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## Liquid Crystals

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### Thermotropic biaxial nematic phases with negative optical character [1]

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## PRELIMINARY COMMUNICATIONS

### Thermotropic biaxial nematic phases with negative optical character [1]

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Two disc-shaped multialkynyl arene ethers (**1** and **2**) with unusual thermomesomorphic properties are presented. Conoscopic studies show that the nematic phases of these new low molecular weight liquid crystals are biaxial and that the sign of their biaxiality is negative. The diether **2** is the first discotic twin liquid crystal which exhibits a nematic phase.

The molecular architecture of thermomesomorphic organic compounds studied in the past 100 years is manifold and nowadays also includes a selection of disc-shaped substances [2]. Among the latter type of molecules are very few species which exhibit not only discotic phases ( $D$ ), but also, or exclusively, nematic phases ( $N_D$ ) [3-7]. The structure of such a  $N_D$  phase is illustrated in figure 1.

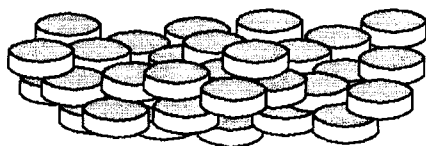
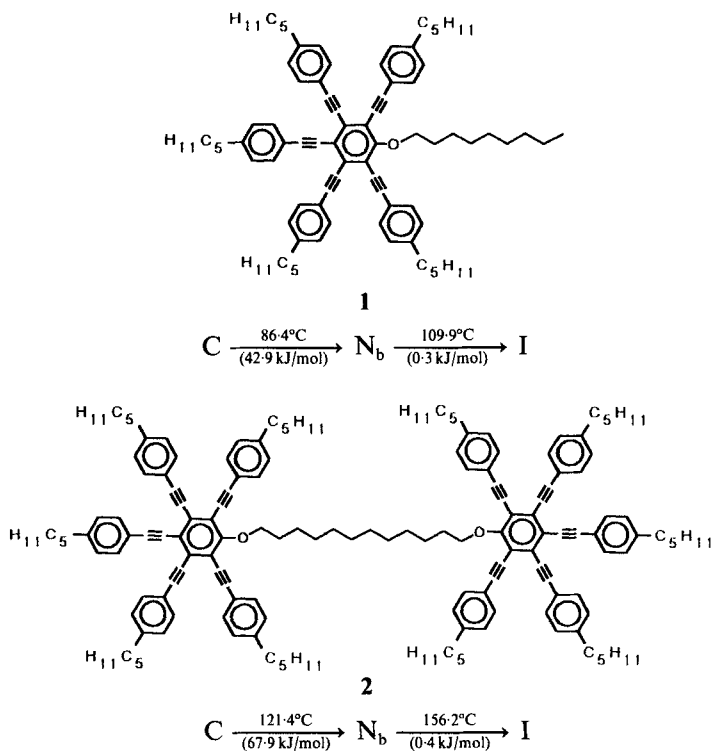


Figure 1. The structure of the discotic nematic phase (schematic presentation).

Recently various examples of a new class of liquid crystal, highly unsaturated substituted hexakis(phenylethynyl)arenes [8] with diameters of their super disc cores of up to about 24 Å, have been synthesized [4-7]. Most of these mesogens exhibit  $N_D$  phases: the larger their core the more likely the formation of a  $N_D$  phase appears to be. Here we present the two relatives **1** and **2** of this family of thermomesomorphic compounds which have an asymmetric molecular geometry contrary to the radially symmetric structure of hexakis(4-alkylphenylethynyl)benzene [4, 5, 7]. Our X-ray investigations show that the mesomorphic phase of these two materials are nematic. It is the aim of this preliminary communication to show that these molecular asymmetries give rise to the biaxiality of the nematic phase in both cases.

(1) Nonyl pentakis[(4-pentylphenyl)ethynyl]phenyl ether (**1**:  $C_{80}H_{94}O$ , 1071.6), and (2) 1,12-bis{pentakis[(4-pentylphenyl)ethynyl]phenyloxy}dodecane (**2**:  $C_{154}H_{174}O_2$ , 2057.1). The monoether **1** as well as the twin ether **2** each contain the large substituted pentayne unit(s) and have been prepared in two step syntheses starting from commercially available pentabromophenol via etherification (using NaH in DMF) which gives the following colourless intermediates: (1) nonyl pentabromophenyl ether,  $C_{15}H_{19}Br_5O$ , m.w. 614.8, m.p. 50.5°C, 63 per cent yield, or (2) 1,12-bis(pentabromophenyloxy)dodecane,  $C_{24}H_{24}Br_{10}O_2$ , m.w. 1143.5, m.p. 138°C, 41 per cent yield. Pd catalysed alkynylations [4–7] of these two bromo ethers with 4-*n*-pentylphenylacetylene gave the yellow crystalline multialkynyl arene ethers **1** and **2** in 34 per cent or 58 per cent yield, respectively; in chloroform or ether they are blue fluorescent. Their structural formulas and phase transition data [9] are



The characterizations of the ethers **1** and **2** are based on a correct elemental analysis and on spectroscopic data, e.g. IR:  $\nu = 2210\text{--}2220 \text{ cm}^{-1}$  which will be published later together with those of homologous derivatives in these series. The bisether **2** is a new example of a rarely described liquid-crystalline dimer or twin with discotic units [10] and is the first discotic twin liquid crystal which exhibits a nematic phase.

On cooling the isotropic phases of **1** or **2**, their nematic phases appear with homogeneous textures which are almost dark between crossed polarizers. These homogeneous textures are sometimes transformed about 20°C below their clearing temperatures into typical schlieren textures, see the example for the twin ether **2** in figure 2.

Conoscopic investigations [11] have been performed on thin layers of homogeneously oriented nematic phases of **1** and **2** between two glass plates, using 23  $\mu\text{m}$

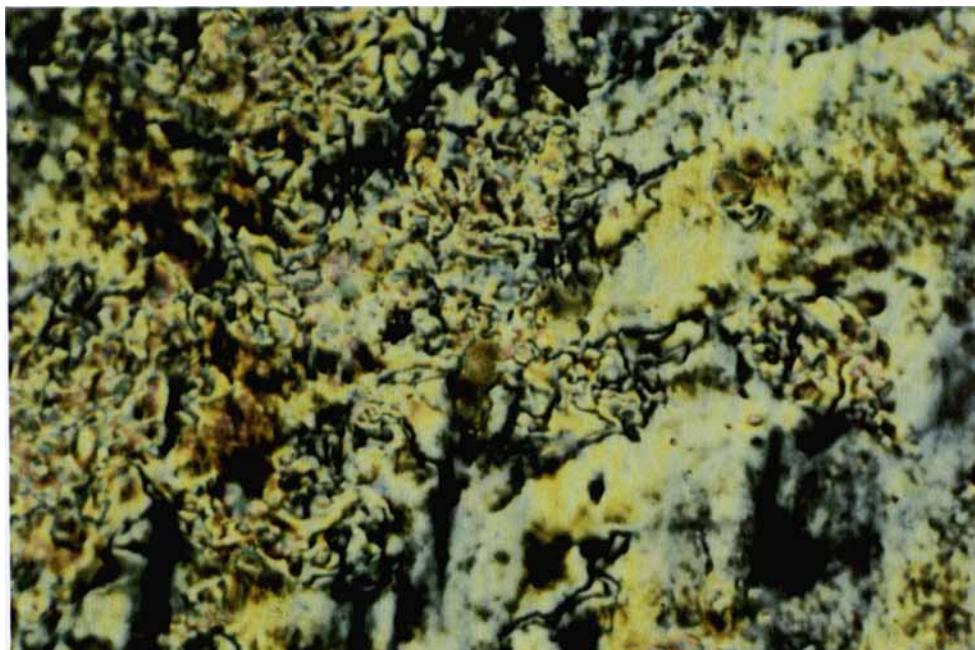


Figure 2. Schlieren texture of the twin ether **2** at 123°C.

thick spacers. For example, figure 3 shows the typical interference pattern of the biaxial nematic phase for the bisether **2**. The isogyres form a cross when the trace of the optic axial plane lies parallel to either cross-wire (extinction position, see figure 3(a)). Rotating the sample by  $\pm 45^\circ$  breaks the cross into hyperbolic brushes (see figure 3(b, c)). The clear splitting into two arcs could be observed only if the glass plates had been rubbed in a uniform direction. Using a sensitive red plate we were able to prove that the sign for the biaxiality is negative in both cases. We want to point out that the separation between the two arcs is enhanced drastically by a flow of the nematic in the direction of the rubbing. The interference figures become diffuse and finally disappear when the schlieren texture is formed from the homogeneous texture. For comparison, the conoscopic pattern in the  $N_D$  phase of radially symmetric hexakis(4-pentylphenylethynyl)benzene [7] shows the typical cross of a uniaxial crystal in which the optic axis is perpendicular to the sample plane. In this case the conoscopic pattern is invariant to the rotation of the sample. We also found by refractometric measurements that the sign of the double refraction for this hexayne is negative as expected for discotic nematic phases.

The biaxiality of nematic phases predicted theoretically 20 years ago [12] was experimentally proved for the first time in amphiphilic systems [13]. Later biaxial nematic phases could also be detected in thermotropic liquid crystals [14–16] as well as in polymeric ones [17–21]. To our knowledge the biaxial nematic phases of **1** and **2** presented here are the first examples of thermotropic optically negative biaxial nematics. The negative sign of the biaxiality in these two cases follows from the molecular geometry and from the structure of the nematic phases. In these cases the short axis  $n_x$  coincides with the direction perpendicular to the plane of the flat molecules which is the direction of the smallest polarizability. The splitting of the other axes is caused by the anisotropic alignment of the discs whereby the direction

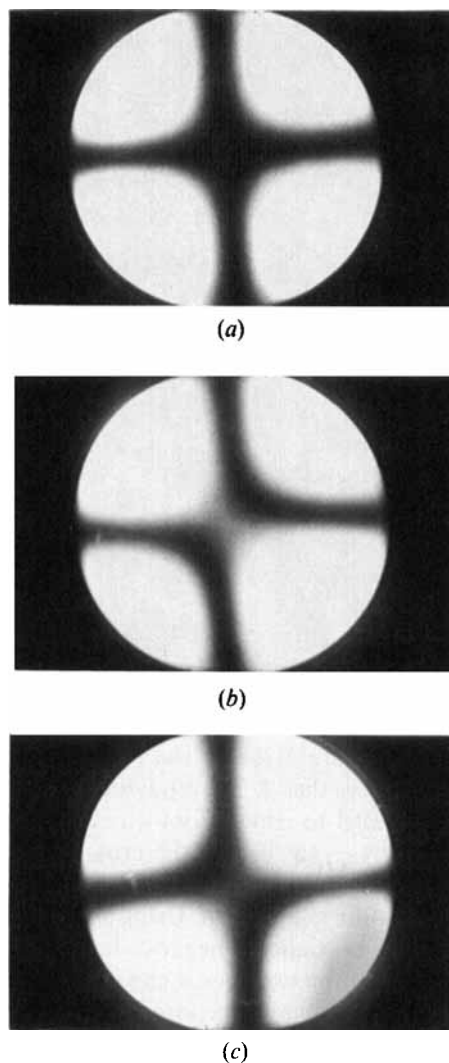


Figure 3. Interference figures of the biaxial nematic phase of compound **2**, section perpendicular with respect to the acute bisectrix ( $T = 137^\circ\text{C}$ ). (a) The trace of the optic axial plane lies parallel to the polarizer or analyser (extinction position). (b) and (c) The trace of the optic axial plane encloses an angle of  $+45^\circ$  or  $-45^\circ$  with the polarizer position.

of the main axis of the indicatrix ( $n_\gamma$ ) lies in the optic axial plane. The direction  $n_\gamma$  is perpendicular to the rubbing direction of the glass plates. Considering the polarizability properties of these two molecules it can be assumed that the rubbing direction coincides with the preferred direction of the nonyloxy or 1,12-dodecyldioxy chain which corresponds to the direction  $n_\beta$  of the indicatrix. Figure 4 shows the probable orientation of the indicatrix with respect to the molecular alignment.

We assume that the surface interactions between the samples and the rubbed glass plates generate a uniform orientation (single crystal) of the initially inhomogeneously oriented biaxial nematic phase and not an artificial induction of biaxiality in a uniaxial nematic phase.

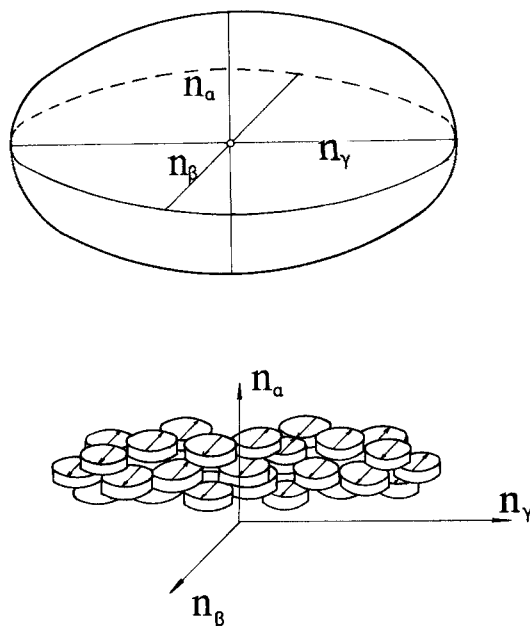


Figure 4. The axes of the biaxial indicatrix with respect to the molecular structure. The arrows drawn in the molecules indicate the preferred direction of the  $-\text{OC}_9\text{H}_{19}$  chain in **1** or of the  $-\text{O}(\text{CH}_2)_{12}\text{O}-$  bridge in **2**.

It should be noted that for the thermotropic biaxial nematic phases published very recently [15, 16] the sign of the biaxiality is positive. In these two cases the nematic phases were oriented by strong electric fields. The field direction obviously coincides with the main axis  $n_\gamma$  of the indicatrix which is the axis of the greatest polarizability. Further investigations of our new compounds **1** and **2** as well as of other examples by additional experimental methods are in progress.

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- [8] Here arene stands for benzene [4, 5, 7], naphthalene [6], and triphenylene [7].
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