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D. Singer[a]; A. Liebmann[b]; K. Praefcke[a]; J. H. Wendorff[b]
[a] Institute of Organic Chemistry, Technische Universität Berlin, Berlin 12, Germany [b] Deutsches Kunststoff-Institut, Darmstadt, Germany

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Disc-shaped dinuclear palladium organyls

Structure and phase behaviour of charge transfer induced mesophases [1]

by D. SINGER, A. LIEBMANN†, K. PRAEFCKE* and J. H. WENDORFF†

Institute of Organic Chemistry, Technische Universität Berlin,
Straße des 17. Juni 135, W-1000 Berlin 12, Germany
† Deutsches Kunststoff-Institut,
Schloßgartenstraße 6, W-6100 Darmstadt, Germany

The recently synthesized non-calamitic/disc-shaped metal organyls containing two palladium atoms and eight flexible side chains represent the first case of metallo-mesogens exhibiting the nematic discotic (N_D) phase [2]. On doping with 2,4,7-trinitrofluorenone (TNF), a strong electron acceptor, the stabilization and/or induction of mesophases was observed. The phase behaviour of these binary systems and the structures of the mesophases displayed by them were studied by means of polarizing microscopy, differential scanning calorimetry, and X-ray scattering.

1. Introduction

The types of thermotropic liquid crystal mesophases are not only determined by the shape of the constituent molecules, but also, as studied to an increasing extent in recent times, by specific intermolecularly directed forces arising, for example, from hydrogen bonding, charge transfer and dipole–dipole interactions [3].

In the field of non-calamitic mesogens, the importance of such directed interactions is well-established, for example, by (i) the formation of hexagonal columnar (H_X) phases by multimerization of promesogenic molecules via hydrogen bonding [4], (ii) the induction of hexagonal columnar (D_{ho}) phases [5], (iii) the formation of even nematic columnar (N_C) phases [6] via charge transfer interactions between disc-shaped molecules and strong electron acceptors, and (iv) the induction of columnar mesophases (D_{ho} and D_{ro}) most probably caused by dipole–dipole interactions [7].

Recently, the two first liquid crystalline discoid metal organyl series—containing two or four palladium atoms—were synthesized [2]. The molecular structures of the dinuclear palladium organyl series **1a–e** and of 2,4,7-trinitrofluorenone (TNF), as a strong electron acceptor, are shown in figure 1. The acetato-bridged member **1a** is bent, whereas the halogeno- and thiocyanato-bridged systems (**1b–e**) are rather flat. Investigations of the halogeno- and thiocyanato-bridged members, **1b–e**, by polarizing microscopy, differential scanning calorimetry (DSC), and miscibility studies have shown that they exhibit the nematic discotic type of mesophases [2]. However, due to its non-planar structure, the acetato-bridged member (**1a**) is not liquid crystalline. The phase transition data for these five palladium organyls are summarized in table 1.

Mesophase stabilizations and/or inductions by charge transfer interactions, found recently in various cases [5, 6], were also observed in mixtures (contact method) of each of the halogeno- or thiocyanato-bridged palladium nematogens, **1b–e**, with 2,4,7-trinitrofluorenone (TNF) [2].

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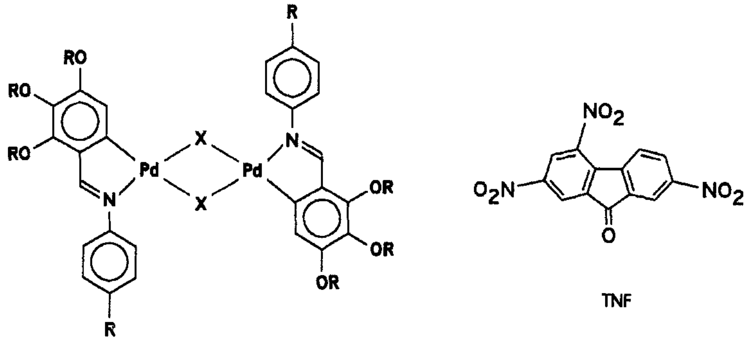
* Author for correspondence.



1a: *X*=OAc
b: *X*=Cl
c: *X*=Br
d: *X*=I
e: *X*=SCN

R=hexyl

Figure 1. Structures of the dinuclear palladium organyls **1a–e** as electron donors and of 2,4,7-trinitrofluorenone (TNF) as electron acceptor.

Table 1. Phase transition temperatures (°C)† and enthalpies (J g^{-1}) of the undoped dinuclear palladium organyls **1a–e**.

Pd organyl	*X*	C		N$_D$		I
1a	OA$_c$	●	55·8 (57·7)	—		●
1b	Cl	●	79·2 (24·9)	(●	43·5 (0·1))	●
1c	Br	●	72·6 (26·3)	(●	27·9 (0·1))	●
1d	I	●	97·4 (32·8)	(●	27·2 (0·1))	●
1e	SCN	●	96·1 (26·9)	(●	≈45 (—))‡	●

† Mettler TA 3000/DSC 30 S, enthalpies in parentheses.

‡ This monotropic transition occurs via a biphasic range and could be detected by hot stage polarizing microscopy only.

In this communication we report first results on the structures and behaviour of the mesophases of charge transfer complexes formed between the metallo-organyls, **1a–e**, and 2,4,7-trinitrofluorenone.

2. Results and discussion

2.1. *Preparation of the charge transfer complexes*

The charge transfer complexes of the dinuclear palladium organyls, **1b–e**, with TNF were prepared by dissolving appropriate amounts of both compounds separately in dichloromethane, mixing their solutions, and evaporating the solvent. The change of colour of the solutions during mixing indicates the formation of the electron donor acceptor complexes. Those mixtures containing 60 mol% TNF or more were homogenized by heating them into the isotropic phase and subsequent rapid cooling to room temperature.

2.2. *Experimental techniques*

The thermal behaviour of the mixtures was studied by the following methods.

(i) polarizing microscopy, using a Leitz Laborlux 12 Pol microscope equipped with a Mettler FP 82 hot stage (heating rate 2–5 K min^{-1}, crossed polarizers);
(ii) differential scanning calorimetry (DSC) in a Mettler TA 3000/DSC 30 S with Graph-Ware TA 72 (heating rate 5 K min^{-1}).

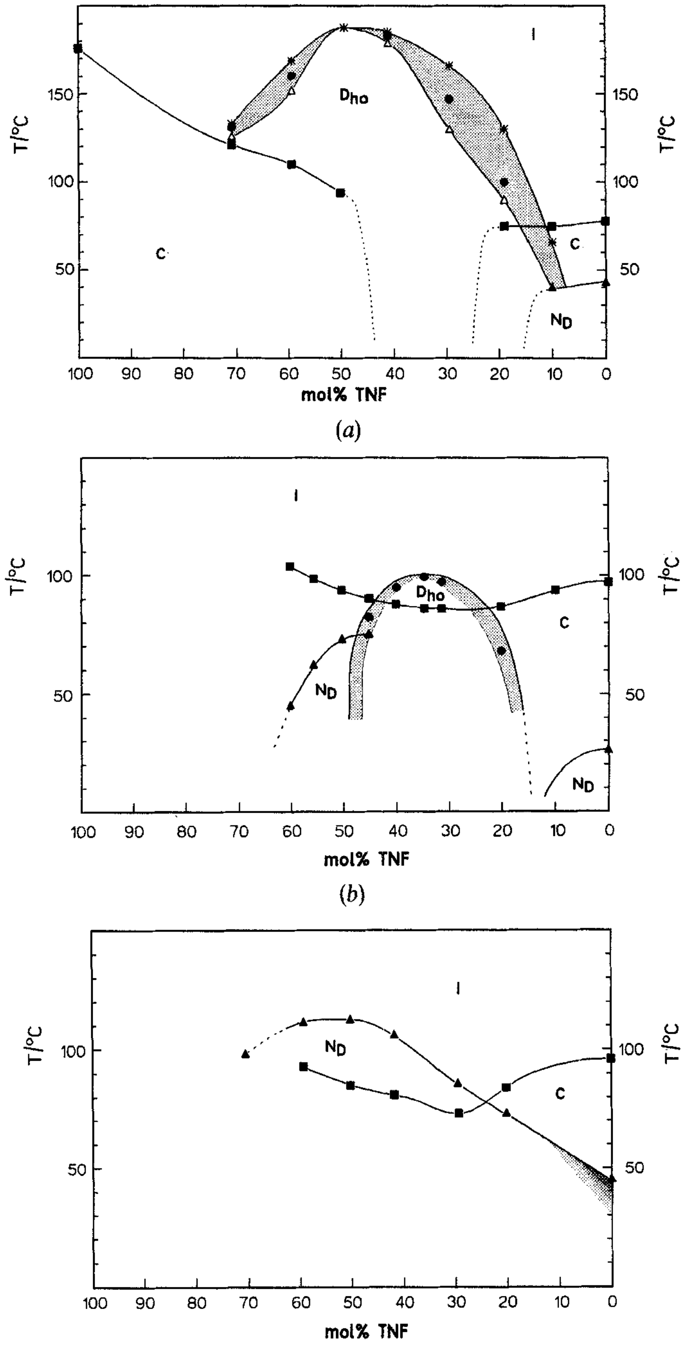
The structures of the induced mesophases were studied by X-ray diffraction using a Siemens D-500 wide angle goniometer and Ni-filtered Cu–K$_\alpha$ radiation ($\lambda = 0{\cdot}154$ nm). The X-ray patterns of oriented samples were recorded by the flat chamber technique with Ni-filtered Cu–K$_\alpha$ radiation ($\lambda = 0{\cdot}154$ nm). The orientation of the samples resulted spontaneously by surface interactions and flow effects in the capillaries.

2.3. *Phase behaviour of the charge transfer complexes*

All of the dinuclear palladium organyls, **1a–e**, form charge transfer complexes with the strong electron acceptor 2,4,7-trinitrofluorenone (TNF), as is indicated for such mixtures by a change of colour. A stabilization and/or induction of mesophases with TNF was observed in the cases of the planar halogeno- and thiocyanato-bridged palladium organyls, **1b–e**. On the other hand, the bent acetato-bridged member, **1a**, proved not to be liquid crystalline both in its pure state and the TNF-doped state [2].

The phase diagrams of the binary systems **1b**/TNF, **1d**/TNF, and **1e**/TNF are shown in figure 2 and are based on examinations of mixtures with defined acceptor contents and contact preparations between them. The assignments of the charge transfer induced and/or stabilized mesophases observed here are based on texture studies and X-ray scattering results (see § 2.4). The types of induced mesophases found are strongly influenced by the bridging groups *X* in **1b–e**. In principle, three variations of the mesophase behaviour were observed:

(i) The N_D phase of the undoped chloro-bridged palladium organyl, **1b**, vanishes for TNF concentrations higher than 10 mol% (see figure 2 (*a*)); a highly ordered mesophase is induced in the concentration range between 10 mol% and about 70 mol% TNF. This is a well-known behaviour for such doped systems [5]. On cooling from the isotropic phase, droplets with linear defects as well as homeotropic star-shaped domains with hexagonal symmetry appeared, developing into a mosaic texture similar to that shown in figure 3 (*a*). This behaviour is typical for hexagonal ordered (D_{ho}) phases. Mixtures containing more than 60 mol% TNF are thermodynamically unstable due to phase separation by crystallization of TNF. Therefore, at least in this concentration range, the phase diagram (see figure 2 (*a*)) reflects metastable situations. This is true for all binary systems studied here. The maximum clearing temperature (188°C) was found for the equimolar composition showing a rather narrow transition into the isotropic state (cf. table 2). For mixtures of non-equimolar compositions, the phase transitions D→I occur over wide biphasic ranges (cf. figure 2 (*a*)). A qualitatively very similar phase behaviour was observed for the bromo-bridged palladium organyl, **1c**, doped with TNF. Here, the maximum of the clearing temperature was about 143°C for the equimolar composition (cf. table 2 and figure 2 (*b*)).
(ii) In the case of the iodo-bridged mesogen, **1d**, doped with TNF, the situation is more complex. This particular binary system exhibits two mesophases (see



(a)

(b)

(c)

Figure 2. Phase diagrams of the binary systems of (*a*) the chloro-bridged palladium organyl, **1b** (top), (*b*) the iodo-bridged, **1d** (middle), and (*c*) the thiocyanato-bridged nematogen, **1e** (bottom), each doped with 2,4,7-trinitrofluorenone (TNF), based on examinations of mixtures with defined acceptor contents, as well as of contact preparations between them. ■ = melting points, ● and ▲ = clearing temperatures of the D_{h_o} and N_D phases, respectively. Shaded areas mark biphasic regions. For the binary system, **1b**/TNF (see (*a*)), the start (△) and the end (*) of the clearing processes are also marked.

figure 2 (*b*) and 3). As expected, the original N_D phase vanishes immediately by doping and an induced D_{ho} phase (cf. figure 3 (*a*)) is found in the concentration range between 20 and 45 mol% TNF. In contrast to the doped palladium organyls, **1b** or **c**, here, in the case of **1d**, the maximum clearing temperature (96°C) is observed for a complex containing 35 mol% TNF and not for the equimolar mixture. Increasing the TNF content above 45 mol% leads to the induction of a nematic phase revealed by its schlieren texture with strong thermal fluctuations (cf. figures 2 (*b*) and 3 (*b*)).

(iii) By doping the thiocyanato-bridged compound, **1e**, with TNF no new mesophase is induced, but the original monotropic N_D phase of the undoped compound (see table 1) is now enantiotropic, i.e. stabilized. This is a very unusual phase behaviour. The maximum of the clearing temperature (112°C) was observed for the equimolar composition (cf. figure 2 (*c*)). In comparison with the halogeno-bridged compounds, **1b–d**, and other nematogens showing $N_D \rightarrow I$ transitions, the thiocyanato-bridged compound (**1e**) in its pure state displays an unusual clearing behaviour. The clearing temperature of **1e** is not sharp as expected for such transitions; the clearing process of **1e** occurs over a biphasic temperature range of about 5 K (see table 1), most probably caused by the composition of this nematogen, i.e. it is a mixture of two structural isomers [2]. It is remarkable that the biphasic temperature range for the clearing process shrinks with increasing TNF content; it even disappears in mixtures of **1e** with more than about 15 mol% TNF (cf. figure 2 (*c*)).

It is interesting to note that the nematic discotic charge transfer complexes of **1d** or **e** with TNF show very sharp phase transitions into the isotropic state (cf. figures 2 (*b*) and (*c*)). The clearing enthalpies, of the order of 0·1 $J g^{-1}$, are of the magnitude often found for $N_D \rightarrow I$ transitions [8] and seem to be independent of the acceptor concentration.

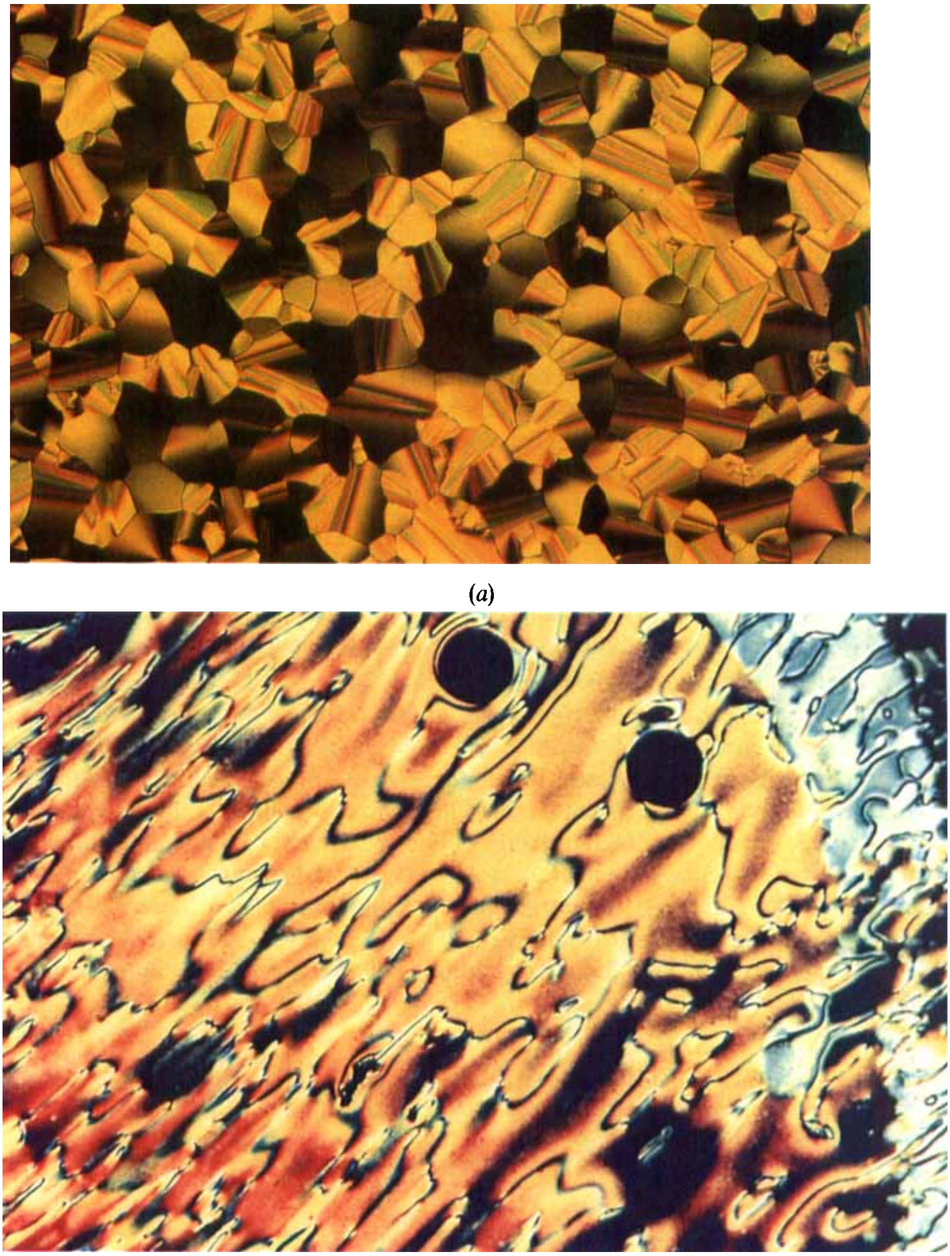
Each of the four binary systems studied here shows a complex multimorphism in the solid state—not documented in figure 2. The coexistence of liquid crystalline and crystalline phases over wide temperature and concentration ranges was observed. In addition, the crystallization of charge transfer complexes of the halogeno-bridged palladium organyls, **1b–d**, with around 50 mol% TNF is very slow. Moreover, mixtures of **1a** with 30 or 40 mol% TNF did not crystallize at all after weeks at room temperature (cf. figure 2 (*a*)).

Table 2. Phase transition temperatures (°C)† and enthalpies ($J g^{-1}$)† of charge transfer complexes generated by mixing the dinuclear palladium organyls of type **1** with 2,4,7-trinitrofluorenone (TNF).

TNF complex of [*X*]	TNF content/mol%	C		D_{ho}		N_D		I
1b[Cl]	50	●	93·7 (8·2)	●	188·2 (3·1)	—		●
c [Br]	50	●	99·3 (9·3)	●	142·5 (1·8)	—		●
d [I]	35	●	≈85 (—)‡	●	95·7 (1·4)	—		●
d [I]	50	●	83·6 (8·2)	—		(●	73·2 (0·1))	●
e [SCN]	50	●	85·0 (20·2)	—		●	112·0 (0·2)	●

† Mettler TA 3000/DSC 30 S (heating rate 5 K min^{-1}), enthalpies in parentheses.

‡ Because of very slow crystallisation this melting point could only be estimated (polarizing microscopy).



(*a*)

(*b*)

Figure 3. Textures of the charge transfer induced mesophases obtained by doping the iodo-bridged palladium organyl, **1d** with 2,4,7-trinitrofluorenone (TNF); magnification × 32 in a 24 × 36 mm microscope camera (Photoautomat Wild MPS 51), and crossed polarizers; (*a*) mosaic texture of the D_{ho} phase at 85°C of a mixture of **1d** with 40 mol% TNF, (*b*) schlieren texture of the nematic discotic (N_D) phase at 62°C of a 1 : 1 mixture of **1d** with TNF.

2.4. *Structural analysis of the charge transfer induced mesophases*

X-ray scattering experiments on mixtures of the halogeno- and thiocyanato-bridged palladium organyls, **1b–e**, with TNF at various temperatures confirm the induction of two different types of mesophase.

The wide angle scattering curve of the equimolar charge transfer complex of chloro-bridged **1b** with TNF in its mesophase is shown in figure 4. Essentially similar curves were obtained for mixtures of the bromo-bridged **1c** with an equimolar amount of TNF and of the iodo-bridged **1d** doped with 38 mol% TNF in their mesophases. In the small angle region, a sharp intensive reflection and two weak reflections of higher order were observed. These reflections have to be assigned to a hexagonal arrangement of columns on a two dimensional lattice. The hexagonal lattice constants a_{hex} are summarized in table 3. Additionally, a peak in accordance with a spacing of 3·5 Å is observed and refers to a regular stacking within the columns. The correlation lengths [9] for the inter- and intra-columnar order were calculated from the X-ray scattering curves and are also listed in table 3. These results clearly verify that the charge transfer induced columnar mesophases observed in mixtures of the halogeno-bridged palladium organyls, **1b–d**,

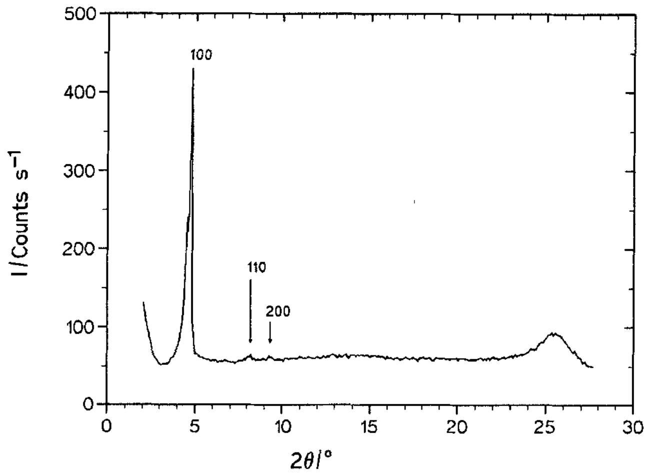


Figure 4. Wide angle X-ray scattering curve of an equimolar mixture of the chloro-bridged palladium organyl, **1b** with TNF at 100°C; for the peaks the Miller indices (*hkl*) are given above.

Table 3. X-ray data (in Å) of the mesophases exhibited by the charge transfer complexes of the palladium organyls **1b–e** with 2,4,7-trinitrofluorenone (TNF). a_{hex}: hexagonal lattice constant, L_{inter} and L_{intra}: inter- and intra-columnar correlation lengths.

CT-complex of [*X*]	TNF content/mol%	d_{100}	a_{hex}	L_{inter}	L_{intra}	Type of mesophase
1b [Cl]	50	18·7	21·6	320	37	D_{ho}
c [Br]	50	19·0	22·0	445	34	D_{ho}
d [I]	38	20·0	23·1	356	20	D_{ho}
d [I]	50	18·2	—	40	—	N_{D}
e [SCN]	50	19·6	—	62	—	N_{D}

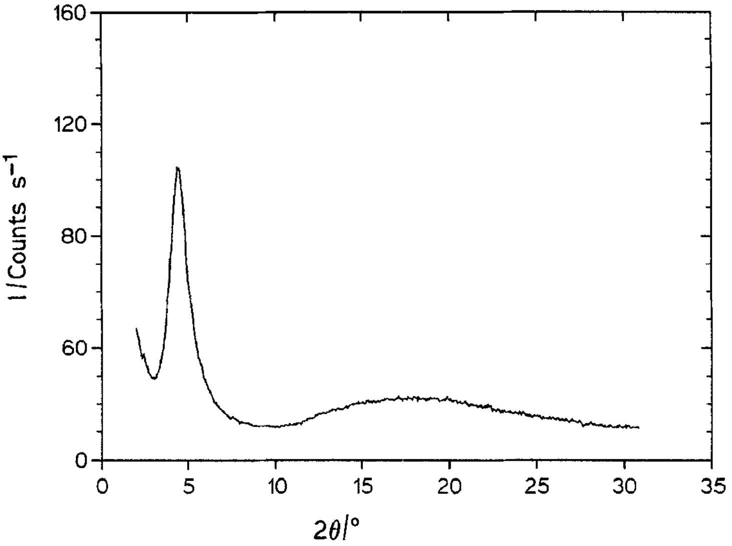


Figure 5. Wide angle X-ray scattering curve of an equimolar mixture of the thiocyanato-bridged palladium organyl, **1e** with TNF at 100°C.

with TNF are of the hexagonal ordered (D_{ho}) type. As expected, the hexagonal lattice constants increase from $X = Cl$ to $X = I$ due to the increasing molecular diameter within this series.

Charge transfer interactions between disc-shaped electron donors and strong electron acceptors are known to cause the induction of different columnar ordered phases [5]. Therefore, the charge transfer induced nematic phases observed in such mixtures composed of the iodo- or thiocyanato-bridged palladium organyls **1d** and **e**, and TNF should give similar results.

Surprisingly, the wide angle scattering pattern of the equimolar charge transfer complex of compound **1e** with TNF in the nematic phase shows the typical pattern (cf. figure 5) for the nematic discotic type of phase, i.e. without positional long range order. In the small angle regime, a rather broad reflection was observed corresponding to a distance of the order of the molecular diameter; in the wide angle range, a halo appeared corresponding to a mean distance of 4·5 Å, typical for a liquid-like arrangement of the aliphatic chains. Similar results were obtained for equimolar mixtures of the iodo-bridged **1d** and TNF. No additional peaks were found in the wide angle regime referring to a columnar order of the molecules in the mesophase. At least, this fact excludes the induction of a nematic columnar phase build-up of ordered columns for these two types of palladium organyl/TNF mixtures. In addition, X-ray patterns of oriented samples of equimolar mixtures of **1d** and **e** with TNF in capillaries display the intercolumnar reflections corresponding to d_{100} parallel to the direction of the capillary axis. Normally, in the case of columnar phases, the columns are oriented parallel to the capillary axis, caused by flow and surface effects and the 100 reflection is observed perpendicular to this axis.

All these features mentioned previously are typical for a nematic discotic (N_D) phase, a characterization also supported by the low clearing enthalpies (about 0·1 J g^{-1}) [8].

3. Conclusions

Based on the results presented, the two different types of charge transfer induced mesophases observed in mixtures of the dinuclear palladium organyls, **1b–e**, with 2,4,7-trinitrofluorenone were identified as hexagonal columnar ordered (D_{ho}) for **1b–d** and/or nematic discotic (N_D) for **1d** and **e**. Thus, this seems to be the first report of stabilization of an N_D phase by charge transfer interaction.

The phase behaviour of the binary systems of the chloro- or bromo-bridged palladium organyls, **1b** and **c**, doped with TNF is consistent with the intercalation model (cf. figure 6) for the induction of columnar phases by charge transfer interactions between disc-shaped donor molecules and strong electron acceptors [5, 6]. The clearing point maximum of the induced D_{ho} phase observed for each of the 1 : 1 compositions in these binary systems strongly supports this model.

For the induction of nematic phases in such systems, additional effects have to be discussed. The nematic columnar type of phase [6] seems to be preferred if elements of steric disturbance attached to the disc-shaped donor [6 (a, c] or to the electron acceptor [6 b] impair the arrangement of columns on a two dimensional lattice.

The formation of the nematic discotic type of mesophase by charge transfer interactions of the iodo- or thiocyanato-bridged palladomesogens, **1d** and **e**, respectively, with TNF is more likely to be a result of geometric changes in the donor molecules than a consequence of electronic effects. The Pd–Pd distance increases from **1b** to **1e**—especially from the iodo-bridged **1d** to the thiocyanato-bridged **1e**—leading to larger molecules, more ellipsoid in shape and with a decrease in space filling both in the core region and in the areas of the side chains; consequently, the association of electron donor and acceptor is altered and the formation of columnar structures is disfavoured.

To understand the difference between the N_D and the N_C phase and to investigate the nature of these phases, miscibility studies were performed. In contact preparations between (i) nematic discotic (N_D) equimolar charge transfer complexes of the palladium organyls, **1d** or **e**, respectively, with TNF and (ii) nematic columnar (N_C) charge transfer complexes of pentakis(phenylethynyl)phenyl tridecyl ether with the same TNF content [6 a] no phase boundaries could be observed in the contact zones. Therefore, these two types of nematic phases observed in such mixtures containing disc-shaped molecules are completely miscible with each other, although their X-ray scattering patterns

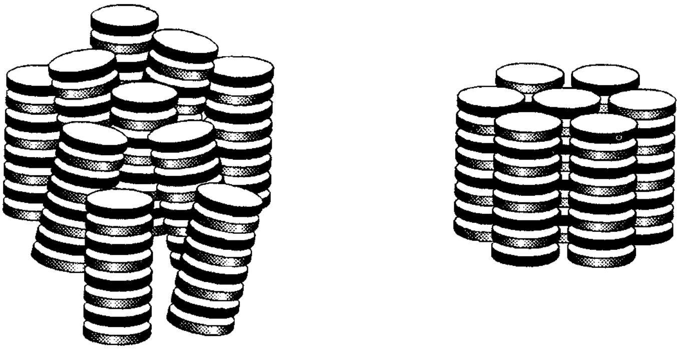


Figure 6. Schematic representations of the thermotropic nematic columnar (N_c) and discotic hexagonal ordered (D_{ho}) phases induced by charge transfer (CT) interactions between a low molecular weight disc-shaped donor compound (marked in black) and an electron acceptor (shaded).

are clearly different. Moreover, in the case of the donor pentakis(4-methylphenylethynyl)phenyl hexadecyl ether—nematic discotic in its pure state—as a component of mixtures with increasing amounts of 2,4,7-trinitrofluorenone as an electron acceptor, columnar aggregates develop without any sign of phase separation or transition.

Further studies on charge transfer induced nematic phases, including new donor and acceptor compounds, are in progress in an attempt to answer the question whether the nematic columnar (N_C) phase is best described as just a nematic discotic phase with columnar cybotactic groups showing a continuous change from the N_D to the N_C phase by intracolumnar aggregation of the molecules or whether a phase transition in real thermodynamic terms is involved.

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References

[1] Part of the contribution A-P4 at the *14th International Liquid Crystal Conference*, June 21–26, 1992, University of Pisa, Pisa, Italy, and part 74 on liquid-crystalline compounds; part 73: JANIETZ, D., PRAEFCKE, K., and SINGER, D., *Liq. Crystals* (in the press).

[2] PRAEFCKE, K., SINGER, D., and GÜNDOGAN, B., 1992, *Molec. Crystals liq. Crystals*, **223**, 181.

[3] See the papers cited in [6 a].

[4] (a) PRAEFCKE, K., LEVELUT, A.-M., KOHNE, B., and ECKERT, A., 1989, *Liq. Crystals*, **6**, 263. (b) FESTAG, R., KLEPPINGER, R., SOLIMAN, M., WENDORFF, J. H., LATTERMANN, G., and STAUFER, G., 1992, *Liq. Crystals*, **11**, 699.

[5] (a) BENGS, H., EBERT, M., KARTHAUS, O., KOHNE, B., PRAEFCKE, K., RINGSDORF, H., WENDORFF, J. H., and WÜSTEFELD, R., 1990, *Adv. Mater.*, **2**, 141. (b) EBERT, M., FRICK, G., BARHR, C., WENDORFF, J. H., WÜSTEFELD, R., and RINGSDORF, H., 1992, *Liq. Crystals*, **11**, 293.

[6] (a) PRAEFCKE, K., SINGER, D., KOHNE, B., EBERT, M., LIEBMANN, A., and WENDORFF, J. H., *Liq. Crystals*, **10**, 147. (b) BENGS, H., KARTHAUS, O., RINGSDORF, H., BAEHR, C., EBERT, M., and WENDORFF, J. H., 1991, *Liq. Crystals*, **10**, 161. (c) PRAEFCKE, K., SINGER, D., LANGNER, M., KOHNE, B., EBERT, M., LIEBMANN, A., and WENDORFF, J. H., 1992, *Molec. Crystals liq. Crystals*, **215**, 121.

[7] PRAEFCKE, K., SINGER, D., and KOHNE, B., *Liq. Crystals* (in the press).

[8] (a) KOHNE, B., and PRAEFCKE, K., 1986, *Chimia*, **41**, 196. (b) PRAEFCKE, K., KOHNE, B., GUTBIER, K., JOHNEN, N., and SINGER, D., 1989, *Liq. Crystals*, **5**, 233. (c) EBERT, M., JUNGBAUER, D. A., KLEPPINGER, R., WENDORFF, J. H., KOHNE, B., and PRAEFCKE, K., 1989, *Liq. Crystals*, **4**, 53. (d) PRAEFCKE, K., KOHNE, B., and SINGER, D., 1990, *Angew. Chem.*, **102**, 200, or 1990, *Angew. Chem. Int. Ed. Engl.*, **29**, 177. (e) PRAEFCKE, K., KOHNE, B., SINGER, D., DEMUS, D., PELZL, G., and DIELE, S., 1990, *Liq. Crystals*, **7**, 589. (f) PRAEFCKE, K., KOHNE, B., GÜNDOGAN, B., SINGER, D., DEMUS, D., DIELE, S., PELZL, G., and BAKOWSKY, U., 1991, *Molec. Crystals liq. Crystals*, **198**, 393. (g) See [2].

[9] GUINIER, A., 1963, *X-Ray Diffraction in Crystals, Imperfect Crystals and Amorphous Bodies* (Freeman).