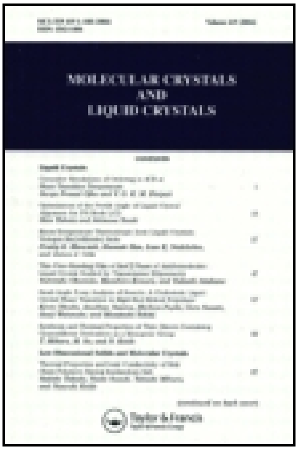

Molecular Crystals and Liquid Crystals

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Carbonaceous Mesophase and Disc-like Nematic Liquid Crystals†

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After a short recall of the mechanism which leads to the formation of the carbonaceous mesophase, some physical properties of this material will be reviewed. In the second part, we would like to show in what way the synthesis of disc-like molecules provides systems which exhibit a fluid nematic phase very similar to the carbonaceous mesophase. Finally, all the results concerning disc-like systems allow us to propose a general classification of the disc-like systems.

1 INTRODUCTION

In 1961 an isotropic fluid phase, made up of flat molecules was evidenced during the thermal treatment of a graphitizable substance.[1,2] A careful study of this carbonaceous mesophase is difficult because of the high temperature (400 to 500°C) and of the lack of chemical stability or organic compounds in this temperature range. Hence apart from optical microscopy and relatively simple physical or analytical measurements nothing quite fancy has been undertaken. 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 a carbonaceous mesophase. We will first review some properties of the carbonaceous mesophase and then show how the recent synthesis of disc-like molecules[25,34] provides systems which exhibit striking analogies with it.

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II CARBONACEOUS MESOPHASE

The chemistry of the liquid-phase carbonization is very complex, but the understanding of the formation of microstructure in cokes and graphite was substantially improved since the role of the mesophase transformation was recognized first by Brooks and Taylor.[1] During carbonization, the transformation takes place in the graphitizable organic materials at temperatures comprised between 350°C and 550°C. During this transformation, the large planar molecules formed by the reactions of thermal cracking and aromatic polymerization, orientate more or less parallel to form an optically anisotropic phase called the carbonaceous mesophase. The life time of this mesophase is limited by its hardening to a semi-coke, but the "mesomorphic" organization of the flat molecules is essential for thermal graphitizability of the pyrolysis product.

A Formation

In the early stages of nucleation and growth the carbonaceous mesophase appears as small spherules suspected in the optically isotropic matrix (Figure 1).

As pyrolysis proceeds the spherules grow and begin to sink through the less dense matrix. When spherules meet, coalescence may occur to produce larger droplets (Figure 2 and 3).

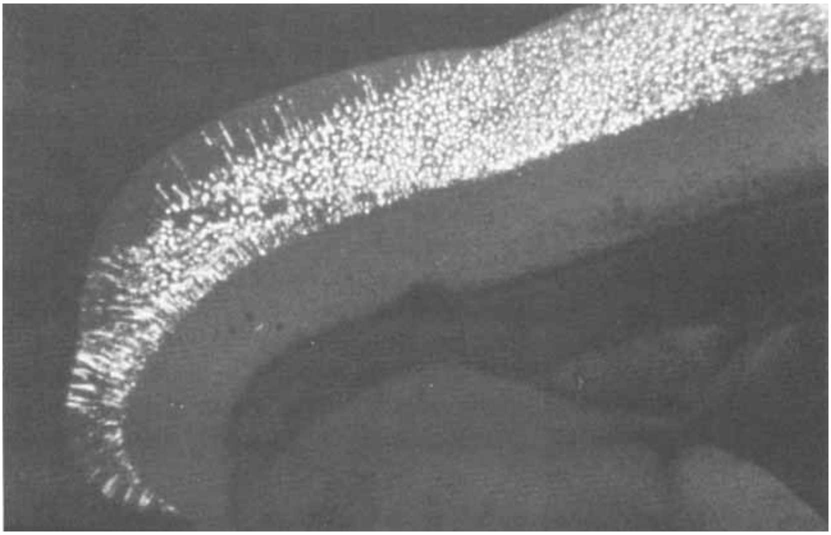


FIGURE 1 Formation of the mesophase

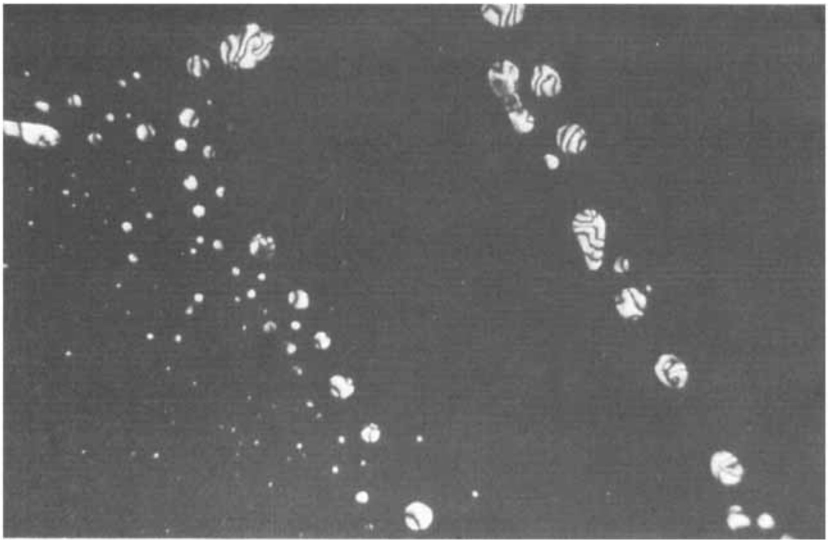


FIGURE 2 Spherules of mesophase

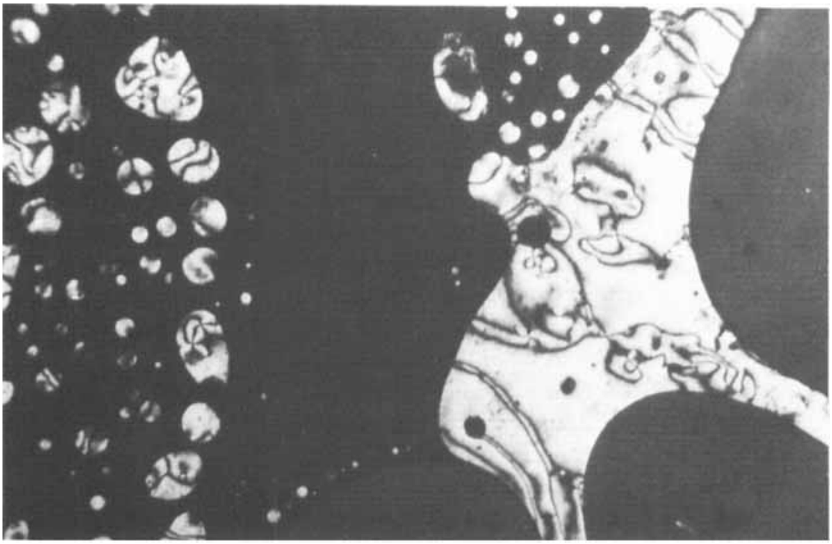


FIGURE 3 Coalescence of the spherules

B Structural characters

The structural features of these mesophase spherule were described by Brooks and Taylor[2] by applying selected area electron diffraction to thin sections of spherules (Figure 4).

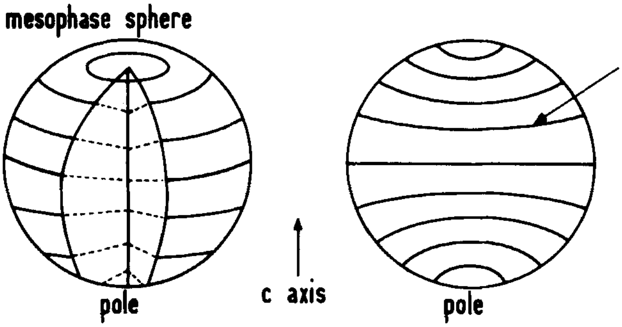


FIGURE 4 Structure of a mesophase spherule.

Recently, Mochida and Marsh[3] described large anisotropic spherules of mesophase and proposed two types of structure for these spherules: the onion-like and the concentric structures.

The various optical textures of cokes indicate that many parameters drive this microscopic aspect. We have to notice: the composition of the pyrolyzed substances, the range of temperature over which the mesophase is fluid, the viscosity values and the physical disturbance within the carbonization system caused by volatile compounds and convection flows. Thus, the approach of White *et al.*[4,5] is to characterize the "defects-structures" found in the industrial prepared cokes with respect to the factors which influence the amount and the dynamic of the mesophase.

This mesophase exhibits many analogies with the classical nematic liquid-crystal, in particular the dynamic behaviour of some disclinations. In addition, it is possible by using polarized-light micrography to inter-relate the defects of the mesophase with those of a classical nematic. White develops, as done in the nematics, the use of co-rotating and counter-rotating nodes and crosses which are labelled as U, Y, O and X respectively (2, 2, 4, 6) (Figure 5).

The density of the carbonaceous mesophase ranges from 1.4 to 1.6 (respectively 1.25 and 1.32 for the isotropic medium).

It has been believed for a long time that the carbonaceous mesophase was insoluble in most solvents and particularly in quinoleine and pyridine which were commonly used in its separation from the isotropic medium. Recent results[7] show that the mesophase solubility depends on the original material from which it is formed and that the percentage of the mesophase is not

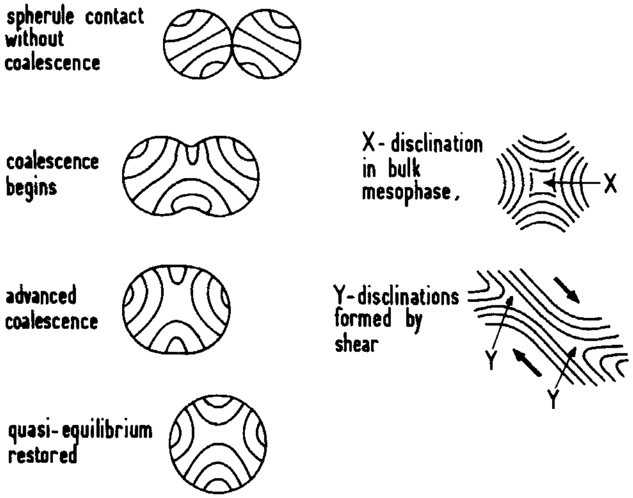


FIGURE 5 Formation and deformation of disclination structures.

necessarily the same as the one of insolubles. Thus, direct optical observations seem to be the way of evaluation of this percentage.

It is difficult to precise the exact chemical composition of the mesophase, it depends on the pyrolized compound and is continually changing during the heat treatment. Mass spectrometry studies have shown the coexistence of numerous chemical substances. The average molecular weight of the mesophase is in the 2000 range, much larger than in the isotropic medium, this value increases with temperature and heat treatment time. The C/H ratio is large, which indicates an important aromaticity percentage. Moreover, some recent results suggest the existence of small aromatic molecules or large molecules composed of small aromatic units linked together with alkyl bones.

C Carbonaceous mesophase and industrial materials

Graphite is usually manufactured from a coke prepared from a petroleum pitch and a binder such as a coal tar pitch. The size, growth and coalescence characteristics of the mesophase spherules influence very closely the physical properties of the final products; so graphite industries are interested in those stages of pyrolisis where mesophase growth and interactions are important. For example, a recent technology is applied in which mesophase still retaining some fluidity is moulded or formed into specific shapes and then graphitized.

Currently the major source of carbon fibers is from synthetic textiles among which polyacrilonitrile is the most important. Economically it is much more attractive to use a raw materials petroleum or coal tar pitch or coal extracts. In order to get carbon fibers with convenient mechanical properties, the best results are obtained by spinning a bi-phase system of pitch and mesophase. The process being such that the mesophase is suitably oriented by the shear forces generated during the spinning.

D Some recent advances

Physical properties of a magnetically oriented carbonaceous mesophase Generally the presence of many defects prevents from generating large single domains, so in order to approach such a structure many investigations concern the properties of a magnetically oriented carbonaceous mesophase. As previously seen, the mesophase is largely composed of polynuclear aromatic molecules the magnetic susceptibility of which is much larger (in absolute value) perpendicularly to the aromatic planes. By rotating the mesophase sample around an axis normal to the magnetic field, we can assume that the aromatic parts like, on average, perpendicularly to this axis. I summarize here some results recently published[8,9] which concern a quenched mesophase. These studies have shown that it is possible to obtain a highly oriented quenched sample by rotating the mesophase in a magnetic field of about 10 kG. The diamagnetic susceptibility and anisotropy results suggest the presence of either small aromatic molecules or larger molecules with small aromatic regions probably connected by aliphatic bridges ($\Delta\chi \simeq -0.80 \cdot 10^{-6}$ uem CGS g^{-1}).

We can remark that the specific heat results indicate the existence of a pregraphitic organization already in the mesophase.

X-ray measurements Concerning the anthracene carbonization from 400 to 800°C, X-ray diffraction experimental diagrams have been recently compared with theoretical curves which have been computed using several types of models. The results show[10] that the aromatic system at 400°C corresponds approximately to the tetramer of the anthracene. From 400°C to 600°C the growth of these systems is not visible and we can suppose that the aromatic species, bridged by atom groups (not necessarily aromatic) are organized in type of "cobweb". The evolution of the material between 400°C to 600°C can be described as the development of this cobweb structure without changing the size of the elementary aromatic species.

Rheological investigations The rheological behaviour is important for controlled growth and coalescence of mesophase spherules. A few measurements deal with rheological characteristics of coal tar pitches during their transformation to mesophase. Mesophase microstructure can be correlated with the flow behaviour followed by rotational viscometry.[11,12] A typical curve shows a maximum of the viscosity around 400°C. Flow curves give evidence that the pitches are newtonian liquids at low temperature, but a non newtonian character appears above ~400°C. Collet and Rand suggest that the system can be regarded as emulsions and the maximum in the apparent viscosity corresponds to the phase inversion point. It is also possible to find similarities with the evolution of the viscosity of thermotropic liquid crystals, for example, with the nematic-isotropic phase transition.[13]

Thus if we sum up the informations collected about the carbonaceous mesophase, we can conclude first that this anisotropic phase present numerous analogies with a nematic phase:

—The optical textures are closely related, with schlieren textures, crosses and nodes defects;

—The phase presents a great mobility which indicates a low viscosity;

—The evolution of this parameter from the isotropic pitch to the anisotropic state can be compared to the variation reported for classical isotropic-nematic transitions;

—A magnetic field orientates the aromatic molecules parallel to each other which allow to evaluate the anisotropy of this medium.

Nevertheless, all these measurements and observations are difficult because of the high formation temperatures of the mesophase joined to gaseous releases which restrict the in situ experiments, and at last because of the chemical complexity of the mesophase obtained by carbonization either of petroleum pitch or of pure aromatic compounds.

III DISC-LIKE MOLECULES

It was interesting to obtain a well defined chemically stable system which could serve as a model for the carbonaceous mesophase.[14,15]

We can define this model as an anisotropic mesophase formed of a pure disc-like aromatic compound obtained at rather low temperature, without chemical transformations.

A Some central cores which lead to disc-like mesogens

Several disc-like mesogens are known at present.[16–26] These molecules possess a central part and flexible side chains, but contrarily to the rod like systems when we can have only two-fold axis parallel or perpendicular to the director, it is possible for disc-like systems to imagine a more diversified symmetry. Up to now only a few series of disc-like mesogens are known which correspond for example to benzene, triphenylene, truxene, ruffigallol, etc.... derivatives (Figure 6). Most of these compounds exhibit an hexagonal or trigonal symmetry, but some of them are characterized by a binary or by a tetragonal symmetry. An exhaustive investigation of the symmetry of these systems had been recently presented by J. Billard.[16]

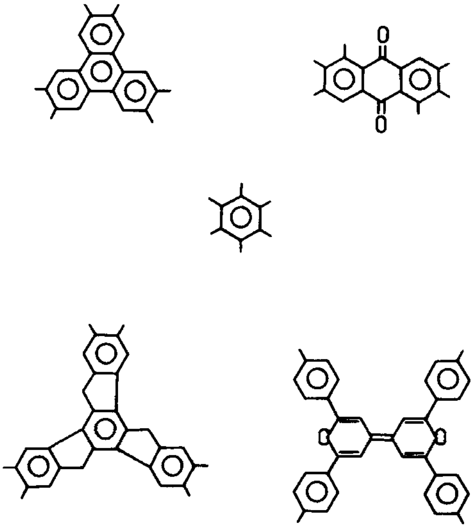


FIGURE 6 Examples of cores which lead to disc-like mesogens.

B Polymorphism of the disc-like mesogens

Actually, only two series (Triphenylene and Truxene derivatives) lead to a nematic phase, but they also show a very general and complex polymorphism

α) *Triphenylene derivatives* By taking the triphenylene serie as example, it is possible to summarize some actual results in the field of the disc-like mesogens.

1) *Columnar phases* The study of the hexa-alcoxy or alcanoyloxy triphenylene series[18-20] (Figure 7) has shown the evidence of a complex polymorphism,[22] but in the most cases the highly viscous and birefringent phases correspond to a columnar arrangement of the disc-like molecules.[23,27-29] On the Figures 8, 9, 10, one can see some textures of the different columnar phases exhibited by these compounds. It is obvious that there is no textural analogy with the micrographies of the carbonaceous mesophase (see, for example, Figure 3). Moreover, the columnar lattice proposed by X-ray experi-

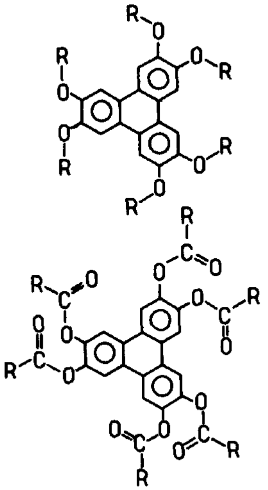
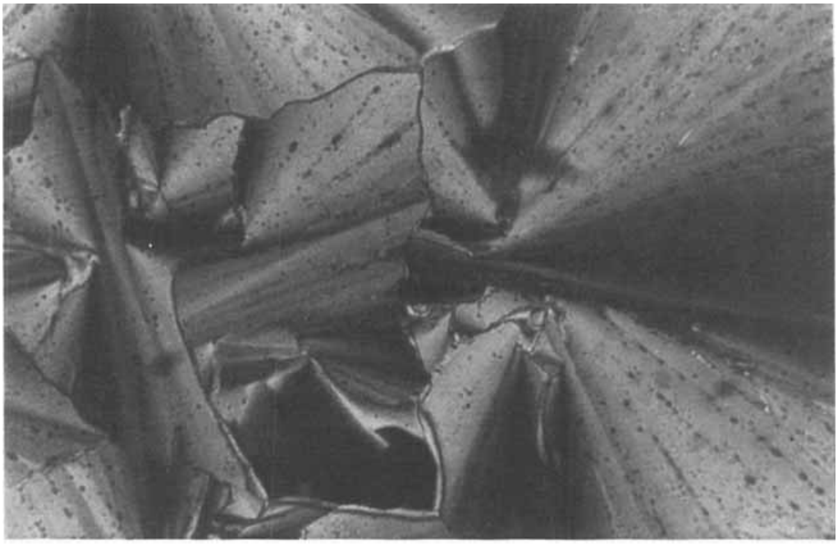


FIGURE 7 Hexa-ether(a) and hexa-ester(b) of triphenylene.



FIGURES 8, 9, 10 Some textures of columnar phases.

ments seems not to agree with the structure of the carbonaceous mesophase which appears essentially fluid.

We shall speak again about the columnar phases when we shall discuss on a possible classification of the disc-like mesogens.

FIGURE 9

FIGURE 10

2) *Nematic phases* In order to obtain a fluid mesophase it was necessary to find a molecular modification which induces the destruction of the columnar packing. In this way, two projects have been developed. First, the substitution of a disc-like core with asymetric substituants; unfortunately, these compounds lead to columnar phases.[24] On the other hand, the subsitution of the triphenylene core with highly sterical hindrance substituents enables us to reveal a new type of fluid mesophase[25] we were looking for in the series of hexa-alkyl or alcoxy benzoates of triphenylenes (Figure 11).

An example of the polymorphism of these compounds is presented in the Table I.[26]

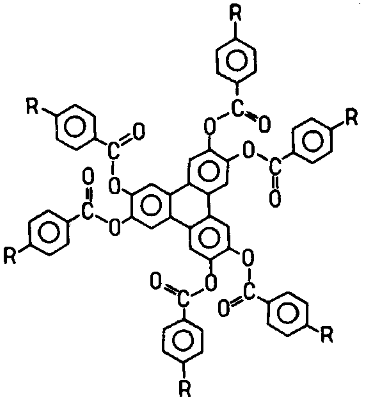


FIGURE 11 Hexa-alkyl (or alcoxy) benzoates of triphenylene.

TABLE I

Transition temperatures and enthalpies of fusion of hexa N-alkoxy or N-alkylbenzoate of Triphenylene

R	K		D_t		D_r		N_D		I	ΔH Kcal/ mole
C_4H_9O	—	257	—		—		—	>300	—	
$C_5H_{11}O$	—	224	—		—		—	298	—	4.55
$C_6H_{13}O$	—	186	—	193	—		—	274	—	2.24
$C_7H_{15}O$	—	168	—		—		—	253	—	2.25
$C_8H_{17}O$	—	152	—		—	168	—	244	—	14.58
$C_9H_{19}O$	—	154	—		—	183	—	227	—	3.24
$C_{10}H_{21}O$	—	142	—		—	191	—	212	—	8.30
$C_{11}H_{23}O$	—	145	—		—	179	—	185	—	6.0
$C_{12}H_{25}O$	—	146	—		—	174	—		—	1.46
C_7H_{15}	—	210	—		—		—		—	
C_8H_{17}	—	208	—		—		—	210	—	
C_9H_{19}	—	175	—		—	183	—	192	—	
$C_{10}H_{21}$	—	185	—		—	189	—		—	

This new fluid phase is labelled N_D because it is quite a nematic phase according to the following arguments.

Microscopic observations The microscopic observations shows a great fluidity of this anisotropic phase and give evidence for schlieren textures very similar to classical nematic ones (Figures 12 and 13).

X-ray diffraction patterns X-ray diffraction patterns of samples of fluid mesophase held in a capillary tube out of the magnetic field are similar to the diffraction patterns of the isotropic liquid phase.[30] We have two broad diffraction rings the inner ring being of high intensity compared to the outer ring.

The outer ring lies at $1/d = 1/4.5\,\text{Å}^{-1}$ while the inner is related to the molecular size and corresponds to $d = 20.5\,\text{Å}$ for the C_6 compound and $d = 26.5\,\text{Å}$ for the C_{11}. This is very similar to the diffraction by a non orientated nematic phase. Nevertheless, a striking difference lies in the relative intensity of the two rings: the inner is of higher intensity in the case of this fluid mesophase of disc-like molecules while the outer is more intense for nematics of rod-like molecules.

In the case of the C_6 derivative, the magnetic field (3 kG) orientates the sample; the best orientation effects are obtained after a rotation of $\Pi/2$ of the capillary tube around its axis which is perpendicular to the magnetic field.

By changing the angle between the X-ray beam and the magnetic field, it was established that the diffraction pattern of the C_6 fluid phase has an infinite rotational symmetry axis parallel to the axis of the capillary tube. One can see two broad discs at $1/d = 1/4.5\,\text{Å}^{-1}$ while the inner ring is split into four broad spots. The structure of the inner ring is similar to the diffraction patterns of a nematic phase of elongated molecules with "skewed cybotactic groups". The two outer discs lying at $1/d = 1/4.5\,\text{Å}^{-1}$ are characteristic of a preferred orientation of the molecular lateral substituents, these elongated substituants lying in the plane of the applied magnetic field (plane perpendicular to the axis of the capillary tube).

Magnetic measurements[30] The magnetic experiments were performed on different samples of the same compounds using two methods. The Faraday device is equipped with an electro magnet providing field up to 15 kG, the rotating magnet gives a field of 11 kG.

First, in order to check the influence of the magnetic field upon the degree of orientation of the nematic phase, we have studied the diamagnetic susceptibility of these compounds. The thermal evolutions of this parameter χ (measured in the direction of the magnetic field, during slow cooling from the isotropic phase) corroborate the existence of a spontaneous orientating effect

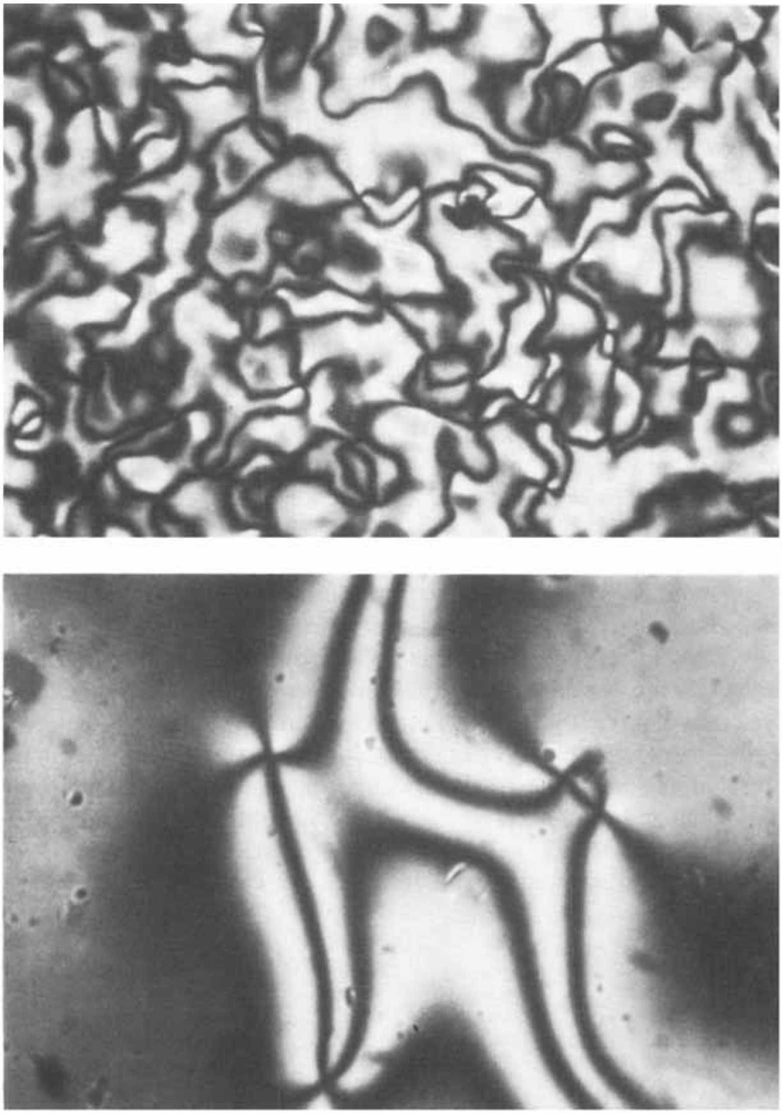


FIGURE 12 and 13 Texture of the disc-like nematic phase in the benzoates of tri-phenylene series

of the applied field at the isotropic-fluid mesophase transition for both C_6 and C_{11} compounds (i.e. a sharp decrease of the absolute value of the diamagnetic susceptibility). In addition, we have to note that, contrarily to the columnar phases of triphenylene derivatives investigated elsewhere, this effect as function of the magnetic field value is saturated for $H \geqslant 5$ kG.

Furthermore, the study of the behavior of a sample hung by a quartz wire in an homogeneous rotating magnetic field of about 11 kG shows that the fluid mesophase is isotropic in the rotation plane of the magnetic field: no magnetic torque occurs and the sample remains in its initial position.[33] Thus, a single domain of this fluid mesophase is obtained with a rotating magnetic field: this medium is magnetically uniaxial with the preferred axis perpendicular to the magnetic field rotation plane. For an uniaxial system, the magnetic anisotropy is defined by

$$\Delta\chi = \chi_{\parallel} - \chi_{\perp}$$

where $\chi_{\parallel}$ is connected to the magnetic susceptibility measured in a direction parallel to the main axis and $\chi_{\perp}$ to the susceptibility measured perpendicularly to this axis.

In the case of this fluid mesophase $\chi_{\perp}$ is the diamagnetic susceptibility in the magnetic field direction thus $|\chi_{\parallel}| > |\chi_{\perp}|$ ($\chi_{\parallel}$ and $\chi_{\perp} < 0$) and the diamagnetic anisotropy in this mesophase is hence negative:

$$\Delta\chi < 0$$

We can note the strong tendency for this mesophase to give extinction between crossed polarizers: this also suggested an optically uniaxial mesophase. Moreover, the upper X-ray study has pointed out that the aromatic cores of the molecules are parallel to the rotation plane of the magnetic field. Thus the preferred axis (i.e. the director) is perpendicular to the molecular core in good agreement with the disc-like molecule symmetry and with the chemical structure of the molecule (the diamagnetism essentially depends on the aromatic part and thus the largest magnetic susceptibility in absolute value is likely perpendicular to the polycondensed rings).

In the limit of our experimental accuracy, the value of the susceptibility

TABLE II

R	K		N_D		D_r		D_h		I
C_6H_{13}	—	112	—	[96]	—	138	—	280	—
C_7H_{15}	—	98	—	[85]	—	140	—	280	—
C_8H_{17}	—	88	—	[87]	—	141	—	280	—
C_9H_{19}	—	68	—	85	—	138	—	280	—
$C_{10}H_{21}$	—	62	—	89	—	118	—	250	—
$C_{11}H_{23}$	—	64	—	83.5	—	130	—	250	—
$C_{12}H_{25}$	—	57	—	84	—	107	—	249	—
$C_{13}H_{27}$	—	58	—	83	—		—	235	—

Transition temperature in Celcius of the different prepared compounds. K = crystal, N_D = nematic "disc-like" phase, D_r and D_k = columnar phases (r = rectangular, h = hexagonal lattice), I = isotropic, [ ] indicate monotropic trasition.

along the magnetic field direction is unchanged after turning the sample around a vertical axis in order to improve alignment. Therefore, the diamagnetic susceptibility measured in the direction of the static magnetic field by the Faraday method seems to correspond to the susceptibility perpendicular to the director (i.e. $\chi_\perp$).

If we assume, as for rod-like nematogenic compounds, that the average magnetic susceptibility does not depend on the temperature and the state of the material, we can write:

$$\bar{\chi}_{\text{isotropic}} = \frac{2\chi_\perp + \chi_\parallel}{3}$$

and then:

$$\Delta\chi = \chi_\parallel - \chi_\perp = 3(\bar{\chi}_{\text{isotropic}} - \chi_\perp)$$

Thus, as for a classical nematic,[32,33] the magnetic susceptibility measurement in the direction of the field, respectively in the isotropic phase and in the fluid mesophase, lead to determine the magnetic anisotropy of this latter phase. In fact, very small amounts of ferromagnetic impurities prevent from obtaining the intrinsic thermal evolution of the disc-like compound anisotropy although, they do not disturb the discontinuity at the transition. Thus near the isotropic phase we find:

C_6 $\Delta\chi = -0.49 \cdot 10^{-7}$ uem CGS g^{-1} $\Delta\chi_M = -7.10^{-5}$ uem CGS mole^{-1}

C_{11} $\Delta\chi = -0.21 \cdot 10^{-7}$ uem CGS g^{-1} $\Delta\chi_M = -4.10^{-5}$ uem CGS mole^{-1}

We can explain the different values of $\Delta\chi_M$ between the C_6 and the C_{11} compounds—first considering that larger the aromatic over aliphatic parts ratio is, larger the molecular anisotropy is—secondly, may be the degree of orientational order at the isotropic phase → fluid mesophase transition has to be taken into account. This difference in the magnetic anisotropies associated to a higher viscosity of the C_{11} could explain that we cannot get orientated X-ray patterns (under 3 kG magnetic field) with this compound contrarily to what is observed for the C_6 compound.

From these arguments, we can claim that this fluid mesophase uniaxial and without translational order is a disc-like nematic phase: N_D.

As for series of rod-like molecules, the low temperature ordered phase which succeeds to the nematic phase can exhibit different structures according to the length of the substituants.

3) *Cholesteric phase* We have to notice that chiral chains in triphenylene series are able to twist the N_D phase of a hexabenzoate of triphenylene. That is the first evidence of a cholesteric phase in disc-like mesogens.[31]

β) Truxene derivatives The complex polymorphism of the disc-like mesogens is confirmed by the recent results which concern the serie of truxene compounds.[34,35] These new disc-like liquid crystals (Figure 14) exhibit both columnar and N_D nematic phases. The N_D nematic phase is the first low temperature one. All these compounds show an inverted nematic-columnar sequence: the fluid N_D nematic phase is observed while heating after the crystalline phase below one or two viscous columnar phases and shows a phenomenon which exists in the reentrant nematic behaviour.

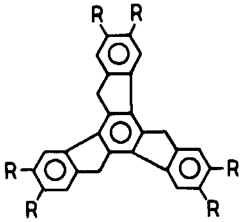


FIGURE 14 Truxene derivatives.

C A classification of the actual results

Actually, three different kinds of mesomorphic phases have been described in the disc-like systems: D (columnar phase), N_D (nematic phase, N_D^* (twisted nematic phase).

Four different D columnar mesophases have been clearly identified by mean of optical texture observations, heat measurements and X-ray diffraction. With respect to a regular (O ≡ ordered) or irregular (*d* ≡ disordered) stacking of discs and considering the symmetry of the two dimensional lattice of columnars: hexagonal (h) or rectangular (r) they are called D_{ho}, D_{hd}, D_{rd} or D_t (this last one is a tilted phase where the discs appear to be tilted versus the columnar axis.[15,23,36] All these D columnar phases are highly viscous and birefringent with optical textures, sometimes very similar to smectics one with striated or non-striated focal conics, finger prints, broken fan or mosaic textures.

On the contrary, the N_D nematic phase is very fluid and presents very typical schlieren textures with classic S: $\pm 1/2$ et ± 1 disclination lines and thermal fluctuations. This phase corresponds (Figure 15) to an original molecular organization very similar to the one proposed for the carbonaceous mesophase. In both cases, the optical and the diamagnetic anisotropy are negative.

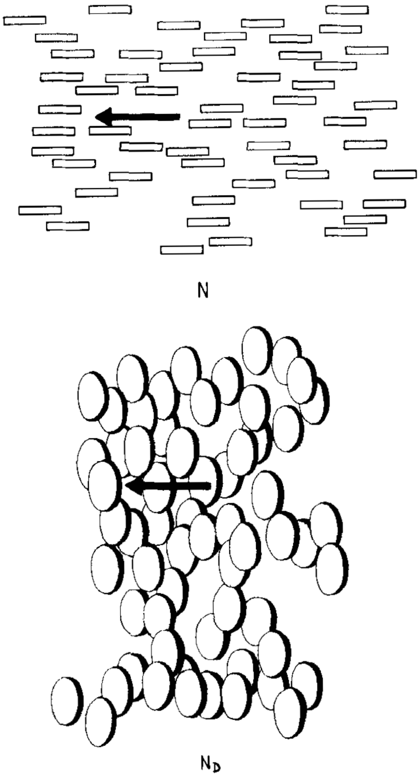


FIGURE 15 Rod-like and disc-like nematics.

IV CONCLUSION

As conclusion, we can observe that the nematic disc-like mesophases, we have just described, present many of the characteristics of the carbonaceous mesophase. It is now important to obtain new series which present such phases based on cores of species participating in the carbonaceous mesophase mixture.

Besides this expected clarification of the carbonaceous mesophase problem, the analysis of the properties of the nematic disc-like mesophase in itself is very stimulating especially because we are in the presence of a new fluid mesophase which we know to be able to orientate in an external field. It is evident that we cannot yet imagine the possible applications of these new materials and it seems very interesting to prospect this new field of research.

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