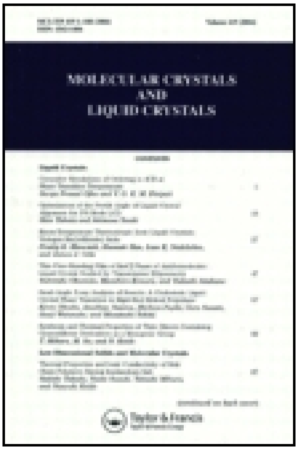

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Carbonaceous Mesophase and Disc-Like Liquid Crystals

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Carbonaceous Mesophase and Disc-Like Liquid Crystals

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The properties of the carbonaceous mesophase are reviewed and some results concerning acenaphthylene pyrolysis are presented. Liquid crystals with disc-like molecules are described and we present a new molecule which exhibits a molecular organization similar to that of the carbonaceous mesophase.

Up to now most mesogenic compounds have been composed of rod-like molecules.[1–3] However in 1961, an anisotropic fluid phase, made up of flat molecules, was evidenced during the thermal treatment of a graphitizable substance.[4–6]

A careful study of this carbonaceous mesophase is difficult because of the high temperature at which it appears (400 to 500°C) and of the lack of chemical stability of organic compounds in this temperature range. Hence, apart from optical microscopy, and relatively simple techniques such as viscosimetry and analytic methods, nothing quite fancy has been undertaken to date. The more serious drawback of this study, is that they are quite often carried out on the anisotropic solid obtained by cooling down the mesophase. To what extent an accurate picture is obtained is not well known yet. Thus there was clearly a need for a well defined chemically stable system which could serve as a model for the carbonaceous mesophase. The past history of our laboratory in both the carbonaceous compounds and the liquid crystal domains prompted us to try an effort in that direction.

In this note we will first review some properties of the carbonaceous mesophase, and then show how the synthesis of disc-like molecules provides systems which exhibit striking analogies with it.

I Carbonaceous mesophase

The mechanisms which take place during the pyrolysis of an organic material has been widely studied[7, 8] but because of their complexity some of them are not well known yet; this is particularly the case for the mesophase formation. This stage of the pyrolysis is characterized by the appearance of anisotropic droplets the diameter of which can reach up to 500 microns when the pyrolized substance is graphitizable.

The viscosity of these units is larger than that of the phase in which they are formed. Using heat treatment time t, and temperature T as parameters, it is possible to draw the existence diagram of the mesophase (Figure 1). Described here is the acenaphtylene case (the mesophase appearance is determined by direct *in situ* observation with a polarizing microscope; a home made programmable heating stage was used.

We show on Figure 2 pictures obtained at different temperatures. One can see that the heating rate slightly affects the temperature at which anisotropic units appears in the isotropic medium. On continued heating they coalesce in larger areas.† This transformation is accompanied by large structural modifications and near 500°C a solid product (coke) is obtained. The density of the mesophase is larger than that of the pyrolyzed medium (called metaphase) and ranges from 1.4 to 1.6 (respectively 1.25 to 1.32 for the metaphase). It was believed for a long time that the carbonaceous mesophase was insoluble in most solvents and particularly in quinoline and pyridine, which were commonly used in its extraction from the metaphase. Recent results[13] show that the mesophase solubility depends on the original material from which it is formed and that the percentage of the mesophase is not necessarily the same as the one of insolubles. Direct optical observation seems to be the best way of evaluation of this percentage.

The exact chemical composition of the mesophase is hard to know. It depends on the pyrolyzed compound and is continually changing. Mass spectrometry studies have shown the existence of numerous chemical substances.[10, 11] The average molecular weight of the mesophase is in the 1800 to 2000 range, much larger than that of the metaphase. This value increases with temperature and heat treatment time. The carbon-hydrogen ratio is large[7] which indicates an important aromaticity percentage. However some recent results[14] obtained from a magnetically oriented mesophase sample, subsequently cooled and studied at room temperature, suggests the existence of small aromatic molecules or large molecules composed of small aromatic units linked together with alkyl bonds. In any case it seems legitimate to consider that the mesophase is a nematic liquid crystal in

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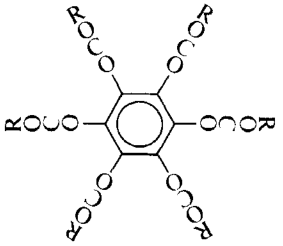
† Large scale preparation of this phase has been achieved in order to perform viscosity, magnetic anisotropy, X-ray and EPR measurements.[9]

which the molecular planes lie on the average perpendicular to the optical axis.

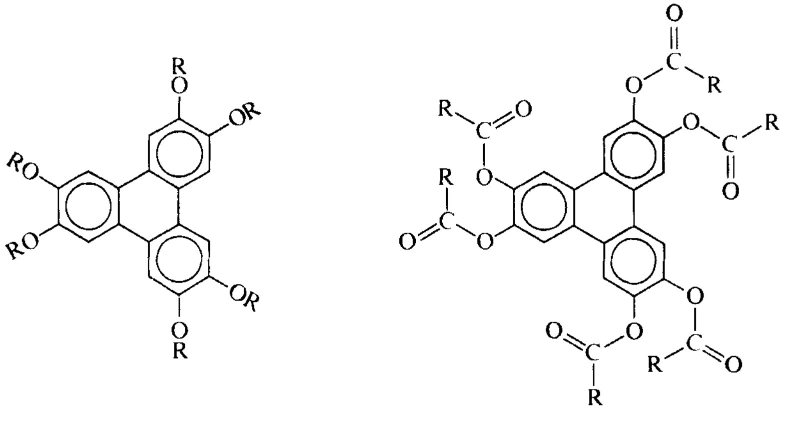
2 Liquid crystals with disc-like molecules

Numerous attempts have been made to obtain mesophases built up with flat molecules. These have been successful recently[15–19] and two different series of molecules have already been studied:

-benzene-*n*-alkanoates:



-hexasubstituted triphenylenes:



In our laboratory we particularly studied the hexaalkoxy and hexaalkanoates of triphenylene and especially the influence of the alkyl chain length ($n = 1$ to $n = 13$) on the nature and the existence domain of the phases.[18]

The existence of a new polymorphism has been shown in the case of several hexaesters with long alkyl chains[18] ($R \geq C_{10}H_{21}$); for these different compounds three mesomorphic phases called D_0, D_1, D_2 have been

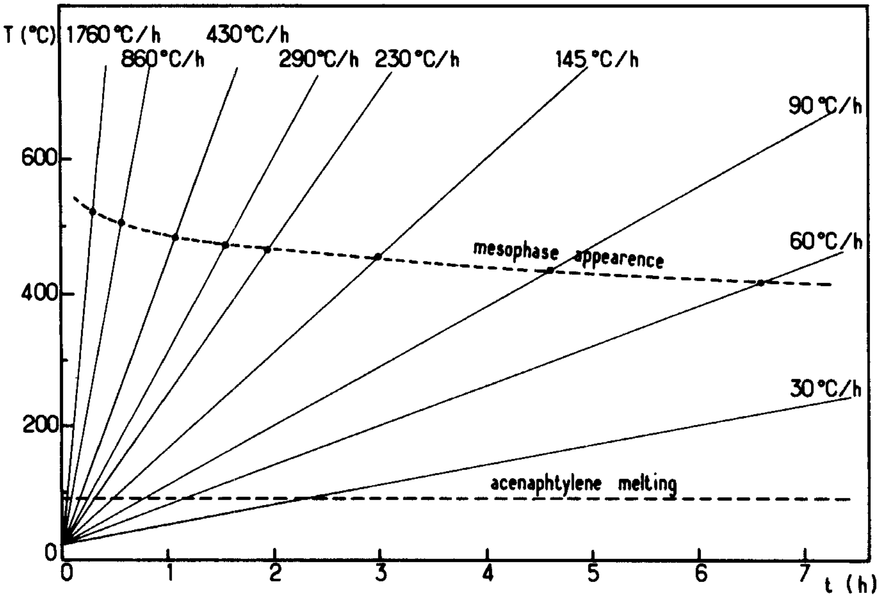
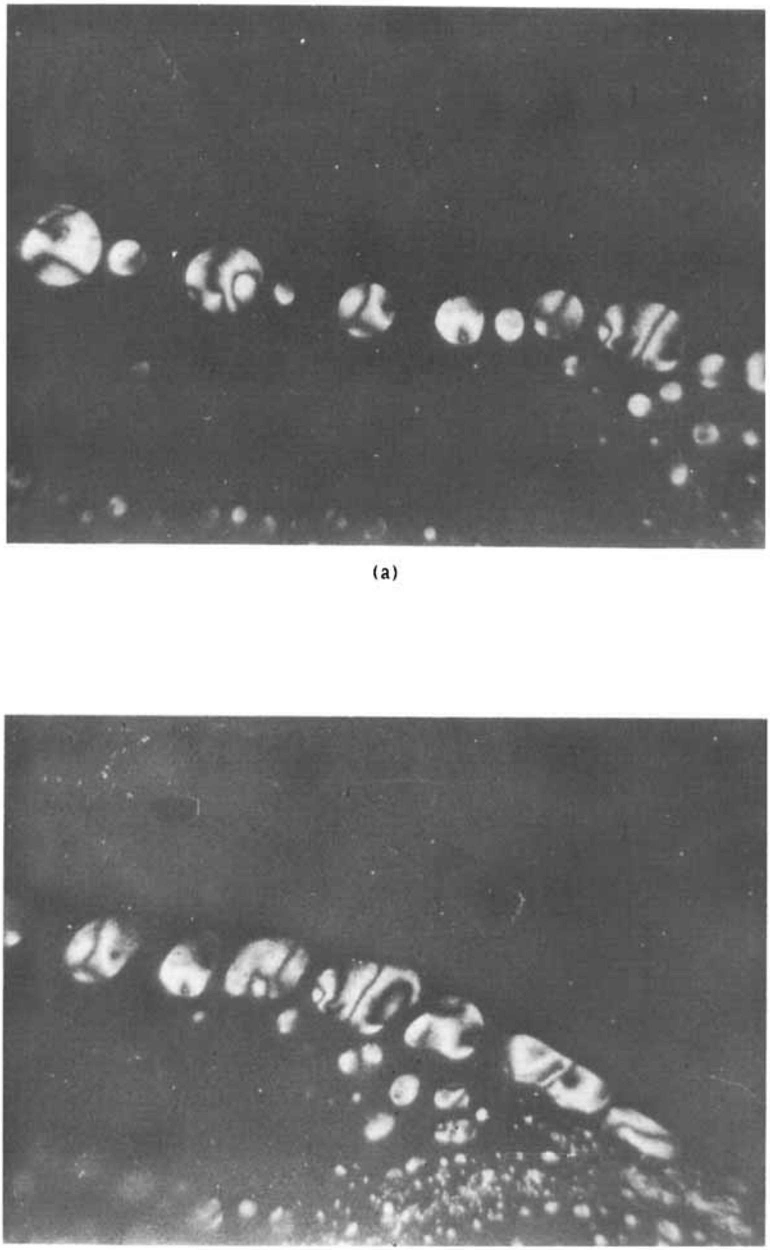


FIGURE 1 Existence diagram of the mesophase obtained by heat treatment of acenaphtylene.

described.[19] Joint studies by X-ray diffraction and by the isomorphic method[23] allows us to propose a classification of these new phases. This classification is based on the symmetry of the piles (hexagonal or rectangular), on the order in the pile and on optical texture.[21] In fact these X-ray measurements have shown this original arrangement of the molecules:[20] they resemble piles of plates. The quasi crystalline cohesion of these piles is caused by the polyaromatic motifs. On the contrary one cannot find any correlations between piles which slide over each other (by means of the quasi liquid alkyl chains). These phases appear to be considerably different from those of the carbonaceous mesophase. A comparison of optical microscopic observations of the disc-like mesophases of the triphenylene derivatives on one hand (Figure 3) and of a carbonaceous mesophase on the other (Figure 2d) is a reliable confirmation that the molecular organization in these mesomorphic phases are not the same. Particularly one cannot find any thread-like textures in the disc-like mesophases.

3 New disc-like molecules with a molecular organisation similar to the carbonaceous mesophase

The hope was that by introducing some kind of disorder in the piles of disc-like molecules, one would eventually get a molecular organisation quite similar to that of the carbonaceous mesophase. Hence the influence of the



(a)

(b)

Figure 2a, 2b Microscopic optical textures of samples with various proportions of anisotropic units.

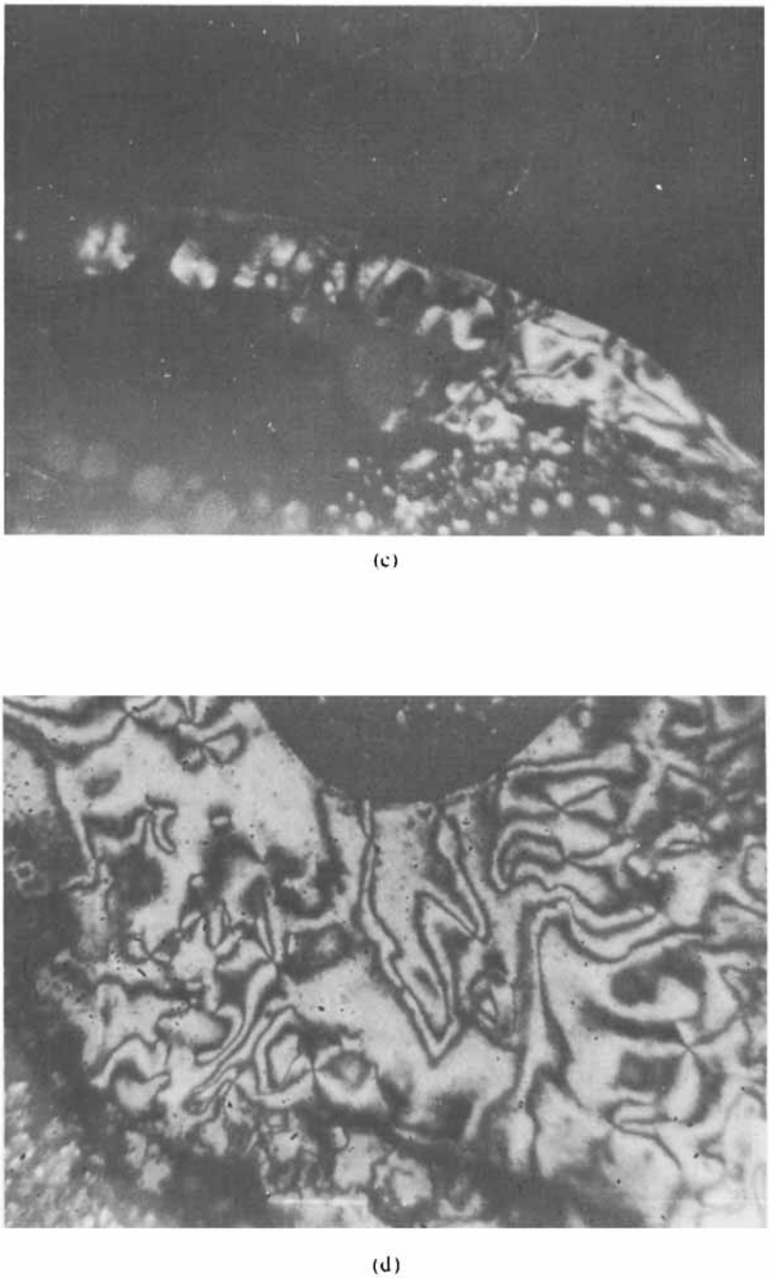


FIGURE 2c and 2d Microscopic optical textures of samples with various proportions of anisotropic units.

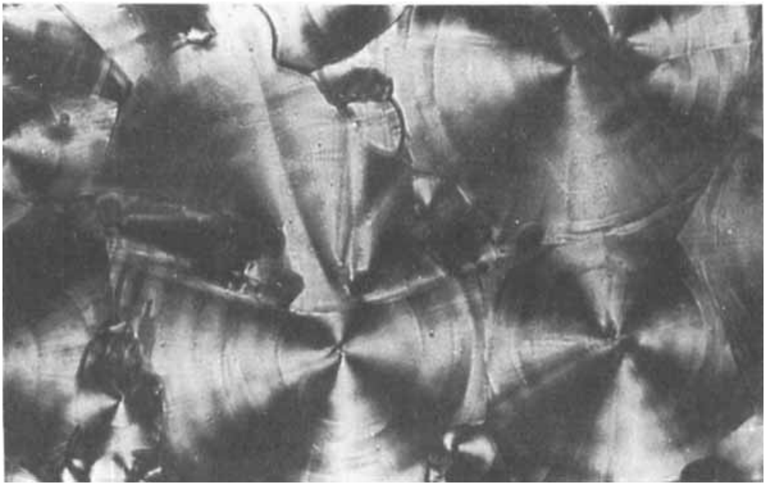


FIGURE 3 Microscopic optical texture of a D_{rd} phase (21) (D_1 phase of Ref. 19): hexa-*n*-dodecanoate of triphenylene at 110°C.

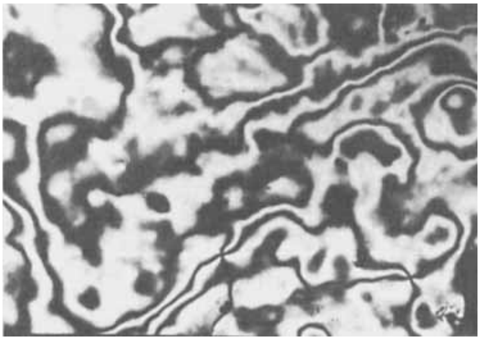


FIGURE 4 Microscopic optical texture of a nematic disc-like compound: hexaoctyl benzoate of triphenylene.

substituents of the triphenylene core has been studied. For example, we present here the results obtained with the hexaoctylbenzoate of triphenylene.[22] The optical texture of this material (Figure 4) is typical of a nematic compound, which indicates a clear analogy with the carbonaceous mesophase. Diamagnetic and structural studies are currently carried out and will allow to refine the analogy between these different materials.

CONCLUSION

The search for pure mesomorphic materials exhibiting the carbonaceous mesophase characteristic properties have led us at first to the synthesis of families of disc-like molecules which exhibit completely novel states of matter. Further synthetic variations allow us to present here the first example of a nematic liquid crystal which bears resemblance with those forming the carbonaceous mesophase, and should constitute a model which is likely to renew the interest for fundamental studies in this field.

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