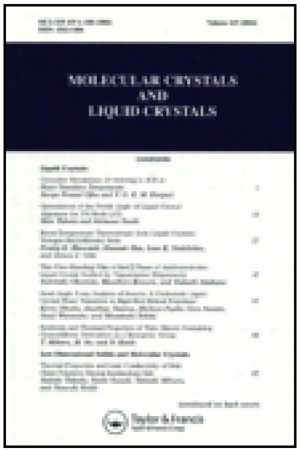

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Disc-Like Mesogen Polymorphism

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Version of record first published: 20 Apr 2011.

To cite this article: C. Destrade , P. Foucher , H. Gasparoux , Nguyen Huu Tinh , A. M. Levelut & J. Malthete (1984): Disc-Like Mesogen Polymorphism, Molecular Crystals and Liquid Crystals, 106:1-2, 121-146

To link to this article: http://dx.doi.org/10.1080/00268948408080183

Mol. Cryst. Liq. Cryst., 1984, Vol. 106, pp. 121–146
0026-8941/84/1062-0121/$18.50/0

Printed in the United States of America

Disc-Like Mesogen Polymorphism†

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(*Received June 21, 1983; in final form October 17, 1983*)

Among the various mesogenic polyaromatic cores, only benzene, triphenylene, truxene and anthraquinone hexasubstituted derivatives exhibit one or several D *columnar* phases and/or a N_D *lenticular* nematic phase. A simple scheme of nomenclature is suggested for the six different types of columnar phase requiring only two structural parameters: firstly the symmetry of the lattice (*hexagonal*: D_h, *rectangular*: D_r, *oblique*: D_{ob}), and secondly the order or disorder within the column. Several examples of disc-like compounds which form phases D_{ho}, D_{hd}, $D_{rd(P2_1/a)}$, $D_{rd(P2/a)}$, $D_{rd(C2/m)}$, $D_{ob.d}$ are described and a discussion of the specificity of the corresponding optical textures is given. Then the complex polymorphism of these new mesogenic materials (*normal*, *inverse*, *reentrant* columnar–nematic sequences) is reviewed. Finally, a simple classification of the various types of lyotropic and thermotropic phase is proposed, based on the shape of the structural element (finite or infinite cylinder, disc, infinite sheet, globule).

1. INTRODUCTION

The existence of mesophases built up from disc-shaped molecules has been predicted for a number of years. One can visualise flat aromatic

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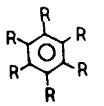
†Invited lecture at the Ninth International Conference on Liquid Crystals, Bangalore, India (1982).

or alicyclic molecular units capable of giving mesomorphic structures similar to those observed in some lyotropic systems (columns, ribbons, discs...).[1-6]

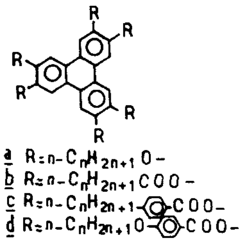
The discovery around 1960[7-10] of an anisotropic fluid phase formed during the pyrolysis of graphitizable substances such as heavy petroleum residues suggested the presence of flat polyaromatic molecules at high temperature. This mesophase shows optical textures very similar to the nematic phase, but its unstable nature did not allow careful structural investigations. So there was an evident need for the synthesis of stable pure mesogens giving this type of phase.[11]

This research succeeded around 1977–1978 in several laboratories with the synthesis of hexa-substituted benzenes (1)[12] and triphenylenes (2a)[13-15] which exhibited a very viscous and birefringent mesophase between the solid and liquid phases. The structure of this mesophase corresponds to stacks of molecular discs forming parallel columns in a hexagonal lattice.[12-16]



R : $n\text{-}C_nH_{2n+1}COO\text{-}$

1



2

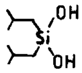
This arrangement is closely similar to those of some lyotropic (M2 Middle phases[1,4]) or thermotropic (neat soaps[17-19]) where we have cylindrical phases in which the aliphatic chains are arranged radially around an infinite cylindrical core formed from the polar end groups.

In 1979, a birefringent fluid mesophase was observed for some hexabenzoyloxytriphenylenes (2c and 2d).[20] From the structural point of view, this is very comparable to the N_L or type II DM mesophases[6] in which the only order is a parallelism between lens-shaped units of soap.

This was rapidly followed by the discovery of a complex polymorphism emphasizing the interest of this new kind of mesogenic material: columnar,[15,21-25] nematic,[20,26] cholesteric phase,[27,28] inverted[29,30] and reentrant sequences.[31,32]

2. NOMENCLATURE PROBLEMS

The term *discotic* was proposed for these mesophases, meaning that they are generated by *disc*-shaped molecules as opposed to *calamitic* phases consisting of elongated molecules.[14,34] Therefore it is probably unnecessary to refer to discotic thermotropic or lyotropic mesophases with a columnar order or a nematic order made with lens-shaped (lenticular) *micelles*, but without disc-like *molecules* such as for instance the cylindrical phases of some neat-soaps and maybe the mesophase of diisobutylsilanediol ($\underline{3}$[35]) or the micellar N_L or type II DM mesophase.[6]



$\underline{3}$

So, in order to avoid any confusion we have founded our nomenclature on the *structural element*, *i.e.* the *column* in the case of cylindrical phases and the *lenticular* (*lens-shaped*) molecule or aggregate for the phases made with discs such as some nematic phases. Consequently the first are named: *columnar phases*[36] and the second *lenticular mesophases*, and we reserve the capital letter D for the designation of phases generated with disc-shaped molecules.

So the nematic phase observed with disc-like compounds is denoted N_D and the columnar phases are denoted D.[37] This review concerns only these two types of mesophase.

The complex columnar polymorphism immediately raises further problems of nomenclature. Two solutions have been suggested. One is similar to the smectic classification based on miscibility criteria; it consists of the letter D with other letters subscripted following generally in alphabetical order (D_A, D_B, $D_C \ldots D_F$, $\ldots D_L$ etc).[23,24,34] The other, we proposed[22,37] previously was based on crystallographic considerations. This is possible because the structures of all the columnar phases are known.[38,39]

Two simple crystallographic parameters are sufficient for the characterization of columnar arrangements: the two-dimensional lattice symmetry (*h*exagonal: D_h, *r*ectangular: D_r or *ob*lique: D_{ob}) and the *o*rder or *d*isorder of the molecular stacking in the columns (Figure 1). Therefore, a hexagonal lattice of columns with ordered disc-like molecules is conveniently denoted D_{ho}, the notations D_{hd}, D_{rd} or $D_{ob.d}$ are then obvious.[40]

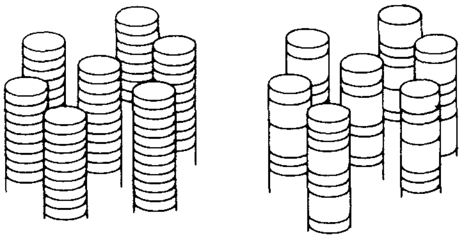


FIGURE 1 D columnar arrangement: (a) ordered; (b) disordered.

In fact three different columnar D_{rd} phases have now been identified. The symmetry of their 2D lattices can be described in terms of the eighty plane space groups.[38] These constitute the sub-set of the 230 space groups where there are no symmetry elements relating to translations in a direction parallel to one of the axes. (This direction would correspond to the axis of the columns.) The most common of these rectangular phases has $P2_1/a$ symmetry while the two other phases have P2/a and (C2/m) symmetry (figure 2). These are the conventional crystallographic notations for space groups (International Tables for X-ray Crystallography, Vol. I, Henry and Lonsdale, Editors, Kynoch press, Birmingham, England 1969). It was established by optical observations that the average molecular plane is not perpendicular to the column axis for all the rectangular phases. The tilt angle is not known with accuracy[38,41] and the relative orientations of the tilt vector in neighbouring columns is included in the space group designation. It is not therefore necessary to mention the tilted character explicitly in the symbol as we used to do in our previous articles.[37] For this reason we consider this notation to be preferable to our previous one, which was based on the seventeen two-dimensional space groups:[37,40] $D_{rd(P2_1/a)} \equiv D_{rd(pgg)}$, $D_{rd(P2/a)} \equiv D_{rd(pmg)}$, $D_{rd(C2/m)} \equiv D_{rd(Cm)}$, in new nomenclature and old respectively.

TABLE I

Nomenclature

K: crystalline phase
N_D: lenticular nematic phase
D_{ho}: hexagonal ordered columnar phase
D_{hd}: hexagonal disordered columnar phase
D_{rd}: rectangular disordered columnar phase
  —$D_{rd(P2_1/a)}$ with the $P2_1/a$ plane space group symmetry
  —$D_{rd(P2/a)}$ with the P2/a plane space group symmetry
  —$D_{rd(C2/m)}$ with the C2/m plane space group symmetry
$D_{ob.d}$: oblique disordered columnar phase

Consequently we have a very simple notation system for a concise and unambiguous classification of columnar phases. Our notation is summarized in Table I.

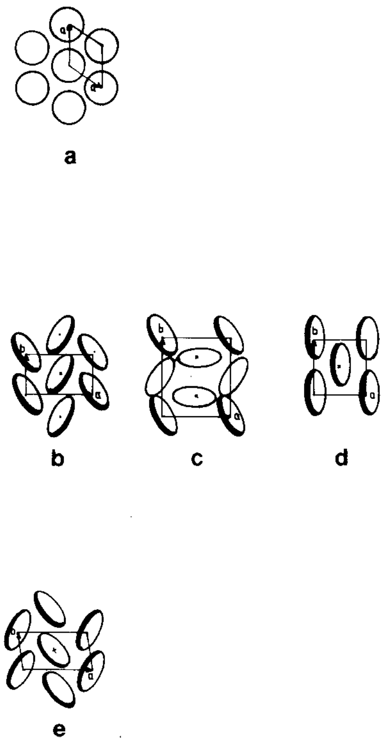


FIGURE 2 Two-dimensional lattice symmetry: (a) hexagonal: D_{ho} and D_{hd}; (b) rectangular: $D_{rd(P2_1/a)}$; (c) rectangular: $D_{rd(P2/a)}$; (d) rectangular: $D_{rd(C2/m)}$; (e) oblique: $D_{ob.d}$.

3. MOLECULAR STRUCTURE OF DISC-LIKE MESOGENS

As for the classical nematic and smectic liquid crystals, disc-like mesogenic molecules are restricted to certain structural types, i.e., flat and more or less disc-shaped central rigid core C usually surrounded by six lipophilic L chains (Figure 3).

3.1. Central cores

Up to now most of the disc-like cores have been more or less aromatic. They are with decreasing symmetry: hexasubstituted benzenes (1)

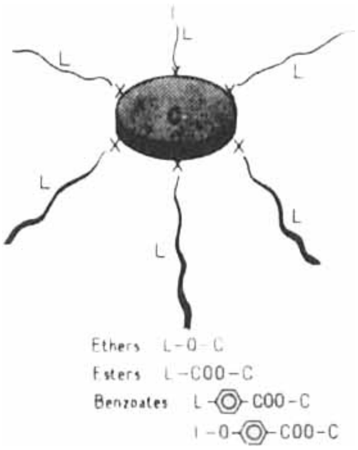
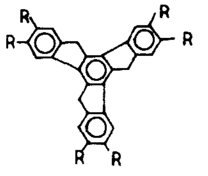


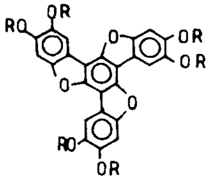
FIGURE 3 Disc-like mesogen molecule.

(hexagonal), 2,3,6,7,10,11-hexasubstituted triphenylenes (2) (trigonal), 2,3,7,8,12,13-hexa-substituted truxenes (4) and the oxygenated homologues: trioxatruxene (5) (trigonal) and 1,2,3,5,6,7-hexasubstituted anthraquinones (6) (with two-fold rotational symmetry).



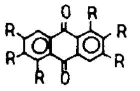
a $R = n\text{-}C_nH_{2n+1}O-$
b $R = n\text{-}C_nH_{2n+1}COO-$
c $R = n\text{-}C_nH_{2n+1}\text{-}\langle O\rangle\text{-}COO-$

4



$R = n\text{-}C_{13}H_{27}CO-$

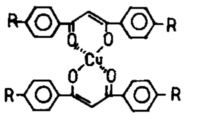
5



$R{:}\ n\text{-}C_nH_{2n+1}COO-$

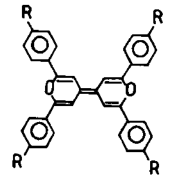
6

Some additional flat mesogenic cores have been described. For example the copper complex (7)[42] and some tetraarylbipyranylidenes (8)[43] with only four paraffinic chains exhibit some very ordered thermotropic phases, the structures of which have not yet been resolved.



$R = n\text{-}C_{10}H_{21}\text{-}$

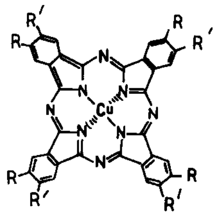
7



$R = n\text{-}C_nH_{2n+1}\text{-}$

8

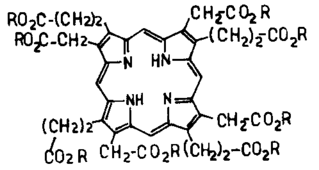
Recently Piechocky *et al.*[44] reported on an octasubstituted phthalocyanine copper complex (9a) which exhibits a D_{hd} columnar phase over a very large temperature range. A mesophase could be observed, on cooling, 0.1°C before crystallization, with the porphyrin (10).[45] Several tetrathiafulvalene derivatives (11) are however devoid of any mesogenic properties.[46] Finally an example of a lyotropic disc-like mesogen has been reported: tetracarboxylated copper phthalocyanine (9b).[47]



a $R = R' = C_{12}H_{25}OCH_2\text{-}$

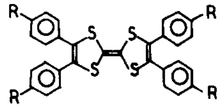
b $R = \text{-}COO^{\ominus}$, $R' = H$

9



$R = n\text{-}C_{12}H_{25}\text{-}$

10



$R = n\text{-}C_nH_{2n+1}O$

11

All these results suggest that columnar and N_D nematic orders require at least six paraffinic substituents around the central rigid core.

3.2. Lateral chains

It appears that a dense paraffinic crown is necessary for the manifestation of any columnar or N_D nematic mesomorphic properties.

The normal aliphatic chains (with, at least, five carbon atoms) are bound to the central aromatic part by an ether or ester linkage.

The chemical nature of the chain probably has a decisive influence on the appearance of mesomorphic properties. For example some hexasubstituted benzenes with polyheteroatomic chains seem to be devoid of mesomorphism.[48]

The chains can also be linked to the central part by mean of benzoyloxy groups. These very bulky substituents are probably responsible for the appearance of the N_D nematic phase.[20]

In the present review, the mesomorphic properties which will be discussed are those of hexa-*n*-alkanoyloxybenzenes (HAB) (1),[12,49], 2,3,6,7,10,11-hexa-*n*-alkoxytriphenylenes (HET) (2a),[14,15] 2,3,6,7,10, 11-hexa-*n*-alkanoyloxytriphenylenes (HAT) (2b),[15,21] 2,3,7,8,12,13-hexa-*n*-alkoxytruxenes (HETX) (4a),[50] 2,3,7,8,12,13-hexa-*n*-alkanoyloxytruxenes (HATX) (4b),[29,33] 2,3,6,7,10,11-hexa(4-*n*-alkyl- or -alkoxybenzoyloxy) triphenylenes (HBT) (2c or 2d),[20,26] 2,3,7,8,12,13-hexa(4-*n*-alkoxybenzoyloxy) truxenes (HBTX) (4c)[32] and 1,2,3,5,6,7-hexa-*n*-alkanoyloxyanthraquinones (6).[23,24] Finally, the first example of a new disc-like mesogen family was recently described: 2, 3, 7, 8, 12, 13-hexa-*n*-tetradecanoyloxy-5,10,15-trioxatruxene (HATXO) (5).[25]

4. D COLUMNAR PHASES†

We shall present only the main features of the optical textures of the different columnar phases, *i.e.* "finger prints" which should enable the chemist to make an immediate assessment of the nature of the observed phases. For a more detailed account the reader should refer to some interesting publications by specialists in defect structures.[52-55]

Concerning X-ray measurements we shall give only a few characteristic data relating to the lattice parameters (Table II); for more details see ref. 38.

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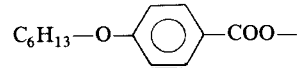
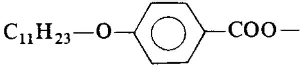
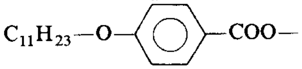
†This section concerns only normal substituents, although we have described some chiral columnar phases, see ref. 51.

TABLE II

		Columnar lattice			Specific area per column $cm^2/g \times 10^7$
Cores	Paraffinic substituents	Symmetry	Parameters in Å	Temperatures °C	
	$C_8H_{17}O$—	$P_6\,2/m\,2/m$	$a = 23,3$	≃ 80	2, 87
Triphenylene	$C_7H_{15}COO$—	$P\,2_1/a$	$a = 37,8$ $b = 22,2$	100	2, 34
	$C_{11}H_{23}COO$—	$P\,2_1/a$	$a = 44,9$ $b = 26,4$	105	2, 52
		$P_6\,2/m\,2/m$	$a = 26,3$	117	2, 54
Anthraquinone	$C_7H_{15}COO$—	$P\,2_1/a$	$a = 34,8$ $b = 18,1$	114	1, 78
		$P\,2/a$	$a = 34,9$ $b = 36$	95	1, 78
		$P_6\,2/m\,2/m$	$a = 30$	160	2, 75
Trioxatruxene	$C_{13}H_{27}$—COO—	$P\,2_1/a$	$a = 49,2$ $b = 29,3$	76	2, 55
		P_1	$a = 49,7$ $b = 28,0$ $\gamma = 97,5$	68	2, 44
Triphenylene		$C\,2/m$	$a = 30,7$ $b = 28,4$	185	1, 48
		$P\,2_1/a$	$a = 51,8$ $b = 32,6$	165	2, 58
Truxene		$P\,2_1/a$	$a = 44,1$ $b = 32,7$	94	2, 08
		$C\,2/m$	$a = 50,6$ $b = 33,8$	180	2, 47

4.1 D_h hexagonal phases

4.4.1. D_{ho} ordered hexagonal phase. This is the most ordered columnar phase with a perfect hexagonal lattice (Figure 2); this phase is uniaxial[14,16,34,52,56] ($\Delta_n < 0$[14,52] $\Delta\chi < 0$[56,57]).

The microscopic identification of the D_{ho} phase is rather easy: on slow cooling between glass slides, the mesophase grows from small homeotropic hexagons which develop into digitated stars which then merge, on further cooling, into a mosaic of domains[52] characteristic of this type of phase with some linear birefringent defects (Figure 4).

This mesomorphic arrangement is strongly ordered, and as a corollary the $D_{ho} \rightarrow I$ transition heats are high.[15] For example 2.04 kcal. mol^{-1} for C_5HET (2a, $n = 5$).

This phase type usually only occurs when the linkages are not very bulky, such as the six oxygens of hexa-alkoxytriphenylenes (2a)[14,15] or truxenes (4a),[50] but there are exceptions, e.g., short chain hexa-alkanoyloxytruxenes (4b).[29,30]

4.1.2. D_{hd} disordered hexagonal phase. Once more the uniaxial character of this phase leads to large homeotropic domains. On cooling from the isotropic liquid, this phase grows like a crystal (i.e., in geometrical domains with straight boundaries) but without mosaic texture: in most cases focal conic or fan-shaped textures are observed (Figure 5). Some X-ray lattice parameters are given in Table II.

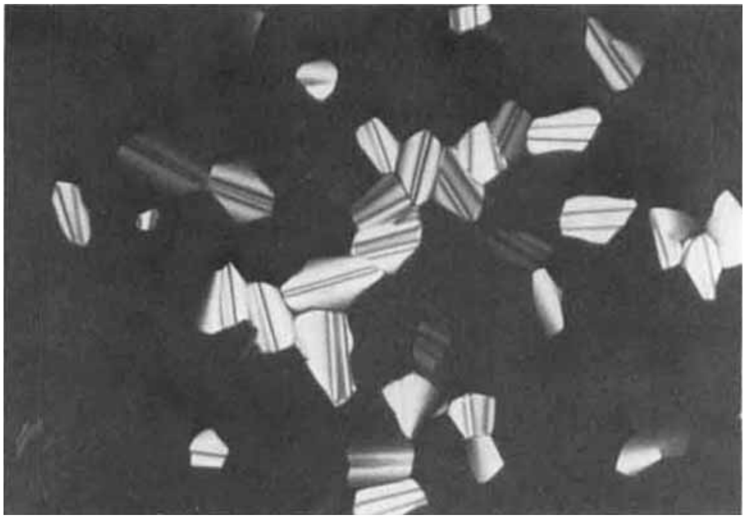


FIGURE 4 Optical texture of the D_{ho} phase: 2a, $n = 5$, 82 °C.

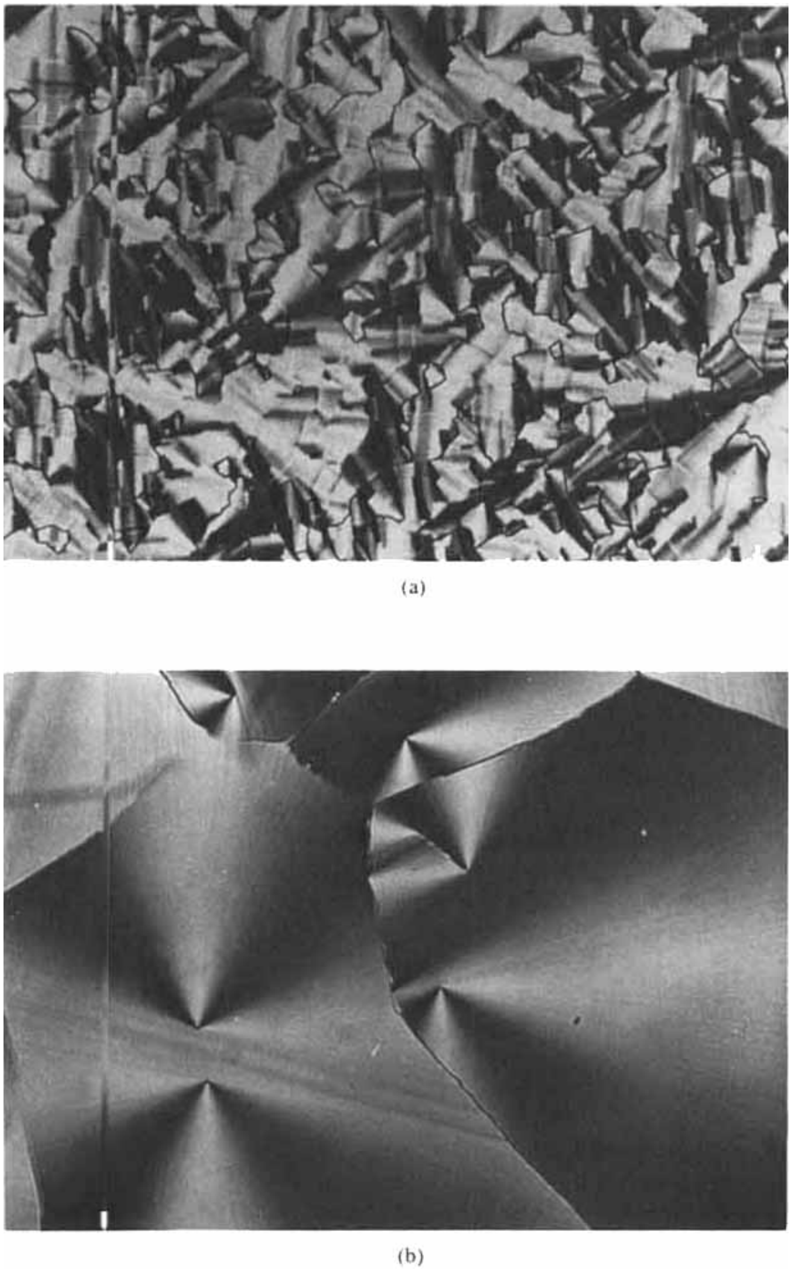


FIGURE 5 Optical textures of the D_{hd} phase: (a) 5, $n = 13$, 163°C; (b) 2b, $n = 11$, 112°C.

Up to now this phase has only been encountered for some long chain hexa-alkanoyloxytriphenylenes (2b) and truxenes (4b) ($n > 10$). The $\Delta H_{D_{hd \to I}}$ is weaker than $\Delta H_{D_{ho \to I}}$ (typically 0.3 kcal.mol^{-1} [15]).

4.2. D_r rectangular phases

Here the situation is more complex: three D_{rd} phases have been identified with different two-dimensional space groups: $P2_1/a$, $P2/a$, $C2/m$ (X-ray lattice parameters are given in Table II). These three phases are biaxial and more or less tilted ~ 55° for the $D_{rd(C2/m)}$ phase in one HBT (2d, $n = 6$[22,37,56]).

The $D_{rd(C2/m)}$ phase exhibits a typical mosaic texture very similar to some S_G phases (cf. 58) (Figure 6).

It is rather difficult to give typical textures for the other D_{rd} phases; some examples are given in Figure 7 in the case of the $D_{rd(P2_1/a)}$ phase.

4.3. $D_{ob.d}$ disordered oblique phase

In this case we cannot again propose a specific texture for the phase, first described for the hexatetradecanoyloxytrioxatruxene (5).[25] The X-ray parameters are given in Table II.

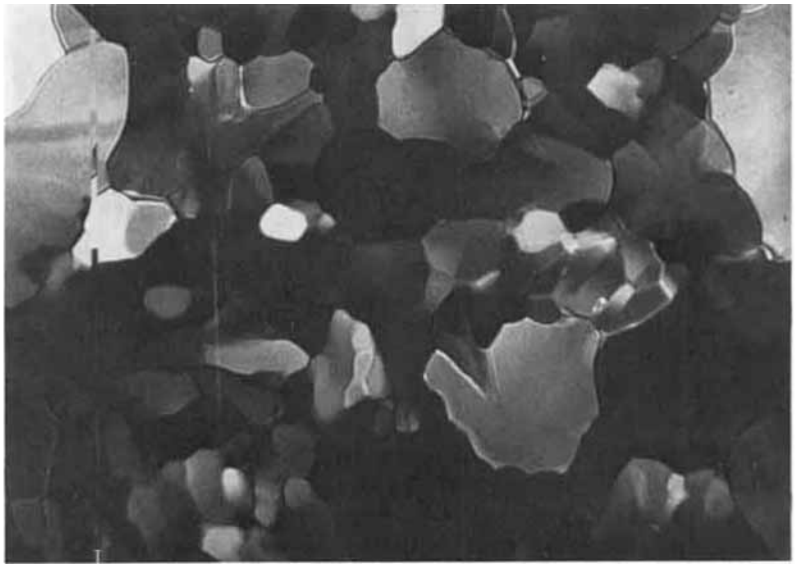
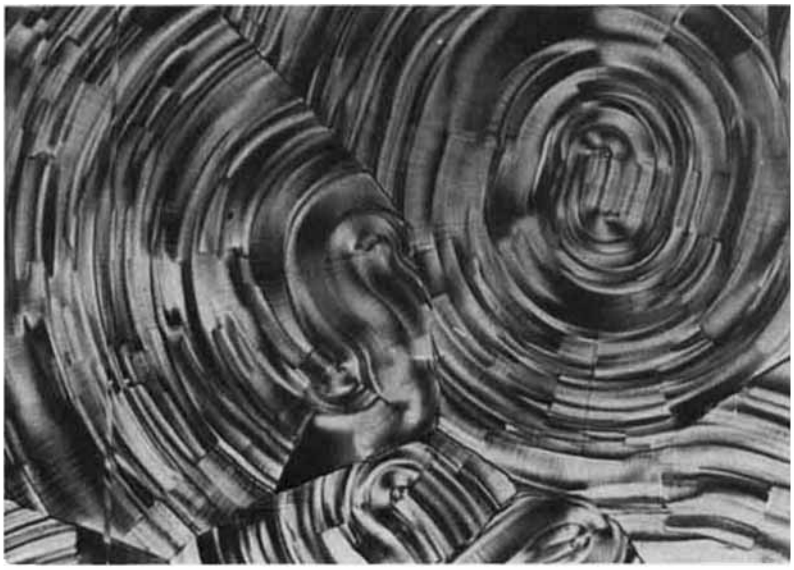
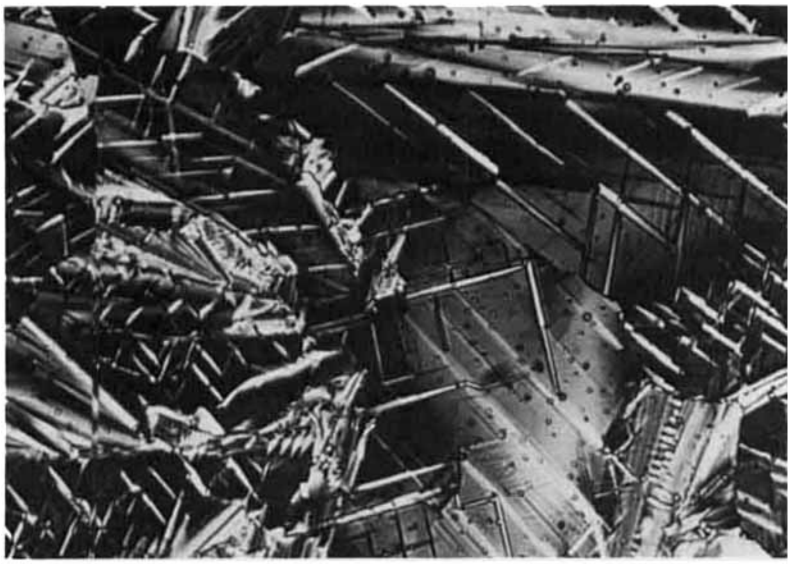


FIGURE 6 Optical texture of the $D_{rd(C2/m)}$: 2d, $n = 6$, 190 °C.



(a)



(b)

FIGURE 7 Optical textures of the $D_{rd(P2_1/a)}$ phase: (a) 2b, $n = 11$, 104 °C (finger prints); (b) 4b, $n = 10$, 101 °C (striated texture); (c) 4b, $n = 9$, 137 °C (broken fan-shaped).

FIGURE 7 *Continued*

5. N_D LENTICULAR NEMATIC PHASE

The fluid N_D nematic phase was discovered in 1979 with some hexabenzoyloxytriphenylene derivatives (2c and 2d) above the D_{rd} columnar phases.[20] The texture is in every way similar to that of the common nematic phases: marbled or threaded texture (Figure 8) with $S \pm 1$, $\pm 1/2$ disclination lines and strong thermal fluctuations especially at the $N_D \rightarrow I$ transition.

This phase corresponds to a molecular organization in which the different flat molecules have complete orientational and rotational freedom but their planes are on average parallel to each other (Figure 9). This description is topologically identical to the classical nematic one, and was confirmed by some X-ray and magnetic measurements.[38,56] Some electrooptical effects have been demonstrated;[59] the analogy with the carbonaceous mesophase has been largely developed.[11]

Nevertheless the optical and diamagnetic anisotropies Δn and $\Delta\chi$ are negative, and the macroscopic viscosity markedly higher than that of the classical nematic state.[60] Finally, we must emphasize that the N_D phase is not entirely miscible with the nematic phase of the

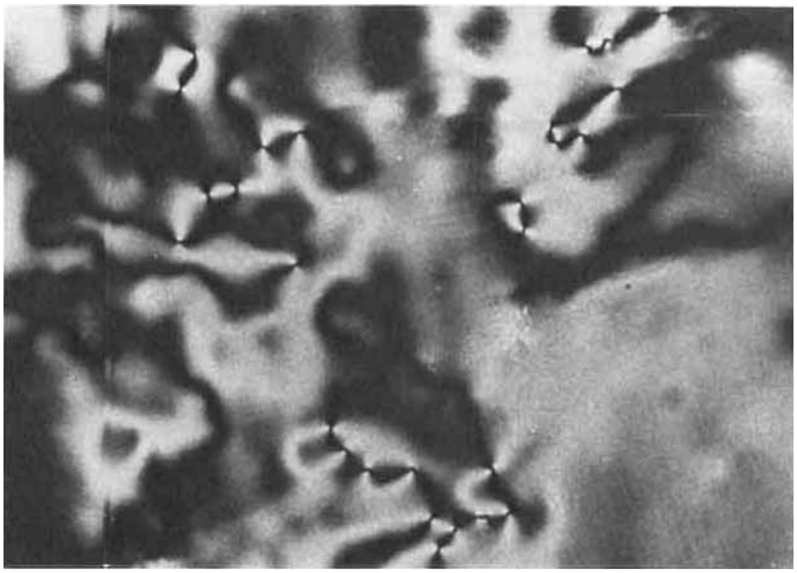
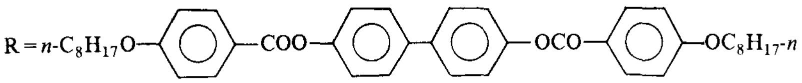


FIGURE 8 Optical texture of the N_D nematic phase (4b, $n = 13$, 65 °C).

one-dimensional analogue (12) of C_8OHBT (2d, $n = 8$).[26]



12

A convincing confirmation of the nematic nature of the N_D phase has been given by obtaining a N_D^* cholesteric phase.[27,28]

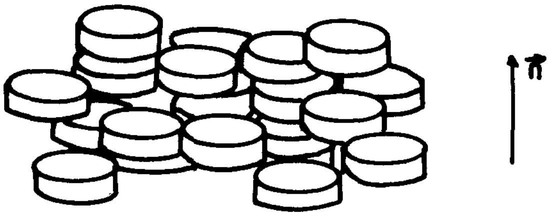


FIGURE 9 Molecular structure of the N_D nematic phase.

6. POLYMESOMORPHISM OF DISC-LIKE COMPOUNDS

6.1. Monomorphism

Let us recall the monomesomorphism encountered:

—Hexa-alkanoyloxybenzenes (HAB) (1)[12] exhibit a D_{rd} phase, probably $P2_1/a$,[38] with a short temperature range. For example, C_5HAB (1, *n* = 5):[12]

$$K \xrightarrow{68.3^\circ} D_{rd(P2_1/a)} \xrightleftharpoons{86^\circ} I;\ \Delta H_{D_{rd}\rightarrow I} = 4.77\ \text{kcal. mol}^{-1}$$

—Hexa-alkoxytriphenylenes (HET) (2a)[14,15] give a D_{ho} phase for the whole series. For example, C_5HET (2a, *n* = 5):

$$K \xrightarrow{69^\circ} D_{ho} \xrightleftharpoons{122^\circ} I;\ \Delta H_{D_{ho}\rightarrow I} = 2.4\ \text{kcal. mol}^{-1}$$

—Hexa-alkanoyloxytriphenylenes (HAT) (2b)[15] with short chains exhibit a $D_{rd(P2_1/a)}$ phase. For example, C_7HAT (2b, *n* = 7):

$$K \xrightarrow{66^\circ} D_{rd(P2_1/a)} \xrightleftharpoons{126^\circ} I;\ \Delta H_{D_{rd}\rightarrow I} = 0.68\ \text{kcal. mol}^{-1}$$

—Hexabenzoyloxytriphenylenes (HBT) (2c and 2d) with short alkyl chains exhibit a N_D nematic phase or a N_D^* cholesteric phase.[20,26-28] For example, C_7HBT (2d, *n* = 7):

$$K \xrightarrow{168^\circ} N_D \xrightleftharpoons{253^\circ} I$$

—Let us mention finally the hexa-alkoxytruxenes (HETX) (4a)[50] with a D_{ho} columnar phase over a large temperature range. For example, C_{10}HETX (4a, *n* = 10):

$$K \xrightarrow{67^\circ} D_{ho} \xrightleftharpoons{260^\circ} I$$

We must point out the consistent relationship which seems to exist between the diameter of the central rigid part and the mesomorphic temperature range (Table III).

TABLE III

Central cores and increasing mesomorphic temperature domains (° C)

HAB	(benzenes 1)	16
HET	(triphenylenes 2a)	53
HAT	(triphenylenes 2b)	60
HBT	(triphenylenes 2c, 2d)	92
HETX	(truxenes 4a)	193
HBTX	(truxenes 4c)	> 210

6.2. Di and trimorphism D-D

The hexa-alkanoyloxytriphenylene series (2b) with long chains ($n \geq 10$) provided us with the first example of a complex columnar polymorphism. In fact, three different columnar phases were identified by mean of optical texture observations and were originally denoted D_0, D_1, D_2.[15,21] X-ray diffraction measurements were performed on these substances and showed that D_2 phase is D_{hd} and D_1 is $D_{rd(P2_1/a)}$, but the structure of the so-called D_0 phase is still unknown. The C_{11}HAT derivative[21] (2b, $n = 11$) exhibits the following sequence:

$$K \xrightarrow[12.5]{80^\circ} D_0 \xrightleftharpoons[(0.00)]{93^\circ} D_{rd(P2_1/a)} \xrightleftharpoons[(0.034)]{111^\circ} D_{hd} \xrightleftharpoons[(0.30)]{122^\circ} I$$

$\Delta H(\text{kcal.mol}^{-1})(\text{in bracket})$

Another example of columnar polymorphism was described for one rufigallol derivative (6, $n = 7$),[24] and provides an interesting transition between D_{rd} disordered rectangular columnar phases:

$$\begin{tikzcd}
K \arrow[r, "107.5^\circ", "(11.3)"'] & D_{rd(P2_1/a)} \arrow[r, shift left, "127.5^\circ"] \arrow[d, shift left, "95^\circ(0.00)"] & I \arrow[l, shift left, "(3.3)"] \\
& D_{rd(P2/a)} \arrow[u, shift left] &
\end{tikzcd}$$

$\Delta H(\text{kcal.mol}^{-1})(\text{in bracket})$

6.3. D-N_D polymorphism

6.3.1. Normal sequence. Let us recall that it was within the hexabenzoyloxytriphenylene series (2c and 2d) that the first example of a N_D nematic phase[20,26] was found. Three different types of mesomorphic sequence are encountered with compounds (2d):

$$K \xrightarrow{186^\circ} D_{rd(C2/m)} \overset{193^\circ}{\rightleftharpoons} N_D \overset{274^\circ}{\rightleftharpoons} I \qquad (2d,\ n = 6)$$

$$K \xrightarrow{152^\circ} D_{rd(P2_1/a)} \overset{168^\circ}{\rightleftharpoons} N_D \overset{244^\circ}{\rightleftharpoons} I \qquad (2d,\ n = 8)$$

Finally, with (2d, $n = 12$), the N_D nematic phase disappears and a direct $D_{rd \to I}$ transition occurs:

$$K \xrightarrow{146^\circ} D_{rd} \overset{174^\circ}{\rightleftharpoons} I$$

This behaviour recalls the classical nematic case where the nematic phase tends to disappear with growing chain length.

These sequences are arbitrarily named *normal* because the viscous highly ordered columnar phases are observed at lower temperatures than the more fluid nematic phases.

6.3.2. Inverted sequences. Hexa-alkanoyloxytruxenes (4b)[29, 30] exhibit an *inverted* sequence: the N_D nematic phase is observed at lower temperatures than the columnar phases with chain lengths between $n = 6$ and $n = 11$, and have very large mesomorphic temperature ranges. For example with (4b, $n = 9$):

$$K \xrightarrow[5.1]{68^\circ} N_D \underset{0.24}{\overset{85^\circ}{\rightleftharpoons}} Drd_{(P2_1/a)} \underset{\sim 0}{\overset{138^\circ}{\rightleftharpoons}} D_{ho} \underset{\text{(decomposition)}}{\overset{280^\circ}{\rightleftharpoons}} I$$

$\Delta H(\text{kcal. mol}^{-1})$

This peculiar behaviour poses an interesting theoretical question. Furthermore, the existence of a "low temperature" N_D phase may be useful for experiments on this kind of phase.

Another example of inverted sequence with a more complex columnar polymorphism was recently described for one hexasubstituted trioxatruxene (5):[25]

$$\begin{tikzcd}
K \arrow[r, "74^\circ", "(22.3)"'] & D_{rd(P2_1/a)} \arrow[r, shift left, "158^\circ"] \arrow[dl, shift left, "(0.1)"] & D_{hd} \arrow[l, shift left, "(0.03)"] \arrow[r, shift left, "166^\circ"] & I \arrow[l, shift left, "(0.6)"] \\
D_{obd} \arrow[ur, shift left, "71^\circ"] \arrow[d, shift left, "(0.3)"] & & & \\
N_D \arrow[u, shift left, "58^\circ"] & & &
\end{tikzcd}$$

$\Delta H(\text{kcal. mol}^{-1})$
(in bracket)

6.3.3. Reentrant sequences. The presence of a N_D nematic phase at lower temperature than the columnar phase[29,30] offered some analogy with the well-known reentrant phenomena (with for example a S_A phase re-observed above the nematic[61]). As expected, some hexa-alkanoyloxytruxenes (4b) with long chains ($n \geq 12$) exhibited a D_{hd} reentrant columnar phase.[31] For example (4b, $n = 13$):

$$\begin{tikzcd}
K \arrow[r, "61^\circ"] & N_D \arrow[r, shift left, "84^\circ"] \arrow[r, leftarrow, shift right] & D_{rd(P2_1/a)} \arrow[r, shift left, "112^\circ"] \arrow[r, leftarrow, shift right] & D_{hd} \arrow[r, shift left, "241^\circ"] \arrow[r, leftarrow, shift right] & I \\
D_{hd} \arrow[ur, shift left, "56^\circ"] \arrow[ur, dash, shift right] \arrow[urrr, leftrightarrow] & & & &
\end{tikzcd}$$

It is important to note the perfect superposition of low and high temperature optical textures of the D_{hd} phases (Figure 10).

Another example of a reentrant sequence was described owing to a simple consideration: hexa*benzoyloxy*triphenylenes (2c or 2d) present a high temperature N_D nematic phase above a D_{rd} columnar phase (for example: 2d, $n = 8$, N_D from 168 °C to 244 °C). On the other hand, hexa-alkanoyloxy*truxenes* (4a) exhibit a low temperature N_D phase under a D_{rd} phase (for example 4b, $n = 9$ from 68 °C to 85 °C). So one could imagine that hexa*benzoyloxytruxenes* (4c) would offer a reentrant nematic phase. In effect, some compounds (4c) have the expected reentrant sequence; for example (4c, $n = 11$):[32]

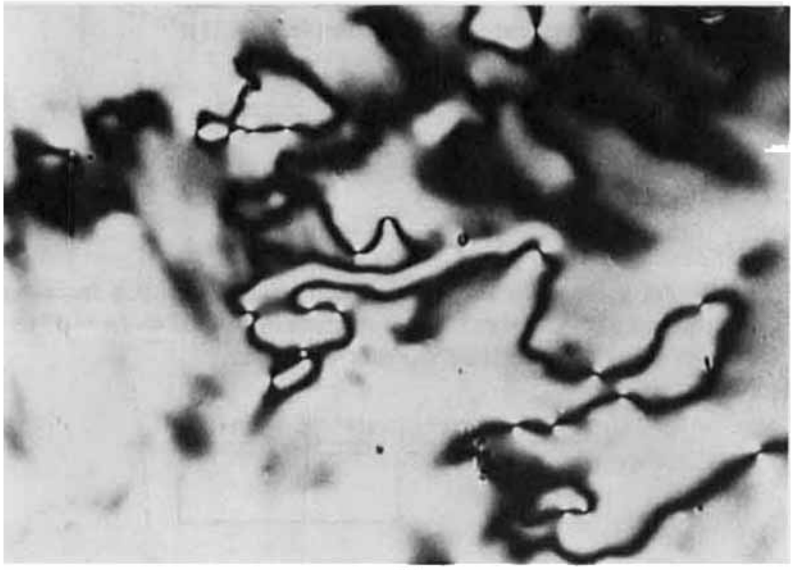
$$\begin{tikzcd}
K \arrow[r, "90^\circ"] & D_{rd} \arrow[r, shift left, "137^\circ"] \arrow[r, leftarrow, shift right] & N_D \arrow[r, shift left, "171^\circ"] \arrow[r, leftarrow, shift right] \arrow[rr, leftrightarrow, bend right=40] & D_{rd} \arrow[r, shift left, "274^\circ"] \arrow[r, leftarrow, shift right] & N_D \arrow[r, shift left, "297^\circ"] \arrow[r, leftarrow, shift right] & I
\end{tikzcd}$$

Finally, let us recall a very unexpected sequence with a *reentrant isotropic* liquid phase. For example a mixture of 87% of 4b ($n = 13$) + 13% of 4c ($n = 12$) shows the following sequence:[33]

$$\begin{tikzcd}
K \arrow[r, "67^\circ"] & N_D \arrow[r, shift left, "112^\circ"] \arrow[r, leftarrow, shift right] & I \arrow[r, shift left, "129^\circ"] \arrow[r, leftarrow, shift right] \arrow[rr, leftrightarrow, bend right=40] & D_{hd} \arrow[r, shift left, "214^\circ"] \arrow[r, leftarrow, shift right] & I
\end{tikzcd}$$

In this concentration range (Figure 11), the D_{hd} columnar phase shows a transition from mesophase → isotropic liquid by increasing (214 °C) *and* by decreasing (129 °C) the temperature!

(a)



(b)

FIGURE 10 Optical textures of the reentrant D_{hd} phase, 4b, $n = 13$: (a) 95 °C; (b) intermediate N_D nematic phase at 65 °C; (c) 57 °C.

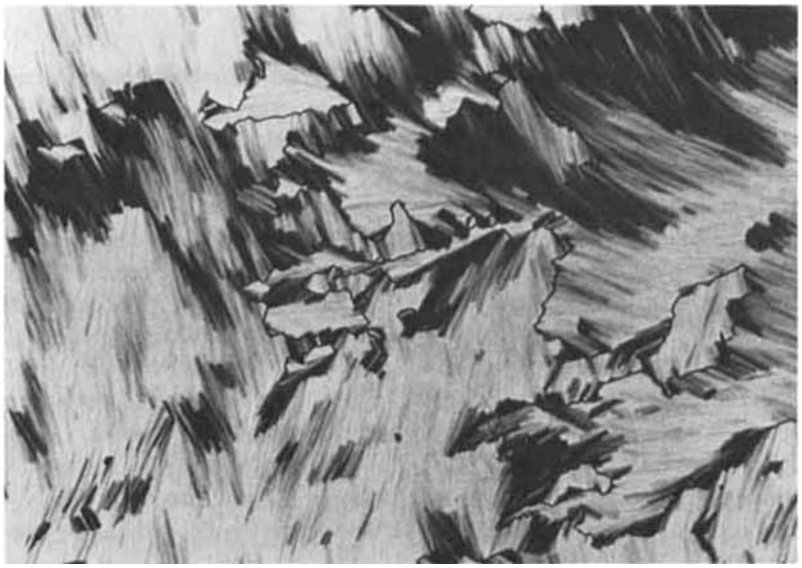


FIGURE 10 *Continued*

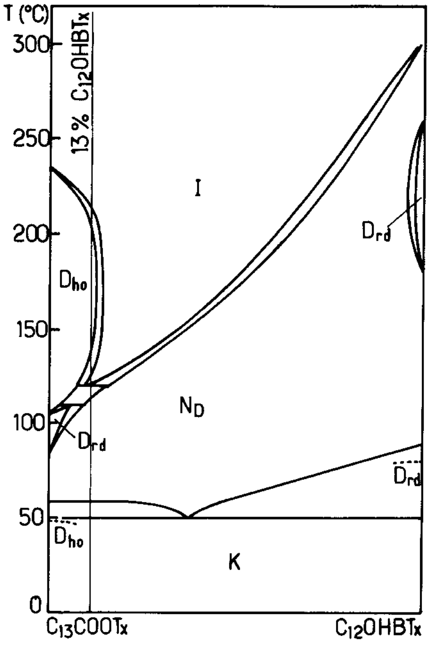


FIGURE 11 Binary phase diagram between 4c, $n = 12$ and 4b, $n = 13$.

7. ISOMORPHISM

The X-ray diffraction method is a very sure but slow and complicated technic for the determination of mesophase structure. Therefore complementary methods are extensively used: the observation of the microscopic textures, and of course the measurement of the transition heat, and studies of isomorphism by the contact method.[62]

Several authors have tried to use this latter method for the N_D and columnar phases. This technique is successful in the case of two members of the same chemical series: benzenes (1),[63] triphenylenes (2),[14,15,26,37] and truxenes (4).[20,30,37] Recently, some examples of total miscibility between mesophases of chemically different disc-like compounds have been described.[23,26,28] A very interesting example concerns the isomorphism between the two N_D phases of a hexabenzoyloxytriphenylene (2d) and the N_D phase of an hexabenzoyloxytruxene (4c):[32] the miscibility is complete between the N_D nematic phase on one hand and between the two D_{rd} phases on the other hand.

Nevertheless we must underline two important limitations of this method in the case of disc-like mesogens:

—The small number of reference substances (~ 70).[40]

—The necessity for considerable similarity between the two compared substances (in terms of chemical nature, diameter).

So, when the molecular diameters of two compounds in contact are too different, even in an homologous series, the isotropic phase usually separates the two mesomorphic domains[15] each however with the same structure. Consequently the isomorphism method must be used step

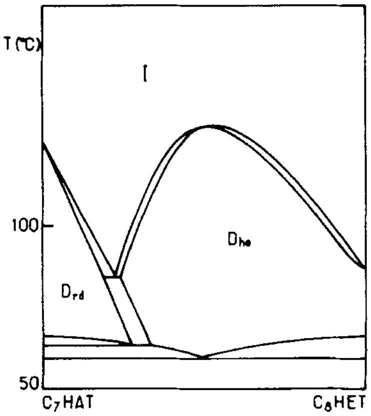


FIGURE 12 Binary phase diagram between 2a, $n = 8$ and 2b, $n = 7$.

TABLE IV

Mesomorphic types

PHASE TYPE	STRUCTURAL ELEMENT (only one molecule in the case of thermotropic bacillar and lenticular nematics)	MOLECULE(S) OF THE STRUCTURAL ELEMENT AND CORRESPONDING MESOMORPHIC PHASES	
		Thermotropic phases	Lyotropic phases[a]
BACILLAR	FINITE CYLINDER	1 rod → nematic *n* rods → cubic phases[68]	*n* rods → CM Mesophase[6] (nematic) *n* rods → cubic phases[69, 70]
LENTICULAR	DISC	1 disc → N_D nematic	*n* rods → DM Mesophase[6] (nematic) → monoclinic,[19] or orthorombic[18] phases
LAMELLAR	INFINITE SHEET	*n* rods → smectics (except S_D)	*n* rods → lamellar phases[4]
COLUMNAR	INFINITE CYLINDER	*n* rods → diisobutylsilanediol phase[35] *n* discs → columnar phases	*n* rods hexagonal, ribbon phases(4,17–19)

[a] Under this item are included neat soaps, intermediate between thermotropic and lyotropic phases.

by step between pairs of similar diameter. For example, with (2a): $n = 6 + n = 8$; $n = 8 + n = 10$.[15,37]

Finally, as in the case of classical mesogens,[64] strongly non-ideal behaviours have been observed[16,65,66] (Figure 12).

8. CONCLUSION

From these results, a clear analogy can be drawn between these thermotropic mesophases and some lyotropic ones: lens-shaped units and indefinite cylinders—consisting of rod-like amphiphilic molecules (lyotropic systems) or disc-like molecules (thermotropic systems)—are the structural elements encountered in both cases. Moreover, the same remark can be made about the lamellar lyotropic and thermotropic mesophases: in both cases the structural element is the sheet consisting of rod-like molecules, respectively amphiphilic (with or without solvent) and hydrophobic[67] (Table IV).

In thermotropic systems, the presence of a more or less polar rigid molecular core-oblate (disc-like mesogens with at least six paraffinic chains) or prolate (rod-like mesogens with one or two chains)—gives a richer mesomorphic polymorphism than in lipid systems. For example tilted mesophases displayed by disc-like compounds with $P2_1/a$, $P2/a$ and $C2/m$ space groups are unknown in lyotropic systems.

Nevertheless, the mesomorphic phases can be classified in four main categories (five if the plastic crystals are included) based upon the structural element (Table IV), molecular aggregate or molecule: *bacillar* phases consisting of finite cylinders, *lenticular* phases (discs), *lamellar* phases (infinite sheets), *columnar* phases (infinite cylinders).

Therefore it is easy to understand why, in spite of the small number of disc-like mesogens which have been synthesized up to now, this new type of material is of great interest to physicists.

Acknowledgments

We are indebted to Drs. Y. Bouligand, J. Jacques, M. Kleman, L. Liebert, L. Mamlok, P. Oswald and J. Prost, for stimulating discussions, comments and helpful discussions.

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