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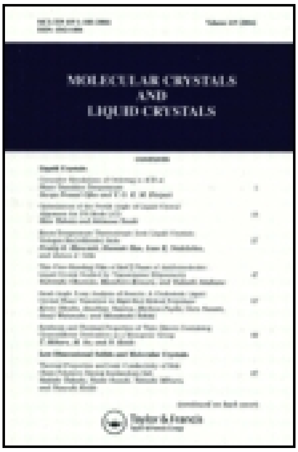

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Further Low Mass Liquid Crystal Systems with Nematic Columnar (N_C) Phase [1]

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Further Low Mass Liquid Crystal Systems with Nematic Columnar (N_C) Phase [1]

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A number of new disc-like pentaynes **1**-**4** with super-disc cores are presented. These new non-mesogenic electron donors doped with 2,4,7-trinitrofluorenone (**5**) form charge transfer complexes showing enantiotropic nematic and hexagonal columnar mesophases.

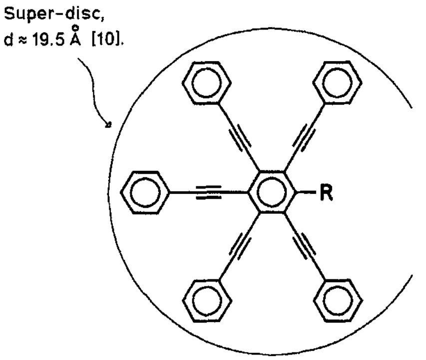
Keywords: charge transfer complexes, disc-like multiynes, mesophase induction

The occurence of thermotropic liquid-crystalline properties of organic materials is determined by the shape of its constituent molecules [2] and, as realized to an increasing degree during the last three decades, also by specific interactions of various kind between them [3]. Electronic and steric interactions determine the formation and stability of supramolecular structures in organized systems especially in higher ordered mesophases, *e. g.* of columnar types.

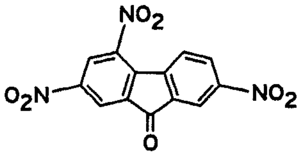
Recent studies in our two research groups led to the discovery of the nematic columnar (N_C) type of thermotropic mesophases in binary low molecular weight systems composed of highly unsaturated, large disc-like electron donor and small acceptor molecules, for instance **1b,e** and **5**, by itself not liquid-crystalline [4]. Independently, Ringsdorf and coworkers have found other examples of binary low molecular weight systems forming the same N_C phase [5]; a similar type of mesophase is also known for polymeric systems [6].

All these electron donor components - mono- or polymeric -, as applied here thus far, have alkoxy substituents of different number in common.

Several more large pentakis(phenylethynyl)phenyl derivatives of the structures **1-4** without side chains in the periphery usual for discotic systems have now been synthesized in palladium catalyzed one-pot coupling reactions [4, 7-9] from the corresponding pentabromoarenes and phenylacetylene; experimental and analytical details of the five new compounds (**1c,d**, **2-4**, yields between 65 and 76 per cent) will be published elsewhere.


Super-disc,
d ≈ 19.5 Å [10].

1-4



Cr 176°C I

5: TNF

	R	Cr → I (°C)
1a	OC_5H_{11}	227.3
1b	OC_9H_{19}	125.8
1c	$OC_{10}H_{21}$	117.6
1d	$OC_{11}H_{23}$	113.6
1e	$OC_{13}H_{27}$	109.1
2	CH_3	194.5
3	CF_3	182.3
4*	CN	201.4

*Compound **4** exhibits a monotropic phase transition: D_h 191.8°C I

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These eight electron donor compounds **1**-**4** were doped with 2,4,7-trinitrofluorenone (**5**) under formation of charge transfer complexes and inductions of at least two types of enantiotropic mesophases, *i. e.*, the exhibition of nematic and hexagonal columnar phases (*e. g.*, N_c and D_{ho}) was observed. Schematic representations of two of these types of thermotropic mesophases are shown in figure 1.

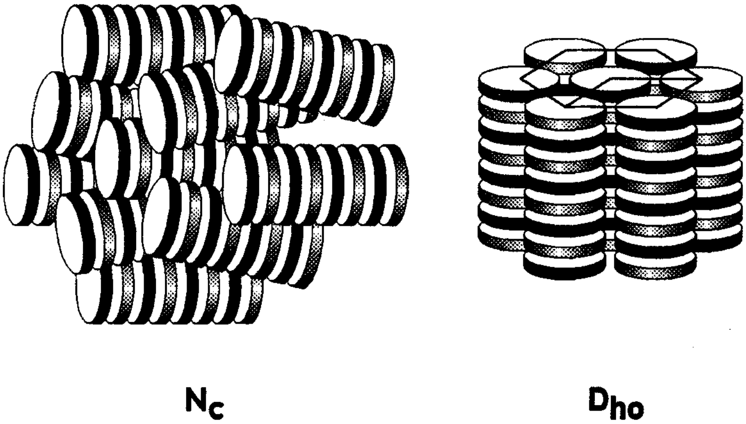

Figure 1. Schematic representations of a thermotropic nematic columnar (N_c) and a thermotropic discotic hexagonal ordered (D_{ho}) phase induced by charge transfer (CT) interactions between two low molecular weight compounds, for instance between a large electron donor of the pentayne type **1** [4] (in black) and **5** (TNF) as an electron acceptor (shaded).

From X-ray data [4] we conclude that in case of the pentayne ethers **1a**-**e** these disc-like non-liquid-crystalline compounds and the relatively small electron acceptor 2,4,7-trinitrofluorenone (**5**) aggregate in such a way that ordered columns are formed giving rise to the induction of two different enantiotropic mesophases. The origin for the alternate stacking of donor and acceptor molecules in these columns is the charge transfer interaction perpendicular to their molecular planes. The nematic (N_c) or hexagonal (D_{ho}) arrangements of these columns observed here are controlled by the length of the one alkoxy group, a factor of steric disturbance in the aggregation of these columns to a two-dimensional lattice [4]. The stronger this disturbance, *i. e.*, the longer

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this flexible alkoxy group, the more the nematic columnar (N_c) phase consisting of separated/mobile columns (cf. figure 1) is formed preferably. Thus, the binary system **1a**/**5** (TNF) exhibits an induced D_{ho} phase only, similar to charge transfer complexes of hexakis(alkylphenylethynyl)benzene or hexaalkoxytriphenylene, respectively, with **5** (TNF) [11]. With longer alkoxy chains present in the donor compounds **1b** and **c** (n = 9 or 10, respectively) the nematic columnar (N_c) phase along with the D_{ho} phase is developed in the charge transfer complexes with **5** (TNF), cf. figure 2. If the alkoxy group, in case of the undecyloxy (**1d**) or the tridecyloxy (**1e**) pentayne, sticks out far enough the charge transfer complexes of these donor molecules with **5** (TNF) exhibit just the new type of enantiotropic N_c phase [4].

Furthermore, concerning these mesophase inductions we want to refer to first observations of electro-optical effects and measurements of dielectrical elastic properties in the fluid nematic phases of our charge transfer complexes [12]. Details of these new findings obtained recently will be published in due course.

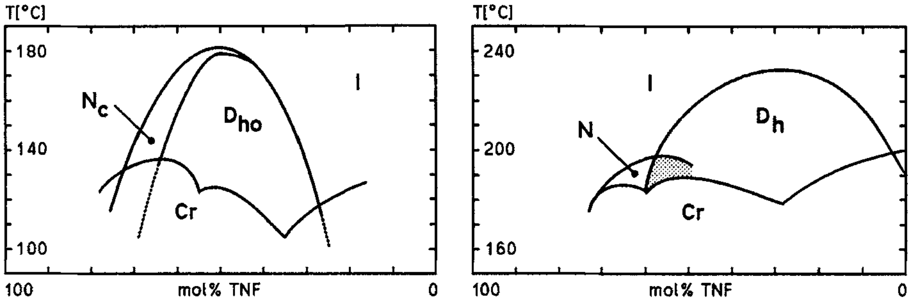

Figure 2. Simplified phase diagrams of the two binary systems of the nonyloxy-pentayne **1b** [4] (left) or of the cyano-pentayne **4** (right) both doped with 2,4,7-trinitrofluorenone (**5**), based on mixtures with definite acceptor contents; Cr: crystalline, D_h: discotic hexagonal (o: ordered), N: nematic (type not yet clarified), N_c: nematic columnar, I: isotropic liquid; the shaded field: a biphasic N and D_h area.

In binary mixtures with the electron acceptor **5** (TNF) also the non-liquid-crystalline pentaynes **2** and **3** as well as the monotropic liquid-crystalline cyano-pentayne **4** form charge transfer complexes exhibiting enantiotropic nematic and hexagonal columnar liquid crystalline phases (cf. figure 2 and 3).

The monotropic D_h phase of the cyano-pentayne **4** is stabilized up to acceptor concentrations of about 67 mol% **5** (TNF). In contrast to the binary systems obtained

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from **1a**-**e**, here, the maximum of the clearing temperature of 232°C is not found for the equimolar charge transfer complex, but at a lower acceptor concentration (around 30 mol%). In mixtures from **4** containing more than about 67 mol% **5** (TNF) a nematic phase is induced. Charge transfer complexes with acceptor concentrations between 50 and 60 mol% exhibit a biphasic area N/D_h (cf. figure 2, right hand side), not yet studied in detail; the types of mesophases formed here have not been clarified either, *e. g.*, by X-ray diffraction.

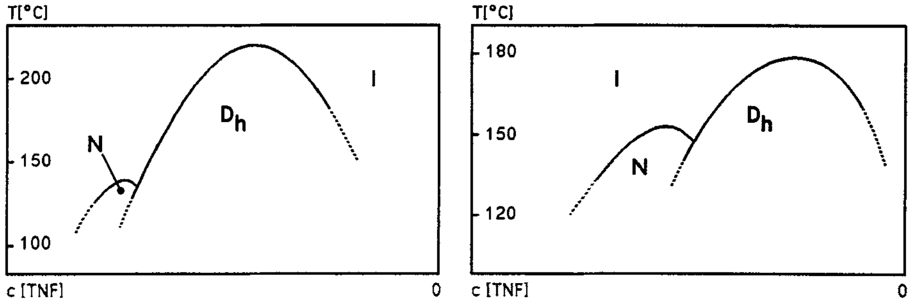

Figure 3. Preliminary simplified phase diagrams of the binary systems of the toluene centered pentayne **2** (left) or of the analogous trifluorotoluene derivative **3** (right), both doped with 2,4,7-trinitrofluorenone (**5**), sketched on the basis of mixtures obtained by the contact method; Cr: crystalline, D_h: discotic hexagonal, N: nematic (type not yet clarified), I: isotropic liquid.

The non-liquid-crystalline super-disc-shaped compounds **2** and **3** exhibit a similar mesophase behavior in contact preparations with **5** (TNF), was was observed in case of the monotropic mesogenic cyano-analogue **4**. At lower acceptor concentrations broad D_h phases are formed followed by nematic phases at higher acceptor concentrations. Up to now, the nature of these two mesophases could not yet be determined precisely; their preliminary classification is based on polarizing microscopy only. (cf. figure 3).

Further work on the induction, stabilization, and variation of mesophases by charge transfer complexation of various non-calamitic materials is in progress.

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