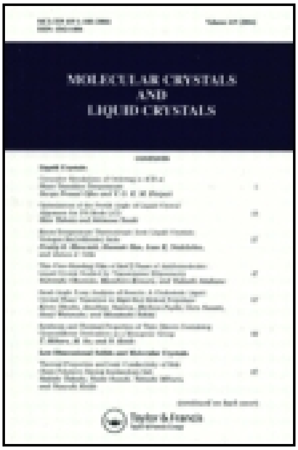

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Orientation of Discotic Mesophases

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Orientation of Discotic Mesophases†

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The orientation of some fluid (D_F) and optically uniaxial columnar (D) discophases by surfaces is examined by optical microscopy. The test materials are 2,3,6,7,10,11 hexa-substituted triphenylenes, including two new compounds exhibiting mesophases at room temperature, and a binary mixture with a D_F phase stable between 57 and 100°C. The alignment with the directors perpendicular to the walls can be obtained on glass surfaces coated with flat molecules possessing six polar side-functions. Similar homeotropic alignments for the D_F phase and total normal orientations for the D phase are observed on faces of cleaved apophyllite and muscovite crystals. For the D_F phase, the uniform alignment with the directors parallel to the surfaces is obtained using glass surfaces coated with silicon oxides deposited at oblique incidence. Mutual orientations of the D and D_F phases are noted. Between two slides and with the parallel alignment, left or right handed twisted fluid discophases with only an infinite-fold screw symmetry axis can be obtained. Displays using optically negative mesophases can be envisaged.

1 INTRODUCTION

Nematic and different smectic mesophases can be obtained with elongated and flexible molecules[1]: *calamitic* mesophases (from *χαλαμοσ*: reed). We can obtain also some kinds of anisotropic mesophases with discoïd molecules: *discotic* mesophases (from *δισχοξ*: quoit).[2] Mounted between untreated glass slides by melting, cooling or dissolution, these phases appear with a non-uniform orientation.[3] The achievement of uniformly oriented nematic,

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‡ Equipes associées au C.N.R.S.

smectic A, C and B mesophases simplifies physical studies and permits many applications. Until to day, there have been observed for discophases, only:

—microscopical areas with the main symmetry axis perpendicular to the walls: normally oriented areas, obtained by slow cooling of the isotropic phase of 2,3,6,7,10,11 hexa-alkoxytriphenylenes,[4]

—orientation of the mesophase formed from aqueous solutions of the sodium salt of the tetracarboxylate of copper phtalocyanine by glass slides rubbed in one direction[5] and

—orientational effects of intense magnetic fields on the mesophases of some triphenylene derivatives.[6,7]

We study here the orientation of some thermotropic discotic mesophases by treated glass slides and crystalline surfaces obtained by cleavage.

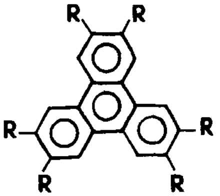
2 DISCOTIC MESOPHASES STUDIED

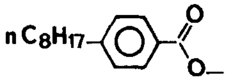
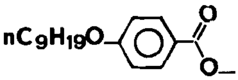
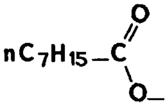
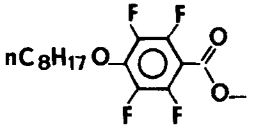
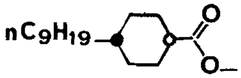
To simplify the observation of the orientational effects with a polarizing microscope (Leitz, Panphot) equipped with a heating stage (Mettler, FP 52), we have tested optically uniaxial discophases. The compounds used are 2,3,6,7,10,11-hexa-substituted triphenylenes: Table I. The fluid discotic mesophases D_F^2 of **1** and **2** exhibit, between uncoated glass slides, threads and schlieren-like textures with curved $s = \pm 1/2$ and $s = \pm 1$ disclination lines.[10] By cooling, the D_F mesophase of **1** forms another mesophase D with a mosaïc-like texture. Two growing domains which come into contact collapse. The decomposition of compound **2** in the presence of air, under atmospheric pressure, begins before the clearing point. The columnar mesophase of this compound was previously confused with a solid phase.[8] By cooling, the D_F mesophase of **2** gives a birefringent, non-rigid mesophase with defects having a rectilinear axis. This mesophase appears in domains exhibiting two parallel rectilinear sides and two irregular sides. These domains are birefringent with a uniform extinction parallel to the rectilinear sides in accordance with a binary symmetry. Compound **3** exhibits only a D_B mesophase.[2]

The phase diagram of mixtures of compounds **1** and **3** at atmospheric pressure (Figure 1) is established by observation of a contact preparation.[11] The mixture containing ~72 moles % of **3** has a stable D_F mesophase between 57 and 100°C. Mixtures of **2** and **3** exhibit a stable D_F phase only over 110°C. Mixtures with other known discogenic compounds exhibit D_F phases at higher temperatures.

TABLE I

Compounds used



Compound number	R	K		D		D_F		L	References
1		.	125	.	179	.	222	.	8
		. .	147 *4.0*	. .	182 *1.45*	.	230	.	8
3		.	66 *4.72*	.			126 *.68*	.	9
4	$nC_5H_{11}-O-$	.	69 *7.76*	.			122 *1.94*	.	4
5				.			300 *2.15*	.	
6				.			>345	.	

The phases exhibited by a compound (solid K, columnar discotic mesophase D, discotic fluid mesophase D_F and liquid L) are indicated by a point in the corresponding column. The transition temperatures are given in Celsius degrees and the transition molar enthalpies (*in italics*) in kcal/mol.

The discophase of **4** is uniaxial.[4,12] Compounds **5** and **6** are synthesized by reacting the corresponding acid chlorides with 2,3,6,7,10,11-hexahydroxytriphenylene in pyridine. The acids are prepared by methods previously des-

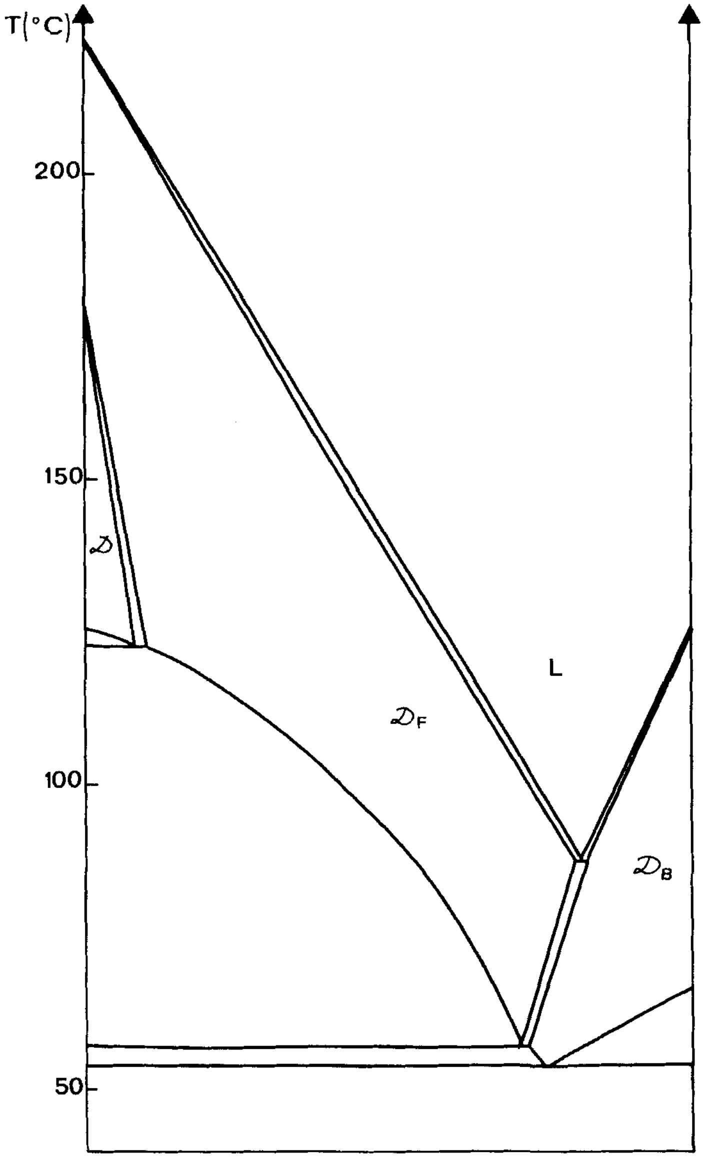


FIGURE 1 Isobaric phase diagram for binary mixtures of compounds **1** (on the left) and **3** (on the right).

cribed[13] for **5** and[14] for **6**. At room temperature the compounds are birefringent pastes. Mixtures of **5** with benzene exhibit fluid mesophases at room temperature. By slow cooling, the liquid phases of **5** and **6** give optically negative uniaxial domains with a sixfold or threefold symmetry and defects with rectilinear axes. Although we have not obtained the compounds crystalline, these discophases are probably supercooled at room temperature. Thermal decomposition of **6** begins before the clearing point.

3 NORMAL ALIGNMENT BY COATED GLASS SURFACES

Homeotropy[15,16] is obtained for calamitic mesophases with long chain surfactants.[17,18,19] For flat discogenic molecules, the director is perpendicular to the molecular plane[2] and perpendicular to the average directions of the side chains, and glasses coated with polysiloxanes have no orientational effect on the D_F phase of **1** and the columnar[12] discophase D of **4**.[4]

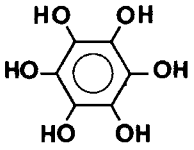
A situation similar to homeotropic alignment of calamitic molecules by long chain surfactants can be obtained for discogens with a sheet of flat molecules with their directors perpendicular to the surface, i.e., with the plane molecules parallel to the surface. One way is to use flat molecules with six polar side-functions which give a good anchorage to the glass. For example hexphenol; mellitic acid; 2,3,6,7,10,11-hexahydroxytriphenylene and rufigallol: Table II.

The glass slides are firstly cleaned with acetone and treated in boiling water for half an hour. After immersion for ten minutes in the appropriate solution at 20°C, the slides are rinsed with the solvent, drained and dried for one hour at 110°C in nitrogen. The coating solutions are hexaphenol 1 % and mellitic acid 5 % by weight in pure water; 2,3,6,7,10,11-hexahydroxytriphenylene 0.25 % and a saturated solution (< 0.1 %) of rufigallol in ethanol.

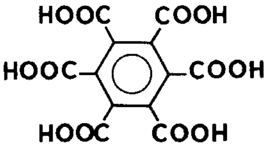
Compounds **1**, **2** and the mixture of **1** and **3** are heated between these slides and observed between crossed polarizer and analyser. The D_F mesophases appear birefringent in the flowing parts (threads parallel to the flow direction) and black in the stationary areas. Cooling the liquids give D_F phases with some disclination lines. By pressing the D_F phase, defects are produced. In all cases, these defects relax spontaneously in a few minutes and the preparations become totally black. By conoscopic observation with a Bertrand's lens and a wave retardation plate, these mesophases appear totally uniaxial and negative. The optic axis is perpendicular to the slides. This direction is an infinite fold symmetry axis for all the observed properties,[2] and the orientations of D_F on glass surfaces coated with the surfactants in the Table II are *homeotropic*.

TABLE II

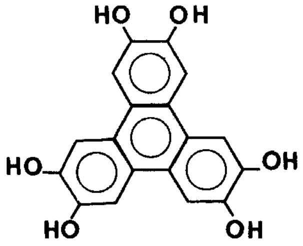
Surfactants used to obtain normal alignment



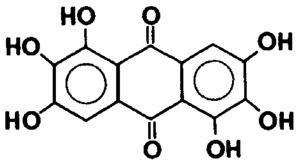
Hexaphenol
melting point over 300°C



Mellitic acid
decomposition at 286°C
before melting



2,3,6,7,10,11 hexahydroxy-
triphenylene



Rufigallol

By cooling D_F between glass slides coated with hexaphenol, only **1** gives a columnar, mosaïc-like discophase. Most of the grains have their optic axes perpendicular to the slides: *normally orientated areas.*[4] After crystallization and melting, the same texture is observed. On further heating the D_F phase becomes totally homeotropic: orientation of D_F by surfactants is predominant.

By cooling, the liquid phase of **4** gives, between slides coated with mellitic acid, a mesophase with only normally oriented areas. By pressing the cover slip, a weak birefringence appears and the limits between the areas can be distinguished between crossed polarizers. By suitable cooling, crystal growth proves that the preferred directions[4] of the different normally oriented areas are not correlated. Glasses coated with mellitic acid orient only the column axes of the discophase normally to the surface: *normal alignment.* By cooling between glass slides covered with hexaphenol, the liquid phase of **5** gives discotic domains, in the most part with normal alignment. No effect is observed with **6** because of the thermal decomposition before the clearing temperature.

These coated glass slides have no orientational effect on the nematic mesophases of tolanes and 4-*n*-heptylbenzoïc acid.

To summarize, flat molecules having six polar side-functions are surfactants which induce a homeotropic alignment of D_F and a normal alignment of the columnar discophases of **1**, **4** and **5**. These data establish the optical uniaxiality of these discophases.

4 ORIENTATION BY CRYSTALLINE SURFACES

With glass surfaces coated with flat molecules, we have obtained only the normal alignment for columnar discophases, but the remarkable (preferred) directions are not oriented around the optical axis. The orientation of calamitic mesophases by crystalline surfaces is well known.[20] We have tested this method to obtain a total orientation of optically uniaxial discophases.

The crystalline surfaces used are the perfect cleavage (001) of apophyllite, a lamellar tetragonal silicate,[21,22] and the perfect cleavage of muscovite, a monoclinic mica.

These surfaces have no orientational effect on the D_F phase of **2**. For **1** perfect homeotropy is observed for D_F and normal alignment for D. Over fresh muscovite cleavage, the discophase of **5** obtained by cooling the liquid has a normal alignment. By cooling from the liquid phase, the columnar discophase of **4** is obtained with a normal alignment over freshly cleaved apophyllite. By further cooling, all the fine crystalline needles appearing in the discotic preparation are parallel to one of only six equally spaced directions. This discophase is totally oriented by the apophyllite (001) face.

5 PARALLEL ALIGNMENT BY TREATED GLASS SURFACES

The alignment of the director parallel to the streaks of a rubbed surface[23–26] minimize the elastic energy of a mesophase[27] from calamitic molecules. The same technique was applied to the discotic mesophases. Between glass slides scratched with diamond powder ($\leqslant 2\ \mu$m) only partial parallel alignment was observed for the D_F phase of **1** and **2**.

Another way is to use glass slides coated with silicon oxides deposited in the usual way[28] (the angle between the beam and the slide plane is 20°). Such slides have no net orientational effect on the D_F phase of **2** and the columnar discophases of **3** and **4**. The D_F discophase of **1** heated between two slides with parallel streaks appears birefringent with some threads parallel to the flow. In motionless preparations, the defects relax spontaneously and a uniform birefringence appears. The neutral lines are respectively parallel and perpendicular to the streaks. From the cooled liquid phase, the D_F mesophase appears in spherical droplets with different orientations and defects. After total transformation, the defects relax and the birefringence is uniform. Glass slides coated with silicon oxides deposited at an oblique incidence orient on contact the D_F phase of **1** with the optic axis parallel to the streaks: *parallel alignment*. A similar orientation is obtained, at lower temperature, with the D_F discophase of the mixture of **1** and **3**.

By cooling, the oriented D_F phase of **1** gives a columnar discophase with a mosaïc-like texture. Most of the grains have their neutral lines parallel and perpendicular to the streaks. On rotation of the stage, these different uniaxial areas exhibit different colours. After heating, a D_F phase with a parallel alignment is obtained; only a few threads appear at the location of the previous limits of the mosaïc.

6 OTHER ORIENTATIONS FOR DISCOPHASES

For compound **1** between untreated slides, normally oriented domains of D give, on heating, homeotropic D_F areas. From oblique mosaïc grains of D appear D_F regions with practically uniform extinction. Conversely, by decreasing the temperature the nuclei of the mosaïc-like mesophase, appearing in a uniformly oriented D_F area, develops into D grains with the same orientation. In mixtures of **1** and **3**, where the organized discophase rich in **1** is in equilibrium with D_F (Figure 1), these two mesophases have the same extinction directions. We can conclude that a reciprocal orientation of these mesophases occurs similar to that observed with nematic and smectic B calamitic mesophases.[29]

An electric field orients the discophases of **1** and **2** to give the directors parallel to the field.[30]

7 TWISTED DISCOPHASES

The first anisotropic and twisted medium studied was the twisted nematic.[15,16,31] Twist of normal or tilted columnar discophases is difficult; conversely, for the D_F phase, without columnar organization, twist is possible. To obtain a helical disposition of the director, it is necessary to have different orientations for the molecular planes (Figure 2). A possibility is to use two plane limits with parallel alignment in different directions.

The D_F phases of pure **1** and of **1** mixed with **3** are aligned between glass plates coated by silicon oxides with non-parallel streaks. Light extinction is

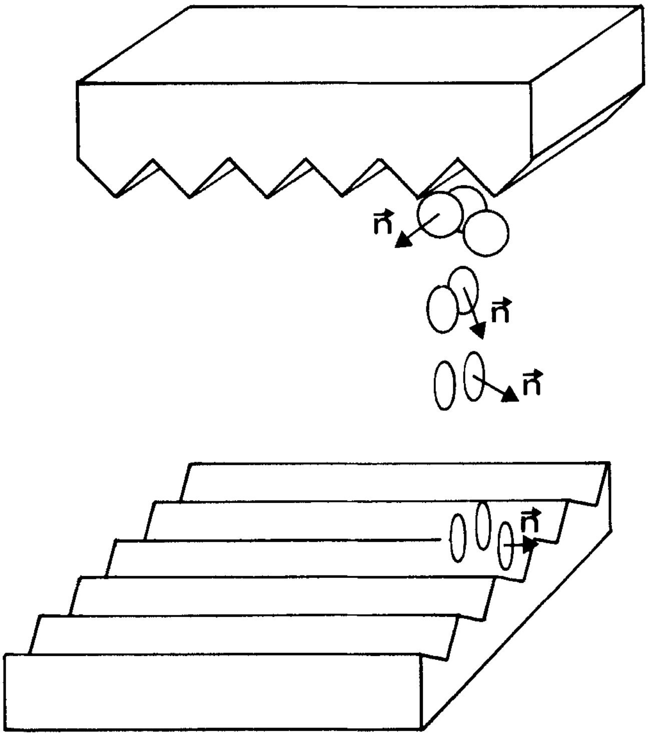


FIGURE 2 Orientation of the molecules in a twisted fluid discophase D_F^*. The molecules are represented by disks perpendicular to the directors *n*.

possible only if the analyser is rotated through an angle equal to that of the streaks. This is not exactly a rotatory power: for an arbitrary stage orientation, coloured light is transmitted. This is a twisted birefringent preparation, i.e., chiral D_F^* with a left handed (D_{Fl}) or right handed (D_{Fr}) twist depending of the rotation sense for the plates. These observations confirm the parallel alignment given by slides coated with silicon oxides. An untwisted D_F phase exhibits an ∞/mm symmetry; with a twist, the symmetry planes disappear and there remains only an infinite-fold, screw symmetry axis. By this method, the twist angle is limited to 90°. No selective reflection of visible light has been observed: the pitch is too large or the thickness is too small to give a significant intensity of reflected light.

By cooling chiral D_F^* phases, columnar discophases appear with uniform extinction between crossed polars: twisted fluid discophases give rise to untwisted columnar discophases. By heating, these untwisted phases give D_F^* phases: orientation of D_F by rubbing is dominant.

8 CONCLUSION

To study the orientation of discophases by convenient surfaces, six hexa-2,3,6,7,10,11-substituted triphenylenes, including two new compounds (**5** and **6**, Table I), are used. The discogens **1** and **2** exhibit fluid D_F and the compounds **1**, **4** and **5** give columnar D optically uniaxial discophases. A binary mixture (**1** and **3**) exhibiting a D_F phase between 57 and 100°C is also used. Reciprocal orientations of fluid and columnar discophases are observed.

Glasses coated with flat molecules having six polar side-functions orient D_F phases homeotropically and some optically uniaxial D discophases with the director perpendicular to the walls: normal alignment. Total orientation of columnar discophases can be obtained by freshly cleaved surfaces of crystals: apophyllite and muscovite mica. These surfaces can be also used to obtain homeotropic alignment of D_F.

The uniform orientation of D_F with the director parallel to the surfaces can be observed between glass slides coated with silicon oxides deposited at oblique incidence. Between two slides so coated and with non-parallel streaks, left or right handed twisted fluid discophases with only one infinite-fold screw symmetry axis can be obtained.

These orientations by surfaces facilitate physical studies of discophases. The existence of fluid discophases at low temperature and the orientating effects by walls and an electric field allow us to envisage displays using optically negative mesophases.

Acknowledgements

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