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LYOMESOMORPHIC BEHAVIOUR OF SELECTED DI-PALLADIUM ORGANYLS IN HYDROCARBONS[1]

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Abstract The lyotropic phase behaviour of selected lath-like di-palladium organyls and of an almost linear one in mixtures with linear, saturated or cyclic, unsaturated hydrocarbons has been studied. The ratio of the length of the aliphatic chains of the metal complexes vs. the length of the respective solvent molecules appeared to be important for the mesomorphism of such binary mixtures. During this study it became clear that the formation of lyotropic phases is controlled in two ways: 1) by the thermomesomorphic behaviour of the pure material being preserved in apolar organic solvents used here or 2) by the influence such solvents have on the development of different architectures of them. As an example for one case of the first family X-ray data are included.
Beyond that, further details of a first case of lyotropic twisted nematic (N*) phase formation in a binary system composed of a non-chiral di-palladium organyl and a chiral hydrocarbon, (R)-(+)-limonene, are also reported.

INTRODUCTION

Geometric elements as for instance molecular shape, length, width, and thickness determine substantially the supramolecular arrangement of mesogenic molecules in their mesophases. Thus, *disc*-like octasubstituted metal complexes of phthalocyanine and porphyrin derivatives[2] or various other flat multi-metal organyls[3] spontaneously form *columns*, both in thermotropic and in lyotropic liquid-crystalline phases. *Rod*-like metallomesogens, however, mostly exhibit thermotropically *layered* kinds of phases,[4] whereas the *lamellar* or the *hexagonal* mode of building is typical for their lyotropic phases.[5]

We have already published data concerning the influence of the molecular structure (e.g., of the length of substituents and type of bridging or spacer groups) on the appearance of lyotropic phases in systems composed of *disc*-like **tetra**-metal organyls and apolar organic solvents (saturated hydrocarbons).[3]

The investigation discussed here is an extension of our ongoing interest in this particular type of structure-property relationship and deals with different types of **di**-palladium organyls, for instance, with the *lath*-(*twin*-)like chlorobridged, only *four* aliphatic substituents carrying di-palladium organyl **1** in solvents as mentioned above. Besides, we compare the lyomesomorphism of **1a-c** with the lyotropic phase behaviour of two other di-palladium organyls in identical media, in fact with **2** (slightly folded, possessing *five* hexylchalkogeno substituents) and **3**, almost *linear* in shape and equipped with *six* long alkyloxy chains.

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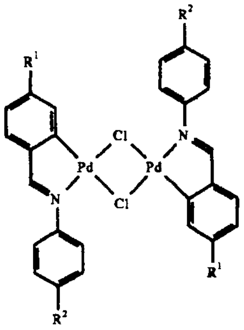
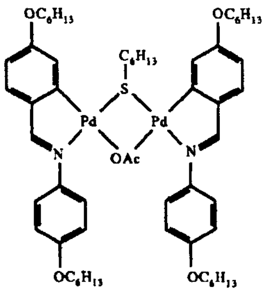
[1] See reference[1]



1

1a: $R^1 = OC_{10}H_{21}$, $R^2 = C_6H_{13}$
1b: $R^1 = OC_6H_{13}$, $R^2 = C_6H_{13}$
1c: $R^1 = OC_{10}H_{21}$, $R^2 = C_{10}H_{21}$



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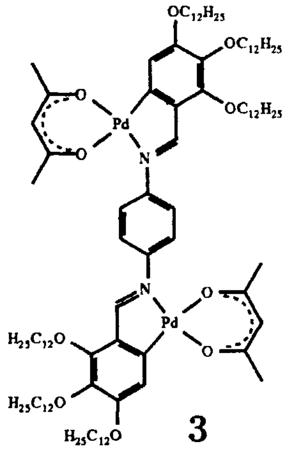

3

MATERIALS AND METHODS

The easily accessible dinuclear Pd(II) organyls **1a-c**[6] and **2**,[6] and **3**[7] were prepared by procedures published in references quoted here.

These three types of di-palladium organyls are different in their basic molecular structures; none of them can be depicted as clearly rod- or disc-like. Series **1** and compound **2** are well related in the *lath-* or *twin-*like shape of their molecular cores, but are different in 1) their core geometries (series **1**: fully planar; compound **2**: slightly folded), 2) their configurations (series **1**: *anti*; compound **2**: *syn*), 3) the number and type of elements bridging the palladium atoms, 4) the number, kind, and length of their aliphatic substituents (alkyl, alkoxy, and alkylthio), series **1** carries *four* substituents (alkyl and/or alkoxy groups) whereas **2** possesses *five* (four alkoxy groups and one alkylthio function). In comparison to these two foregoing structures organyl **3** is completely different: it is a bis-β-diketonato di-palladium(II) complex, the first of this kind,[7] and the longest one of all metal organyls studied here, is almost linear, but not typically rod-shaped, however, quite flexible, and carries *six* long alkoxy chains in two groups at its terminal phenyl rings.

Their phase behaviour was investigated by polarizing microscopy using a Leica DMRB microscope with crossed polarizers equipped with a Mettler FP 90 hot stage (heating rates 1-5 K min^{-1}) and by differential scanning calorimetry (Perkin Elmer DSC 7, heating rate 5 K min^{-1}). The texture photograph shown has been taken with a CCD Hitachi KP - C 501 videocamera equipped with a Sony UP 5000P videoprinter. We applied the well known contact method[3,8,9] to explore the lyomesophase behaviour of our di-palladium organyls using the following apolar organic solvents: linear alkanes (octane, decane, dodecane, or pentadecane), 1,5-cyclooctadiene, or (R)-(+)-limonene. As an electron acceptor in charge transfer complexes 2,4,7-trinitrofluorenone (TNF) was used. The phase diagram of the **1c**/pentadecane system was developed on the bases of polarizing microscopy and DSC studies of eleven defined mixtures containing the di-palladium organyl between 15 wt% and 89 wt% in these compositions. The preparation of homogeneous mixtures was achieved as described previously.[3c] X-ray diffraction patterns were recorded photographically (Polaroid

Table 1: Optical, thermal, and thermodynamic data[a] of the di-palladomesogens **1**-**3**.

Metallomesogen	Cr^1	Cr^2	S_C	S_A	N	Iso
1a	• 106.6 (31.8)	–	–	• 263.4[c]	–	•
1b	• 101.2 (7.1)	• 127.5[b] (26.1)	–	• 210.0[c]	–	•
1c	• 95.0 (26.7)	• 112.4 (3.3)	• 135.0[b]	• 237.6[c]	–	•
2	• 154.4 (13.7)	–	–	• 168.9	• 173.2 (2.5)[d]	•
3	• 41.7 (55.0)	• 59.2 (6.0)	–	–	–	•

[a] Temperatures in °C, enthalpies ($kJ \cdot mol^{-1}$) in brackets. Cr^1,Cr^2 = crystalline phases; S_A = smectic A phase; S_C = smectic C phase; Iso = isotropic liquid. [b] Optical microscopy data. [c] Decomposition. [d] The sum of enthalpies for both transitions above S_A.

type 57 sheet film, ASA 3000) using Cu-K_α radiation collimated by a glass collimator (beam diameter 0.4 mm). The samples were placed in sealed Mark-capillaries (diameter 0.7 mm). Heating was achieved by a Bruker ER4111VT Variable Temperature Unit with an accuracy of ± 1 °C.

RESULTS

1. Thermotropic behaviour

Compound **1a** with each two hexyl and decyloxy substituents exhibits a smectic A phase with myelinic figures and spherulites in a temperature range of almost 157 K. The metal organyl **1b** with four hexyl chains instead of which two are bridged via oxygen also displays a smectic A phase but less stable and wide (82.5 K only). The third metallomesogen of this kind, **1c**, carrying now four decyl chains, two of them again via oxygen, is dimesomorphic and shows the smectic C phase in a broken fan-shaped texture and at higher temperature also the smectic A phase with myelinic figures and spherulites; the total mesophase range is here about 125 K.[6] The slightly non-planar dinuclear palladium complex **2** with five hexylchalkogeno chains shows another polymorphism: apart from an almost 15 K wide S_A phase, the Schlieren texture of a narrow nematic phase can be observed in a temperature range of about 4 K.[10]

The almost linear compound **3** is non-mesomorphic at all in its pure state, but exhibits a highly viscous induced mesophase in charge transfer complexes with the electron acceptor TNF.[7] Further details and observations regarding the thermotropic behaviour of these metallomesogens are compiled in Table 1.

2. Lyotropic behaviour

The di-palladium organyl **1a** does not form any lyomesophase in contact preparations with *linear alkanes* as for instance with octane, decane, dodecane, or pentadecane; here, only dissolution on heating or crystallization on cooling can be observed. On the other hand, **1b** or **1c** show lyomesomorphism under these conditions; in their contact zones with such alkanes one type of lyomesophase appears displaying myelinic figures and spherulites. On heating, the temperatures of phase transition into the lyomesophase observed in contact preparations of **1b** with octane or decane are lower (42 or 64.3 °C) than those (76 or 80 °C) for analogous contact preparations of **1c**, cf. Figure 1. However, in similar investigations using dodecane

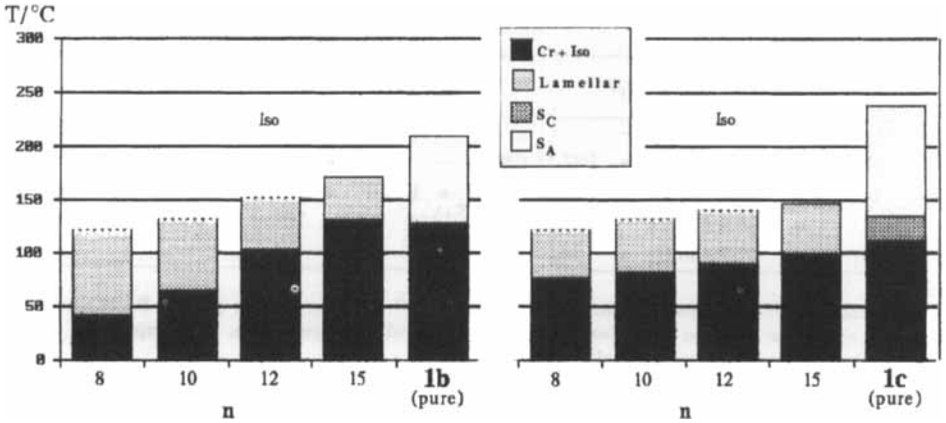

Figure 1: Relationship between the lamellar phase existence and the chain length of the solvent used in binary systems of the di-palladium organyls **1b** or **1c** and linear alkanes; observations in contact preparations on heating. - n = number of carbon atoms of the alkanes. Cr = crystalline phase, Iso = isotropic liquid phase. Note: The dotted lines on top of six columns indicate the limits of observation due to solvent evaporation in each of these cases.

or pentadecane the situation is inverse: the corresponding transitions with **1b** are higher (120 and 130.5 °C) than for **1c** (90 and 99 °C). On cooling, these lyomesophases stay in their contact preparations down to ambient temperature.

From the phase diagram of the **1c**/pentadecane system, shown in Figure 2, it is possible to conclude that the supramolecular packing in the lyotropic phase with myelinic figures remains the same as in the thermotropic smectic phase, however, the S_C to S_A transition temperature drops.

The layer distance of **1c** in dependence on the amount of solvent at 108 and 140 °C is shown in Figure 3. We think that these results can be explained by models for the insertion of alkanes into the mesophases of **1c** as indicated in Figure 4*a-d*. In the region up to 30% of solvent, the addition of the alkane leads to a remarkable jump of the spacing from about 32 Å (in the crystalline phase, cf. Figures 3 and 4*a*) up to about 41 Å (cf. Figures 3, 4*b* and *c*). Here, the alkane seems to insert between the paraffinic chains of **1c** more or less parallel to them pushing the planes of the layers apart.

Despite growing concentration of pentadecane in the region between 30 and 70% the layer spacing remains more or less constant until a last, only weak increase up to 41.5 Å occurs in the area of the lamellar phase.

The following description may shed some light on the mixing process (cf. Fig. 4):

At the beginning, the mesophase swells on addition of solvent like a sponge does, inserting the alkane into the paraffinic section by enlarging the distance between the layers, i.e., the alkane penetrates nearly parallel to the alkyl chains of this derivative of this type of *four-*tailed di-palladomesogen. This situation is depicted in Fig. 4*b*.

Further increase of the alkane concentration in this system does not lead to a remarkable change of the layer distance. Additional alkane forces the molecules of **1c** to enlarge the intermolecular distance in the lamellar planes; cf. Figure 4*c*. Besides, the alkyl chains become more disordered. Both processes allow the layer distance to remain constant, despite substantial increase of the paraffinic area space demand; cf. Figure 4*c*.

In the lamellar case, now, the alkane continues to penetrate into the middle of the paraffinic

Table 2: Lyotropic phase behaviour of the *five*-tailed, slightly folded di-palladium organyl **2** in selected hydrocarbons.

Hydrocarbon/	Heating					Cooling				
Solvent	Cr		M		Iso	Iso		M		Cr
Octane	●	86	–		●	●	79	N		–[a]
Decane	●	100	N	145	●	●	115	N	82	●
Dodecane	●	114	N	150	●	●	118	N	89	N+Cr
Pentadecane	●	125	N	173	●	●	165	N		–[a]
(R)-(+)-Limonene	●	93	N*	147	●	●	143	N*		–[a]

M = type of mesophase; N = nematic phase; N* = twisted nematic phase. [a]Here, the mesophase is still observed at ambient temperature.

section, even independent of the alkyl chains of **1c** (not parallel) causing again a slight increase of the layer distance; cf. Figure 4*d*. The phase indication "lamellar" is based on optical and thermodynamic investigations, though the border between the thermotropic and lyotropic state of matter in this system is vanishing.

In contact preparations of the *five*-tailed, slightly non-planar di-palladium organyl **2** with above mentioned linear alkanes the *nematic* lyotropic phase with Schlieren texture is observed. The widest temperature range of the N-phase existence is observed in the **2**/*penta*decane system, i.e., 48 K or 143 K on heating or cooling, respectively. Moreover, on cooling the nematic phase remains in this system till room temperature.

The almost linear di-palladium organyl **3** in its pure state does not exhibit any lyotropic mesophases in binary systems with the linear alkanes being used. However, charge transfer complexes of **3** with various amounts of TNF behave differently! Now, such mixtures in linear alkanes exhibit two columnar lyomesophases: 1) a two dimensional ordered one (similar to the chromonic M phase) and 2) a nematic columnar phase![7]

In contact preparations with the apolar, *un*saturated (non-planar, strongly folded) solvent 1,5-*cyclo*octadiene neither **1** nor **2** display any lyomesophase at all. In part, however, this situation changes when another *cyclic*, apolar, unsaturated, and *chiral* solvent, (R)-(+)-limonene, is used. Whereas both **1a** or **1b**/(R)-(+)-limonene systems do also not exhibit lyomesomorphism, the **1c**/(R)-(+)-limonene system now displays a lamellar phase with myelinic figures.

Moreover, in preparations of **2** with the apolar solvent (R)-(+)-limonene a *chiral* nematic lyomesophase (N*) is obtained existing in very broad ranges of temperature both on heating and cooling and displaying fingerprint, Grandjean, and focal-conic cholesteric textures, cf. Figure 5 and Table 2. Qualitatively, the cholesteric pitch is here quite large; its size could be changed by adding different amounts of above mentioned linear alkanes.

The occurrence of myelinic figures in contact preparations of **1b** or **1c** with apolar organic solvents is most probably connected with the formation of a lamellar lyotropic phase. In this case, the symmetry of the layered structure of the thermotropic smectic phase is kept in the lamellar lyotropic one. The lyotropic phase formation can be described as similar to the expansion of the arrangement existing in the absence of solvent (swelling process). The same could be the case for the metal organyl **2** in similar mixtures displaying nematic mesomorphism in both the thermotropic and lyotropic state.

This is considered to be the *first* way of lyotropic phase formation in binary mixtures of the metal organyls **1** or **2** with apolar organic solvents.

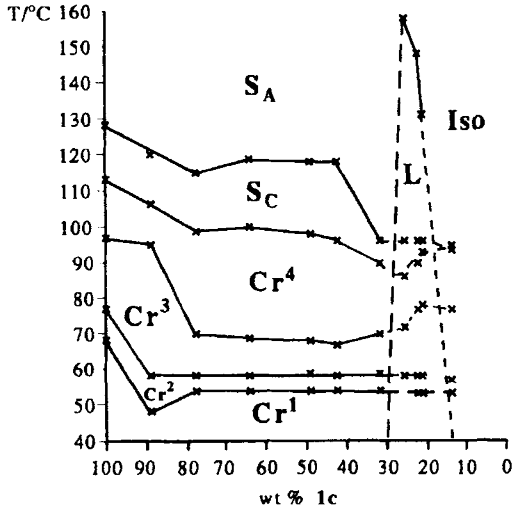

Figure 2: Simplified phase diagram of the di-palladium organyl **1c**/pentadecane system in the region of the lyomesophase formation, based on optical microscopy and DSC measurements on heating of binary mixtures with defined contents of the two components. Cr^1-Cr^4 = crystalline phases, S_A = smectic A phase, S_C = smectic C phase, L = lamellar phase, Iso = isotropic region.

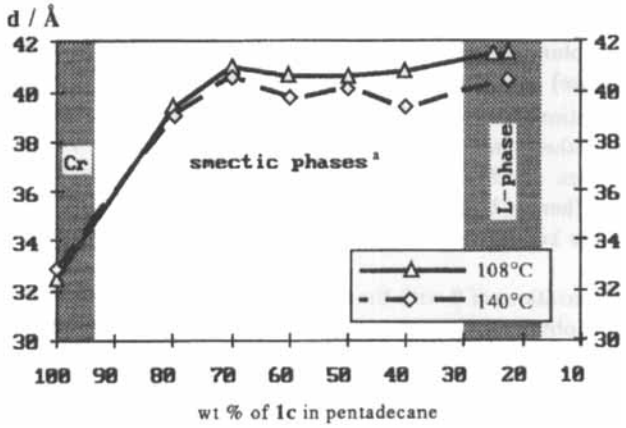

Figure 3: Layer distances between the molecules of **1c** in pentadecane (defined mixtures) at 108 °C or 140 °C. ^{a}Compare the region of S_A and S_C in Figure 2. - Cr = crystalline phase; L = lamellar phase.

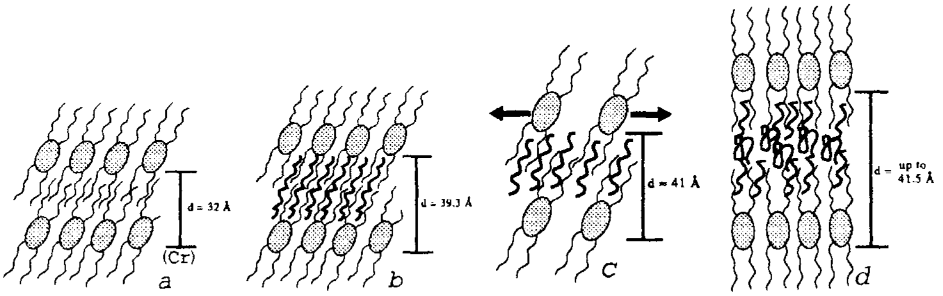

Figure 4: Preliminary models for the insertion of alkanes into the mesophase of the organyl **1c** sketched for examples at 108 °C; Cr = crystalline. *a*: the solvent free state; *b*: the mixture with about 20% solvent; *c*: mixtures with ≥ 30% solvent; *d*: the situation in the "lamellar" region.

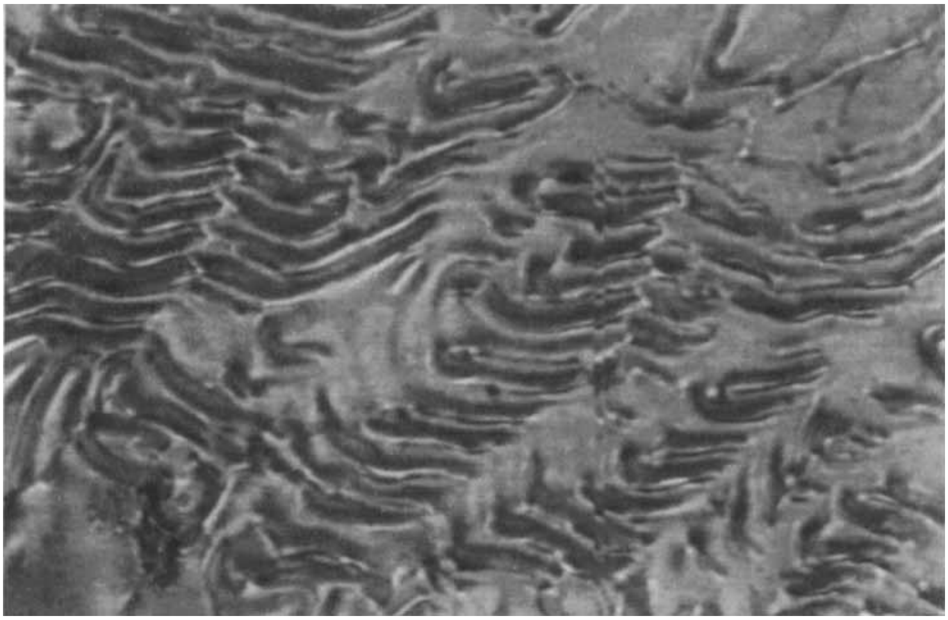

Figure 5: Fingerprint texture of the twisted nematic phase at 22 °C formed in contact preparations of the *five*-tailed, slightly folded di-palladium organyl **2** with (R)-(+)-limonene on cooling, magnification x 200. (See Colour Plate VI).

Table 3: Types of lyomesophases displayed in binary mixtures of the four dipalladomesogens[§] **1a-c** or **2** and apolar organic solvents.

Hydrocarbon/Solvent	1a	1b	1c	2
Octane	-	L	L	(N)
Decane	-	L	L	N
Dodecane	-	L	L	N
Pentadecane	-	L	L	N
1,5-Cyclooctadiene	-	-	-	-
(R)-(+)-Limonene	-	-	L	N*

[§] See their differently long alkyl and alkylchalcogeno groups shown in their chemical formulas which are also of different configuration, see text. - L = lamellar phase; N = nematic phase; N* = twisted nematic phase; ( ) = monotropic character of the mesophase indicated.

Still more interesting, however, is the occurrence of new types of supramolecular organizations in the lyotropic state which are not characteristic for the pure materials. Such situations represent a *second* way to the formation of lyomesophases. An attractive example for this alternative way is the induction of the cholesteric phase in the binary mixture of **2** and the *chiral* limonene, see above.

An overview of the lyotropic behaviour of our four metal complexes **1a-c** or **2** in mixtures with the several hydrocarbons applied here is given in Table 3.

In comparison to recently reported[3,9] first cases of cholesteric phase inductions in lyotropic systems of non-chiral *disc*-like metallomesogens and apolar organic solvents our findings with **2**, reported here, are the first ones regarding a non-chiral, but *lath*-(twin-)like metallomesogen. These inductions were achieved with the chiral, non-mesogenic dopant (+)- or (-)-TAPA[11] or with the mentioned chiral hydrocarbon, respectively; the system/mixture was ternary in the previous or binary in the latter instance.

Finally, it can be concluded that the periphery of the metallomesogens, i.e., the number and length of their aliphatic substituents in relation to the length and structure of the apolar organic solvents used have a significant influence on the type of lyomesophase formed and on the temperatures of the phase transitions.

In the lyotropic binary systems/mixtures discussed here two possibilities for the formation of lyotropic phases in apolar organic solvents/hydrocarbons are given:

- Due to a kind of swelling process after the addition of such solvents the symmetry of both a certain thermotropic and the lyotropic phase formed remain the same, i.e., an effect of symmetry preserving seems to be involved.
- The addition of solvents or of an electron acceptor plus solvent creates new kinds of supramolecular packings, *here*: a nematic or a twisted nematic one being both different in structure compared to how the pure materials would self-assemble thermotropically.

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[11] TAPA: 2-(2,4,5,7-Tetranitro-9-fluorenylideneaminoxy)propionic acid; both enantiomers are commercially available.