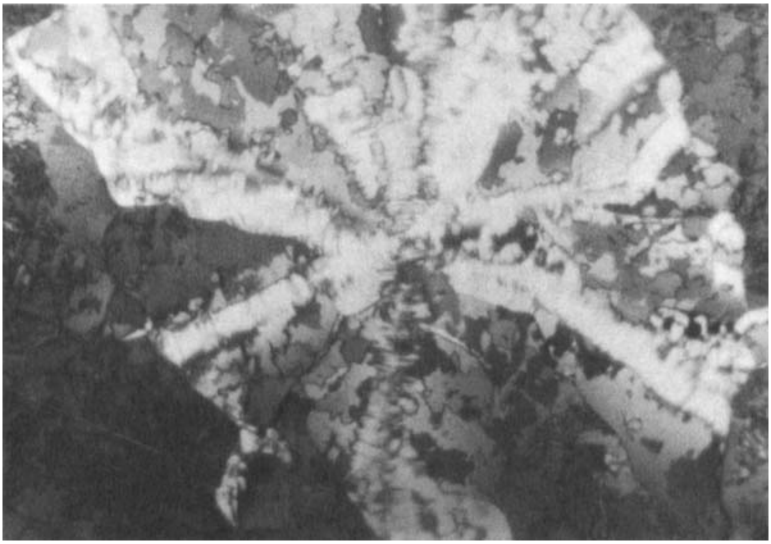

FIGURE 3 Striated flower-like texture at 175 °C (same plate as in Fig. 2, simply cooled down from 190 °C). Crossed polarizers, ×250.

TABLE I

X-Ray Diffraction

	d (Å) obs. at 125 °C	d (Å) Obs. at 225 °C	d (Å) calc.
1	27.1	26.9	27.0
extra	20.5	—	—
$\sqrt{3}$	15.6	15.6	15.6
$\sqrt{4}$	13.5	13.5	13.5
$\sqrt{7}$	—	10.3	10.2

located in the small angle region and corresponding to reciprocal spacings in the ratio $1:\sqrt{3}:\sqrt{4}:\sqrt{7}:\sqrt{9}$ (Table I). In the wide angle region, they contain a diffuse ring located at about 4.8 Å, which is compatible with the disordered state of the paraffin tails. The sharp reflections indicate the presence of a two-dimensional hexagonal crystal lattice as is quite frequently the case for discotic liquid crystals with hexagonal packing of the columns[1-4] (Figure 4). The distance between the axes of two neighboring piles of molecules is found to be $D = 31.2$ Å, in agreement with the geometrical parameters of the molecules reported above. From this value, it is easy to calculate the mean stacking distance h of the disc-like molecules along the axis of the columns using the relation:

$$\frac{\sqrt{3}}{2}D^2h = \frac{M}{\rho\mathfrak{N}}$$

where M is the molecular weight of the product ($M = 2{,}101.35$), ρ its specific gravity and π the Avogadro's number ($\mathfrak{N} = 6.02 \times 10^{23}$). The value of the specific gravity at 225 °C ($\rho_{225} = 0.89 \pm 0.05\ \mathrm{g \cdot cm^{-3}}$) was deduced from that measured at room temperature assuming for the substance the usual thermal expansion coefficient of about 5 to $8.10^{-4}\ \mathrm{K^{-1}}$ and an extra expansion of the volume of about 5 to 8% to take into account the melting of the flexible chains. The mean stacking distance h was thus found to be $h = 4.6 \pm 0.2$ Å. This value coincides with the value of the average interatomic distance found with paraffins in the disordered state. As a consequence, the diffuse ring observed in the wide angle region of the X-ray patterns–which is due to the flexible chains–might very well contain also a contribution from the one-dimensional liquid-like distribution of the flat parts of molecules within the columns. Let us recall here the case of the copper derivative of the phthalocyanine[6] where the repeat distance of the aromatic core

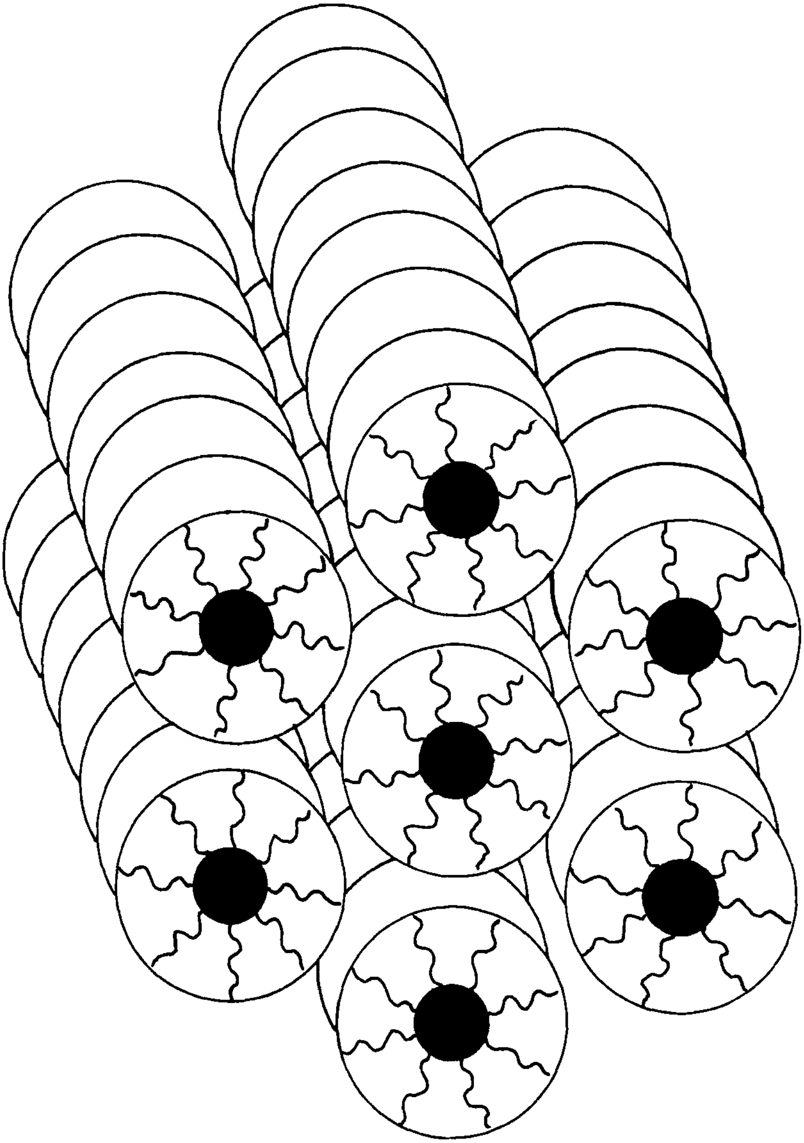

FIGURE 4 Schematic representation of the discotic mesophase.

was only 3.8 Å and where a diffuse ring specifically attributed to the internal structure of the columns was visible separately from that related to the paraffin tails.

With regard to the structural parameters of the discotic mesophase at 225 °C, it is good to calculate S, the area occupied by each flexible chain at its anchoring point on the cylindrical surface of the columns. Knowing the radius R of the aromatic cores ($2R = 15$ Å, as mentioned above), it is clear that

$$S = 2\pi Rh/8$$

The value found ($S = 27.3$ Å^2) is in accordance with that generally measured for disordered aliphatic chains in smectic phases.[9]

At 125 °C, not very far above the transition from the crystal into the discotic mesophase, the X-ray patterns are identical to those registered at 225 °C; however, they contain one more sharp Bragg reflection at 20.5 Å. This extra peak which is unrelated to the hexagonal lattice is observed regardless of whether the sample has been cooled from temperatures higher than 180 °C or heated from the room temperature. It is clear, therefore, that the phase observed at 125 °C is different from that observed at 225 °C, the change from one to the other being reversible in agreement with the optical observations presented above. However, exactly in the same way as with the optical textures (see above), the extra peak indicative of this phase shades off after a few cycles of heating or cooling the sample. From the parameters of the two-dimensional hexagonal lattice $D = 31.2$ Å (identical to that measured at 225 °C), and from the specific gravity $\rho_{125\,°\mathrm{C}} = 0.95 \pm 0.03$ g $\cdot$ cm^{-3} (calculated as previously), the mean stacking distance $h = 4.4 \pm 0.15$ Å was determined. As with the high temperature discotic mesophase, the value of h is in agreement with the position of the outer diffuse ring which has shifted from 4.8 Å at 225 °C to 4.6 Å at 125 °C.

The sharp reflection at 20.5 Å certainly deserves special discussion. At first sight, this could be interpreted to indicate the existence of a three-dimensional lattice. Still arranged laterally according to a two-dimensional hexagonal lattice, the columns could possibly be further correlated as far as their mutual longitudinal positioning is concerned. But the following features go against this interpretation. First, the repeat distance of 20.5 Å, does not correspond to an integral number ($20.5/4.4 = 4.65 \pm 0.15$) of molecules superposed within the columns. Second, the distribution of the molecules within the piles is not regular, as suggested by the absence of a narrow reflection at 4.4 Å.

And third, the columns are embedded in an extended continuous matrix of disordered paraffin chains; so the correlations between them are significantly reduced.

Very likely, the sharp reflection at 20.5 Å is connected with the internal structure of the columns. Indeed, apart from the Bragg reflections due to the hexagonal packing, all the X-ray scattering comes from the electron-density distribution within the columns, provided these can slide freely along their axes. Incomparably sharper than the diffuse outer ring, the reflection at 20.5 Å cannot possibly be attributed to a helicoidal stacking of the molecules on top of one another, as has been observed with other discotic mesophases[2]; rather, it may be attributed to a periodic variation of the electron-density, decoupled from the liquid-like distribution of the molecules. This modulation does not come from the delocalization of the electrons of the aromatic cores (which, as a rule, involves a very small number of electrons); instead, it may come from a periodic distortion of the columns, with a wave-length of 20.5 Å. Of course it should be stressed at once, that the experimental evidence presently available is by no means sufficient to prove definitely this interpretation. Further studies are necessary for that purpose, notably X-ray diffraction measurements on oriented samples and measurements as a function of temperature of the position, the profile, and the intensity of the sharp reflection at 20.5 Å, especially in the neighborhood of the *transition* between the two discotic mesophases at 180 °C.

CONCLUSION

From the observations reported in this paper, it becomes clear that phthalocyanine molecules substituted with several, rather long, flexible chains are perfectly able to exhibit discotic mesophases. It is of interest to note that the chemical and the structural stability of the system seems to be reasonably preserved within a very large range of temperatures. Among the two discotic mesophases identified in this work, the low-temperature one corresponds to what is probably a new type of discotic organization with a short-range liquid-like distribution of the molecules along the columns and a supra-molecular modulation of the electron-density along the same direction.

One of the interesting aspects of phthalocyanines used as discogenic materials is their ability to form stable complex with a wide variety of metal ions, opening up in this way a new area of research, especially in the field of one-dimensional conductors. The introduction of bumps and ramifications in the molecules should probably lower the transition temperatures, so that to permit the formation of discotic mesophases at room temperature.

Acknowledgments

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Note

A theoretical analysis of the longitudinal modulation of the electron density distribution along the axis of the columns was recently presented by P. G. de Gennes (*J. de Phys., Lettr.*, **44**, 567 (1983)).

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