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Induction of nematic cholesteric (N*) phases by charge transfer complexation of disc-shaped multiynes [1]

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Based on charge transfer interactions with the (chiral) electron acceptor (−)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid ((−)-TAPA), our easily accessible disc-shaped electron rich multiynes (for example, **1** and **2**) give rise to two types of cholesteric nematic phases. Thus, the *binary* mixture of the nematic discotic (N_D) pentakis-(4-methylphenylethynyl)phenyl hexadecyl ether (**2**) with (−)-TAPA exhibits its twisted variant (N_D^*). Likewise, but now in a *ternary* mixture, the homologue **1**—peripherically unsubstituted and *non*-mesogenic—with the two electron acceptors (−)-TAPA and 2,4,7-trinitrofluorenone—both also *non*-liquid crystalline—shows cholesteric nematic properties, most probably however of a columnar type (N_C^*). First results concerning these charge transfer induced cholesteric–nematic properties, including phase diagrams and the helical twist of the two systems presented here, are discussed on the basis of data obtained by polarizing microscopy and differential scanning calorimetry.

1. Introduction

The structures of twisted nematic (cholesteric) phases (N*) exhibited by chiral nematogens, for example, cholesteryl derivatives, or by mixtures of achiral nematic liquid crystals and chiral dopants have been well studied for materials composed of rod-shaped molecules [2]. Also in the field of lyotropic liquid crystals, twisted nematic phases are known both from several types of pure chiral amphiphiles [3] and from achiral lyotropic phases through induction by chiral dopants [4]. In fact, the cholesteric type of thermomesomorphic state was the first one to be observed in the middle of the last century [2*c*].

Because of their unique properties connected with the helical twist, chiral mesophases are of strongly growing interest both in basic research and for the purposes of applications in recent time [5]. However, up to now, there are only a few examples of the twisted *nematic discotic* (N_D^*) type of phase formed by chiral disc-shaped mesogens [6] or induced by chiral dopants [7].

Benzene-, naphthalene-, or triphenylene-centred multiynes are the disc-shaped mesogens of choice, when appropriately structured, for studies on this N_D^* phase because of their preferred nematogenic character [8], and it is especially noted that the first observation of selective light reflection and even of 'blue phases' in mixtures of such a disc-like multiyne with a cellobiose derivative as a chiral dopant have been reported just recently [9].

Another topic of current liquid crystal research on *disc-shaped mesogens* being studied with increasing intensity concerns mesophase induction or stabilization

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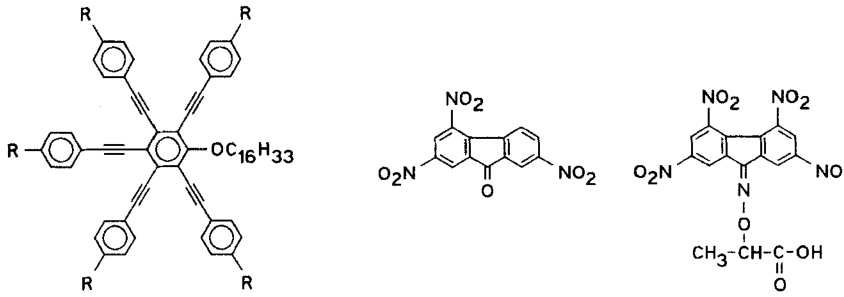


1: R = H
2: R = CH_3
TNF
(–)-TAPA

Figure 1. Structures of the hexadecyl pentayne ethers **1** and **2** as electron donors as well as of 2,4,7-trinitrofluorenone (TNF) and (–)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy) propionic acid ((–)-TAPA) as acceptors.

processes created by specific intermolecular interactions, as for instance by charge transfer (CT) [10] or dipole–dipole [11] situations. Thus, the induction of a columnar type of nematic phase (N_C) [10 (e)–(g)] and observations of the stabilization/induction of a nematic discotic (N_D) phase [10 (h), (i)], both caused by charge transfer interactions between different types of disc-shaped electron donors—for example, of pentayne ethers in the first case or of dinuclear palladium organyls in the latter—and 2,4,7-trinitrofluorenone (TNF) as a strong electron acceptor, encouraged us to start studies on the influence of chirality on such induced nematic phases.

Hence, here we report our first results on the cholesteric nematic behaviour of charge transfer complexes of the homologous disc-shaped pentayne ethers **1** or **2** containing the chiral electron acceptor (–)-TAPA—see the molecular structures shown in figure 1.

2. Results and discussion

2.1. *The access to the materials*

The materials used in this study are mixtures of new, highly unsaturated, apparently easily polarizable, and non-radially symmetric alkyl pentayne ethers **1** or **2**, the electron donors, with 2,4,7-trinitrofluorenone (TNF) and/or (–)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid ((–)-TAPA), the electron acceptors; see figure 1.

The two-step synthesis of **1** and **2** started from pentabromophenol, gave the corresponding hexadecyl pentabromophenyl ether as an intermediate, and ended with fivefold palladium catalysed alkynylations in a well-known manner [8, 10(e)]. Spectroscopic data (IR, ^{1}H and ^{13}C NMR and MS) confirm the structures of these two yellow crystalline compounds—see experimental.

The commercially available electron acceptors TNF and (–)-TAPA were used after drying, without further purification. The mixtures from the pentaynes **1** or **2** and these dopants were prepared by mixing their solutions in dichloromethane as solvent.

2.2. *The mesomorphic properties of the new materials*

The peripherically unsubstituted hexadecyl pentayne ether **1** shows no liquid crystalline properties by itself; even with cooling rates as high as 100 K min^{-1}, no

Phase transition temperatures (°C)† and enthalpies (kJ mol^{-1})†‡ in parenthesis of the pentayne ethers **1** and **2**, as well as of selected mixtures of them with TNF and/or (−)-TAPA. C, crystalline; N_D, nematic discotic; N_C, nematic columnar; I, isotropic phase; *, cholesteric.

1	C	94·9	(23·3)				I
2	C	162·3	(55·7)	N_D	192·5	(0·2)	I
1/TNF (50 mol%)	C	118·0	(21·6)	N_C	140·0	(1·1)	I
2/TNF (50 mol%)	C	129·0	(17·0)	N_C	184·1	(1·0)	I
1/TNF/TAPA (38/12 mol%)	C	108·9	(10·0)	N_C^*	118·1	(1·1)	I
2/TAPA (20 mol%)	C	155·5	(16·3)	N_D^*	169·8	(0·2)	I

† Determined by differential scanning calorimetry (DSC, heating rate 5 K min^{-1}) and confirmed by polarizing microscopy.

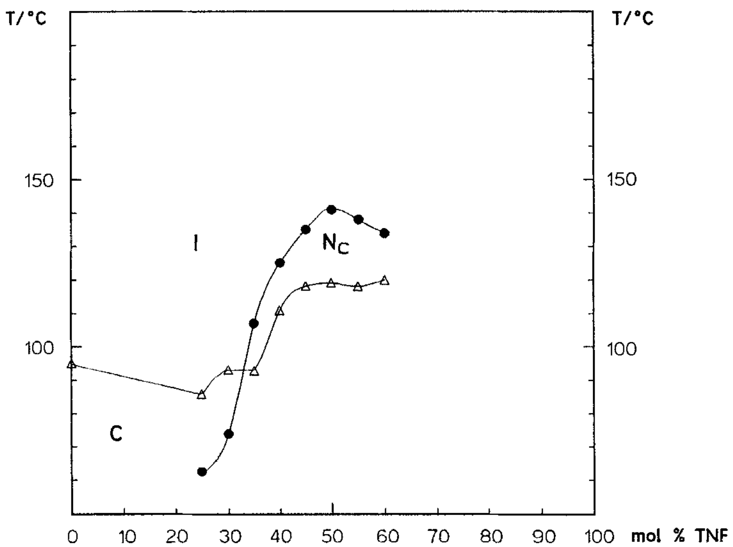
‡ The transition enthalpies of the charge transfer complexes of **1** and **2** are given in kJ mol^{-1} of the *complex*.

mesophase could be detected by polarizing microscopy. With the exception of pentakis(phenylethynyl)benzonitrile [10(g)] which exhibits a monotropic columnar mesophase, other phenylethynyl multiyne derivatives without lateral *aliphatic* substituents are non-mesomorphic.

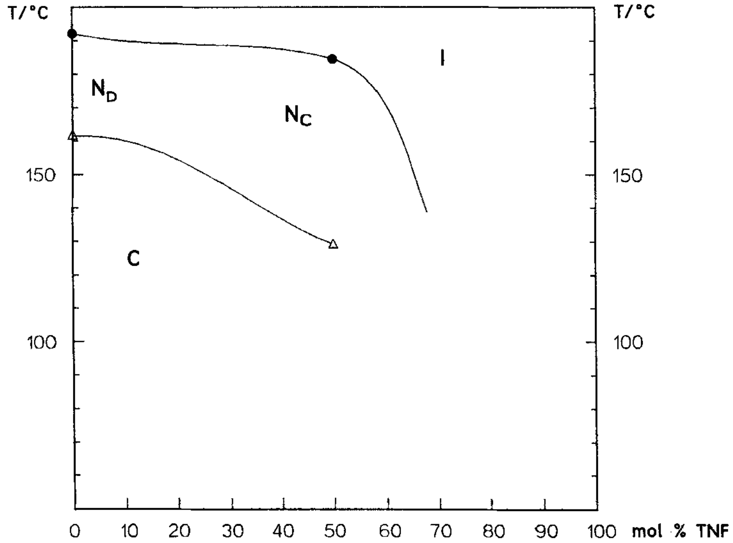
The introduction of just five methyl groups as in **2** leads to a strong increase in the melting temperature and to the formation of an enantiotropic *nematic discotic* (N_D) phase, cf. the table. On heating the pentayne ether **2** above its melting temperature, typical marble or schlieren textures are obtained, showing characteristically strong thermal fluctuations. Miscibility studies (contact method) of **2** with other multiyne nematodiscogens [8] confirm the phase classification given here. As found for other nematic discotic mesogens of the multiyne [8] or dinuclear palladium organyl type [10(h)], the enthalpy of the clearing process is also about 0·1 kJ mol^{-1}.

The non-liquid crystalline pentayne ethers of type **1** are known to form induced mesophases in mixtures with strong electron acceptors, as for example TNF [10(e)]. The type of such induced phases strongly depends on the length of the one alkyloxy chain present in **1**. Following the intercalation model [10(e)] for this type of charge transfer-induced mesophase in binary systems containing disc-shaped donors, this aliphatic chain is an element of steric disturbance preventing the aggregation of CT-based columns into a two-dimensional lattice such as occurs, for example, in the discotic hexagonal ordered (D_{ho}) mesophase, the most common CT-induced phase of a columnar type [10(b)–(j)]. As expected, the phase behaviour observed for the binary system **1**/TNF is therefore similar to that of the tridecyloxy homologue [10(e)]—see the table and cf. figure 2(*a*). Just the nematic columnar type (N_C) of mesophase is observed; the maximum clearing temperature of 140°C occurs for the 1 : 1 molar ratio of the donor **1** and the acceptor TNF.

A different kind of mesophase induction behaviour is observed in mixtures of nematic discotic (N_D) pentayne ethers of family **2** with TNF. Besides a slight decrease in the clearing temperature of the N_D phase with increasing acceptor content, only the pentyloxy homologue of **2** exhibits an additional induced D_{ho} phase. The hexadecyloxy substituted pentayne **2** shows no mesophase induction in mixtures with TNF, see the table and figure 2(*b*). Similar phase diagrams are observed for the related tridecyloxy and nonyloxy derivatives doped with TNF. But, first X-ray scattering experiments on the nematic phase of charge transfer complexes of the tridecyloxy homologue of **2** with


T/°C
T/°C
150
150
100
100
I
N$_C$
C
0
10
20
30
40
50
60
70
80
90
100
mol % TNF

(*a*)


T/°C
T/°C
I
N$_D$
N$_C$
150
150
C
100
100
0
10
20
30
40
50
60
70
80
90
100
mol % TNF

(*b*)

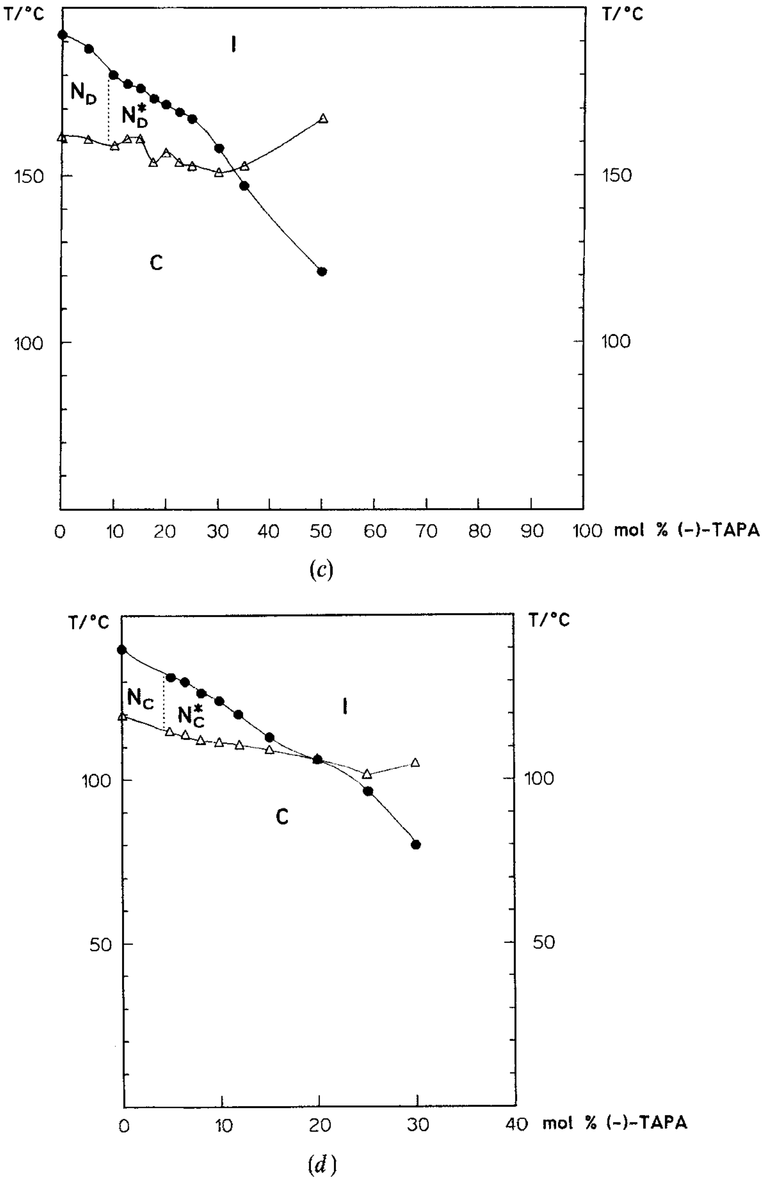


Figure 2. Phase behaviour of (*a*) the hexadecyloxy pentayne **1** doped with 2,4,7-trinitrofluorenone (TNF), (*b*) the methyl substituted hexadecyloxy pentayne **2** doped with TNF (*c*) the binary system of the pentayne ether **2** in mixtures with (−)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid ((−)-TAPA), and (*d*) the ternary system of the pentayne ether **1**/TNF/(−)-TAPA with an over-all acceptor concentration of 50 mol%. Dashed lines indicate a change in textures, but not a phase transition or phase boundary.

TNF prove the existence of columnar aggregates in mixtures containing more than about 27 mol% TNF [12]. However, no phase boundaries within the nematic area could be detected by polarizing microscopy, cf. figure 2 (*b*), although the clearing enthalpy of, for example, the equimolar CT-complex of **2** with TNF is significantly higher than that of the undoped pentayne ether **2**—see the table. Furthermore, the nematic phases of the equimolar charge transfer complexes of **1** or **2** with TNF are completely miscible with each other, as well as with the CT-stabilized *nematic discotic* phase of a thiocyanato-bridged dinuclear palladium organyl doped with TNF [10 (i)].

With the electron acceptor TAPA, *inductions* of the hexagonal (D_{ho}) phases are observed for charge transfer complexes with benzene, naphthalene, or triphenylene centred hexaynes. The same is true for such mixtures with some dinuclear disc-shaped palladium organyls [10 (h), (i)]. CT-complexes of peripherally unsubstituted pentayne ethers of type **1** with TAPA exhibit no mesophase. Up to now, no example of an *induced nematic phase* in mixtures of TAPA with disc-like compounds is known. On the other hand, mixtures of the methyl substituted pentayne **2** with (−)-TAPA do show a phase behaviour similar to that observed with TNF as dopant. Up to dopant contents of around 35 mol%, an *enantiotropic* nematic phase is observed, showing *cholesteric* properties with acceptor concentrations above 10 mol% see the table and figures 2 (*c*) and 3.

Contact preparations of an equimolar TNF charge transfer complex of **1** with (−)-TAPA also exhibit textural features of a cholesteric nematic phase in the contact zone. Therefore, the phase behaviour of this *ternary* system composed of *three non-liquid crystalline* compounds has been studied for an *overall acceptor concentration* of 50 mol%, cf. figure 2 (*d*). Mixtures of the pentayne **1** with up to 20 mol% (−)-TAPA and, therefore, 30 mol% TNF, are enantiotropic nematic. Above a (−)-TAPA content of 6·5 mol% (43·5 mol% TNF), a twisted nematic phase is formed, cf. figure 2 (*d*). A comparison of the phase diagrams in figure 2 and of the clearing temperatures in the table reveals that both the nematic discotic (N_D) phase of **2** and the nematic columnar (N_C) phase of **1**/TNF are *destabilized* if TAPA is added. A similar behaviour is observed with 2,4,5,7-tetranitrofluorenone as dopant. Therefore, it seems clear that the efficiency of such tetranitro-substituted electron acceptors in building columnar charge transfer complexes is much lower compared with that of TNF. These findings also hold for the CT-stabilized D_{ho} phases of their mixtures with hexa(pentyloxy)triphenylene [13].

The cholesteric type of the nematic phase exhibited by samples of the binary system **2**/(−)-TAPA or the ternary system **1**/TNF/(−)-TAPA is clearly proved by their fingerprint textures and associated strong thermal fluctuations—see figure 3. It is interesting to note that with increasing (−)-TAPA content, a change takes place in the orientation of the mesogens between glass surfaces. Samples with low (−)-TAPA concentrations (for example, 15 mol% in **2**/TAPA or 6·5 mol% in **1**/TNF/(−)-TAPA) show a strong tendency to give a homeotropic orientation (director perpendicular to the glass surface), leading to a texture characterized by broad parallel lines, cf. figure 3 (*a*), which may degenerate into a pattern of point defects [14]. Sometimes an unwinding of the helical twist occurs in such samples, resulting in a dark homeotropic nematic texture when observed between crossed polarizers.

With higher (−)-TAPA concentrations, in both systems studied here, focal-conic like textures showing typical fingerprint lines are obtained, cf. figure 3 (*b*). Therefore, the orientation changes and becomes more inhomogeneous. In cases of (−)-TAPA concentrations above 18 mol% in the binary system **2**/(−)-TAPA or 25 mol% in the ternary system **1**/TNF/(−)-TAPA similar textures are exhibited but without evaluable

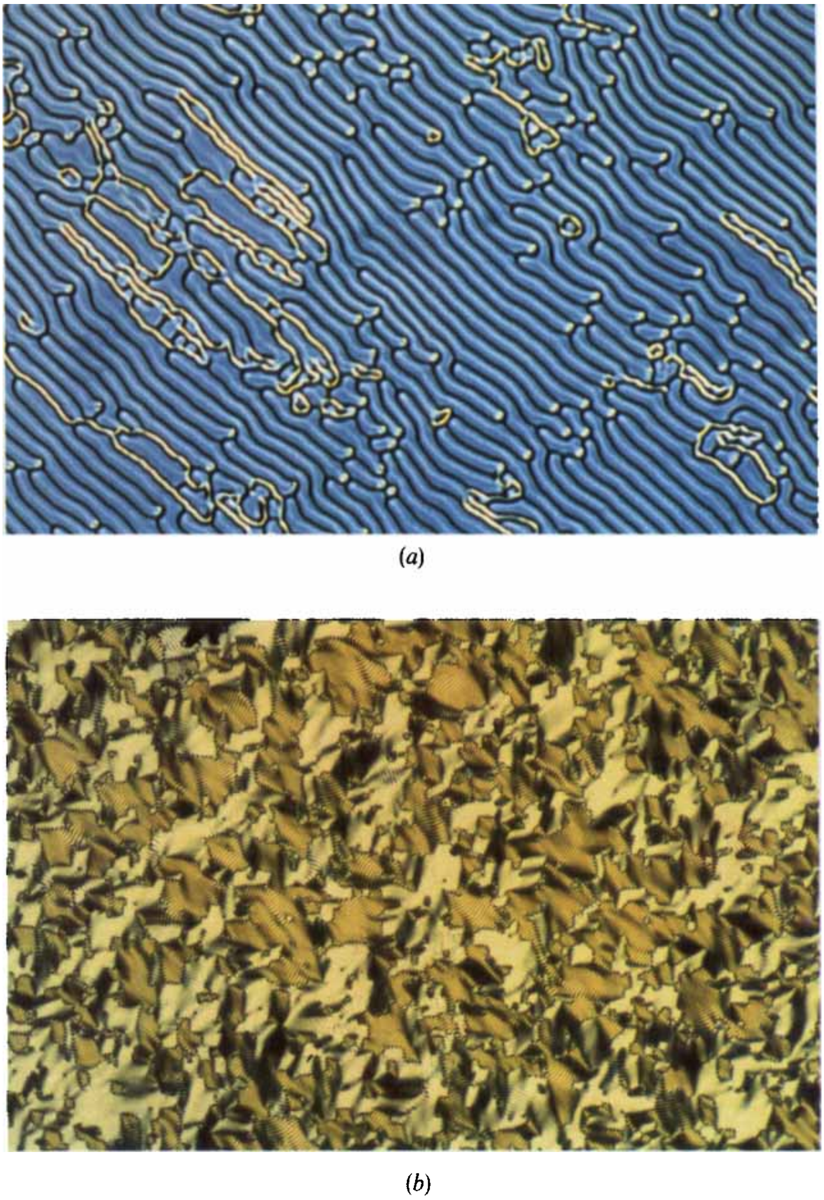


Figure 3. Textures of the cholesteric nematic phases exhibited by charge transfer complexes of the pentayne ethers **1** and **2** with the chiral electron acceptor (−)-TAPA: (*a*) 'strain' texture of a mixture of **2** with 15 mol% (−)-TAPA at 148°C on cooling from the isotropic liquid, *b*) focal-conic like texture of the ternary system **1**/TNF/(−)-TAPA containing 35 mol% TNF and 15 mol% (−)-TAPA at 104°C on cooling from the isotropic phase.

fingerprint lines. Such mixtures with high (−)-TAPA contents, for example, **2** containing 50 mol% (−)-TAPA or **1** doped with 30 mol% (−)-TAPA plus 20 mol% TNF, sometimes give aligned samples showing a homogeneous texture of a white opalescent colour without any fingerprint lines or defects. Analogous observations were previously reported for mixtures of chiral benzene, triphenylene, or truxene derivatives with the 2,3,6,7,10,11-hexa(heptyloxybenzoate) of triphenylene in their N_D^* phases [7 (a)]. Surface treatment, as, for example, by unidirectional rubbing or silanization, has nearly no effect on the alignment of the mesophase. Hitherto, we could not obtain homogeneous planar orientations necessary for examinations by the Cano method.

In order to estimate the helical twisting power (HTP) of (−)-TAPA in our cases and the temperature dependency of the helical pitch p, a systematic investigation of the fingerprint textures has been carried out. For this purpose, defined textures have been obtained by slowly cooling (1–2 K min^{-1}) thin samples of the charge transfer complexes of **1** or **2**, between glass plates and cover slips, from the isotropic into the twisted nematic phase and annealing there if necessary. Photographs of the defect textures of several mixtures differing in their (−)-TAPA contents have been taken at various temperatures. The distances between the fingerprint lines were measured by comparison with photographs taken from a graduated scale. The average line distance should be equal to half of the pitch p, but at least for samples with low (−)-TAPA contents, often multiples $np/2$ were observed, for example, in samples of mixtures of **2** containing 15 mol% (−)-TAPA, besides line distances d correlated to $p/2$, also those for $d = 3p$ and $d = 6$p occurred, most probably due to the formation of superstructures forming a type of 'strain' texture [15]. The pitch p in both systems, **2**/(−)-TAPA and **1**/TNF/(−)-TAPA, seems to show only a weak temperature dependency not exceeding the statistical spread in these measurements which is estimated to be in the order of 10–20 per cent.

The results concerning the helical pitch p as a function of the (−)-TAPA concentration are summarized in figure 4. Both the binary system **2**/(−)-TAPA and the ternary system **1**/TNF/(−)-TAPA show absolute minima of their helical pitches p of 2·7 and 2·3 μm, respectively, at (−)-TAPA concentrations of about 20 mol% in the former and around 12–15 mol% in the latter case.

In most of the examples of cholesteric nematic phases of mixtures of calamitic nematogens with a chiral dopant, the relationship between the pitch p and the dopant concentration c may be described by the equation $1/p = \beta_m \cdot c$, in which β_m is the helical twisting power for c in mol%. As expected, a plot of $1/p$ versus the (−)-TAPA concentration leads to linear curves, but with deviations for high (−)-TAPA contents because of the pitch minima mentioned above, cf. figure 4. For the mixture of **1** containing 10 mol% (−)-TAPA and 40 mol% TNF, the observed pitch is too high, but the value fits with 3/2 of p.

Two surprising features of the curves observed for the systems studied here should be emphasized and can be described by the following equations:

$$1/p = 0{\cdot}021\ c_{(-)\text{-TAPA}} - 0{\cdot}08 \quad \text{for the binary system } \mathbf{2}/(-)\text{-TAPA}$$

and

$$1/p = 0{\cdot}043\ c_{(-)\text{-TAPA}} - 0{\cdot}08 \quad \text{for the ternary system } \mathbf{1}/\text{TNF}/(-)\text{-TAPA}.$$

(1) Both curves do not cross the concentration axis at the zero point, but at about 2 mol%.

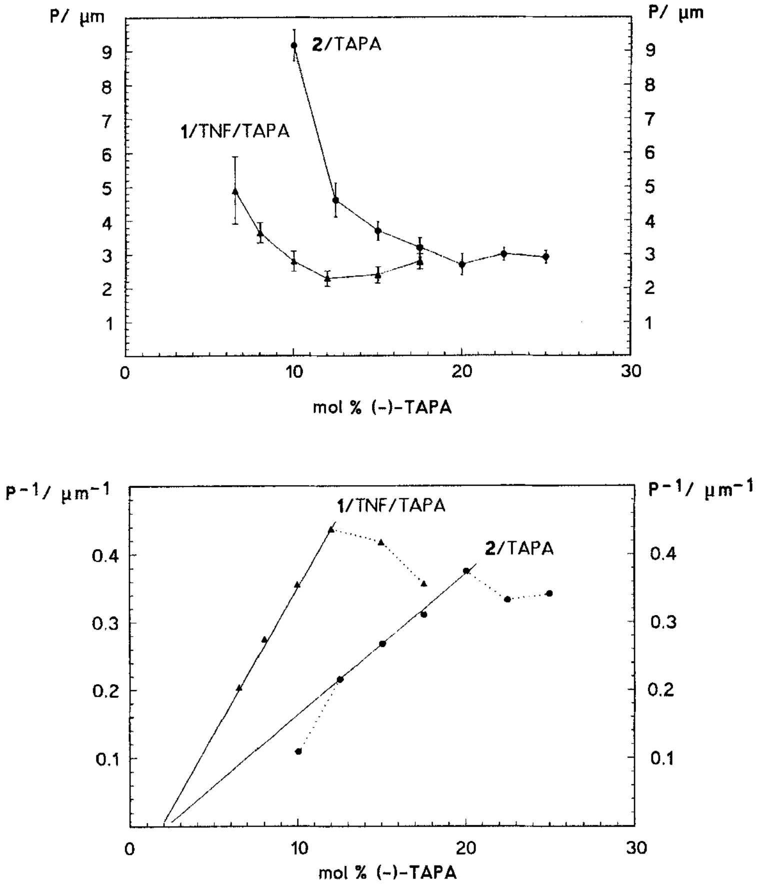


Figure 4. The helical pitch p as a function of the (−)-TAPA concentration in the binary system **2**/(−)-TAPA or in the ternary system **1**/TNF/(−)-TAPA (both top) and the resulting plots $1/p$ versus the (−)-TAPA content in these two systems (bottom).

(2) The slope β_m (= helical twisting power) of 0·043 mol%$^{-1}\mu$m^{-1} for the ternary system **1**/TNF/(−)-TAPA is twice that of the binary system **2**/(−)-TAPA of 0·021 mol%$^{-1}\mu$m^{-1}. For this reason, the pc-product of 23·3 μmmol% of the ternary system is just half that of the binary one (pc = 47·6 μmmol%).

We have no reasonable explanation for the first result. The different HTPs β_m for (−)-TAPA in the nematic systems studied here clearly show the importance of the nematic matrix to induced cholesteric properties in such systems. Because of the higher overall acceptor concentration in the ternary system **1**/TNF/(−)-TAPA, in comparison with that of the binary one **2**/(−)-TAPA, the helical twisting power β_m may depend on the length of the columnar aggregates, assuming the (−)-TAPA molecules also intercalate in columnar structures (cybotactic groups) formed by charge transfer interactions. For rod-like thermotropic nematogens, favouring of the helical twisting by smectic-like clusters is assumed [2(c), 16]. In the case of a lyotropic system exhibiting a nematic columnar (N_C) and a nematic lamellar (or lenticular) (N_L) phase the opposite behaviour was observed with brucine sulphate as a chiral dopant. For the same dopant concentration the pitch of the N_C^* phase is twice that of the N_L^* phase [3(b)].

3. Concluding remarks and outlook

These first results presented here concerning cholesteric nematic properties induced by a *chiral charge transfer acceptor* on disc-shaped compounds and, in the case of the ternary system **1**/TNF/(−)-TAPA, exhibited even for mixtures of *non-liquid crystal* materials, show the possibilities of mesophase variation or induction based on charge transfer interactions between disc-like donor molecules and strong electron acceptors. This kind of molecular interaction seems to be one of the most useful ways for changing the molecular aggregation, at least in the field of disc-shaped compounds, even if one must admit that the nature of the CT-induced nematic type of mesophase which we denote N_C is not yet fully clear.

The pure enantiomers of TAPA are commercially available, but it should be noted that this acceptor compound decomposes at higher temperatures. Thus, we consider that their easily accessible esters may be more suitable as chiral dopants for further studies.

More accurate measurements—using for example the Cano method, selective light reflection or spectroscopic techniques—of the pitch dependency on temperature or dopant concentration and the determination of the helical sense will be necessary. Based on the binary and ternary systems introduced here, systematic studies on the influence of charge transfer interactions and the role of columnar aggregates in cholesteric nematic phases of disc-shaped compounds are possible. A comparison of the HTPs β_m of chiral CT-acceptors with those of chiral non-acceptor dopants in a nematic discotic (N_D) pentayne matrix (for example, **2**) or in a charge transfer induced nematic columnar (N_C) phase (for example, **1**/TNF), may help us to understand the basic features of the chiralization of mesophases by chiral dopants. Eventually, based on reports of chiral columnar mesophases [17], it should be possible to obtain tilted chiral columnar phases in mixtures of TAPA or TAPA derivatives with suitable discogens, as, for example, with tetranuclear disc-shaped palladium organyls [10(h)]. As a first result of such attempts, we have observed *lyotropic nematic cholesteric* properties in contact preparations of an equimolar (−)-TAPA charge transfer complex of such a metallo-mesogen with pentadecane.

4. Experimental

4.1. *The synthesis of the electron donor compounds* 1 *and* 2

The alkyl pentakis(phenylethynyl)phenyl ethers **1** and **2** were prepared in two steps: Reaction of commercially available pentabromophenol with hexadecyl bromide (sodium hydride in dimethylformamide) yielded *hexadecyl pentabromophenyl ether*, $C_{22}H_{33}Br_5O$ (FW 670·9), m.p. 70°C, in 79 per cent yield, as colourless crystals from acetone. The structure was confirmed by elementary and spectroscopic data. Fivefold alkynylations of this pentabromophenyl ether (5 mmol) were carried out with excess (> 50 mmol) of phenylacetylene and 4-methylphenylacetylene, respectively, in Pd-catalysed CC-coupling reactions [8, 10(e)] (refluxing with 250 mg $PdCl_2(PPh_3)_2$, 250 mg Cu_2I_2, and 500 mg PPh_3 in 50 ml of degassed triethylamine, bath temperature 100°C, argon atmosphere, for 18 h (**1**) or 48 h (**2**)); this furnished the yellow crystalline (greenish-blue fluorescence in solution) pentayne ethers **1** or **2** 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 and from heptane. Their phase transition data are compiled in the table.

Hexadecyl pentakis(phenylethynyl)phenyl ether (**1**); $C_{62}H_{58}O$ (FW 819·1): yield 78 per cent. IR (CCl_4): $\tilde{\nu}_{C\equiv C} = 2220\,cm^{-1}$. ^1H NMR (Bruker WH 400, $CDCl_3$: $\delta = 7·65$–7·58, 7·41–7·33 (2m; phenyl H), 4·39 (t, $J \approx 6·5$ Hz; O–CH_2), 1·94 (tt, $J \approx 6·5$ and 7 Hz; 2 H, β–CH_2), 1·62 (tt, $J \approx 7$ and 8 Hz, respectively; 2 H, γ–CH_2), 1·36 (tt, $J \approx 7$ and 8 Hz; δ–CH_2), 1·31–1·19 (m; the remaining CH_2), 0·88 (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR (Bruker AM 270, $CDCl_3$): $\delta = 160·55$ (s; quart. aromatic C–O), 131·80, 131·69, 131·64, 128·92, 128·81, 128·69, 128·55, 128·41 (8d; tert. aromatic C), 128·92, 124·03, 123·41, 123·25, 123·18, 120·20 (6s; quart. aromatic C), 99·38, 99·26, 97·18 (3s, ratio 2:2:1; the inner ethynyl Cs), 87·43, 86·98, 84·51 (3s, ratio 2:1:2; the outer ethynyl Cs), 74·87, 31·92, 30·62, 29·71, 29·37, 26·37, 22·69, 14·14 (7t, 1q; the hexadecyl chain). MS (Varian MAT 711, 70 eV, 330°C, high resolution): $m/z = 818·448766$ (M^+), calculated 818·448765.

Hexadecyl pentakis(4-methylphenylethynyl)phenyl ether (**2**); $C_{67}H_{68}O$ (FW 889·3): yield 71 per cent. IR (CCl_4): $\tilde{\nu}_{C\equiv C} = 2210\,cm^{-1}$. ^1H NMR (Bruker WH 400, $CDCl_3$): $\delta = 7·54$–7·48, 7·20–7·15 (2m; phenyl H), 4·36 (t, $J \approx 6·5$ Hz; O–CH_2), 2·39 (s; CH_3-phenyl), 1·92 (tt, $J \approx 6·5$ and 7·5 Hz; 2 H, β–CH_2), 1·61 (tt, $J \approx 7·5$ Hz each; 2 H, γ–CH_2), 1·40–1·20 (m; the remaining CH_2), 0·88 (t, $J \approx 7$ Hz; CH_3). ^{13}C NMR (Bruker AM 270, $CDCl_3$): $\delta = 160·26$ (s; quart. aromatic C–O), 138·96, 138·83, 138·65 (3s, ratio 2:2:1; quart. aromatic $\underline{C}$–CH_3), 131·74, 131·59, 131·54, 129·17 (4d; tert. aromatic C), 128·71, 124·01, 120·49, 120·32, 120·27, 120·08 (6s; quart. aromatic C), 99·42, 99·30, 97·20 (3s, ratio 2:2:1; the inner ethynyl Cs), 87·04, 86·56, 84·04 (3s, ratio 2:1:2; the outer ethynyl Cs), 74·77, 31·92, 30·60, 29·73, 29·68, 29·36, 26·37, 22·68, 14·11 (8t, 1q; the hexadecyl chain), 21·58 (q; $\underline{C}H_3$–phenyl). MS (Varian MAT 711, 70 eV, 330°C, high resolution): $m/z = 888·527016$ (M^+), calculated 888·527015.

4.2. *Preparation of the various mixtures*

Preparations were carried out by mixing the pentayne ethers **1** or **2** with the desired amounts of the electron acceptors (−)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy) propionic acid ((−)-TAPA) and/or 2,4,7-trinitrofluorenone (TNF) in solutions of dichloromethane. The various solutions were concentrated and the orange to red residues dried *in vacuo*, subsequently mechanically homogenized and heated into the isotropic phase for half a minute, 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 1–5 K min^{-1}, crossed polarizers, and
(ii) differential scanning calorimetry (DSC) using a Mettler TA 3000/DSC 30 S with GraphWare TA 72·5; heating rate 5 K min^{-1}.
(iii) Photographs of defect textures were taken with a 24 × 36 mm microscope camera, Photoautomat Wild MPS 51; overall magnification 420 ×.

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