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Charge transfer induced nematic columnar phase in low molecular weight disc-like systems [1]

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Two large pentakis(phenylethynyl)phenyl alkyl ethers, without side chains as is usual for discotic systems, were synthesized in palladium catalysed one pot coupling reactions. These low molecular weight and non-liquid-crystalline electron donor compounds were doped with 2,4,7-trinitrofluorenone under the formation of charge transfer complexes. The induction of two types of enantiotropic mesophases (i.e. nematic and hexagonal columnar phases (N_c and D_{ho})) was observed. These charge transfer-induced mesophases were characterized by polarization microscopy, differential scanning calorimetry, and X-ray analysis; phase diagrams of the binary systems were also recorded as well as the hexagonal columnar to nematic columnar transition as a function of the length of the disturbing alkoxy group. It is considered possible now to study low molecular mass N_c phases by tailor-made two component mixtures on the basis of our easily accessible disc-shaped multiynes.

1. Introduction

The occurrence of thermotropic liquid-crystalline properties of organic materials is determined by the shape of their constituent molecules [2] and, as realized to an increasing degree during the past three decades, also by specific interactions of various kinds between them [3]. The fundamental classes of such molecular interactions which have emerged are for instance based on (i) ionic structures (salts) [4], (ii) electronic causes and permanent dipoles [5], (iii) charge-transfer situations [6] which open fascinating possibilities in research and the application of binary liquid crystal systems of various geometries, (iv) hydrogen bonding [7] producing shape stabilization and mesophase formation, for example, by multimerization of promesogenic molecules, a subject of growing interest in the past 10 years [8], and (v) steric effects [9], for example the influence of methyl groups [9(b)-(g)] in exposed positions on the existence of mesophases. Electronic and steric interactions determine the formation and stability of supramolecular structures in organized systems especially in higher ordered mesophases, for example of columnar types.

It is interesting to note that some of the scientific successes, recently achieved, also concern low molecular weight materials exhibiting thermotropic nematic mesophases, the appearance of which led to the systematic exploration of liquid crystals about a hundred years ago [10, 11]. Thus, huge numbers of rod-shaped (calamitic) compounds [2] with a nematic phase were followed in recent times by disc-shaped ones of various

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structures forming a nematic discotic phase [12–14]. It turned out here that the larger the core diameter of such disc-like mesogens, 24 Å is the largest found so far for multiynes [14], the more likely is the exhibition of this N_D phase, the second type of nematic phase. In contrast to the uniaxial behaviour of these nematic phases a special group with biaxial properties (N_B) is formed by mesogens of various geometries based on their shape anisotropy and/or suitable substitution pattern. A review of the developments in this promising third family of thermotropic nematogens is to be published shortly [15].

The very latest studies in our two research groups led to the discovery of a fourth type of thermotropic nematic phase, the nematic columnar (N_C) phase, even though expected [16], of a binary non-polymeric system composed of highly unsaturated, large, disc-shaped electron donor and small acceptor molecules, each one non-liquid-crystalline, which is the subject of this paper. Independently, Ringsdorf and coworkers examined another example of a binary low molecular weight system consisting of a disc-shaped donor mesogen and a non-mesogenic acceptor also exhibiting this N_C phase which is published in the following paper [17]. Prior to these findings this group described a similar type of mesophase in a polymeric system [6(m)].

2. Results and discussion

2.1. Synthesis of the donor compounds and their charge transfer complexes

The materials employed in this study are the two new, highly unsaturated, apparently easily polarizable, and non-radially symmetric alkyl pentayne ethers **1 (a)** and **(b)** as electron donors and the commercially available 2,4,7-trinitrofluorenone (TNF) used here as the electron acceptor [18]; all three compounds are non-liquid-crystalline. The syntheses of **1 (a)** and **(b)** were carried out starting from pentabromophenol via the corresponding alkyl pentabromophenyl ethers and subsequent fivefold palladium catalysed one pot alkynylations in a well known manner [12–14]. Spectroscopic data (IR, ^1H and ^{13}C NMR, UV, and MS) confirm the constitutions of these two yellow crystalline compounds (see Experimental). Their charge transfer complexes with TNF were prepared in solution. The mesophase behaviour was characterized via polarization microscopy, differential scanning calorimetry (DSC) and X-ray analysis.

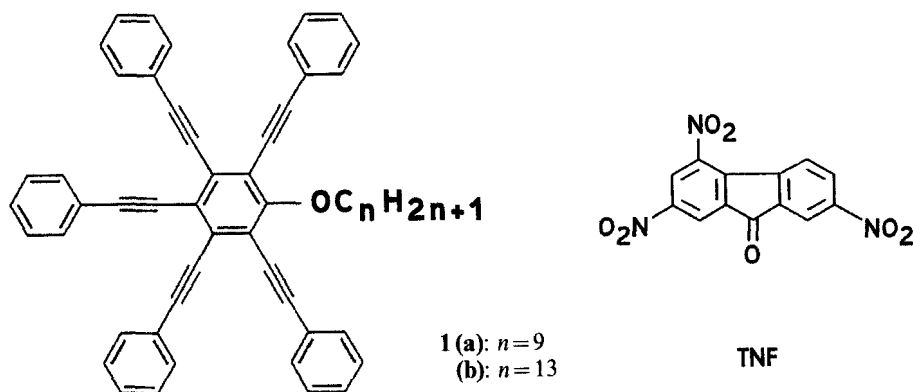


Figure 1. Structures of the alkyl pentakis(phenylethynyl)phenyl ethers **1 (a)** and **(b)** as electron donors and of 2,4,7-trinitrofluorenone (TNF) as an acceptor—all three compounds are non-liquid-crystalline.

2.2. Phase behaviour of the charge transfer complexes

Both new non-liquid-crystalline pentayne ethers **1(a)** and **(b)** exhibit induced mesophases by charge transfer interactions with 2,4,7-trinitrofluorenone. Contact samples of the nonyl ether **1(a)** with TNF show the induction of two different mesophases in the contact zone (cf. figure 2) and a deep red colour indicating the formation of electron donor acceptor complexes. The induced phase on the side of lower TNF concentrations exhibits a typical D_{ho} texture on cooling from the isotropic phase. Towards higher TNF contents another liquid-crystalline phase with schlieren texture and strong thermal fluctuations, typical of a nematic phase, is observed (see the left half of the upper photograph in figure 2). In the contact zone of the tridecyloxy pentayne **1(b)** with TNF just this nematic phase is formed. The phase diagrams of the binary systems **1(a)**/TNF and **1(b)**/TNF are shown in figure 4 and are based on examinations of definite mixtures.

Doping the nonyloxy pentayne **1(a)** with more than 25 mol% TNF causes a mesophase induction; up to 45 mol% TNF leads to monomesomorphic mixtures only, i.e. a highly viscous columnar phase is induced. On cooling from the isotropic phase typical textures of a D_{ho} phase with homeotropic regions (see figure 2) are observed. The hexagonal ordered type of this mesophase is confirmed by X-ray analysis (see the next section).

In mixtures of **1(a)** with TNF containing more than 45 mol% of the electron acceptor an additional mesophase above the D_{ho} phase occurs which has been characterized as nematic because of its schlieren texture (see figure 3) with strong thermal fluctuations. The clearing temperature increases continuously with increasing acceptor concentration and is 179°C for the equimolar mixture at its maximum (cf. figure 4).

The ranges of temperature and concentrations of these two induced mesophases for **1(a)** are shown in figure 4. Moreover, in the solid state of such mixtures a complex multimorphism is observed, but not documented. In all mixtures, the various phases are separated from each other by biphasic regions which are not shown in figure 4. Mixtures containing more than 60 mol% TNF are thermodynamically unstable (phase separation due to crystallization of TNF from the nematic or isotropic phase), therefore, the simplified phase diagrams shown in figure 4 reflect metastable situations at least in this concentration range.

Induced mesophases formed by charge transfer interactions between electron acceptors and disc-shaped donors are composed of ordered columns due to enhanced forces between the single molecules [6 (k), (l)]. Microscopic and X-ray analysis (see next section) proves that the induced nematic phase, too, consists of such ordered columns. These columns display a positional short range order and an orientational long range order which are the characteristics of a nematic (N_c) phase. In this situation the columns play the role of calamitic-like rod shaped mesogens.

In contrast to the binary system **1(a)**/TNF the electron donor acceptor complexes of the tridecyloxy substituted pentayne **1(b)** with TNF are monomesomorphic, just the new type of nematic columnar (N_c) phase is formed (cf. figure 4). Here, the induction of the N_c phase is observed in a concentration range between 25 and 75 mol% TNF; an equimolar composition shows the maximum of the clearing temperature (154°C) (as before, mixtures containing more than 60 mol% TNF are thermodynamically unstable). Mixtures of **1(b)** and TNF with acceptor concentrations higher than 45 mol% show sharp transitions into the isotropic state. However, this process is more complex in samples containing TNF between 25 and 45 mol%; with decreasing TNF con-

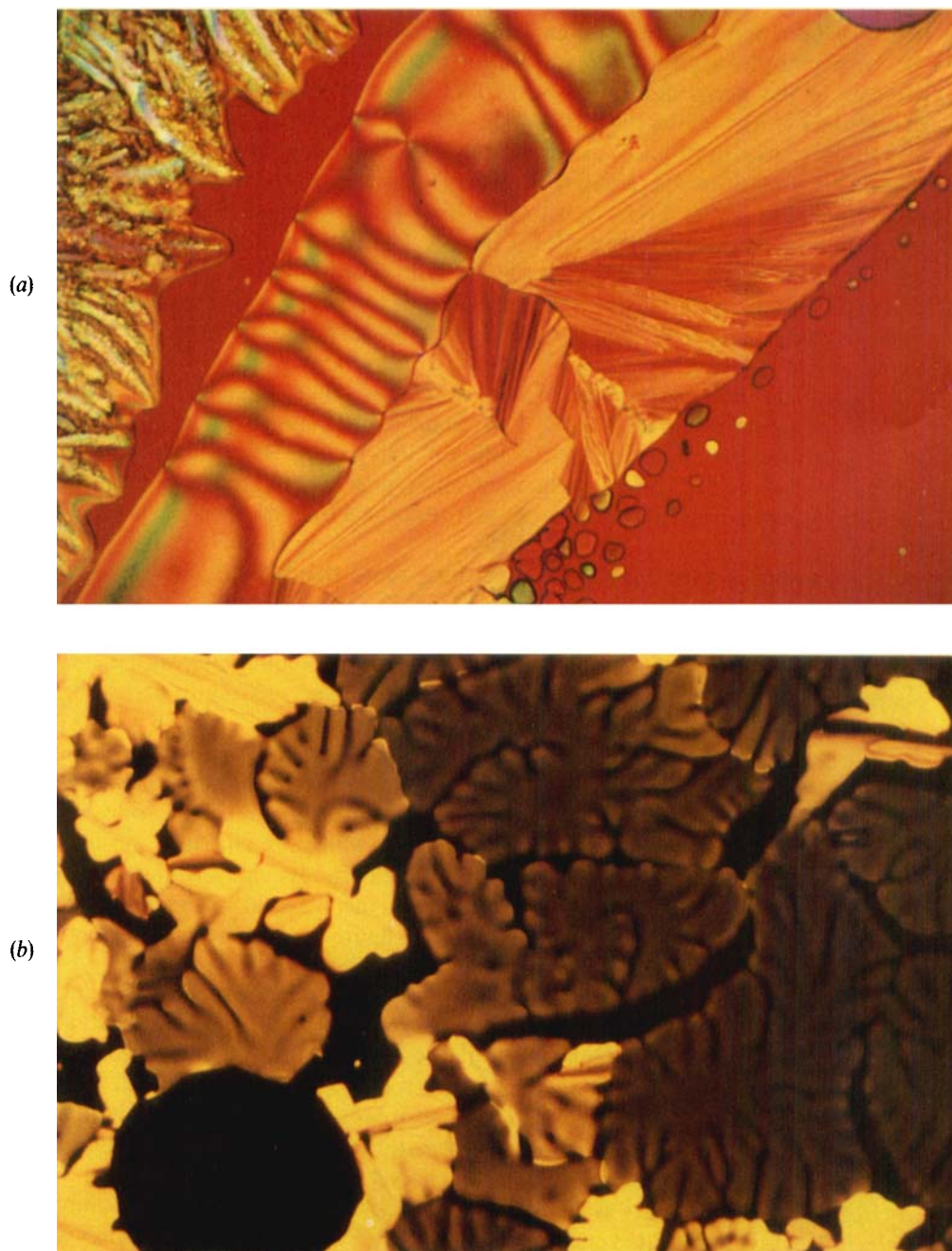


Figure 2. Textures of the charge transfer induced mesophases obtained by doping the nonyloxy pentayne **1** (a) with 2,4,7-trinitrofluorenone, magnification $\times 32$ in a 24×36 mm microscope camera, Photoautomat Wild MPS 51, crossed polarizers. Part 1: (a) A contact sample at 140°C (λ -plate used), showing the phase sequence from left to right crystalline (TNF) \bullet nematic columnar (N_c) \bullet hexagonal columnar (D_{ho}) \bullet isotropic liquid (I); (b) D_{ho} phase texture of an equimolar charge transfer complex of **1** (a) with TNF at 172°C on cooling from a biphasic N_c/I state.

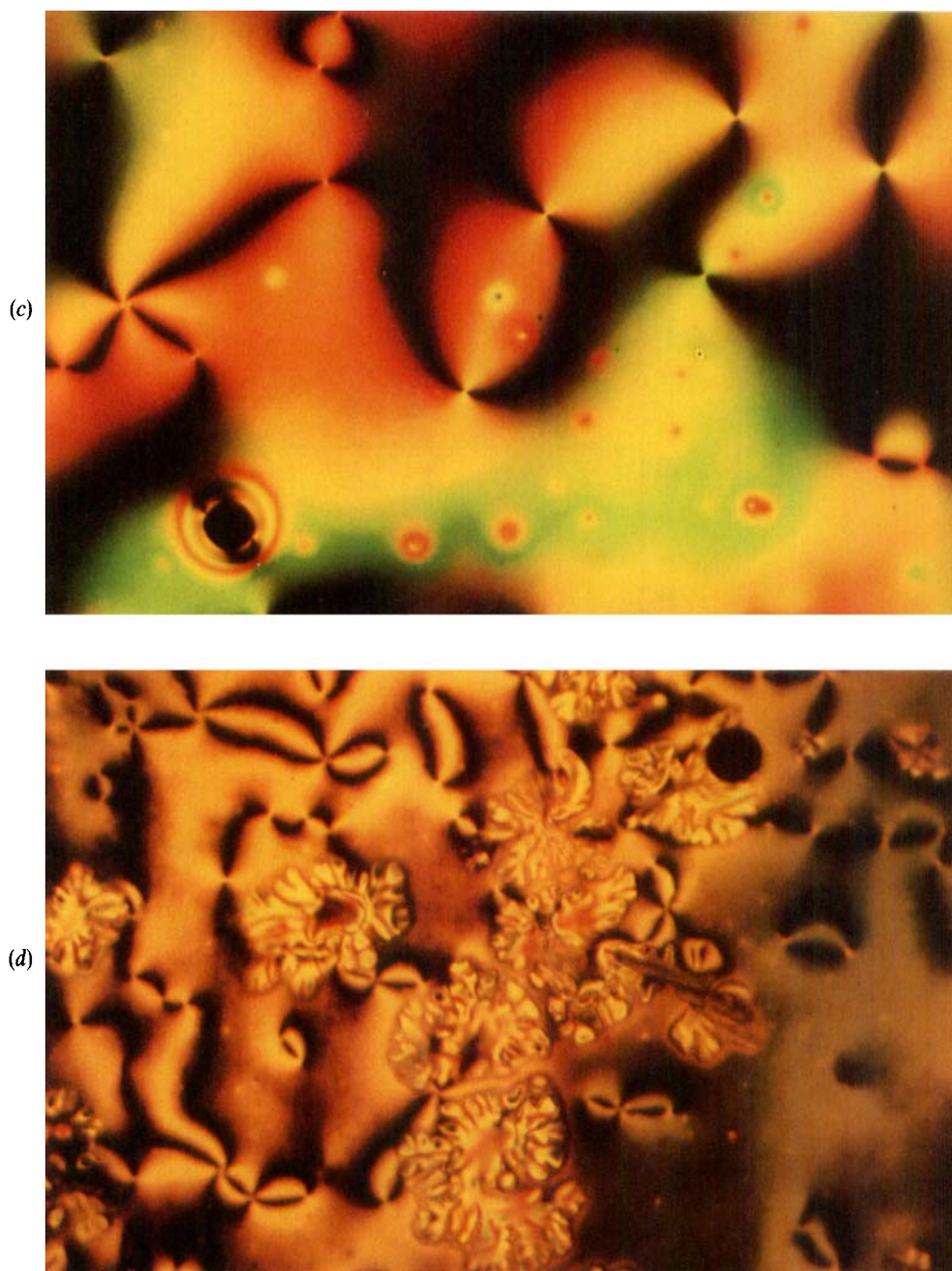


Figure 3. Textures of the charge transfer induced mesophases obtained by doping the nonyloxy pentayne **1** (**a**) with 2,4,7-trinitrofluorenone, magnification $\times 32$ in a 24×36 mm microscope camera, Photoautomat Wild MPS 51, crossed polarizers. Part 2: (c) schlieren texture of the nematic columnar (N_c) phase of an equimolar charge transfer complex of **1** (**a**) with TNF at 174°C on heating; (d) schlieren texture of the nematic columnar (N_c) phase of an equimolar mixture of **1** (**a**) with TNF at 176°C , but containing D_{bo} domains, on cooling from the nematic columnar (N_c) phase.

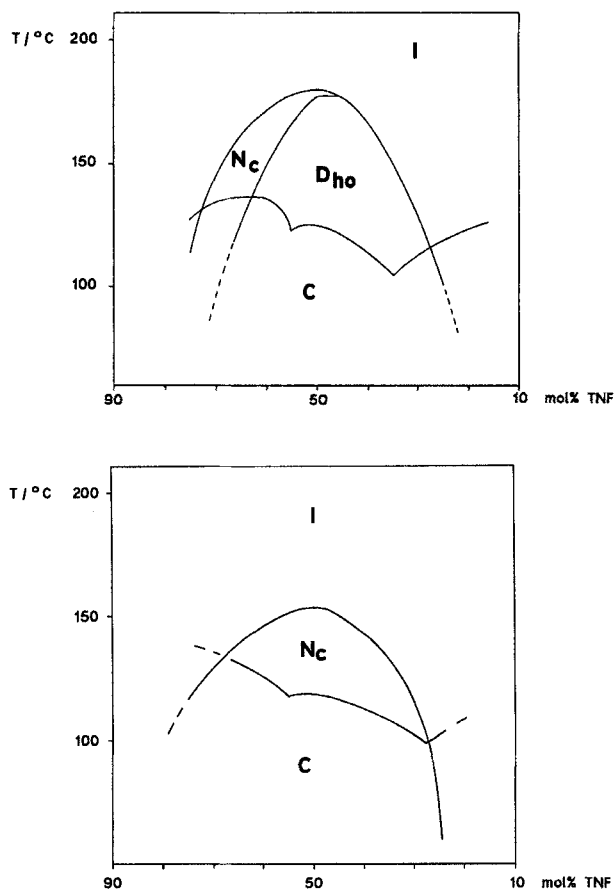


Figure 4. Preliminary simplified phase diagrams of binary systems of the nonyloxy pentayne **1(a)** (top) or the tridecyloxy pentayne **1(b)** (bottom) both doped with 2,4,7-trinitrofluorenone (TNF); C, crystalline; D_{ho} discotic hexagonal ordered; N_c nematic columnar; I, isotropic liquid.

Phase transition data[†] of the equimolar charge transfer complexes of the pentayne ethers **1(a)** or **1(b)** with 2,4,7-trinitrofluorenone (TNF).

Pentayne	C	D_{ho}	N_c	I
1(a)	● 119 [†] /124.3 (37.1)	● 172 [†] /176.3 (6.8) [§]	● 179.0/179.5 (1.6) [§]	●
1(b)	● 118.7/119.4 (59.9)	—	● 153.3/153.4 (0.8)	●

[†] Transition temperatures (°C) determined by polarization microscopy/DSC; transition enthalpies (kJ mol^{-1} of the complex) are shown in parentheses.

[‡] In this case, the phase transition proceeds via a biphasic temperature range of about 4°C.

[§] An estimated enthalpy value because of an overlap with the neighbouring peak of the transition $D_{ho} \rightarrow N_c$ or $N_c \rightarrow I$, respectively.

C, crystalline; D_{ho} , discotic hexagonal ordered; N_c , nematic columnar, I, isotropic liquid.

centration in this range the N_c and the isotropic liquid phases are separated by a biphasic region which grows steadily in width. This biphasic area as well as the noticed multimorphism in the solid state are not given in figure 4.

The phase transition data of the equimolar charge transfer complexes of the alkyloxy pentaynes **1 (a)** and **(b)** with TNF are summarized in the table. As expected, the enthalpies of the transition $N_c \rightarrow I$ are significantly smaller than those of $D_{ho} \rightarrow I$ transitions in related charge transfer complexes [6j] due to the lower order of the N_c phase. The clearing enthalpies of the order of 1 kJ mol^{-1} of these new N_c phases are of a magnitude characteristic for classical nematic phases exhibited by calamitic, rod-like liquid crystals, but are about eight to ten times larger than those of N_D phases known from disc-shaped multi-ethynylarenes [12–14].

2.3. Structural analysis of the charge transfer induced mesophases

X-ray scattering experiments on mixtures of the nonyloxy pentayne **1 (a)** with TNF at various temperatures confirm the induction of two different types of liquid-crystalline phases (cf. figure 4). The first mesophase (60 mol% TNF, 140°C) with a texture typical of discotic hexagonal ordered phases is characterized by (i) sharp small angle reflections corresponding to a two dimensional hexagonal lattice (lattice constant $a_{\text{hex}} = 1.65 \text{ nm}$, independent of the acceptor concentration), (ii) a diffuse halo (due to the short range order of the aliphatic chains, Bragg distance 0.49 nm), and (iii) the typical intracolumnar reflection in the wide angle region ($d_{\text{intra}} = 0.352 \text{ nm}$) which corresponds to the regular stacking of acceptor and donor molecules on top of each other (see figures 5 and 6). Thus, this induced mesophase is clearly identified as a D_{ho} type phase.

The X-ray scattering pattern of the nematic phase (60 mol% TNF, 166°C) again displays an intracolumnar reflection corresponding to the formation of columns by regularly stacked acceptor and donor molecules with an intracolumnar spacing of 0.357 nm (cf. figures 5 and 6). In contrast to the scattering pattern of the D_{ho} phase the small angle reflections are no longer sharp, but rather diffuse and broad, typical for a liquid-like arrangement of the molecular groups. The intracolumnar reflection is perpendicular to the small angle reflection, therefore, the columns are nearly oriented parallel, having only a short range positional order characteristic for nematic systems. The mean intercolumnar distance ($a = 1.66 \text{ nm}$) is about the same as for the D_{ho} phase previously assigned. In accord with the appearance of an intracolumnar reflection and the diffuse small angle reflection this nematic phase has to be classified as nematic columnar (N_c). Mixtures of the tridecyloxy pentayne **1 (b)** with TNF show similar results for the X-ray diffraction pattern proving also in this case the nematic columnar type of mesophase. The significant parameters of the N_c phase found for an equimolar mixture of the pentayne ether **1 (b)** with TNF at 129°C are 1.62 nm for the mean intercolumnar distance, 0.357 nm for the intracolumnar spacing, and 0.50 nm for the halo.

3. Conclusions

The examination of the relation between molecular structure and the mesophase behaviour of discoid amphiphiles six years ago [16] produced factors governing the formation and stability of lyotropic micellar nematic phases (N_c and N_D) and were used successfully to design novel mesogens of this kind which, in few examples, also gave rise to stable N_c phases (on dissolution in water, i.e. in two component mixtures). Also thermotropics can stack as in fact expected [16(b)] into columnar aggregates forming an N_c phase, realized very recently in polymeric systems for the first time, i.e. in

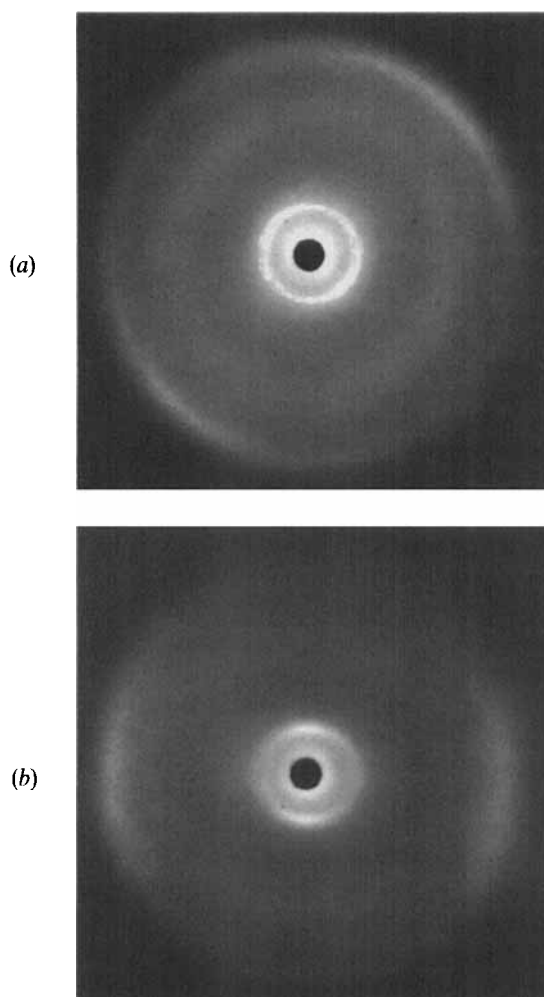


Figure 5. X-ray diffraction pattern of oriented samples of charge transfer complexes of the nonyloxy pentayne **1** (a) containing 60 mol% 2,4,7-trinitrofluorenone in their induced mesophases. (a) The discotic hexagonal ordered phase at 140°C and (b) the nematic columnar phase at 166°C.

amorphous discoid main chain polymers doped with 2,4,7-trinitrofluorenone (TNF) [6(m)]. In this paper and in another publication regarding other types of donor and acceptor molecules [17] the first low molecular weight examples are described. In such a case there is a direct correspondence in the mechanisms of nematic to hexagonal transitions [16].

From X-ray data we conclude that our two large, non-liquid-crystalline, disc-like electron donor molecules **1** (a) and (b) free from the usual side chains, but apart from one linear alkoxy group fixed in the centre of the super-disc (cf. figure 7), and the relatively small non-liquid-crystalline electron acceptor 2,4,7-trinitrofluorenone (TNF) aggregate to form ordered columns which give rise to the induction of different enantiotropic mesophases. The origin for the alternate stacking of donor and acceptor molecules is the charge transfer interaction perpendicular to their planes [6(k), (l)].

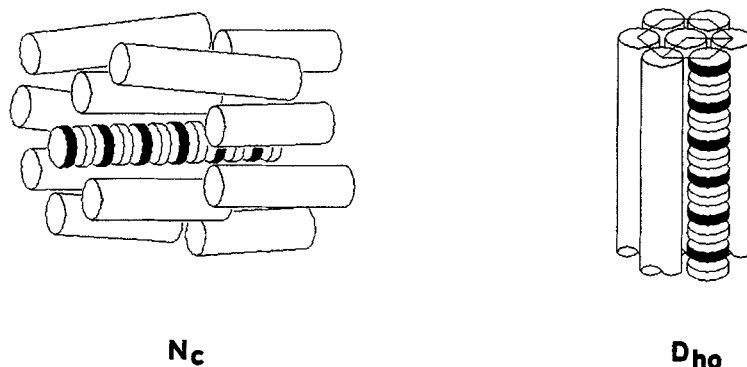


Figure 6. General schematic representations of thermotropic nematic columnar and discotic hexagonal ordered phases induced by charge transfer interactions between a low molecular weight disc-shaped donor compound (marked in black) and an electron acceptor, see for instance the molecular structures in figure 1. In the cases studied here both the donor and the acceptor are non-liquid crystalline.

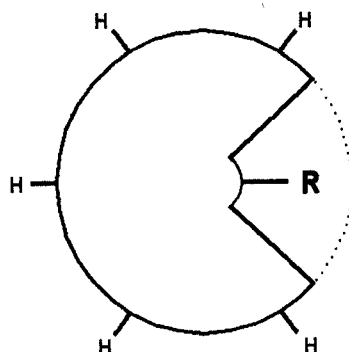


Figure 7. Schematic representation of the super-disc-like electron donor of type **1** (cf. figure 1); R = flexible groups, here a linear alkoxy chain. On the assumption of a stretched conformation (Dreiding models) a pentyloxy group is located just inside this super-disc with a diameter of about 19.5 \AA whereas a nonyloxy (in **1(a)**) or a tridecyloxy group (in **1(b)**) sticks out of the disc by approximately 5 \AA or 10 \AA , respectively.

The nematic (N_c) or hexagonal (D_{ho}) arrangement of these columns observed here is governed by the length of the only alkoxy group, an element of steric disturbance in the aggregation of these columns to a two dimensional lattice (cf. figure 6). The stronger this disturbance, i.e. the longer this flexible alkoxy group, the more the nematic columnar (N_c) phase consisting of separated/mobile columns (cf. figures 6 and 7) is formed preferably or vice versa. Thus, for instance the binary system **1(b)**/TNF exhibits an enantiotropic N_c phase only, whereas that made of **1(a)** and TNF, with a somewhat shorter alkoxy group, predominantly develops an enantiotropic D_{ho} phase along with the N_c phase (depending on the TNF concentration, cf. figure 4). If the alkoxy group, in the case of pentyloxy, does not stick out of the pentayne disc of **1** (figure 1, $n = 5$ or figure 7, $R = \text{OC}_5\text{H}_{11}$) the charge transfer complexes of this particular donor molecule with TNF exhibits an enantiotropic D_{ho} phase only [19]! In between these cases put forward

here other situations of nematic columnar to hexagonal columnar transitions as a function of such a steric disturbance are not only possible, but easy to realize, i.e. thermotropic low molecular weight N_c phases can now be tailor-made, in particular, on the basis of these easily accessible types of electron-rich disc-like donor molecules.

4. Experimental

4.1. Synthesis of the electron donor compounds

The alkyl pentakis(phenylethynyl)phenyl ethers **1 (a)** and **(b)** were prepared in two steps starting from commercially available pentabromophenol. The reaction of pentabromophenol with nonylbromide and tridecylbromide (sodium hydride in dimethylformamide), respectively, yielded the two ethers as colourless crystals from acetone.

- (i) nonyl pentabromophenyl ether, $C_{15}H_{19}Br_5O$ (FW 614.8), mp 50°C, 63 per cent yield,
- (ii) tridecyl pentabromophenyl ether, $C_{19}H_{27}Br_5O$ (FW 670.9), mp 62°C, 50 per cent yield.

Fivefold alkynylations of these pentabromophenylethers (5 mmol each) with excess of phenylacetylene (50 mmol) in palladium-catalysed reactions [12–14] (refluxing with 250 mg of $PdCl_2(PPh_3)_2$, 250 mg of Cu_2I_2 and 500 mg of PPh_3 in 50 ml of degassed triethylamine at a bath temperature of 100°C under argon for 24 h) furnished the new yellow crystalline, in solution greenish-blue fluorescent, pentayne ethers **1 (a)** and **(b)** after dissolving each reaction mixture in chloroform, washing with dilute hydrochloric acid and water, drying over magnesium sulphate, filtration, evaporation and repeated recrystallization from acetone.

- (i) Nonyl pentakis(phenylethynyl)phenyl ether **1 (a)**, $C_{55}H_{44}O$ (FW 721.0): yield 60 per cent, mp 125.8°C (ΔH 55.5 kJ mol⁻¹, DSC purity 99.9 mol%). IR (CCl_4): $\nu_{c\equiv c} = 2220$ cm⁻¹. ¹H NMR (Bruker WH 400, $CDCl_3$): $\delta = 7.66$ – 7.58 , 7.40–7.33 (2 m; 10 and 15 H, respectively, phenyl H), 4.39 (t, $J \approx 6.5$ Hz; 2 H, O–CH₂), 1.94 (tt, $J \approx 7$ and 6.5 Hz; 2 H, β -CH₂), 1.62 (tt, $J \approx 7.5$ Hz each; 2 H, γ -CH₂), 1.36 (tt, $J \approx 7.5$ and 7 Hz; 2 H, δ -CH₂), 1.30–1.18 (m; 8 H, remaining CH₂), 0.87 (t, $J \approx 7$ Hz; 3 H, CH₃). ¹³C NMR (Bruker AM 270, $CDCl_3$): $\delta = 160.61$ (s; 1 C, phenyl C–O), 131.85, 131.74, 131.69, 128.87, 128.75, 128.61, 128.46 (7 d; 20 C, phenyl CH) 128.98, 124.08, 123.46, 123.30, 123.23, 120.25, (6 s; 10 C, phenyl C), 99.44, 99.32, 97.23 (3 s; 2, 2 and 1 C respectively, inner ethynyl C), 87.46, 87.01, 84.54 (3 s; 2, 1 and 2 C respectively, outer ethynyl C), 75.95, 31.91, 30.64, 29.64, 29.34, 26.39, 22.69, 14.14 (7 t, 1 q; 9 C, nonyl chain). MS (Varian MAT 711, 70 eV, 160°C): m/z (per cent) = 720 (69; M^+), 59 (100). UV/VIS (Cary 118, CH_2Cl_2): λ_{max} . [nm] (lg ϵ) = 330 (5.087), 360 (4.719, sh), 410 (4.093, sh).
- (ii) Tridecyl pentakis(phenylethynyl)phenyl ether **1 (b)**, $C_{59}H_{52}O$ (FW 777.1): yield 44 per cent, mp 109.1°C (ΔH 62.4 kJ mol⁻¹, DSC purity 99.2 mol%). Its spectra are in good agreement with those of **1 (a)**.

4.2. Preparation of the charge transfer complexes

Their preparations were carried out by mixing the pentayne ethers **1 (a)** or **(b)** with the desired amounts of the electron acceptor 2,4,7-trinitrofluorenone in solutions of purified tetrahydrofuran; the developed orange colour indicates the formation of the expected electron donor acceptor complexes. The greenish-blue fluorescence of the

dissolved **1 (a)** or **(b)** disappears at higher concentrations of the complexes, but reappears on addition of further solvent. The solid red residues were dried in vacuum, subsequently homogenized by heating into the isotropic phase followed by rapid cooling to room temperature.

4.3. Instrumental

The thermal behaviour of these samples was investigated by:

- (i) polarizing microscopy, using a Leitz Laborlux 12 Pol equipped with a Mettler FP 82 hot stage, heating rate $2\text{--}5\text{ K min}^{-1}$, using crossed polarizers, and
- (ii) differential scanning calorimetry (DSC) on a Perkin Elmer DSC 4 with a heating rate of 20 K min^{-1} .

The measurements of the phase transition data of the pure compounds **1 (a)**, **1 (b)** and of their equimolar complexes with TNF were carried out using a Mettler TA 3000/DSC 30 S with GraphWare TA 72 with a heating rate of 5 K min^{-1} .

The X-ray structural analyses (Siemens D 500 wide angle diffraction goniometer and a flat film camera, nickel filtered Cu-K_α irradiation, $\lambda = 0.154\text{ nm}$) were performed on unoriented as well as on macroscopically oriented samples in glass capillaries. The orientation was achieved by spontaneous surface interactions and improved by annealing the samples in their mesophase ranges.

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Note added in proof.—In cooperation with Mrs Dipl.-Chem. B. Sabaschus, from the research group of Professor G. Heppke, it has now been found that the fluid nematic phase of our charge transfer complex between the disc-like pentayne **1 b** and 2,4,7-trinitrofluorenone shows electric field effects similar to those reported recently for N_D phases exhibited by two types of pure disc-shaped hexaynes (HEPPKE, G., RANFT, A., and SABASCHUS, B., 1991, *Molec. Crystals liq. Crystals Lett.*, **8**, 17). Details of these new findings will be published at a later date.

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