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1980, Gordon and Breach, Science Publishers, Inc.
nted in the United States of America

THE DISCOTIC PHASE OF URO-PORPHYRIN I OCTA-n-DODECYL ESTE

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Abstract: A number of materials which exhibit the relatively new discotic phase have recently been discovered. All of the materials known which show this type of phase have molecular structures that are flat and hexagonal in shape. In this current work, we have shown that a porphyrin compound, uro-porphyrin I octa-n-dodecyl ester, which has a flat, octagonally shaped molecular structure can also exhibit a discotic phase. This is the first report of the discotic liquid crystal phase being exhibited by porphyrin compounds.

INTRODUCTION

In recent years a number of new materials have been discovered that exhibit the discotic mesophase.[1-3] The majority of these compounds have molecular structures that consist of a flat central core structure with six terminal alkyl chains symmetrically placed around the outside edge of the core (for example, benzene-hexa-n-heptanoate). Recently, Lydon et al.[4] have shown that diisobutylsilanediol also exhibits a discotic mesophase. In this case the central core structure has only four peripheral (branched) alky chains attached to it. Furthermore, results obtained by Goodby and Gray,[5] for compounds with molecular structures that are flat and triangular in shape, have shown that it is very unlikely that materials with this type of structure will exhibit discotic phases.

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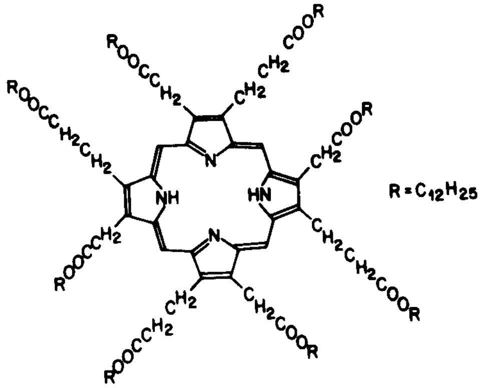
In this present study we have attempted to produce a compound that has a larger central core structure than those previously studied, and which, therefore can accommodate a larger number of n-alkyl, peripheral, carbon-chains. For this purpose we chose to study the melting behavior of the octa-n-alkyl esters of uro-porphyrin I. In this investigation we report the preparation, optical, and thermal behavior of one member of this series, namely, uro-porphyrin I octa-n-dodecyl ester (OCTUPOR-12) (A)



(A)

RESULTS AND DISCUSSION

The melting behavior of uro-porphyrin I octa-n-dodecyl ester was examined firstly by optical microscopy. The transition temperatures obtained by thermal microscopic investigation were as follows:

$$\text{Crystal} \xrightarrow{107^\circ} \text{Isotropic Liquid} \xrightarrow{96.8^\circ} \text{Discotic} \xrightarrow{96.7^\circ} \text{Crystal}$$

The phase exhibited, almost on the point of recrystallization, was classified as being of the discotic type. The phase was characterized by investigation of its microscopic textures, by miscibility experiments, and by differential scanning calorimetry.

Optical studies determined that the compound melted directly from the crystal to the isotropic liquid. However, on cooling, a phase initially separated from the isotropic liquid. The phase separated in a "fronded" type of pattern (plate 1) which developed to give a mosaic and pseudo-fan type texture. On further slight cooling, the phase nucleated crystallization. The exothermal heat of fusion of this process, effectively, melted the phase and crystallization took place directly from the liquid. However, the microscopic textures of the phase were found to be similar to those of the discotic phase.

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PLATE 1. The separation of the discotic phase from the isotropic liquid for uro-porphyrin I octa-n-dodecyl ester (X100).

The phase exhibited by uro-porphyrin I octa-n-dodecyl ester (OCTUPOR-12) was confirmed as being of

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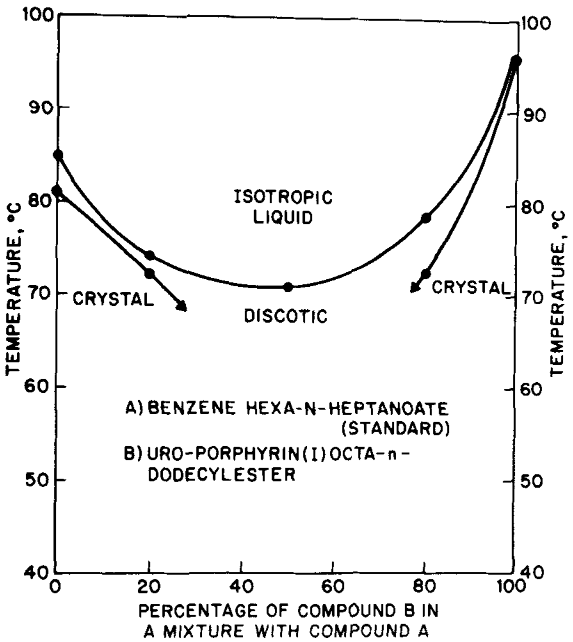

FIGURE 1. Miscibility diagram of state for mixtures (wt.%) of benzene-hexa-n-heptanoate (A) with uro-porphyrin I octa-n-dodecyl ester (B).

the discotic type from miscibility experiments with materials known to show discotic phases. A typical miscibility diagram of state for binary mixtures of the test material with benzene-hexa-n-heptanoate as the standard material is shown in Figure 1. In a similar way to the pure test material some of the mixtures recrystallized at the same time as the transition from the isotropic liquid to the discotic phase. In an attempt to suppress the solidification process in binary mixtures a miscibility experiment was carried out using

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the contact method. By allowing the isotropic liquids of the two pure components to flow together to form a contact a considerable suppression of the recrystallization temperatures for the binary region was obtained. In the two component area, at a temperature of 72°, a continuous region of the discotic phase was obtained (plate 2).

PLATE 2. The contact region between the discotic phase of benzene-hexa-n-heptanoate (top left) and uroporphyrin I octa-n-dodecyl ester (bottom right) (X100).

Finally, differential scanning calorimetry was used to confirm the transition temperature of uroporphyrin I octa-n-dodecyl ester (OCTUPOR-12). The recrystallization temperature was found to be lowered by fast cooling rates (10°/Min.) in comparison to those of slower cooling rates, thus indicating that it is possible to obtain the phase at lower temperatures by quenching the sample. The enthalpy associated with the isotropic liquid to the discotic phase transition was found to be quite large suggesting that the transition

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is probably first order in nature. The values for the enthalpies of transition, in kcal mol^{-1}, are given in Table 1.

TABLE 1

ΔH_{mp}	ΔH_{I-D}	ΔH_{Rec}
7.92	1.01	7.51

CONCLUSIONS

Uro-porphyrin I octa-n-dodecyl ester exhibits a well-defined discotic phase for a narrow temperature range. The fact that this compound exhibits a discotic phase suggests that systems having flat, octagonal shapes will also exhibit discotic phases. As the porphyrin ring system is a widely known structure in the life sciences, it may be used in order to produce new discotic materials.

EXPERIMENTAL

The uro-porphyrin I octa-n-dodecyl ester was prepared from uro-porphyrin I dihydrochloride (Strem) by acid-catalyzed esterification and chromatographed on silica eluting with chloroform. Its purity was confirmed by elemental analysis, UV-visible and infra-red spectroscopy. Microscopic investigations were made using a Zeiss Universal polarizing microscope in conjunction with a Mettler FP52 hot-stage and control unit. Differential Scanning Calorimetry was carried out using a Perkin Elmer DSC 2 thermal analyzer.

REFERENCES

1. S. Chandrasekhar, B. K. Sadashiva, and K. A. Suresh, Pramana, 9, 471, 1977.

2. C. Destrade, M. C. Mondon, and J. Malthete, J. de Physique, 40, 17, 1979.
3. A. Beguin, J. Billard, J. C. Dubois, Huu Tinh Nguyen, and A. Zann, J. de Physique, 40, 15, 1979.
4. J. E. Lydon, J. D. Bunning, J. W. Goodby, G. W. Gray, and C. Eaborn, to be published.
5. J. W. Goodby and G. W. Gray, unpublished results.

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