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The first case of a lyotropic twisted nematic (N*) phase induced by a chiral charge transfer complex [1]

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The disc-shaped tetra-palladium organyl **1** forms optically active charge transfer complexes in equimolar mixtures with the enantiomers of the π-acid electron acceptor **2**, (+)- or (−)-TAPA, exhibiting lyotropic cholesteric nematic properties in apolar organic solvents. These ternary systems are the first examples in which such a lyomesophase has been induced by charge transfer interactions.

1. Introduction

Studies on lyotropic cholesteric phases traditionally are associated with aqueous systems of rod-shaped amphiphilic compounds [2]. The formation of such twisted nematic phases (N*) usually was achieved in two ways:

(1) by adding chiral dopants, for example brucine sulphate [2(a), (b)] or sugars 2(c)] to aqueous lyotropic nematic systems leading to the induction of a helical twist,
(2) by dissolving chiral surfactants [2(d)–(f)] or chiral macromolecules, for example, poly-peptides, -saccharides or -nucleotides [2(g)], in (mostly) aqueous media.

A topic of increasing interest in the field of lyotropic liquid crystals is the mesophase formation of disc- or lath-shaped molecules. The mesomorphic properties of aqueous binary mixtures of planar polyaromatics [3(d)], discotic [3(b), (c)] or discoid [3(d)] compounds, indicated as 'chromonics', stem from the column-type stacking of their more or less flat molecules or aggregates, as well as from the nematic-like arrangement or the different two-dimensional packing of these columnar units, respectively. Up to now, descriptions of successful attempts to generate cholesteric behaviour of a lyotropic nematic phase based on disc-like compounds seem not to exist in the literature [3(d)]. However, a 'chromonic' N* phase has been observed in aqueous solutions of a cyclic dinucleotide [3(e)].

Just as little is known about lyotropic nematic properties of disc-shaped compounds in apolar organic solvents [4]; only one case, of an induced cholesteric type, of a nematic lyomesophase (N*) or rhodium eicosanoate in the chiral solvent (+)-camphene has been reported in poster presentations a short while ago [4(b)].

In a recent paper, the existence of lyotropic nematic properties of the tetranuclear palladium organyl **1** [1] and related pallado-discogens, as well as of their charge transfer complexes with 2,4,7-trinitrofluorenone (TNF) over wide concentration and

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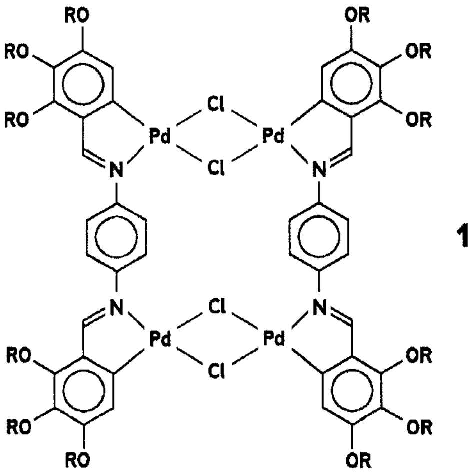
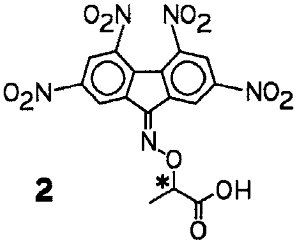
temperature ranges was proved. It should be emphasized here that nematic ordering does exist over wide concentration and temperature ranges in binary mixtures of **1** with pentadecane; the same is true for the ternary system: **1**/TNF/pentadecane.

In *thermotropic* nematic discotic (N_D) and nematic columnar (N_C) systems, doping with a chiral electron acceptor, for example (−)-2-(2,4,5,7-tetranitro-9-fluorenylideneaminooxy)propionic acid [(−)-TAPA, (−)-**2**], was shown to be an interesting new way to obtain cholesteric properties [5]. This success encouraged us to apply our method to a *lyotropic* type of nematic phase made up by mixing **1** in different apolar organic solvents.

Our first results concerning this new work on the cholesteric nematic (N*) behaviour of mixtures of the pallado-organyl **1** with the two pure enantiomers of **2**, as strong electron acceptors, in solutions of aliphatic hydrocarbons are reported here.



1 (R = $C_{12}H_{25}$)



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2. Results and discussion

2.1. *Materials and instrumental*

The synthesis of the metallo-mesogen, the tetranuclear palladium organyl **1**, is described elsewhere [6]. The commercially available electron acceptors (+)-TAPA [(+)-**2**] and (−)-TAPA [(−)-**2**] were used after drying without further purification.

The equimolar charge transfer complexes of **1** with (+)-**2** or (−)-**2** were prepared by dissolving appropriate millimolar amounts in dichloromethane and evaporating the solvent in vacuo. The various lyomesomorphic samples of defined compositions were obtained by adding the required amounts of the solvent, for example, heptane, pendadecane or eicosane, to the appropriate crystalline CT complexes of **1**, followed by homogenization in an ultrasound bath for 90 min at 80°C.

The thermal behaviours of these samples were studied by polarizing optical microscopy (Leitz Laborlux 12 Pol equipped with a Mettler FP 5 hot stage, heating rate 2 K min^{-1}, crossed polarizers). The texture photographs were taken using a 24 × 36 mm microscope camera, Photoautomat Wild MPS 51; the overall magnification was × 320.

2.2. *Lyotropic cholesteric (N*) properties of the ternary system* **1**/*TAPA* (**2**)/*apolar organic solvent of the tetra-palladium organyl* **1**

Contact preparations of the equimolar CT complexes (composed of **1** and (−)-**2**) with heptane, pentadecane, or eicosane, respectively, clearly proved the existence of a lyotropic cholesteric (N*) phase in these ternary systems. The nematic character of these fluid lyomesophases was obvious because of *visible* fluctuations. Different types of texture were observed as, for example, polygonal or fingerprint-like (see figure 1); along the border of such contact samples, structures similar to Grandjean-terraces were formed. In order to estimate the helical pitch **p** and its temperature dependence, a systematic investigation of the pitch line distances $d = 1/2\mathbf{p}$ in the fingerprint and polygonal textures of such samples was carried out. For this purpose, photographs of defined textures obtained by slow cooling from the isotropic liquid of contact preparations between glass plates and cover slips were taken at various temperatures. The distance between the fingerprint lines was measured by comparison with photographs taken of a graduated scale. The results of these studies on the metallorganyl **1** are summarized in figure 2(*a*).

The temperature range of the N* phase of the heptane solutions was too small to determine the temperature dependence of the pitch **p**. Besides, problems also arose from the volatility of this solvent, and the pitch **p** for the ternary system **1**/(−)−**2**/heptane could only be estimated to be about 3·7 μm. As is obvious from figure 2(*a*) with pentadecane or eicosane, the pitch **p** increases with rising temperature. We would like to point out that comparable relations for $p = \mathrm{f}(T)$ were found for aqueous cholesteric (N*) solutions of potassium dodecanoyl l-alaninate or l-serinate [2 (e)]. It is interesting to note that for the charge transfer complex of **1** with (+)-**2** in pentadecane solution, a significantly smaller pitch **p** was observed compared to that for the CT complex of **1** with (−)-**2** in the same solvent: $\bar{\mathbf{p}} \approx 2{\cdot}8$ and 3·9 μm, respectively. This difference of about 1 μm may arise from different optical purities of the two enantiomers of this electron acceptor **2**. However, contact preparations of the (+)-TAPA and the (−)-TAPA charge transfer complex of **1** in pentadecane show compensation of the helical twist **p**.

In order to determine the phase behaviour and the influence of the solvent concentration on the helical pitch **p**, we extended these studies to mixtures of the equimolar charge transfer complex of **1**/(−)-**2** with defined amounts of pentadecane. The results of these studies are summarized in the pseudo-binary phase diagram in figure 3. The mesogen concentration in wt % of the equimolar CT complex **1**/(−)-**2** in relation to the pentadecane content was varied from 60 to 28 wt %. In this concentration range the phase transition from the solid into the mesomorphic state occurs at 50–55°C. The nematic phase region is subdivided by us into three parts:

1. the twisted nematic area of the different cholesteric nematic textures, for example, polygonal or fingerprint, cf. figure 1,
2. an intermediate range between N + I and N* exhibiting the nematic schlieren texture together with cholesteric textures, and
3. the biphasic region N + I in which the nematic phase coexists with the isotropic phase.

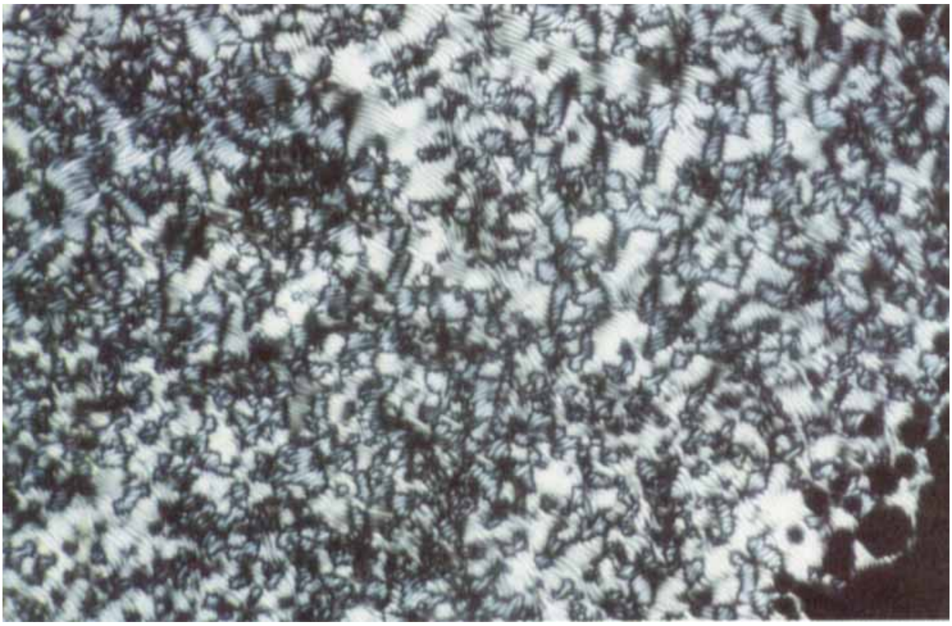


Figure 1. The fingerprint texture of the equimolar mixture of **1**/(−)-**2** in a contact preparation with pentadecane, $T = 39{\cdot}9^\circ C$ on cooling, magnification ×320.

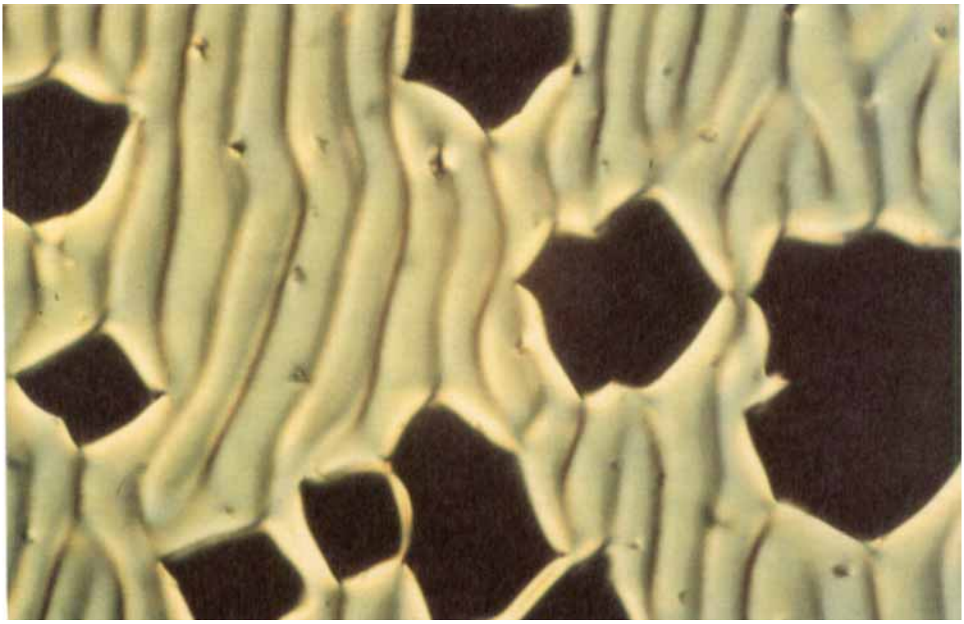


Figure 4. The strain texture of the **1**/(−)-**2**/pentadecane system (**c** = 47 wt% of the equimolar charge transfer complex in pentadecane), $T = 70{\cdot}4^\circ C$ on cooling, magnification ×320.

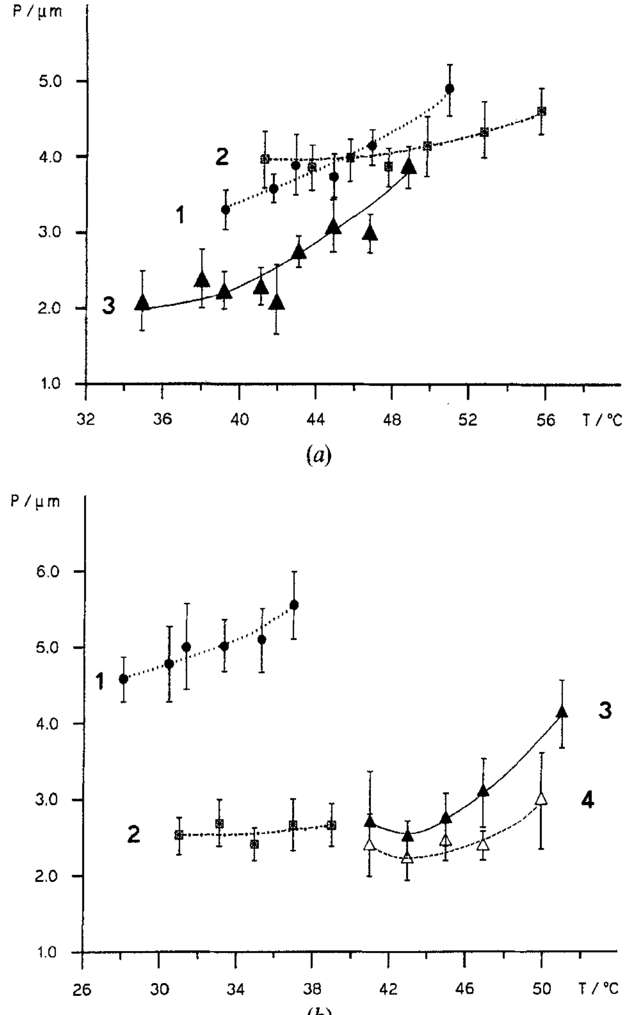
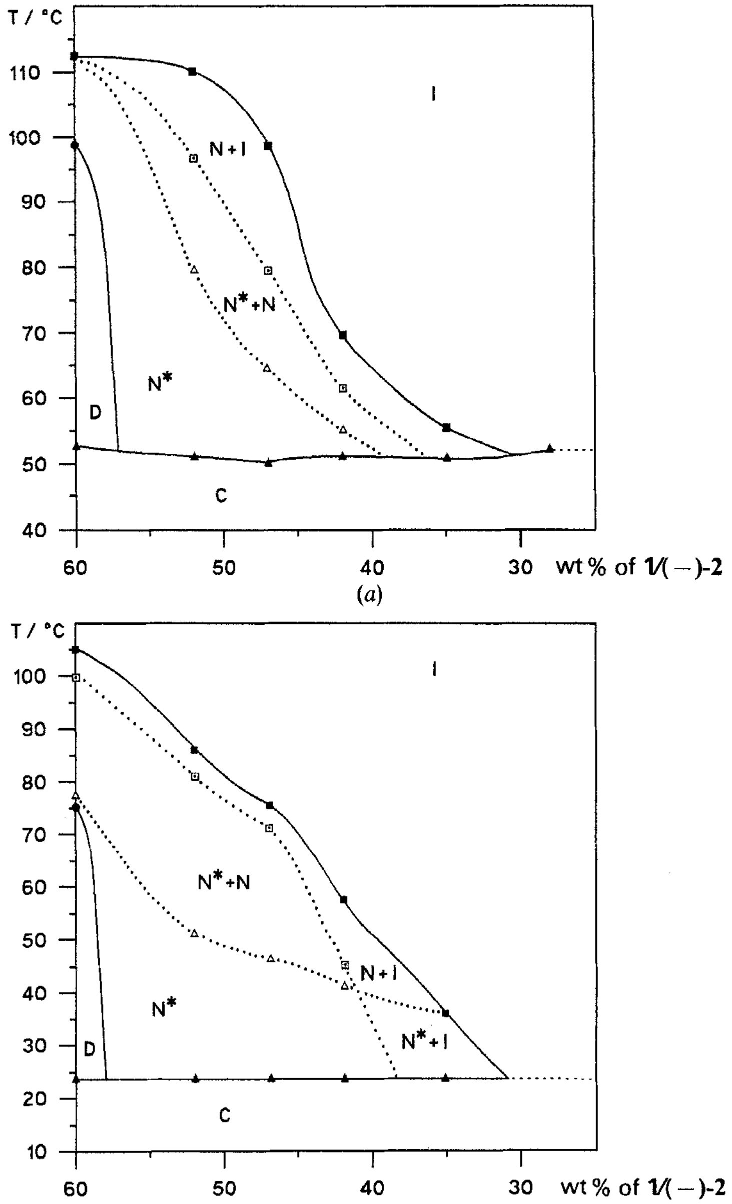


Figure 2. The helical pitch **p** as a function of temperature in the ternary systems made up from the equimolar charge transfer complexes **1**/TAPA (**2**) with alkanes: (*a*) Contact preparations: (1) **1**/(−)-**2**/pentadecane; (2) **1**/(−)-**2**/eicosane; (3) **1**/(+)-**2**/pentadecane; (*b*) The ternary system **1**/(−)-**2**/pentadecane containing the following amounts of the equimolar charge transfer complex **1**/(−)-**2**: (1) 35 wt %, (2) 42 wt %, (3) 47 wt %, (4) 52 wt %.

It should be emphasized here that in all of these mixtures a significant supercooling of the formation of the cholesteric nematic textures is observed, cf. figure 3 (*b*). The temperature dependencies of the helical pitch **p** of the four compositions studied here [35, 42, 47 and 52 wt % of the equimolar charge transfer complex **1**/(−)-**2**] and sketched in figure 2 (*b*) were derived from the fingerprint lines obtained on cooling from the isotropic phase. The data obtained for the 35 wt % mixture at the border to the biphasic region, N* + I, correlate with those derived from contact preparations. It is important to note that for the pentadecane solutions containing 42, 47 and 52 wt % or the CT complex **1**/(−)-**2**, the formation of 'strain'-textures—similar to those of thermotropic cholesteric (N*) phases of rod- [7] or disc-shaped [5] molecules—is observed near their



(*a*)

(*b*)

Figure 3. Pseudo-binary phase diagram of the ternary system made up by the equimolar charge transfer complex **1**/(−)-TAPA [(−)-**2**] with pentadecane in the area of the N* phase; *top* on increase in temperature, *bottom*: on decrease in temperature.

clearing temperatures, see figure 4. There seems to be an increase of the pitch **p** with rising pentadecane content, as well as with temperature.

3. Conclusions

Based on the presented results, the induction of cholesteric properties by charge transfer interactions in a lyotropic nematic system composed of disc-shaped molecules and of apolar organic solvents has been proved here for the first time.

Electron acceptors, as for example TAPA (**2**) or 2,4,7-trinitrofluorenone are known to favour the formation of columnar phase structures by intercalation between disc-shaped molecules, for example, thermotropic hexagonal columnar (D_{ho}) or nematic (N_C or N_D) phases [8]. Therefore, columnar aggregates may also be assumed as the basic units of the cholesteric nematic lyomesophase of the ternary systems **1**/TAPA (**2**)/alkanes studied here. More accurate studies on the structure and properties, for example, the helical sense of this type of N* phase, are necessary. Because of the higher thermal stability, the easily accessible esters of the commercially available enantiomers of **2** may be more suitable as chiral dopants for further investigations.

But, the results presented here, and a recent study of thermotropic nematic phases of disc-shaped multiynes [5] clearly prove that charge transfer interactions with chiral electron acceptors, as, for example, with **2**, are an effective new way of introducing cholesteric properties in nematic phases of discotic compounds.

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