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Lyotropic phase behaviour of disc-shaped tetra-palladium organyls in apolar organic solvents [1]

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The lyomesomorphic behaviour in apolar organic solvents of members of two series **1** and **2** of disc-shaped palladium organyls—the syntheses of four of them are new (**1d**, **f** and **2a**, **e**) and are described here—each carrying twelve long lipophilic chains have been studied. Their lyomesomorphism appeared to be complex and has been observed here for the first time with metal organyls. As can be seen by polarizing microscopy, most of the binary mixtures investigated here exhibit *nematic* properties. For two members of series **1**—the chloro-bridged **1b** and its bromo-analogue **1c**—there is even evidence for the existence of *two* different nematic lyomesophases side by side showing reversible transitions between them. In ternary systems, i.e. after the addition of 2,4,7-trinitrofluorenone (TNF, a strong electron acceptor), the nematic phases are stabilized, suggesting that their mesophase structures are made up by columns with intercalated TNF molecules (charge transfer complex formation). Influences of structural features of the pallado-mesogens on the one hand and of the type of solvent on the other on the molecular self-aggregation in the observed types of lyotropic mesophase formed are discussed in detail.

1. Introduction

Mesomorphic properties of lyotropic liquid crystals are mostly determined by specific interactions of *amphiphilic* molecules with each other as well as with the solvent and play an important role in biological systems [2]. Classical ionic or non-ionic amphiphiles, therefore, build supramolecular structures, for example, micelles, as basic units of a wide variety of lyomesophases. Common examples of this type of lyomesomorphism are aqueous solutions of surface active substances (for example, soaps) [3] or lipids [3 (c)]. Together with such supramolecularly structured lyomesogens also solutions of rod-shaped macromolecules [4], for example, polypeptides [4 (a)] nucleic acids [4 (a)–(d)], or polysaccharides [4 (a), (e)], and even macromolecular assemblies such as for example tobacco mosaic virus [5] also display lyomesomorphic properties both in aqueous and organic solvents.

A topic of increasing interest in the field of lyotropic liquid crystals is the mesophase formation by solutions of molecules of disc- or lath-like geometry. In aqueous solutions, the mesomorphic properties of such systems denoted as 'chromonics' are based on the stacking of such flat molecules or their aggregates on top of each other, so

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building up columnar units. These columns may arrange *nematic-like* or on a *two-dimensional* lattice [6], for example, of a hexagonal or rectangular type. But, up to now, there are only very few reports on the lyotropic behaviour of disc-shaped compounds in *apolar* organic solvents [7, 8 (a), (c)].

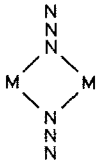
Hence, here we report our first results on the lyomesomorphism of tetranuclear palladium organyls of the types **1** [8 (a), (c)] and **2** [8 (b), (c)] in apolar organic solvents (for example, heptane, pentadecane, or eicosane) in general and of the chloro-bridged derivative **1b** in particular.

2. Results and discussion

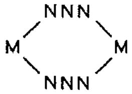
2.1. *Access to and properties of the tetra-pallado-mesogens*

The tetranuclear palladium organyls of type **1** or **2** were obtained by fourfold *ortho*-palladations of the corresponding bisimine ligands with palladium(II) acetate in acectic acid. Subsequent exchange of the acetato-bridges in **1a** and **2a** with isopropanolic hydrochloric acid in dichloromethane led to the chloro-bridged key compounds **1b** and **2b**, as described elsewhere [8 (a), (b)]. The preparations of **1c–f** and **2c–e** were carried out by treatment of **1b** and **2b**, respectively, with suitable alkali metal salts in dichloromethane/acetone, cf. [8 (a), (b)] and experimental section.

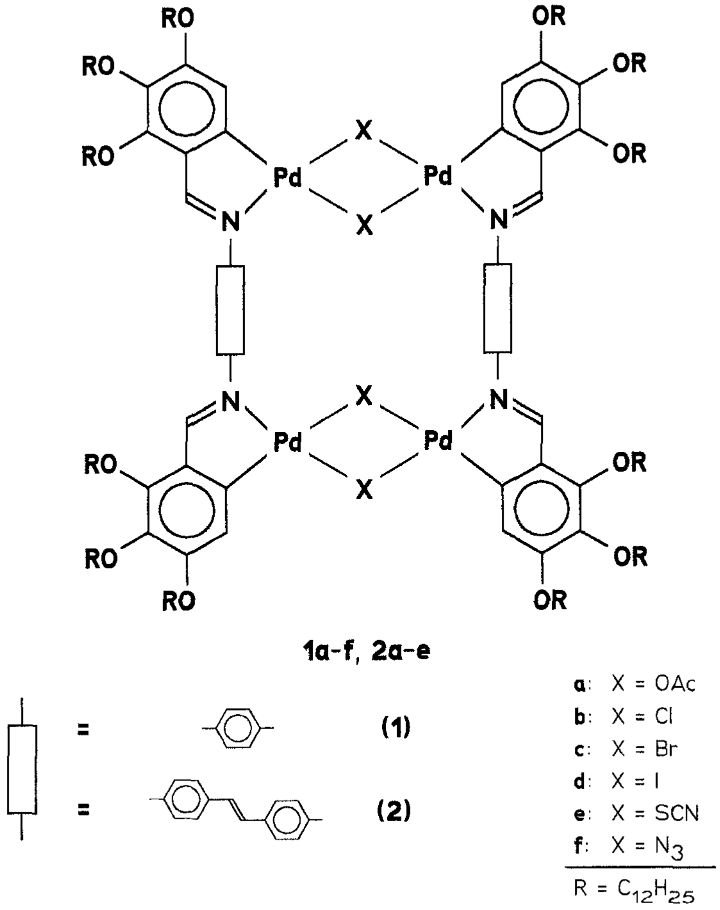
A:



B:



The non-oligomeric, macrocyclic molecular structure of this type of palladomesogen is proved by osmometric molecular weight determination and by single crystal X-ray analyses of homologous bromo- [9 (a)] and iodo-bridged [9 (b)] compounds of type **1** carrying shorter alkyl chains. It should be noted here that **1f** is the first example of a pallado-mesogen containing bridging azido groups, cf., figure 1. In principle, two different bridging modes of the two azido groups (cf. **A** and **B**) between the metal atoms M are known [10]. Usually, the formation of four-membered rings (type **A**) is observed [10 (a)–(c)], but there are also a few examples [10 (a), (d)] of azido-bridges of mode **B** leading to a larger ring. A reasonable distinction between both types in the case of the macrocyclic **1f** seems to be difficult. The IR and Raman spectroscopic data of this new palladium organyl—especially the difference of $\Delta\tilde{\nu} \approx 850\,\mathrm{cm}^{-1}$ between the asymmetric N_3 stretching vibration $\tilde{\nu}_{as}$ (IR) and the symmetric one $\tilde{\nu}_s$ (Raman), cf. experimental section—suggest the type **A** bridging mode [10 (c)]. But, on the basis of geometrical considerations, the existence of the type **B** bridging modus also looks reasonable. The distance between the two palladium atoms along the same bisimine ligand was found to be about 815 pm [9 (b)]. Therefore, on the basis of structural data for the di-μ-azido-bis-[diazidopalladate(II)] anion [10 (d)], a coplanar arrangement of the two inner azido bridges in the type **A** mode is not possible and a final decision about this concerning **1f** has still to be taken. (For the three-atomic thiocyanato-bridges in **1e**, a strictly *antiparallel* orientation of not only the two μ-SCN structures connecting the palladium atoms, but also of the whole bridges to each other is assumed and in full agreement with the NMR data [8 (a)] of this tetranuclear Pd compound. Therefore, the four palladium atoms in each of these molecules do not form a rectangle as in the halogeno-bridged analogues **1b–d**, but a distorted quadrangle, because of the difference in the length of the Pd–S compared to the Pd–N bond. In contrast to these findings, an



1a-f, 2a-e

a: X = OAc
b: X = Cl
c: X = Br
d: X = I
e: X = SCN
f: X = N_3

R = $C_{12}H_{25}$

Figure 1. Molecular structures of the tetra-nuclear palladium organyls **1a–f** and **2a–e**.

isomeric composition is proved for the stilbenyl derivative **2e** by ^1H NMR decoupling experiments. The two resonances for the protons at the tris-(dodecyloxy)-substituted phenyl rings or at the imino functions in a ratio of about 1 : 0·42 support the presence of two isomers of similar high symmetry, most probably caused by the difference in orientation of the two Pd–(μ-SCN)$_2$–Pd units relative to each other.)

The thermotropic liquid crystalline properties of the pure disc-shaped tetranuclear palladium organyls **1** and **2** are summarized in table 1. The bent acetato-bridged derivatives **1a** and **2a** exhibit complex thermal behaviours; their phase transitions are non-reversible. Most probably, at least one of their phases seems to be of a liquid crystalline type. The structures of these phases are not yet known in detail. The planar pallado-discogens **1b–e** and **2c–e** are thermotropically mono-mesomorphic over very broad temperature ranges, whereas the chloro-bridged **2b** exhibits an additional high temperature mesophase, cf. table 1. It should be noted here that the mesophases of the two acetato-bridged derivatives **1a** and **2a** show no similarities to those of the halogeno- or thiocyanato-bridged members of both series. The new azido-bridged pallado-discogen **1f** exhibits a highly viscous mesophase with a non-defined, unchanged texture—similar to those of the D_{ob} phases of the other members of series **1**—

Table 1. Phase transition temperatures† (°C) and enthalpies† (kJ mol^{-1}) of the pure tetra-nuclear palladium organyls **1d–f** and **2d–f**; C, crystalline; D, discotic columnar; *M*, a highly viscous phase of as yet unknown type, *I*, isotropic.

Pd organyl	*X*	C			D			M			I	
1a [8(a),(c)]	OAc	●	71	(127·8)	●	114	(1·1)	●	≈230	(≈2)	●	dec.
b [8(a),(c)]	Cl	●	71	(86·7)	●	301	(45·7)	—			●	dec.
c [8(a),(c)]	Br	●	69	(111·5)	●	279	(28·3)	—			●	dec.
d [8(c)]	I	●	62	(111·5)	●	265	(11·3)	—			●	
e [8(a),(c)]	SCN	●	50	(128·7)	●	≈290		—			dec.‡	
f	NNN	●	60	(129·4)	●	87§	(8·7)	●	>150		dec.‡	
2a [8(b),(c)]	OAc	●	44	(32·3)	●	75	(8·1)	●	143	(2·7)	●	dec.
b [8(b),(c)]	Cl	●	125	(57·0)	●	242	(7·5)	●	260	(8·6)	●	dec.
c [8(b),(c)]	Br	●	126	(54·6)	●	242	(19·8)	—			●	dec.
d [8(b),(c)]	I	●	99	(65·2)	●	237	(15·0)	—			●	dec.
e [8(c)]	SCN	●	≈54¶		●	>240		—			dec.‡	

† Mettler TA 3000/DSC-30 S; on heating at 1 K min^{-1} (**1a**) or 5 K min^{-1} (**1b–f, 2a–e**), respectively, for melting and 20 K min^{-1} for clearing processes. Strong decomposition takes place in the isotropic phases of **1a–f** and **2a–e**. The phase transition enthalpies are in parentheses.

‡ Because of strong decomposition this transition temperature could only be estimated (polarizing microscopy and DSC, heating rate 20 K min^{-1}).

§ This phase transition could only be detected by DSC. Polarizing microscopy shows only a decrease of the viscosity.

¶ This phase transition could only be detected by DSC. Polarizing microscopy shows only a slow softening of the sample up to about 190°C.

between 60°C (m.p.) and its decomposition temperature above 150°C. However, DSC measurements show an additional endothermic peak at 87°C on heating, most probably due to a reversible phase transition showing a significant supercooling of about 7 to 10 K; thus, this palladomesogen may be *di-mesomorphic*. X-ray diffraction studies on the halogeno- and the thiocyanato-bridged members **1b–e** and **2b–e** in their mesomorphic states [11] are in agreement with two-dimensional oblique arrangements of columns (D_{ob}) and not with a hexagonal arrangement as assumed in an earlier report [8(a)]. Within these columnar supramolecular structures the molecules are arranged in a liquid-like disordered fashion.

All members of the series **1** and **2** form charge transfer complexes with strong electron acceptors, for example, 2,4,7-trinitrofluorenone (TNF). A similar behaviour, combined with mesophase induction and/or stabilization, is known for dinuclear disc-shaped pallado-mesogens [12]. Mixtures of the planar palladium organyls **1b–f** or **2b–e** with TNF exhibit a highly viscous type of columnar mesophase, whereas analogous mixtures of the acetato-bridged members **1a** or **2a** are non-liquid crystalline. First X-ray results on the mesophase of such a CT complex of **1c** with TNF seem to indicate a change of the two-dimensional lattice of the columns from oblique (**1c**) to hexagonal (**1c**/TNF).

2.2. *Lyomesomorphic properties of the tetra-pallado-mesogens*

The planar members **1b–f** and **2b–e** of both families of these disc-shaped metallomesogens exhibit lyotropic mesophases with apolar organic solvents; however, no lyomesomorphism was found for the acetato-bridged palladium organyls **1a** and **2a**.

Contact preparations of the chloro-bridged tetranuclear palladium organyl **1b** with alkanes, such as, for example, heptane, pentadecane, or eicosane, clearly prove the formation of lyotropic mesophases. In areas of high concentrations of **1b**, a highly viscous mesophase similar to the thermotropic $D_{ob,d}$ phase is observed. With decreasing contents of **1b** *two* fluid phases exhibiting *both* schlieren textures and visible thermal fluctuations are even displayed. Further results of our studies of such contact preparations, as well as of solutions with defined concentrations of **1b** in pentadecane furnished the phase diagram shown in figure 2. Because of the larger temperature and concentration intervals of their lyomesophases, pentadecane was chosen for these studies. All phase transition temperatures were obtained by polarizing optical microscopy of samples sealed in cells, cf. experimental section.

It is interesting to note that in contact preparations with more polar solvents (for example, octanol, octadecanol, or stearic acid), only a viscous, most probably columnar mesophase is observed. On cooling such samples from the isotropic solution into their mesophase ranges, unusually shaped domains of this lyomesophase are developed over a broad biphasic region. Besides spherulitic domains—in part similar to some textural features of the thermotropic $D_{ob,d}$ phase—uniquely structured domains with elongated 'heads' and long, partially screwed 'tails' are formed, cf. figure 3(*a*).

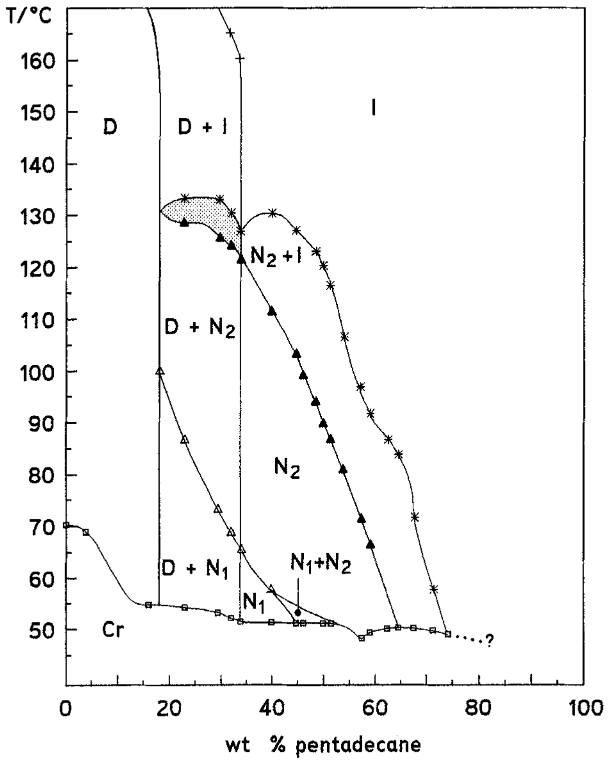
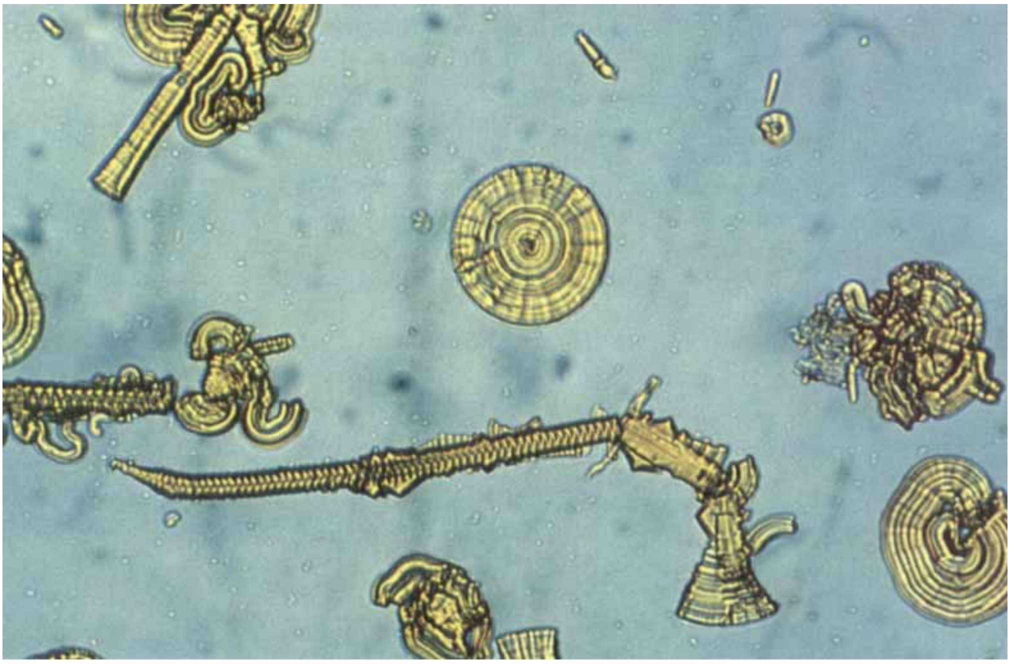
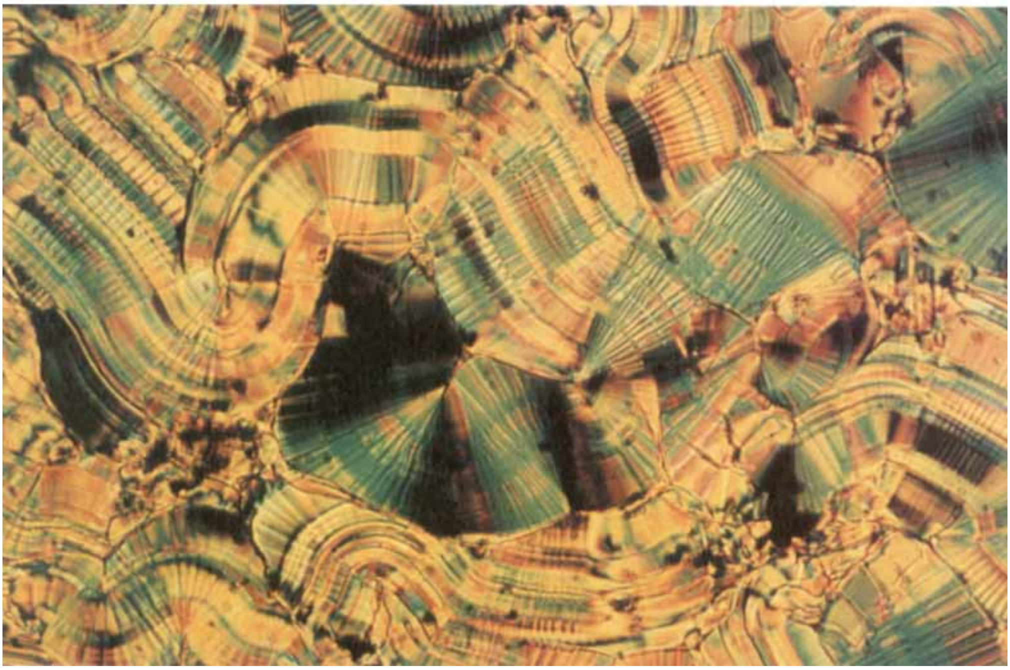


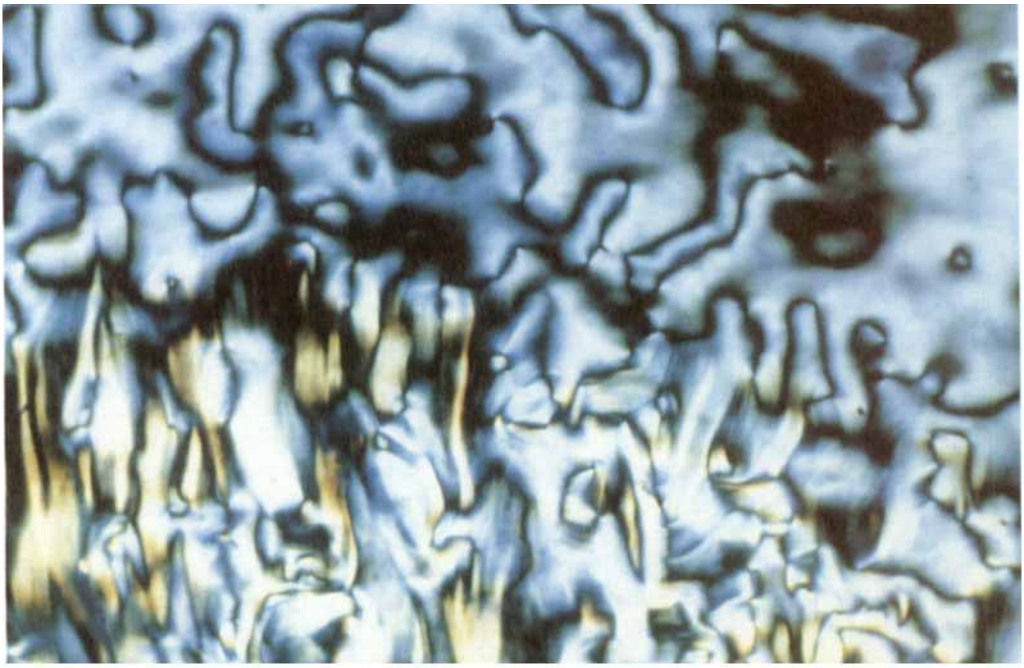
Figure 2. Simplified phase diagram of the tetra-nuclear palladium organyl **1b**/pentadecane system based on examinations of mixtures with defined solvent contents. The phase transition temperatures were obtained by polarizing microscopy on heating. C, crystalline; D, discotic columnar; N_1 and N_2, two different nematic type mesophases; and I, isotropic phase. The shaded area marks a *triphasic* region D–N_2–I. The multimorphism observed in the solid state is not represented.



(*a*)



(*b*)



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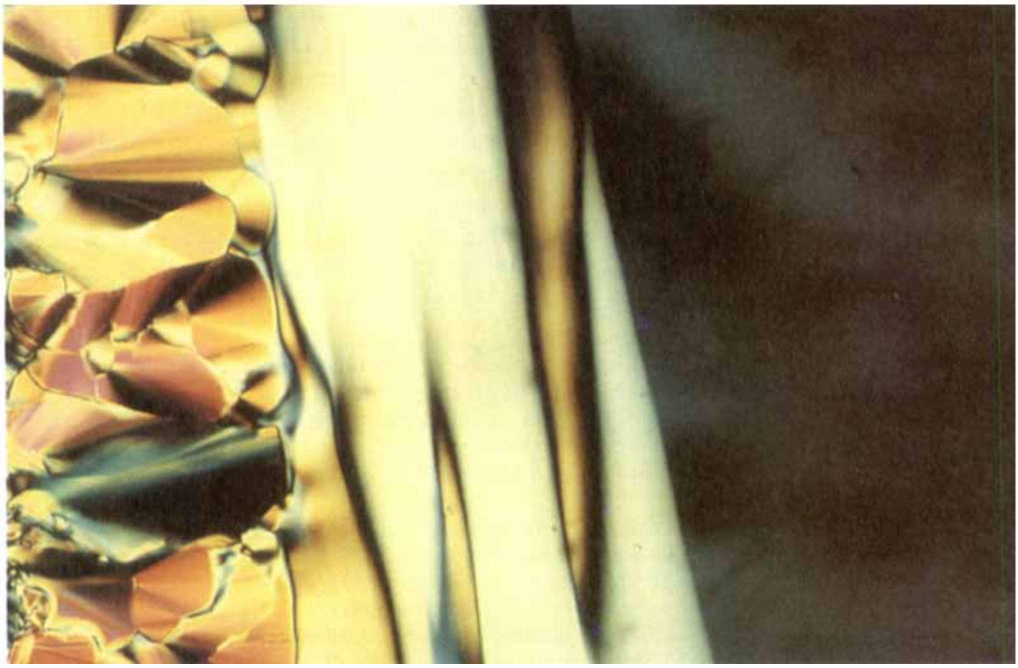

(*b*)

With pentadecane contents up to about 17 wt%, the tetranuclear chloro-bridged palladium organyl **1b** exhibits only a highly viscous columnar mesophase with mostly undefined textures similar to those of the thermotropic $D_{ob,d}$ phase, but sometimes containing focal-conic-like regions with spherulitic areas, cf. figure 3 (*b*). No phase boundaries are observed in this concentration range; therefore, we assume that a kind of swollen thermotropic D phase is formed there. With increasing pentadecane content, the melting temperature drops from 71°C for pure **1b** to about 55°C for a crystal solvate in this region. Mixtures containing more than about 20 wt% of pentadecane show phase separation on crystallization; the crystal solvate occurs along with the isotropic solvent. The observed multimorphism of the solid state is not depicted in figure 2.

Mixtures of **1b** with 17 to 32 wt% of pentadecane melt into a biphasic mesomorphic state; besides domains of the D phase, areas with schlieren texture and visible thermal fluctuations are observed. On further heating, these nematic areas show an abrupt and reversible change in their texture, most probably due to a phase transition from the low temperature nematic phase (preliminary notation N_1) to a different high temperature N_2 phase. The $N_1 \rightarrow N_2$ transition temperature depends strongly on the solvent content of the samples and decreases from 98°C to about 64°C. In this concentration range, the clearing of the N_2 phase occurs at about 130°C over wide biphasic intervals, whereas the D phase domains remain until temperatures above 160°C; thus, a triphasic (shaded) area D–N_2–I results in the phase diagram, cf. figure 2. This behaviour is very unusual for a binary mesomorphic system and may indicate a non-equilibrium state in terms of thermodynamics. Even under very careful conditions of observation and with an optimized experimental set-up, this phenomenon could result from slight temperature and concentration gradients in the samples sealed in sandwich cells.

Samples of **1b** containing more than 32 wt% solvent only display nematic mesomorphic behaviour. Up to about 40 wt%, sharp $N_1 \rightarrow N_2$ transitions are observed (on cooling), and a further increase in the pentadecane content leads to a biphasic region of coexistence between both nematic phases, while from 45 to about 53 wt%, only biphasic behaviour $N_1 + N_2$ is found below the N_2 phase. Heating mixtures of **1b** with 53 to 65 wt% pentadecane over their melting temperatures leads to the observation of just the N_2 phase; on further increase of the solvent content, biphasic behaviour (N_2 + I) and finally (> 75 wt%) just isotropic solutions are observed.

The clearing process of the N_2 phase always occurs via wide biphasic temperature intervals preventing successful DSC measurements. It should be noted that the clearing temperatures of the N_2 phase show two distinct maxima at about 130°C each, cf. figure 2 in the triphasic area of coexistence with the D and the isotropic phase, one at pentadecane concentrations of 25 to about 32 wt% and a second around 40 wt%.

Figure 3. Textures of the highly viscous, most probably columnar lyomesophases exhibited by mixtures of the tetranuclear palladium organyl **1b** with organic solvents: (*a*) spherulitic and unusually shaped elongated domains in a contact preparation of the chloro-bridged **1b** with stearic acid at 81°C on cooling from the isotropic liquid, without polarizer; (*b*) focal-conic-like texture of the chloro-bridged **1b** with 30 wt% pentadecane at 50°C on cooling from the isotropic phase.

Figure 4. Textures of the two nematic lyomesophases N_1 and N_2 of the chloro-bridged tetranuclear palladomesogen **1b** with pentadecane: (*a*) transition from the N_2 (upper part) into the N_1 phase (lower part of this picture) in a mixture of **1b** with 40 wt% pentadecane at about 60°C; (*b*) phase sequence (f.l.t.r.) discotic columnar (D)–N_1–N_2 of a 60 wt% mixture of **1b** with pentadecane at 58°C on cooling in an open sandwich cell with an undulating micro-structure surface of SiO_x evaporated on an angle of 60°; concentration gradient obtained by evaporation of the solvent.

All phase transitions depicted in figure 2 are reversible and show remarkable supercooling effects of 5 to 10 K. In order to answer the question as whether the textural changes within the nematic state of this binary system are connected with a phase transition, further textural and thermoanalytical studies were performed on mixtures of **1b** with 40 to 45 wt% of pentadecane that show sharp transition temperatures. The high temperature N_2 phase exhibits a characteristic schlieren texture with only a significant small number of disclinations. The nematic character of this phase is clearly proved by the visible thermal fluctuations at elevated temperatures. On heating, the transition into the isotropic state occurs via a broad biphasic temperature range characterized by a reticulated texture caused by the isotropic domains and described earlier for aqueous chromonic lyomesogens near the phase transition $N_{chr} \rightarrow I$ [6 (d)]. On cooling from the isotropic phase, the N_2 phase first occurs as small droplets. It is important to note that the textural features of the N_2 phase depend on the thermal history of the sample. For example, only on cooling at small rates, for example, 1 K/min, a microdomain texture with a remarkably large number of defects is exhibited; a similar type of texture is reported for aqueous nematic solutions of caesium perfluoro-octanoate [13]. A further decrease in the temperature or use of high cooling rates leads to typical schlieren textures with mostly $\pm 1/2$ singularities characterized by two dark brushes. The thermal fluctuations are of a remarkable strength for a lyotropic system and are comparable to those of thermotropic nematic discotic (N_D) phases, for example, of disc-shaped multiyne nematogens [14], or to those of charge transfer induced nematic columnar (N_c) ones [15].

The transition from this N_2 in the N_1 phase on cooling is indicated by the occurrence of narrow parallel lines partially disturbing the schlieren texture, cf. figure 4 (*a*). At the transition temperature $N_2 \rightarrow N_1$, these bars are nearly perpendicular to the phase boundaries caused by slight temperature or concentration inhomogeneities in such samples of defined composition. Furthermore, in contact preparations they are more or less parallel to the concentration gradient. But, more significant than those textural changes, cf. figure 4 (*d*), is the strong and abrupt *increase* in the thermal fluctuations on *cooling* from the N_2 into the N_1 phase. Usually, the thermal fluctuations of nematic phases *increase* slowly with *rising* temperature. It should be emphasized that the optical impression of these fluctuations in the N_1 phase is 'anisotropic', reminding on a flow directed parallel to the bars.

No DSC peaks connected with the textural change were found, therefore; if there is a phase transition in terms of thermodynamical physics, the transition enthalpy seems to be very small.

But, the textural changes at the $N_1 \rightarrow N_2$ transition are reversible over repeated heating/cooling cycles, with a supercooling of up to 4 K at a rate of $2\,\mathrm{K\,min^{-1}}$. In addition, the relatively sharp transition temperatures of samples of **1b** containing for example 40 wt% pentadecane are nearly independent of the different orientations of both nematic phases obtained by treatments of the glass surfaces of the cells. Especially in cells with undulating microstructured surfaces of SiO_x evaporated on at an angle of 60°, the phase transition becomes obvious, because the directions of the planar oriented optical axes of these two nematic phases form an angle of about 33°, see figure 4 (*b*).

In order to answer the question whether one or both of the nematic lyomesophases of the **1b**/pentadecane system are built up by *columnar aggregates*, UV/VIS spectrometric measurements were performed on diluted isotropic, as well as on different nematic solutions. The spectrum of a 0·07 wt% solution of **1b** in pentadecane at 65°C shows two significant absorption maxima at 349 nm and 412 nm. Due to the high dilution, a more or less mono-disperse distribution of the molecules in this solution is assumed. An increase in the amounts of dissolved **1b** leads to a remarkable *bathochromic* shift of the maximum at longer wavelength, but has nearly no influence on the other maximum. A 40 wt% solution at 65°C in the N_2 phase, for example, exhibits these maxima at 352 nm and 440 nm, respectively. A further increase in the concentration of **1b** up to 55 wt% at the same temperature (N_2 phase) alters only the latter maximum to 467 nm—these values remain unchanged on cooling the sample down to 50°C into the N_1 phase. Such a strong bathochromic shift of long wavelength absorption maxima usually indicates the formation of molecular aggregates, here most probably columnar ones [16]. Thus, these first results may indicate a columnar structure for *both* nematic lyomesophases in this system.

It is interesting to note that the lyomesomorphism derived from contact preparations of these planar tetranuclear pallado-mesogens **1b–f** and **2b–e** strongly depends on the type of bridging group *X* and the length of the rigid spacer group. In addition, the formation of nematic lyomesophases is extended by charge transfer interactions with, for example, TNF as electron acceptor. Our first results of polarizing optical microscopy studies in this respect on contact preparations are summarized in table 2. In general, the contact preparations of these disc-shaped compounds with organic solvents show neither a distinct maximum in the clearing temperature of the lyotropic nematic phase nor the biphasic behaviour depicted in figure 2 for the **1b**/pentadecane system. The contact method simply yields the usual type of diagram without the maxima of the transition curves of the nematic phases. The maximum clearing temperature $T_{N\rightarrow I,\mathrm{max.}}$ of the N_2 phase of about 130°C and the triple-point temperature $T_{D-N_1-N_2}$ around 72°C determined for contact preparations of **1b** with pentadecane correspond roughly to the data at the border of the biphasic areas $D+N_2$ and $D+N_1$, respectively, to the N phases given in figure 2. It should be emphasized that the data summarized in table 2 are only lower limits for these temperatures because of the difficulties arising with such contact mixtures, for example, the volatility of the solvent, the decomposition of the samples at high temperatures, the determination of biphasic regions, and, for the charge transfer complexes, the strong concentration gradients in ternary contact zones.

A similar phase behaviour, but with a maximum clearing temperature $T_{N\rightarrow I,\mathrm{max.}}$ of the N_2 phase of about 95°C and a triple-point temperature $T_{D-N_1-N_2}$ of 67°C is also observed in contact preparations of the bromo-bridged **1c** with pentadecane. In contrast to these findings, only *one* nematic phase with a schlieren texture (similar to that of the N_2 phase) is observed up to about 211°C in the system pentadecane/**1e** with thiocyanate as the bridging group. On the other hand, no nematic phase but only a highly viscous columnar phase could be detected in contact preparations of the iodo- and the azido-bridged members **1d** and **1f**, respectively, with apolar organic solvents, for example, pentadecane, heptane or benzene. The elongation of the rigid spacer moiety in series **2**, in comparison with the phenyl spacer in **1b–f**, also disfavours the formation of lyotropic nematic phases; only the chloro- and the iodo-bridged derivatives **2b** and **d** show just one N phase each in contact preparations with pentadecane up to 132°C and 94°C, respectively. The other members of series **2** in such mixtures exhibit only a columnar phase similar to the thermotropic one. In the case of the thiocyanato-bridged pallado-mesogen **2e**, there might be an additional mesophase M conspicuous by its small birefringence and high viscosity. It should be noted here that due to the difficulties in obtaining well defined textures by the contact method, the existence of polymesomorphism in the highly viscous areas preliminarily assigned to D phases can also not be excluded for the systems studied here.

Table 2. Lyotropic phase behaviour of the tetra-nuclear palladium organyls **1b–f** and **2b–e** (upper part), as well as of their charge transfer complexes with 2,4,7-trinitrofluorenone (TNF) (lower part) in pentadecane solutions based on contact preparations; D, discotic columnar; M, most probably a highly viscous mesophase of unknown structure; N, nematic; and I, isotropic phase; $T_{D-N_1-N_2}$, triple-point temperature (D–N_1–N_2); and $T_{N\to I,max}$, maximum clearing temperature of the nematic phase.

Pd organyl	X	TNF	Lyomesomorphism	$T_{D-N_1-N_2}$/°C	$T_{N\to I,max}$/°C
1b	Cl	–	D, N_1 and N_2	72	130
c	Br	–	D, N_1 and N_2	69	95
d	I	–	D, no N phase	—	—
e	SCN	–	D, N	—	211
f	NNN	–	D, no N phase	—	—
2b	Cl	–	D, N	—	132
c	Br	–	D, no N phase	—	—
d	I	–	D, N	—	94
e	SCN	–	D, M, no N phase	—	—
1b	Cl	+	D, N	—	146
c	Br	+	D, N	—	105
d	I	+	D, N	—	152
e	SCN	+	D, N	—	220
f	NNN	+	D, N	—	135
2b	Cl	+	D, N	—	152
c	Br	+	D, N	—	168
d	I	+	D, N	—	172
e	SCN	+	D, M, no N phase	—	—

But, preliminary studies on the *ternary* systems of the planar pallado-discogens **1b–f** and **2b–d** each mixed with 2,4,7-trinitrofluorenone (TNF) *and* pentadecane—also prepared by the contact method—prove the stabilization or even induction of one nematic lyomesophase, cf. table 2. Only the thiocyanato-bridged palladium organyl **2e** shows no nematic behaviour in the ternary system, but a phase sequence similar to that one observed without TNF. In addition, we observed *lyotropic nematic cholesteric* (N*) *properties* for an equimolar charge transfer complex of **1b** with (−)-2-(2,4,5,7-tetranitro-9-fluorenylidenaminooxy)propionic acid ((−)-TAPA) in contact preparations with pentadecane.

3. Conclusions and prospects

Based on the results presented, a complex lyomesomorphism of the disc-shaped tetranuclear palladium organyls of series **1** and **2** with apolar organic solvents, for example, pentadecane, has been established, including the formation of nematic phases. The textural studies of the binary systems of the chloro- and bromo-bridged pallado-mesogens **1b** and **1c** with pentadecane as a solvent indicate the formation of *two different* nematic lyomesophases, each with a reversible transition between them. Up to now, this phase behaviour was only known for aqueous micellar systems showing a transition from an N_c (built up by rod-shaped micelles) to an N_L phase (composed of disc-like aggregates) [17]. However, the structures of the basic units of the two nematic phases of the palladium organyls **1b** and **c** in pentadecane solutions are not yet known in detail. The UV/VIS spectrometric measurements seem to indicate the existence of molecular aggregates in both. First results of X-ray scattering measurements [18] on these two nematic lyomesophases show only as broad halos for the N_1 and N_2 phases, indicating the absence of a long range positional order.

A columnar model is also supported by the fact of the stabilization or induction of a nematic lyomesophase in *ternary* systems containing a strong electron acceptor (for example, TNF) together with a tetranuclear palladium organyl of series **1** or **2** and pentadecane as solvent, cf. table 2. Charge transfer interactions between disc-shaped electron donors with, for example, TNF as acceptor are known to favour the formation of columns based on intercalated TNF molecules, resulting in stabilizations or inductions of thermotropic mesophases [15]. But, recently also, the stabilization of the thermotropic nematic discotic type of mesophase of dinuclear palladium organyls by TNF was found [12]. Thus, a nematic columnar nature for both N phases may be assumed. However, a nematic discotic type similar to the thermotropic N_D phase, at least for the N_2 phase, cannot be excluded. Further studies on the structures and properties of such lyomesophases of disc-shaped compounds in apolar organic solvents, especially those of the nematic kind, are in progress.

In whatever manner, the occurrence of nematic properties for the members of series **1** and **2** in solutions strongly depends on (1) the type of bridging group *X*, most probably due to electronic reasons and different polarizabilities, (2) the length of the rigid spacer moiety, and (3) the type of solvent (for example, long alkanes favour nematic behaviour, whereas the presence of just one carboxy or hydroxy function in stearic acid or octadecanol leads only to a highly viscous columnar phase).

In our opinion, the results presented here, in the context of other recent reports on mesophase inductions/stabilizations by charge transfer [12, 15] and dipole–dipole [19] interactions, allow some general remarks to be made about the mesomorphic aggregation modes of disc-shaped molecules. The self-organization into supramolecular mesomorphic structures of such discotic compounds can widely be modified or even initiated by addition of *non-liquid crystalline* dopants with a suitable interaction profile.

(1) An increase of the 'core to core' interaction caused, for example, by intercalation of electron acceptor molecules (for examples, TNF), favours the formation of columnar structures in such charge transfer complexes. These columns usually aggregate on a two-dimensional lattice resulting in the formation of highly ordered, mostly hexagonal columnar phases (D_{ho}). But, if the association of these columns is disturbed by steric factors, a nematic columnar phase is formed. Furthermore, in CT complexes of nematic discotic dinuclear pallado-mesogens, even the formation of columns (depending on their bridging group) seems to be restrained leading to a stabilization of the N_D phase instead [12].

(2) As reported here, an extension of the aliphatic periphery by addition of apolar organic solvents seems to favour less ordered mesophases, mostly of nematic types. A similar behaviour was observed in mixtures (contact method) of the thermotropic mono-mesomorphic 4-alkyl-substituted biphenylethynyl multi-ynes (D phase) with eicosane, giving a nematic discotic (N_D) phase [8 (c)]. In this connection, a disc-shaped derivative of benzenehexamine exhibiting a mesophase of hexagonal structure and a nematic phase in various lipophilic solvents [7 (a)]—instead of a crystalline one—should also be mentioned, as well as the

observation of a nematic columnar (N_C) phase in mixtures of rhodium(II) or copper(II) carboxylates with apolar organic solvents [7 (b)]. In the latter example, the nematic type of mesophase is also observed thermotropically in mixtures of two derivatives different in their chain lengths. Beside these results on N_C phases in binary systems, one example of a pure compound is also known [20].

Therefore, the types of modification of the mesomorphic self-aggregation of disc- or lath-like molecules mentioned above should increase the interest in such mesogens and could contribute to the improvement of our knowledge of liquid crystalline structures, closing the gap between 'rods' and 'discs'. Taking into account, the great number of possible stacking modes of disc-shaped molecules within a column (for example, ordered, disordered, tilted) and the association types with different ranges of order imaginable for these aggregates, further new types of mesophase can be anticipated. Moreover, nematic phases built up by columnar aggregates of disc-shaped molecules could be promising for designing biaxial nematic phases by varying their length.

Studies on such binary systems seem to be of great importance for the classification of phase types and for the theory of liquid crystals.

4. Experimental

4.1. *The synthesis of the new tetranuclear palladium organyls*

The characterizations of the new compounds presented here are based on correct elemental analyses and on various spectroscopic data, for example, ^1H NMR (Bruker WH 400, $CDCl_3$), ^{13}C NMR (Bruker AM 270, $CDCl_3$), IR (Beckmann 9, CCl_4). Furthermore, we give the description of the new compound **1f**, as well as of **1d**, **2a**, and **2e**, three analogues only discussed in earlier papers [8 (b), (c)]; their phase transition data are compiled in table 1. Only structurally relevant data for these four compounds are given, see below.

$^1L = N,N'$-Bis[2,3,4-tris-(dodecyloxy)phenylmethylidene]-1,4-diaminobenzene.
$^2L = N,N'$-Bis[2,3,4-tris-(dodecyloxy)phenylmethylidene]-4,4′-diaminostilbene.

4.1.1. *The tetranuclear palladium compounds* **1d** *and* **f**

The iodo- and the azido-bridged palladium organyls **1d** and **f** were prepared from their chloro-bridged analogue **1b** [8 (a)] by simple exchange reactions with lithium iodide or sodium azide, respectively, in dichloromethane/acetone under argon at room temperature (**1d**: 0·35 mmol **1b**, 20 mmol LiI, 250 ml CH_2Cl_2, 50 ml acetone, for 8 days; **1f**: 0·20 mmol **1b**, 32 mmol NaN_3, 100 ml CH_2Cl_2, 50 ml acetone for 6 days). After filtration and removal of the solvents under reduced pressure, the crude products were purified by recrystallization from dichloromethane/acetone.

$Pd_4{}^1L_2(\mu-I)_4$ (**1d**), $C_{184}H_{316}N_4O_{12}Pd_4I_4$ (3709·8), yield 90 per cent, yellow orange crystals. ^1H NMR: $\delta = 8{\cdot}13$ (s; 4 HC=N), 7·16, 7·09 (2s; 8 and 4 aromatic hydrogens, respectively), 4·11, 4·10, 3·87 (3t, $J \approx 7$, 6·5, and 7 Hz; 4 OCH_2 groups each), 1·84, 1·72, 1·67 (3tt; $J \approx 7$ Hz each; 4 β-CH_2 groups each). ^{13}C NMR: $\delta = 172{\cdot}20$ (d; 4 CH=N), 156·80, 155·61, 152·93, 148·91, 137·49, 133·30 (6s; 6 types of quaternary aromatic carbon), 124·15, 117·58 (2d; aromatic CH situations), 74·68, 73·66, 68·88 (3t; 3 types of OCH_2 group).

$Pd_4{}^1L_2(\mu-N_3)_4$ (**1f**), $C_{184}H_{316}N_{16}O_{12}Pd_4$ (3370·3), yield 89 per cent, yellow orange microcrystalline solid. ^1H NMR: $\delta = 7{\cdot}95$ (s; 4 HC=N), 7·26, 6·57 (2s; 8 and 4 aromatic hydrogens, respectively), 4·14, 3·88, (2t; $J \approx 7$ Hz each; 8 and 4 OCH_2 groups, respectively), 1·82, 1·73, 1·68 (3tt; $J \approx 7$ Hz each; 4 β-CH_2 groups each). ^{13}C NMR: $\delta = 170{\cdot}90$ (d; 4 CH=N), 156·12, 152·68, 149·46, 148·02, 137·64, 131·97 (6s; 6 types of quaternary aromatic carbon), 123·62, 109·17 (2d; aromatic CH situations), 74·56, 73·68, 68·80 (3t; 3 types of OCH_2 group). Stretching vibrations of the azido-groups: $\tilde{\nu}_{as}(N_3) = 2076$ and $2059\,cm^{-1}$ (IR, CCl_4), $\tilde{\nu}_{as}(N_3) = 2075\,cm^{-1}$ and $\tilde{\nu}_s(N_3) = 1223\,cm^{-1}$ (Raman).

4.1.2. *The tetranuclear palladium compounds* **2a** and **e**

The *ortho*-palladation was carried out in a well-known manner [8(a),(b)] by stirring 2 mmol of the corresponding bisimine ligand ^2L [8(b)] with 1·33 mmol of palladium acetate $Pd_3(OAc)_6$ in 80 ml of glacial acetic acid at 70°C for 20 min under argon. After the complete evaporation of the acetic acid under reduced pressure, the crude product was dissolved in dichloromethane, filtered, and after removal of the solvent in vacuum, recrystallized from dichloromethane/ethanol, avoiding heating above 30°C. Based on the results of ^1H NMR decoupling experiments we assume a composition of two isomers for **2a** in a ratio of 1 : 1.

$Pd_4{}^2L_2(\mu-OAc)_4$ (**2a**), $C_{208}H_{340}N_4O_{20}Pd_4$ (3642·6), yield 64 per cent, orange solid. ^1H NMR: $\delta = 8{\cdot}00$, 7·99 (2s; ratio 1 : 1, 4 HC=N each), 7·12, 7·11, 6·99, 6·89 (4d; $J \approx 8{\cdot}5$ Hz each; ratio 1 : 1 : 1 : 1, aromatic hydrogens of the 4,4′-di-*N*-substituted stilbene units), 6·90, 6·86 (2s; ratio 1 : 1, 4 olefinic hydrogens each), 6·06, 6·05 (2s; ratio 1 : 1, 4 aromatic hydrogens each), 4·10–3·78, 3·81–3·69 (2m; OCH_2 groups), 2·28, 2·27 (2s; CH_3 of the isomeric acetato-bridges). ^{13}C NMR: $\delta = 181{\cdot}82$, 181·73, 180·01, 179·79, 179·58 (5s; isomeric bridging CH_3–$\underline{C}O_2$ groups), 168·84 (d; 4 CH=N), 155·07, 155·02, 152·08, 151·77, 151·70, 151·65, 151·61, 147·97, 147·92, 137·15, 135·79, 135·72, 131·67, 131·61 (14s; quaternary aromatic carbons), 128·17, 127·75, 126·42, 123·37, 123·27, 111·77 (6d; olefinic or aromatic CH situations), 74·60, 74·55, 68·57 (3t; 3 types of OCH_2 groups).

The thiocyanato-derivative **2e** was prepared from its chloro-bridged analogue **2b** [8(b),(c)] (0·36 mmol) by a simple exchange reaction with potassium thiocyanate (36 mmol) in dichloromethane/acetone (150/50 ml) under argon at room temperature over a period of 7 d. After filtration and removal of the solvent under reduced pressure, the crude product was purified by recrystallization from dichloromethane/acetone. Based on the results of ^1H NMR decoupling experiments, we assume a composition of two isomers for **2e** in a ratio of 1 : 0·42.

$Pd_4{}^2L_2(\mu\text{-}SCN)_4$ (**2e**), $C_{204}H_{328}N_8O_{12}Pd_4S_4$ (3638·8), yield 65 per cent, brown micro-crystalline solid. ^1H NMR: $\delta = 8{\cdot}16$, 8·15, 8·02, 8·00 (4s; ratio 1 : 0·42 : 0·42 : 1, HC=N), 7·47, 7·46, 7·27, 7·07 (4d, $J \approx 8{\cdot}5$, and 8 Hz; aromatic hydrogens of the 4,4′-di-*N*-substituted stilbene units), 7·07 (s; olefinic hydrogens) 6·67, 6·66, 6·23, 6·21 (4s; ratio 1 : 0·42 : 0·42 : 1, aromatic hydrogens), 4·18–4·00, 3·92–3·81 (2m; OCH_2 groups). ^{13}C NMR: $\delta = 176{\cdot}48$, 170·72 (2d; CH=N), 157·18, 155·96, 155·50, 152·98, 152·47, 150·19, 149·18, 148·70, 137·81, 136·41, 136·05, 133·75, 131·62, 127·22, 126·93 (15s; quaternary aromatic carbons and SCN groups), 128·45, 127·69, 127·44, 126·75, 126·70, 123·43, 123·34, 123·20, 114·08, 111·95 (10d; olefinic and aromatic CH situations), 74·64, 73·69, 73·64, 69·00, 68·74 (5t; OCH_2 groups). IR (CCl_4): $\tilde{\nu}_{SCN} = 2165$, 2150 and $2145\,cm^{-1}$.

4.2. *The preparation and studies of the mixtures*

Preparations of the various mixtures were carried out by mixing the chloro-bridged **1b** with the desired amounts of pentadecane. The solutions obtained were homogenized in an ultra-sound bath for 90 min at 80°C.

The thermal behaviour of these samples was investigated by:

(i) polarizing optical 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) in a Mettler TA 3000/DSC 30 S with GraphWare TA 72·5; heating rate 5 K min^{-1}.
(iii) Texture photographs were taken using a 24 × 36 mm microscope camera, Photoautomat Wild MPS 51.
(iv) Absorption spectra were measured in a UV/VIS Perkin–Elmer λ 19 Spectrophotometer in the temperature region of 40 to 65°C, using sandwich-cells as well as a 2·0 mm cuvette.

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