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On the nematic–nematic phase transition in mixtures composed of sheet-shaped palladium organyls and apolar organic solvents†

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The three sheet-shaped palladium organyls **1a–c** exhibit lyotropic nematic properties in apolar organic solvents. The occurrence of two nematic lyomesophases was verified by the investigation of the orientational properties of these liquid crystalline systems. In cells with obliquely deposited SiO_x layers, the director of the high temperature phase N_2 is aligned in a homogeneous, planar manner. In the low temperature phase N_1, a different orientational pattern is observed. The specific pattern type depends on the deposition conditions of the SiO_x layers. In samples homeotropically aligned in the N_2 phase, the director is tilted away from the cell normal after the transition into the N_1 phase. These changes of orientation are reversible. The experimental observations presented here support our proposed model for the structural change at the nematic–nematic phase transition.

1. Introduction

In the area of lyotropic mesomorphism, rod-type amphiphiles and lipids have been the classical objects of research for a long time. Typical ionic or non-ionic amphiphiles form supramolecular structures, e.g. micelles as the basic units of their lyomesophases. Today, the mesophase formation of sheet-like molecules in aqueous mixtures is a topic of increasing interest [2]. The mesomorphic properties of such mixtures are caused by the stacking of their flat molecules or aggregates in columns and by the nematic-like arrangement of these columnar units.

Contrary to that of aqueous mixtures, the study of the lyotropic behaviour of sheet-shaped compounds in apolar organic solvents is only in its early stages. Recently, lyotropic nematic properties were observed in systems composed of palladium organyls of type **1**, i.e. **1b** (see figure 1) and pentadecane [3(*a*)]. In a lyotropic system of this kind the appearance of *two* nematic phases was detected for the first time [4]. Similar observations are known only in aqueous lyotropic systems of rod-like molecules with a nematic polymorphism based on the change in the shape of the micelle [5].

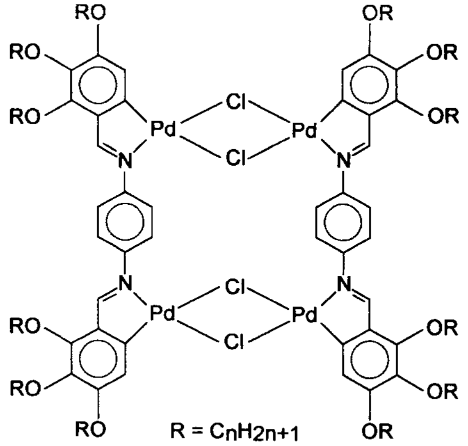

Figure 1. Molecular structure of the tetrapalladium organyl **1** ($R = C_nH_{2n+1}$) differently alkylated; **1a**: n = 10, **1b**: n = 12, **1c**: n = 14.

On heating, the low temperature nematic phase N_1 (see figure 2) is transformed into another (high temperature) nematic phase N_2 with an abrupt and reversible change in the texture. Moreover, the strong thermal fluctuations in the N_1 phase are drastically reduced at this transition. In experimental cells without surface alignment, the low temperature phase shows the typical

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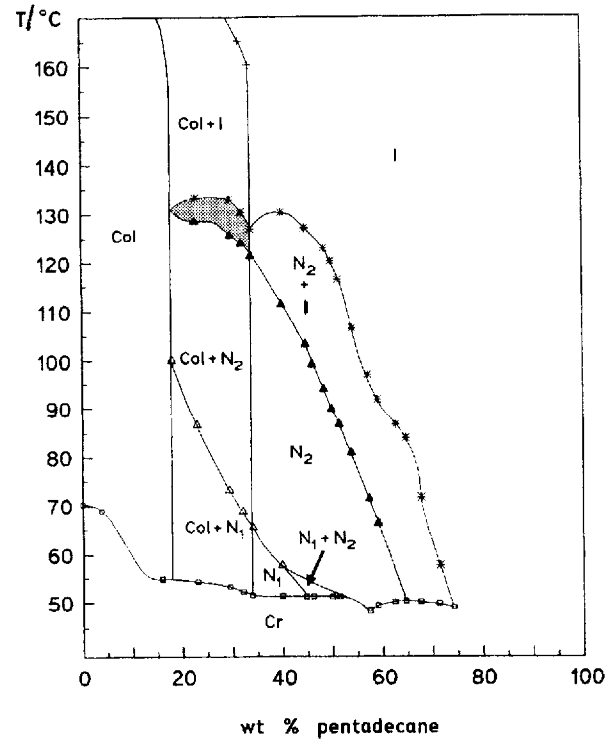

Figure 2. A simplified phase diagram of the tetrapalladium organyl **1b**/pentadecane system [3(*a*), 4, 14]; Cr: crystalline, Col: columnar, N_1 and N_2: two nematic mesophases, and I: isotropic. The shaded area marks a triphasic region Col–N_2–I.

schlieren texture with mostly ±1/2 singularities characterized by two dark brushes. In the N_2 phase, the occurrence of nearly parallel dark and bright bands is observed; these partially disturb the schlieren texture, figure 3(*a*). A model for the supramolecular construction of these two nematic lyomesophases was invented some time ago [6] and will be proved here.

In this paper, we present first results of our investigations on the orientational properties of the two types of nematic lyomesophases. Interfacial effects between the liquid crystalline systems and the walls of the experimental cell were used in this case to detect structural changes at the phase transition. To do this, orientational layers were deposited on the glass substrates of the cells. A homogeneous director orientation could be obtained in the high temperature (N_2) phase because of the specific interaction between the anisotropic surface layers and the molecules of the lyotropic systems. Information on the structural changes at the transition between these two lyomesophases can be derived from the change of director orientation at the phase transition. These data are the basis of a first structural model for our two nematic phases N_1 and N_2.

2. Experimental

2.1. *The syntheses of two new trialkyloxybenzaldehydes, their benzal derivatives from 1,4-diaminobenzene and the tetrapalladium macroheterocycle (series 1)*

2.1.1. *The two new 2,3,4-tri(alkyloxy)benzaldehydes*

Following earlier descriptions [3], their synthesis was carried out in two steps by etherification of pyrogallol (80 mmol) with the corresponding alkyl bromide and subsequent Vilsmeyer formylation on a 20 mmolar scale; overall yields 24 and 40%, respectively, after purification by column chromatography on silica gel, eluting with chloroform or with mixtures of chloroform and petroleum ether up to 70%.

Alkyl = decyl: colourless oil, $C_{37}H_{66}O_4$ (574·9); *alkyl = tetradecyl*: colourless powder, m.p. 52°C; $C_{49}H_{90}O_4$ (742·1); identical ^1H NMR data; solvent CCl_4: $\delta = 10{\cdot}27$ (s; CHO), 7·57, 6·71 (2 d, $J \approx 8{\cdot}5$ Hz; the two aromatic hydrogens), 4·16, 4·03, 3·97 (3 t, $J \approx 7$ Hz; 3 OCH_2 groups), 0·89 (t, $J \approx 7$ Hz; 3 CH_3 groups).

2.1.2. *The two new ligands, 1,4-benzene-bis(2,3,4-trialkoxybenzal)imines*

These ligands were easily obtained [3] by condensation of 1,4-diaminobenzene and 10 mmol of the benzaldehyde derivative; several crystallizations from petroleum ether and ethanol/chloroform mixtures yielded the pure products in yields between 71 and 83%.

Alkyl = decyl: yellow crystals, m.p. 50°C, $C_{80}H_{136}O_6N_2$ (1221·9); *alkyl = tetradecyl*: yellow crystals, m.p. 74°C, $C_{104}H_{184}O_6N_2$ (1558·5); identical ^1H NMR data; solvent CCl_4: $\delta = 8{\cdot}82$ (s; 2 hydrogens, HC=N), 7·87, 6·75 (2 d, $J \approx 8{\cdot}5$ Hz each; 2 aromatic hydrogens each), 7·24 (s; 4 aromatic hydrogens), 4·11, 4·03, 3·99 (3 t, $J \approx 7$ Hz each; 2 OCH_2 groups each), 0·89, 0·87 (4 and 2 t, respectively, $J \approx 7$ Hz each; 6 CH_3 groups); also nearly identical ^{13}C NMR data from $CDCl_3$ solutions around $\delta = 156{\cdot}32$, 154·21, 150·34, 141·23, 123·10 (5 s; 10 aromatic carbons), 155·46 (d, 2 CH=N), 122·30, 121·82, 108·54 (3 d; 2, 4, and 2 aromatic CH situations, respectively), 74·88, 73·68, 68·74 (3 t; 6 OCH_2 groups), 14·09 (q; 6 aliphatic carbons).

2.1.3. *The two new metallomesogens, tetra-μ-chlorobis{μ-[1,4-phenylenebis (nitrilomethylidene-3,4,5-trialkyloxy-2, 1-phenylene)]}tetrapalladium* (**1a**, **c**)

Both compounds were prepared in two steps from the above bisimine ligands (2 mmol) and 4 mmol of palladium acetate, $Pd_3(OAc)_6$, and by subsequent treatment of the respective red intermediate products, obtained in 42 or 72% yield, with a mixture of isopropanol and hydrochloric acid according to a description regarding the dodecyl homologue **1b** published elsewhere [3(*a*)]. The desired metallomesogenes **1a** and **c** were purified by several crystallizations from acetone/dichloromethane and isolated in 32 and 64% overall yield, respectively.

1a (*alkyl = decyl*): yellow powder, m.p. 55°C, cl. p. 316°C, $C_{160}H_{268}N_4O_{12}Pd_4Cl_4$ (3007·4); **1c** (*alkyl = tetradecyl*): yellow powder, m.p. 74°C, cl. p. 277°C, $C_{208}H_{364}N_4O_{12}Pd_4Cl_4$ (3680·6); identical ^1H NMR data; solvent CCl_4: $\delta = 8{\cdot}01$ (s, imine hydrogens), 7·20, 6·68 (2 s, 8 and 4 aromatic hydrogens, respectively), 4·12, 4·07, 3·86 (3 t, $J \approx 7$ Hz each; 4 OCH_2 groups each), 0·88, 0·87, 0·86 (3 t, $J \approx 7$ Hz each; 4 CH_3 groups each); also nearly identical ^{13}C NMR data; solvent $CDCl_3$ around $\delta = 171{\cdot}05$ (d; 4 CH=N), 155·57, 152·26, 150·75, 147·21, 137·59, 132·10 (6 s; 24 aromatic carbons), 123·80, 112·46 (2 d; 8 and 4 aromatic CH situations), 74·60, 73·68, 68·71 (3 t; 12 OCH_2 groups), 14·10 (q; 12 aliphatic carbons).

2.2. *The preparation of lyomesomorphic mixtures of the tetra(pallado)mesogens* **1a–c** *in apolar organic solvents*

Preparations of the various mixtures with commercially available apolar organic solvents (various alkanes) were carried out by mixing the organyls **1** with the desired amounts of solvent. The compositions obtained were homogenized in closed tubes by ultrasonication for 90 min at 80°C. The lyotropic behaviour (the appearance of different mesophases and the phase diagram) of these samples was investigated as described elsewhere [4].

2.3. *The preparation and investigation of the experimental cells*

The inner sides of the glass cells used for the study of the orientational properties were covered with transparent electrodes. SiO_x orientational layers were obliquely deposited onto the electrodes to induce a planar or a tilted alignment [7]. The deposition angles were 60° or 85° because for mesophases of rod-like molecules a planar orientation is usually induced by a 60° deposition, and a tilted one is known to result from a deposition at 85°. The thickness of the cells could be varied by different spacers in the range $d = 3 \sim 10\,\mu m$ and was measured interferometrically. The liquid crystalline mixtures were filled into the cells by capillary action at about 10 K above the transition temperature between the N_1 and N_2 phases.

We tried also to realize a homeotropic orientation of the liquid crystal director. Unfortunately, the well-known techniques for obtaining homeotropic alignment of thermotropic systems of rod-like molecules were not successful in the case of our mesophases. However, a homeotropic orientation of thermotropic systems of disc-shaped molecules was obtained some time ago with molecularly flat surfactants having six polar side functions [8]. In accordance with this approach, the glass substrates of the experimental cells for our lyotropic systems were treated by spin coating with the following solutions:

—mellitic acid, 1% by weight in water;
—hexahydroxytriphenylene, 0·25% in ethanol;
—hexaoctyloxytriphenylene, 0·25% in cyclohexane;
—hexadecyloxytriphenylene, 0·25% in cyclohexane.

The application of an electric field can support the homeotropic alignment in liquid crystals with positive dielectric anisotropy ($\Delta\varepsilon > 0$). Therefore, in some cases we applied an a.c. electric field (100 Hz, 40 V) to the cell electrodes during the filling process.

The investigations were performed using a hot stage and a microscope with crossed polarizers near the transition temperature between N_1 and N_2. In some cells an effect of flow alignment was detected through the presence of defect lines in the direction of the liquid crystal flow during the filling process. But the main alignment is caused by the orientational layers.

3. Results and discussion

3.1. *Lyotropic phase behaviour*

The three palladium organyls **1a–c** possess thermotropic and in apolar organic solvents also lyotropic mesomorphic properties. A simplified phase diagram of the system **1b**/pentadecane is shown in figure 2 [4]. It includes three basic lyomesomorphic areas: a kind of swollen thermotropic columnar phase, and two types of lyotropic nematic phase (N_1 and N_2). The columnar phase shows a fan-shaped texture which is similar to that of the thermotropic $Col_{ob,d}$ phase; see in this context our recently introduced new system of mesophase notation [9].

The occurrence of nematic lyomesophases has now also been studied for two more systems composed of the homologous tetrapalladium organyls **1a** or **1c** with shorter or longer alkyl groups, respectively, compared with those for **1b** [4], see figure 1, and apolar aliphatic solvents of different chain length. The results of this study are compiled in table 1. As it turns out, the

Table 1. The lyotropic nematic polymesomorphism of the homologous tetrapalladium organyls **1a–c** in alkanes of different length as observed in contact preparations; m = monotropic, e = enantiotropic.

	n in $R = C_nH_{2n+1}$ of **1a–c**		
Alkane	10 (**1a**)	12 (**1b**)	14 (**1c**)
Pentane	N_2	N_2	N_2
Hexane	N_2	N_2	N_2
Nonane	N_2	N_2	N_2
Decane	N_2N_1 (m)	N_2	N_2
Dodecane	N_2N_1 (e)	N_2N_1 (m)	N_2
Pentadecane	N_2N_1 (e)	N_2N_1 (e)	N_2N_1 (m)
Heptadecane	N_2N_1 (e)	N_2N_1 (e)	N_2N_1 (e)

appearance of the low temperature phase (N_1) reflects a very sensitive relation between the length of the alkane used and that of the alkoxy chains in **1**. In short chain alkanes, the high temperature phase N_2 is the only one observed. If both chain types are equal, a monotropic transition into the N_1 phase occurs. In longer alkanes reversible transitions between the two nematic phases take place. The broadest temperature range of N_1 is achieved for mixtures in which the solvent molecules are longer by three carbon atoms than the alkoxy chains in **1a–c**. Investigations of similar mixtures with bromo-bridged members of this family of palladomesogens **1** [3(*a*)] or with a tetraplatinum analogue [9] show a comparable lyotropic nematic polymesomorphism. These results indicate that the occurrence of two nematic phases is not restricted to a special case, but is rather a general phenomenon of the lyotropic systems discussed here.

3.2. *SiO_x orientational layers*

For the investigation of the orientational behaviour we used four experimental mixtures with well evolved nematic–nematic phase transitions. Their compositions and phase transition temperatures are given in table 2. The measurements were made 1 K below or above the transition temperature. At first, we discuss the behaviour of mixture III. In cells with 60° deposition of SiO_x ($d = 6\,\mu m$), the N_2 phase is homogeneously oriented. Conoscopic examination of the samples indicated a planar orientation of the optical axis perpendicular to the direction of SiO_x deposition [7]. The macroscopically observed direction of the optical axis can be described by a unit vector, the director **n**. The introduction of a λ-plate into the microscope induced a shift of the interference colour at the diagonal position of the sample. The observed colour change was identical to that expected for systems with negative optical anisotropy [10]. The cell thickness and the optical path difference ($\Gamma = \Delta n \times d$) measured by a rotary compensator yields a birefringence $\Delta n = -0{\cdot}0082$ (at $\lambda = 551$ nm). From symmetry considerations the optical axis can be assumed to be perpendicular to the plane of the spatial extension of the tetrapalladium organyl molecules. Therefore, the sheet-shaped molecules are arranged perpendicular to the walls of the cell. It is known that in the case of rod-like molecules, 60° SiO_x deposition yields a preferred direction on the glass substrates which is perpendicular to the deposition plane [7]. The sheet-shaped molecules are also aligned perpendicular to this direction.

On cooling the sample, the homogeneous planar orientation of N_2 splits at the transition temperature to the N_1 phase, for which two types of domain are present, see figures 3(*b*) and 3(*c*). The alignment inside the domains is, more or less, homogeneous. They are separated by defect lines at which the strong thermal fluctuations of N_1 can be observed. In well-aligned areas the fluctuations are less visible. The defect lines are mobile. Small domains formed at the transition disappear by continuous shortening of their perimeter; only large domains exist in the end. Conoscopic investigation of larger domains showed that the optical axis is again parallel to the cell surface, but is rotated with respect to the direction in N_2, see figure 4(*a*). The only difference between the two domain types is the direction of this rotation. In figures 3(*b*) and 3(*c*) the rotation angles θ of the first and second domain type are nearly $+33°$ and $-33°$, respectively. The value of these angles is not always constant, but varies by some degrees. In figure 3(*b*) the director of the N_2 phase is parallel to the polarizer. In the low temperature phase, the transmissions of both domains are equal because of the same absolute director deviation from the polarizer. A rotation of the sample between the crossed polarizers removes this equality, figure 3(*c*). The movable defect lines indicate that the director orientation in a domain is not absolutely fixed, but may change into the alignment of the other domain type. The deviation from the director direction in N_2 is the only constant value. In both domain types, the optical anisotropy is again negative. The birefringence is increased in comparison with the high temperature phase: $\Delta n = 0{\cdot}0118$.

Table 2. The compositions and phase transition temperatures of the four mixtures I–IV studied; n in $R = C_nH_{2n+1}$ of **1a–c**.

Mixture	n	Solvent	Phase transitions
I	10 (**1a**)	Tridecane (44·3 wt %)	Cr (39°C) N_1 (83°C) N_2 (116°C) $N_2 + I$
II	10 (**1a**)	Pentadecane (45 wt %)	Cr (42°C) N_1 (73°C) N_2 (106°C) $N_2 + I$
III	12 (**1b**)	Pentadecane (40 wt %)	Cr (52°C) N_1 (60°C) N_2 (112°C) $N_2 + I$
IV	14 (**1c**)	Heptadecane (40·8 wt %)	Cr (57°C) N_1 (59°C) N_2 (120°C) $N_2 + I$

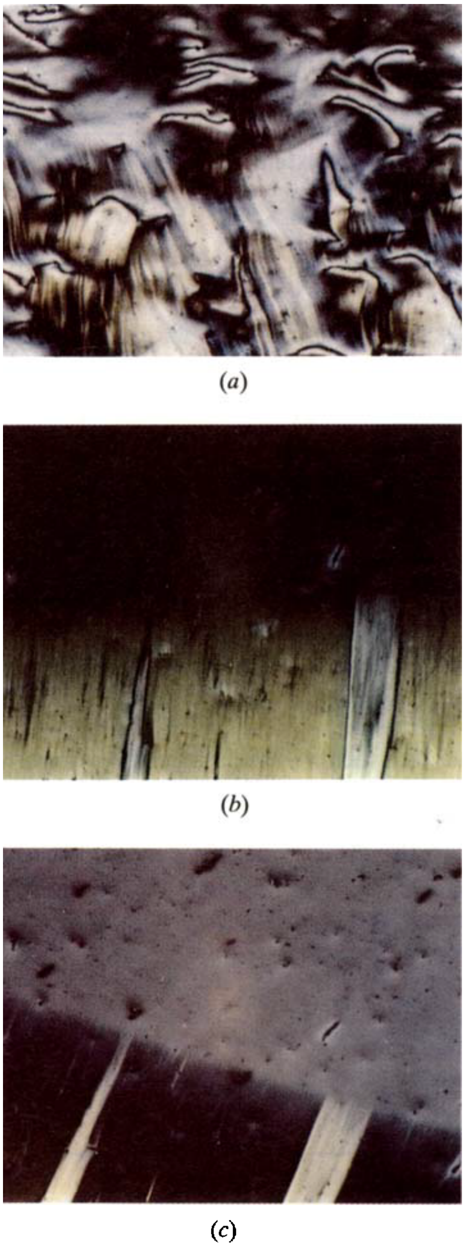

Figure 3. Textures of the two nematic lyomesophases of **1b** with 40 wt % pentadecane: transition from the N_2 (upper part) into the N_1 phase (lower part of the pictures) at 60°C; (*a*) the unoriented sample; (*b*) the sample with 60° deposition of SiO_x with the director in the N_2 phase parallel to the polarizer; (*c*) the same sample rotated between the crossed polarizers.

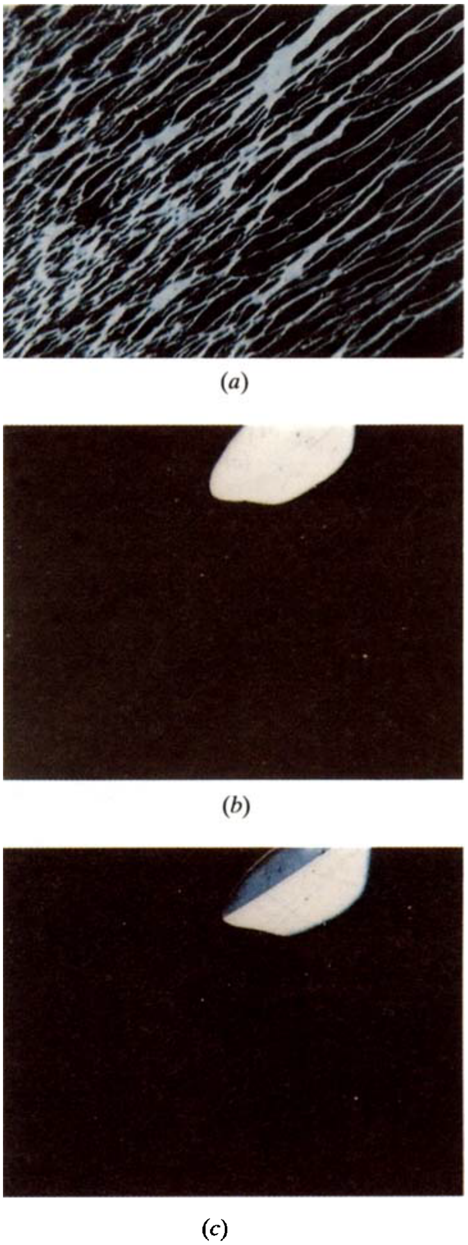

Figure 7. Spontaneous formation of the homeotropic alignment in a thin cell with 60° SiO_x (thickness $d=3{\cdot}7\,\mu m$): (*a*) the first appearence of homeotropic regions in the N_2 phase; (*b*) a small planar oriented region which is enclosed by the final homeotropic alignment in the cell; (*c*) the same area of the cell after the phase transition into the N_1 phase.

Figure 6. The homeotropic domain after the phase transition into the N_1 phase (upper left part of the picture) in a sample having hexaoctyloxytriphenylene coated glass surfaces and filled under an applied electric field.

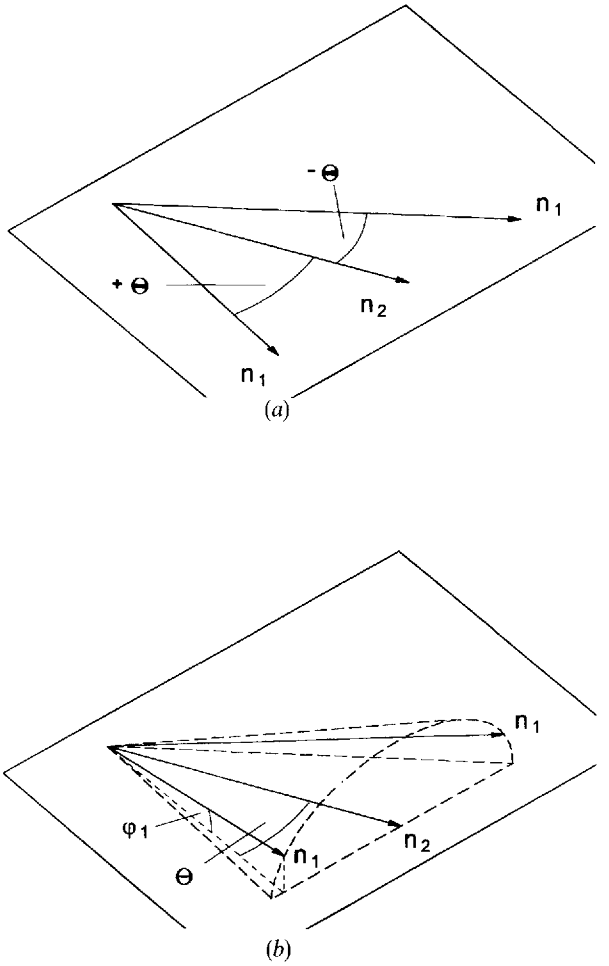

Figure 4. (*a*) Rotation of the director ($\mathbf{n}_1$) in the N_1 phase with respect to the director ($\mathbf{n}_2$) orientation in the N_2 phase for 60° SiO_x orientational layers, θ = rotation angle; (*b*) The tilt angle ϕ_1 and the rotation angle θ in the N_1 phase of mixtures II and IV (cf. table 2) for 85° SiO_x orientational layers.

Table 3. The orientational behaviour of the four mixtures I–IV of **1a–c**, cf. table 2; ψ = deposition angle of $SiO_{(x)}$; HOTP = hexaoctyloxytriphenylene; ϕ_1 and ϕ_2 = tilt angles in the two nematic phases N_1 and N_2, respectively; θ = rotation angle.

Oriental layer	Mixture	ϕ_1	ϕ_2	θ
$SiO_x(\psi = 60°)$	I	0°	0°	15°
	II	0°	0°	19°
	III	0°	0°	33°
	IV	0°	0°	37°
SiO_x ($\psi = 85°$)	I	25°–30°	0°	0°
	II	15°	0°	8°
	III	44°	0°	0°
	IV	~29°	0°	23°
HOTP	I	70°–80°	90°	—
	II	70°–80°	90°	—
	III	60°–70°	90°	—
	IV	65°–75°	90°	—

The other mixtures investigated show a similar behaviour. The only differences are the value of the rotation angle, which increases with increasing chain length (see table 3) and the birefringence. The change of Δn in mixture IV at the phase transition is shown in figure 5. Despite the continuous change of the birefringence, the phase transition seems to be of first order because of the strong increase with decreasing temperature. The slower increase near the transition temperature is probably connected with pretransitional phenomena which may also be responsible for the strong fluctuations in the N_1 phase.

Orientational layers deposited at 85° also induce a homogeneous planar alignment in the N_2 phase of mixture III. In contrast to the 60° layers, the optical axis is in the deposition plane. The measured birefringence ($\Delta n = 0{\cdot}0078$) agrees, within the limits of the experimental errors, with the value in the above case. The transition into the low temperature phase is only visible because strong fluctuations begin here. Conoscopic measurements show that the optical axis of the N_1 phase is tilted to the glass surface at $\phi_1 = 44°$. The alignment of the low temperature phase is similar to the orientational behaviour in mesophases of rod-like molecules. The director of these mesophases is also tilted to cell surfaces covered with 85° SiO_x layers. Measurement of the optical path difference yields an effective birefringence $\Delta n_{\mathrm{eff}} = \Delta n \times \cos^2 \phi$. If ϕ is taken into consideration, a birefringence of $\Delta n = -0{\cdot}0116$ results which again

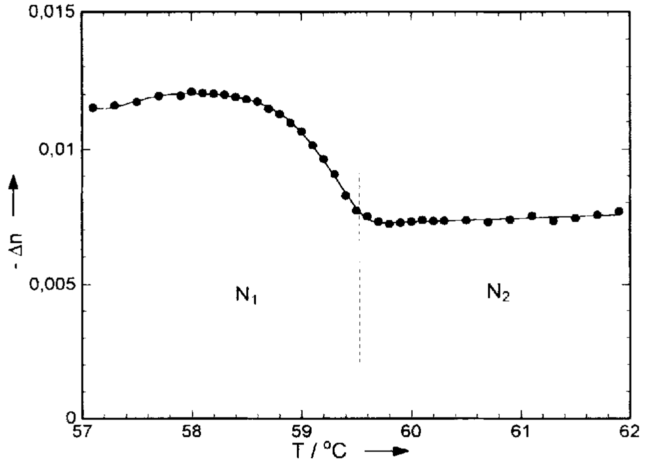

Figure 5. The change of birefringence at the phase transition in mixture IV (cf. table 2) measured in a cell with 60° SiO_x orientational layers.

agrees well with the 60° SiO_x case. Mixture I shows the same behaviour.

In mixtures II and IV, the orientation of the low temperature phase is characterized by the occurrence of two domain types with opposite directions of the director rotation with respect to the director in the N_2 phase, see figure 4(*b*). The picture is similar to the domain formation in cells with 60° SiO_x, but here the director is tilted out of the plane of the glass surface.

3.3. *Homeotropic alignment*

We start the discussion of the homeotropic alignment with mixture III again. In cells of thickness $d > 4\,\mu m$, none of the surfactants used induced a homeotropic orientation of the liquid crystal director; in all cases a planar flow alignment was observed. Application of the a.c. electric field during filling of cells, without surface preparation and having a thickness $d \geqslant 6\,\mu m$, was also not able to induce the homeotropic state in the N_1 or in the N_2 phase. One observes an inhomogeneous, tilted orientation with many defects (e.g. walls between areas with opposite tilt direction). The action of the electric field on the mesophases indicates that in both phases $\Delta\varepsilon > 0$. After switching off the field, the tilted orientational state relaxes into the planar state through nucleation and an increase of planar aligned domains. The same behaviour was observed on the application of the electric field to cells with a hexahydroxytriphenylene coating.

However, the simultaneous influence of an electric field and coating of the substrates with hexaoctyloxytriphenylene or hexadecyloxytriphenylene indeed induces domains of homeotropic orientation in the N_2 phase in cells with $d \sim 6\,\mu m$. Outside the domains, a planar orientation is initiated. The homeotropic domains are dark between crossed polarizers. After switching off the field, their area decreases slowly (during hours). The optical path difference measured in these domains is zero. At the transition (on cooling) into the N_1 phase, one observes a slight increase of the optical transmission. This increase is not constant over the area of a domain (see figure 6), and the transmission distribution changes on rotation of the sample between the polarizers. The measured optical path difference corresponds to a tilt of about 20°–30° with respect to the cell normal.

In very thin cells ($d < 4\,\mu m$) with 60° SiO_x orientational layers or without any surface preparation, one observes a spontaneous formation of the homeotropic alignment. During the filling process planar flow alignment takes place. If the flow stops, the formation of homeotropically aligned parts starts, see figure 7(*a*). Their area increases and, finally, the whole cell is homeotropically aligned, with the exception of small planar parts of the N_2 phase, see figure 7(*b*). At the phase transition, the transmission increases again. In figure 7(*c*) the phase change is visible by the orientational degeneration in the light planar part. The transmission increase in the dark part is too small to be demonstrated in a micrograph. It is constant over the cell area because the 60° SiO_x layer induces a defined direction for the tilt in the low temperature phase.

The behaviour of the other experimental mixtures in homeotropic cells is, in principle, the same as that discussed for mixture III. The measured tilt angles in the low temperature phase are given in table 3.

3.4. *Model for the structural change at the nematic–nematic phase transition*

The orientational behaviour observed in samples with planar or tilted alignment might be discussed in terms of special surface effects, instead of resulting from structural changes at the phase transition between two nematic phases. The conceivable degeneration of orientation would be similar to that investigated in liquid crystalline systems of rod-like molecules [11]. However, the birefringence measurements demonstrated the presence of a phase transition. Deuterium NMR studies [12], as well as investigations on the electrical conductivity [13] also indicate the presence of two nematic phases. Both phases have uniaxial symmetry; however, the experimental error is higher for the N_1 phase than for the N_2 phase [12].

On the basis of UV/VIS spectrometric and small angle X-ray scattering investigations, a columnar nature for the two nematic lyomesophases of **1** with apolar organic solvents may be assumed [4, 14]. The deuterium NMR investigations have shown that the orientational order of the apolar solvent in the N_2 phase is small and is consistent with the alkane being between the (short) columns of the tetrapalladium organyls rather than between the sheet-like molecules forming them [12]. In the N_2 phase, a possible model includes the stacking of the sheet-shaped palladium organyl molecules to give column-like aggregates without intracolumnar molecular order, and also without intercolumnar order between the aggregates. Similar aggregates are known as the basic units of lyotropic 'chromonic' phases in aqueous solutions of different compounds with sheet- or lath-like molecules [2].

On cooling into the low temperature N_1 phase, the orientation of the molecules of series **1** may change with respect to the axis of the aggregates, possibly due to a packing effect of their alkyloxy chains (see figure 8). Thereby, in the bulk of the sample the director can rotate in arbitrary directions. A possible local biaxiality in the low temperature phase is transformed in this way into the uniaxial behaviour of the whole sample. However, near the glass surfaces of the cells, the

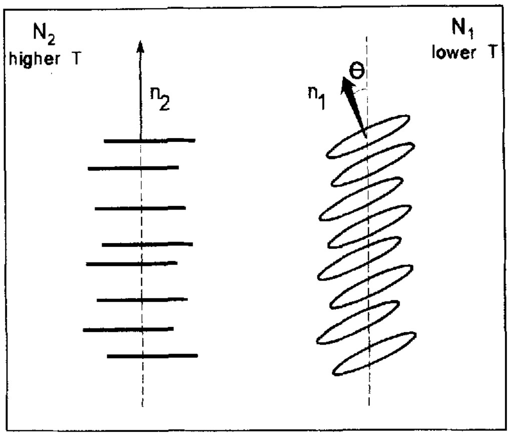

Figure 8. Schematic representations of the rigid cores of the tetrapalladium organyls **1a–c** in their N_1 and N_2 phases (side view).

interfacial forces restrict the arbitrary rotation. If one assumes that the column-like aggregates do not change their position at the phase transition, the observed director shift in our experiments is connected with the change in the molecular orientation with respect to the aggregate axis. Thereby, at the surface, the rotation in one aggregate should be correlated with the change in the neighbouring aggregates to build domains of equal orientation. Until now, such a type of tilted molecular organization has not been observed in chromonic-like phases. Our experiments with anisotropic orientational layers show that this tilted structure is present in the low temperature phase.

At the glass surface of the 60° SiO_x samples, there are only two directions which satisfy the surface condition of the perpendicular arrangement of the sheet-like molecules with respect to the cell walls, as well as the tilt of the molecules with respect to the columnar axis. These two directions correspond to the only two domain types observed in figures 3(*b*) and 3(*c*). The rotation angle θ is a measure for the molecular shift in the aggregates. In the N_2 phase, without the tilt of the molecules, a homogeneous alignment is possible. The column-like aggregates are oriented in that preferred direction in which rod-like molecules would also be aligned. In this sense the column axis plays the same role as the director in thermotropic systems of rod-like molecules, and the aggregate itself, as the basic unit of the lyotropic nematic phases, is the analogy to the molecule in the thermotropic nematic phase. The dimensions of these two types of basic units are, of course, very different. The optical axis, the direction of which is mainly defined by the spatial arrangement of the organyls **1**, deviates from the column axis in the N_1 phase. Because the orientation of the optical axis can be observed immediately, in our experiments, the term 'director' was used for this direction.

SiO_x layers deposited at 85° possess a strongly developed, anisotropic surface topography [7]. This is probably responsible for the tilted orientation in the low temperature phase. If the tilt angle ϕ_1 is of the same order as θ in the case of 60° SiO_x layers, a homogeneously tilted texture is realized. For smaller tilts (mixtures II and IV), a split into two domains (with a rotation in-plane of the surface) occurs as shown in figure 4(*b*). Because of this shift in two directions (in-plane and out-of-plane), the resulting director rotation is again of the same order as θ in the case of 60° SiO_x layers. In the N_2 phase the column-like aggregates with no relative tilt of the molecules are not sensitive to the strong surface topography; a mean, planar alignment is then found.

The study of the homeotropic state, in principle another orientational pattern derived by surfaces with essentially different properties, confirms the model discussed. The homeotropic orientation of the optical axis in the N_2 phase has to transform into a slightly tilted one at the transition into the N_1 phase, if the model of tetrapalladium organyl molecules tilted with respect to the columnar axis is correct. Exactly this behaviour was found experimentally. The increase of the transmission was not constant over the area of the samples due to the arbitrary direction of the tilt.

In conclusion, the experimental results are in agreement with our model [6] for the two intracolumnar modes of organization of sheet-like molecules. The two nematic lyomesophases were provisionally named N_1 and N_2. They could be included into one of the existing classification systems of lyotropic mesophases, e.g. so-called 'chromonics', previously described, however, only in aqueous solutions. Our two nematic lyomesophases N_1 and N_2 could be considered as an extension of the group of 'chromonic' systems: (1) the solvent can now also be of an apolar organic type and (2) 'chromonics' can now also be of a *tilted* build-up. The appearance of the low temperature phase N_1 is mainly defined by the relation between the length of the alkane and that of the alkoxy chains in **1**, and the transition from one nematic into the other nematic lyomesophase is possibly caused by a conformation change of the alkoxy chains. However, the possibility of realizing this N_1 phase is also connected with the structure of the core of the organyls. In systems with a different core structure, or in the presence of charge-transfer complexes, the N_2 phase is the only nematic phase which could be observed [4].

The length of the column-like aggregates is unknown at present. However, it might be possible to get some indication from an observation made during the filling process of the cells: in the N_2 phase the optical axis is parallel to the flow direction. If the basic units of this phase were single molecules of type **1** (mixed with the alkanes) or short column-like aggregates, the orientation of the optical axis should be, probably, perpendicular to the flow and parallel to the cell normal to minimize the effective viscosity. Hence, the length of the columns should be greater than the diameter of the tetrapalladium organyls to realize the observed behaviour. This corresponds to a flow of aggregates with their long axis parallel to the flow direction. The application of an electric field induces an inclination of the columns out of this direction. The effective cross-section with respect to the flow increases, and the flow velocity should decrease. Corresponding experiments have shown a drastic decrease of the flow velocity.

Further investigations are necessary to understand the mechanisms of the formation of the two nematic phases, as well as their structures. Studies on the behaviour of these nematic lyomesophases in electric fields are in progress.

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