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On the molecular and mesophase structures of disc-like tetrapalladium liquid crystals‡

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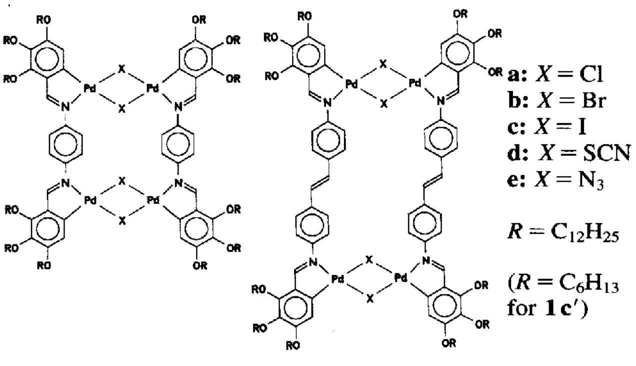
Various members of two series of μ-halogeno-bridged tetrapalladium mesogens each with twelve dodecyloxy chains, but differing in the size of their large disc-like macroheterocyclic cores, **1 a–e** and **2 a–c**, as well as one new short-chained homologue (**1 c′**) of one of the series, as a model compound for single crystal X-ray studies, are presented. Our results on that model compound again unambiguously confirm earlier statements about the unique molecular structure of the core of these flat tetrapalladium complexes. The properties of all thermomesogenic compounds have been studied by differential scanning calorimetry, polarizing microscopy, and also by X-ray diffraction; the latter method reveals an oblique arrangement of disordered columns in most of the mesophases exhibited by the members of both series **1** and **2**.

1. Introduction

Many examples of different classes of substances of varied molecular shape are known to exhibit columnar mesophases [2]. Among such mesogens are likewise metal-containing compounds [3], and these in fact include recently studied palladium or even platinum complexes [4(*a*)–(*d*), 5–8]. Here, we report on the molecular and mesophase structures of two series of tetranuclear halogeno- or pseudo-halogeno-bridged palladium compounds [4(*a*)–(*d*)] of the types **1** and **2** shown in figure 1. Their molecular shapes may also be regarded as consisting of two multicatenar parts linked by metal complexation [4].



1 a–e **2 a–c**

Figure 1. The molecular structures of the two series **1** and **2** of tetrapalladium compounds investigated.

All these compounds were characterized by spectroscopic methods which showed that the significant NMR resonances of the four equal, palladated corner sections of members of both series **1** and **2** with identical bridges *X* between their metal atoms are indeed very much comparable [4(*a*), (*b*)]. In the case of **1 a**, as well as of a lower mass homologue, osmometric or mass spectrometric determinations, respectively, of their molecular weights were made [4(*a*)]. Finally, by succeeding in growing a single crystal of the mesomorphic hexyl homologue of **1 c** (**1 c′**), we were able to prove the macrocyclic structure present in the novel liquid crystal series **1** by X-ray diffraction [5], whereby any possible remaining doubts about the molecular constitution could be eliminated. Our results represent the first example of an X-ray structure analysis of a tetranuclear cyclometallated *iodo*-bridged palladium(II) complex and are in accord with those for a structurally characterized dodecamethoxy bromo-bridged, but *non*-mesomorphic analogue, again obtained by X-ray diffraction [9] carried out in parallel with and independently of our work.

The investigation of the thermotropic phase behaviour of these new palladium organyls was done by differential scanning calorimetry (DSC) and polarizing microscopy.

We want to emphasize here that all these tetrapalladium compounds also form lyotropic liquid crystalline phases

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‡ See [1].

in apolar organic solvents; thus, two members of series **1** even exhibit *two* nematic phases existing side by side with a reversible phase transition between them [4 (*d*), 10]. Furthermore, in ternary lyotropic systems with alkane solvents containing a *chiral* electron acceptor, a cholesteric type of phase is induced which has been studied by polarizing microscopy [4 (*e*)].

2. Experimental

2.1. *Synthetic part*

The characterization of the members of series **1** and **2** and their precursors, see below and figure 1, is based on spectroscopic data obtained by ^{1}H NMR (Bruker WH400, CDCl$_3$) and ^{13}C NMR (Bruker AM270, CDCl$_3$) and correct elemental analyses. These phase transition data compiled in table 2 were determined by DSC (Mettler TA3000/DSC-30 S with TA 72·5 software).

The iodo-bridged palladium organyl **1 c′** with the ligand L = N,N'-bis[2,3,4-tris(hexyloxy)phenylmethylidene]-1,4-diaminobenzene [11] was synthesized in the usual manner by ortho-palladation of that bisimine with palladium acetate, followed by exchange of the bridges X in two steps.

2.1.1. *Tetrakis*[μ-(*acetato-O:O′*)]*bis*{μ-[*1,4-phenylene-bis*[*nitrilomethylidyne*(*3,4,5-tris*(*hexyloxy*)-*2,1-phenylene*)]]}*tetrapalladium.*

The ortho-palladation was carried out by heating under reflux 2·1 mmol of the above ligand [11] with 4·6 mmol of palladium acetate Pd$_3$(OAc)$_6$ in 210 ml of glacial acetic acid for 40 min under argon. After cooling, the orange brown product was filtered off and crystallized from glacial acetic acid/methanol. The solid orange product was obtained in 60 per cent yield as a mixture of two isomers, ratio 85 : 15, dec. at 278°C; C$_{120}$H$_{184}$N$_4$O$_{20}$Pd$_4$ (2428·4). ^{1}H NMR: δ = 8·02, 7·97 (2s; ratio 1 : 0·17, HC = N), 7·00, 6·96 (2s; ratio 1 : 0·19, aromatic hydrogens of the p-di-N-substituted benzene rings), 6·06 (s; 4 aromatic hydrogens), 4·14–3·90, 3·81–3·70 (2m; 12 OCH$_2$ groups), 2·37 (s; CH$_3$ groups of acetato-bridges). ^{13}C NMR: δ = 182·04, 179·22 (2s; 4 bridging CH$_3$–$\underline{C}$O$_2$), 168·84 (d; 4 = CH=N), 155·18, 151·70, 151·58, 151·36, 147·97, 147·24, 137·24, 131·60 (8s; 24 quarternary aromatic carbons), 122·89, 122·75, 111·73 (3d; aromatic CH situations), 74·59, 74·51, 73·48, 68·63 (4t; 12 α-CH$_2$ groups).

2.1.2. *Tetra*-μ-*chlorobis*[μ-{*1,4-phenylenebis*[*nitrilo-methylidyne*(*3,4,5-tris*(*hexyloxy*)-*2,1-phenylene*)]]}*tetrapalladium.*

Treatment of the above acetato-bridged palladium compound (0·33 mmol) dissolved in 100 ml of dichloromethane with 1·3 mmol (13 ml) of 0·1 M isopropanolic hydrochloric acid at room temperature under

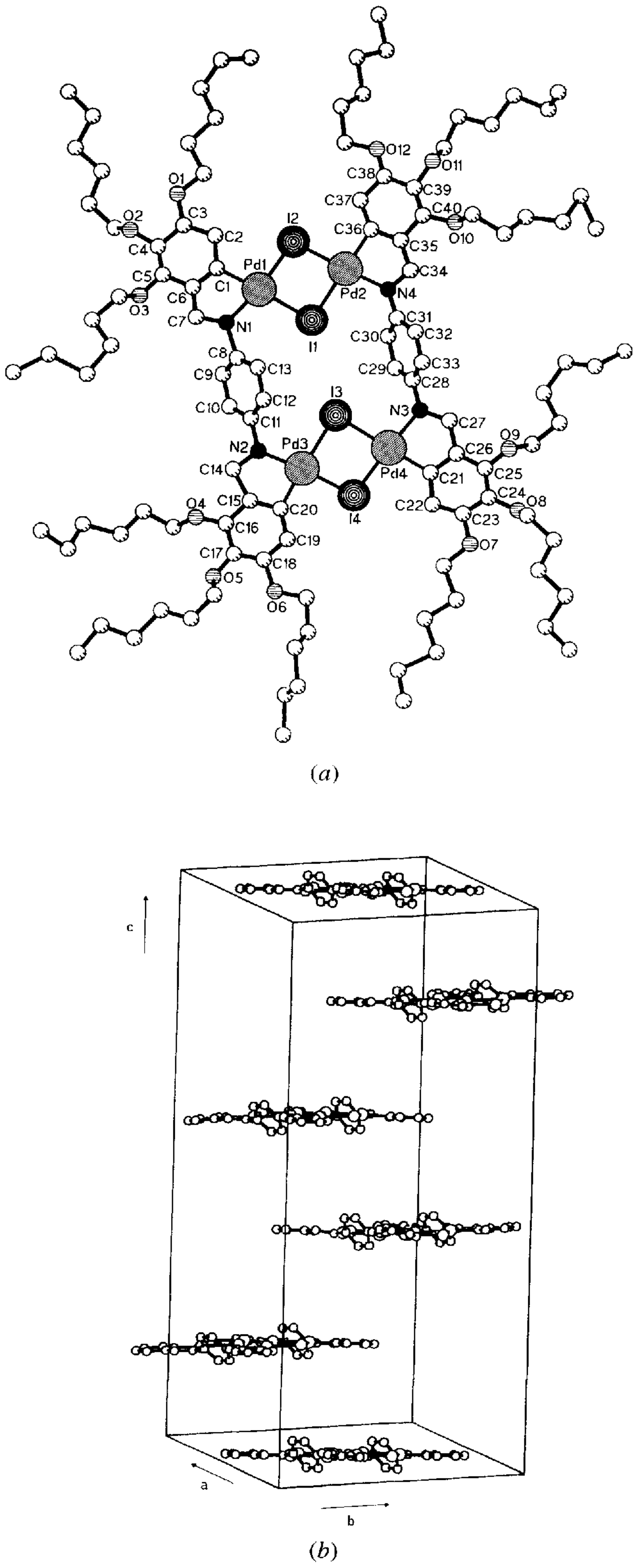


Figure 2. (*a*) The molecular structure and (*b*) the packing in the unit cell of the tetrapalladium liquid crystal **1 c′** (X = I; R = C$_6$H$_{13}$, omitted here however for clarity) according to its X-ray crystal structure analysis.

argon for 66 h furnished the chloro-bridged palladium organyl which was purified by crystallization from ethanol/chloroform. Yield of yellow solid, 57 per cent, dec. at 332°C; $C_{112}H_{172}N_4O_{12}Pd_4Cl_4$ (2334·0).

^{1}HNMR: $\delta = 8{\cdot}01$ (s; 4 HC = N), 7·19, 6·68 (2s; 8 and 4 aromatic hydrogens, respectively), 4·13, 4·08, 3·87 (3t; $J \approx 7$, 6·5 and 7 Hz; 4 OCH_2 groups each), 1·83, 1·72, 1·68 (3tt; $J \approx 6{\cdot}5$, 7 and 7 Hz; 4 β-CH_2-groups each). ^{13}C NMR: $\delta = 171{\cdot}11$ (d; 4 CH = N), 155·62, 152·27, 150·73, 147·26, 137·68, 132·15 (6s; 6 types of quarternary aromatic carbons), 123·80, 112·57 (2d; aromatic CH situations), 74·61, 73·69, 68·75 (3t; 12 α-CH_2 groups).

Table 1. Crystal data for the iodo-bridged tetrapalladium liquid crystal **1 c′** (R = hexyl).

Formula	$Pd_4I_4C_{112}H_{172}N_4O_{12}$
Formula weight	2699·7
Crystal system	Triclinic
Lattice parameters:	
a	1·5122(8) nm
b	2·4895(10) nm
c	4·2876(17) nm
α	92·31(6)°
β	97·66(4)°
γ	99·57(5)°
V	$15742{\cdot}3 \times 10^{-3}\,nm^3$
Molecules per unit cell Z	5
D_{calc}	$1{\cdot}42\,g\,cm^3$
F(000)	6780
Radiation	MoK_α, $\lambda = 0{\cdot}071069$ nm
Absorption coefficient $\mu(MoK_\alpha)$	$14{\cdot}9\,cm^{-1}$
Max. value 2Θ	40°
Scan mode	ω scans
Measured reflections	25 748
Independent reflections	19 070
Observed reflections	9245 with $I > 2\sigma(I)$
Corrections	Lorentz ~, polarization ~, absorption ~
Refinement	$\Sigma w(F_o^2 - F_c^2)$
No. of parameters	1439
$R = \Sigma\|\|F_o\|-\|F_c\|\|/\Sigma\|F_o\|$	0·082
$\Delta\rho_{fin.}$ (max./min)	$0{\cdot}49/-0{\cdot}73\,e\,Å^{-3}$

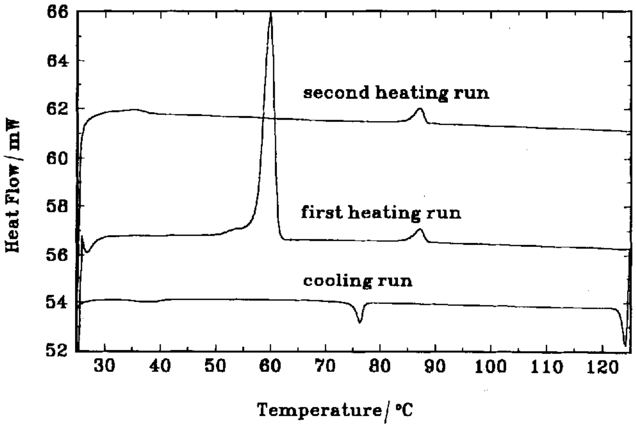


Figure 3. DSC trace (Perkin–Elmer DSC 7) of the azido-bridged tetrapalladium liquid crystal **1 e**.

2.1.3. *Tetra-μ-iodobis{μ-[1,4-phenylenebis[nitrilomethylidyne(3,4,5-tris(hexyloxy)-2,1-phenylene)]]}tetrapalladium* (**1 c′**).

The preparation was carried out by stirring 0·1 mmol of the above chloro-bridged homologue with 20 mmol of lithium iodide in dichloromethane/acetone (75 ml/40 ml) for 144 h under argon at room temperature. After filtration and removal of the solvents under reduced pressure, the crude products were purified by recrystallization from dichloromethane/acetone. Yield of orange crystals 81 per cent, m.p. (Cr → D) 123°C (25·2 kJ mol^{-1}), cl.p. (D → I, decomposition) 360°C; $C_{112}H_{172}N_4O_{12}Pd_4I_4$ (2699·8).

^{1}H NMR: $\delta = 8{\cdot}13$ (s; 4 HC = N), 7·16, 6·99 (2s; 8 and 4 aromatic hydrogens, respectively), 4·12, 4·10, 3·87 (3t, $J \approx 7$ Hz each; 4 OCH_2 groups each), 1·84, 1·72, 1·67 (3tt; $J \approx 6{\cdot}5$, 7, and 7 Hz; 4 β-CH_2 groups each). ^{13}C NMR: $\delta = 172{\cdot}22$ (d; 4 CH = N), 156·80, 155·58, 152·90, 148·90, 137·49, 133·29 (6s; 6 types of quarternary aromatic carbons), 124·12, 117·57 (2d; aromatic CH situations), 74·66, 73·64, 68·78 (3t; 12 α-CH_2 groups).

The syntheses of the other palladomesogens (**1 a–e** and **2 a–c**) were carried out analogously, cf. references [4 (*a*)–(*d*)].

2.2. *Instrumental part*

Intensity measurements for the X-ray structure analysis of **1 c′** (R = hexyl) were carried out at room temperature using a four-circle diffractometer SYNTEX $P2_1$. The lattice constants were obtained from 25 well-centred reflections with high indices. The crystal data are summarized in table 1. The heavy atoms were localized by the Patterson method (SHELXS-86 [12]), and the C, N, and O atoms by subsequent difference Fourier syntheses (SHELX-76 [13]). The least-squares refinement was performed using SHELXL-92 [14], [15]. Because of the high viscosity and the strong decomposition of all compounds, their transition temperatures could only be determined by DSC, using a METTLER TA 3000/DSC-30S for series **1**, and a Perkin–Elmer DSC 7 for series **2**; these data are presented in table 2. Heating rates of 5 K min^{-1} in the regions of the melting temperatures and, due to the strong decomposition of these palladium organyls in the isotropic phases, 20 K min^{-1} for the determination of the clearing temperatures were used.

Textures of the mesophases, see for instance that of the iodo-bridged **1 c** in figure 5, were observed using a Leitz LUX 12 POL S microscope equipped with a Linkam THMS 600 heating stage.

The X-ray investigations of the mesophases were performed using a Huber G644 Guinier goniometer, and

Table 2. Phase transition temperatures (°C) and enthalpies† (kJ mol^{-1}) of the tetrapalladium liquid crystals **1 a–e** and **2 a–c** ($R = C_{12}H_{25}$) [4 (*a*)–(*d*)]; Cr: crystalline, D_1: oblique columnar mesophase, except for **1 e**‡, D_2: rectangular columnar mesophase, except for **2a**, and I: isotropic liquid.

Liquid crystal	*X*§	Cr			D_1			D_2			I
1 a [4 (*a*), (*c*), (*d*)]	Cl	•	71	(86·7)	•	301	(45·7)	—			• dec.
b [4 (*a*), (*c*), (*d*)]	Br	•	69	(111·5)	•	279	(28·3)	—			• dec.
c [4 (*c*), (*d*)]	I	•	62	(111·5)	•	262	(15·1)	—			• dec.
d [4 (*a*), (*c*), (*d*)]	SCN	•	50	(128·7)	•	≈ 290¶		—			dec.
e [4 (*d*)]	N_3	•	60	(129·4)	•	87‖	(8·7)	•	> 150¶		dec.
2 a [4 (*b*)–(*d*)]	Cl	•	126	(51·6)	•	248	(7·3)	•	270	(9·0)	• dec.
b [4 (*b*)–(*d*)]	Br	•	126	(54·6)	•	252	(13·4)	—			• dec.
c [4 (*b*)–(*d*)]	I	•	98	(64·9)	•	244	(15·0)	—			• dec.

† Obtained by DSC on heating at 5 K min^{-1} for the melting and 20 K min^{-1} for the clearing processes. The enthalphy values are in parentheses. Strong decomposition takes place in the isotropic phases of **1 a–c** and **2 a–c**.

‡ A highly viscous phase of as yet unknown type.

§ The bridging group as shown in figure 1.

¶ An estimated temperature because of strong decomposition of the sample (polarizing micrscopy, heating rate 20 K min^{-1}).

‖ At this temperature no remarkable change of the texture could be observed; only the viscosity drops.

a Guinier film camera, as well as a flat film camera. To prevent decomposition of the compounds during sample preparation, the substances were stuffed as solids (not molten) into glass capillaries of ~ 1 mm diameter.

Oriented samples of all members of both series could not be obtained because of the high viscosity of their mesophases and the strong decomposition after the transition from the liquid crystalline into the isotropic phase.

3. Results and discussion

3.1. *The crystal structure of 1 c′* (*R* = hexyl)

The unit cell of this model compound contains five molecules; figure 2 (*b*) shows the arrangement of these molecules in that cell (the twelve hexyl chains are omitted here for clarity). Four molecules occupy general positions, whereas the centre of gravity of the fifth molecule lies on a centre of symmetry in the unit cell. A plot of this molecule is shown in figure 2 (*a*). The Pd_2I_2 groups of these molecules are very nearly planar; the interplanar angle Pd1I1I2/Pd2I1I2 is 179° in the centrosymmetric molecule (cf. figure 2 (*b*)) or has an average angle of only 174° in the cases of the four other molecules. The molecules are essentially planar, and only the two central benzene rings are turned out of the plane of the molecular core. Whereas the core atoms of the ligands could be localized exactly, the hexyl chains are disordered, with an increasing degree of disorder in the direction of the chain ends; this is reflected in rather high and increasing displacement parameters of the chain carbon atoms. The mean non-bonding Pd···Pd distance is 0·3888(2) nm. This value corresponds perfectly to 0·386 nm found for β-palladium(II) iodide [16] and is naturally greater (by about 0·022 nm) than that for the analogous non-bonded

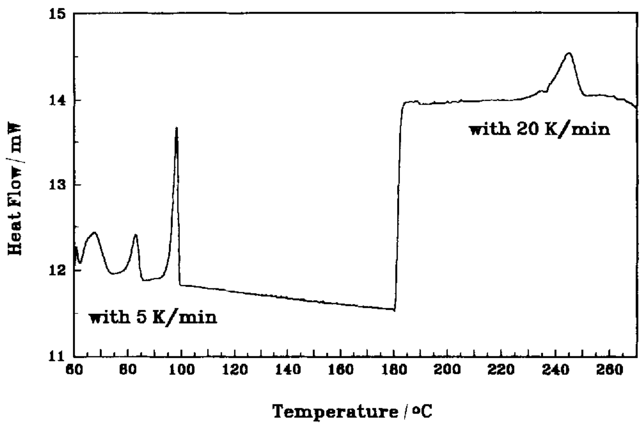


Figure 4. The DSC trace (Perkin–Elmer DSC 7) for the first heating cycle of the iodo-bridged tetrapalladium liquid crystal **2 c**.

Figure 5. The dendritic texture of the mesophase of the iodo-bridged tetrapalladium liquid crystal **1 c** ($R = C_{12}H_{25}$) at 220°C on cooling, magnification × 100.

pairs of palladium atoms in structurally very closely related, but *bromo*-bridged tetranuclear cyclometallated palladium(II) complexes [9]. The Pd–I bond lengths in **1c′** are not equivalent; the bonds directed towards the centre of the molecule (Pd-I1, Pd-I3, cf. figure 2 (*a*)) are significantly longer (average length: 0·272(1) nm) than the bonds directed away from the centre (0·258(1) nm), a result of the different *trans* influences of the phenyl carbon and nitrogen atoms of the imine ligands. This phenomenon was also found in other multinuclear multi-μ-bromo- or -chlor-palladium(II) complexes [9, 17]. Considering only the central planar core of the molecules of **1 c′** without the alkyl chains, their molecular planes are separated by appr. 0·86 nm and lie parallel to the *a–b* plane. The X-ray data for the structure analysis of **1c′** are given in table 1.

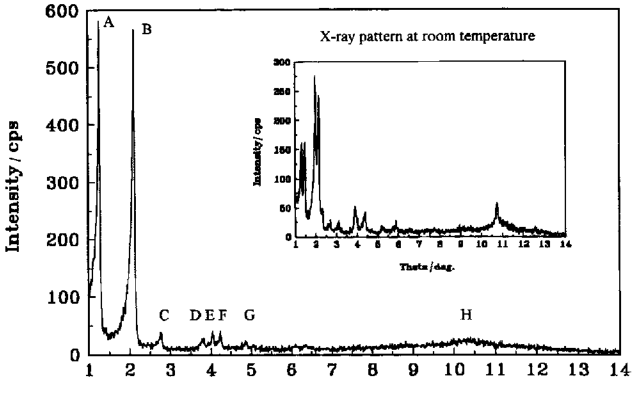


Figure 6. The X-ray pattern of the liquid crystalline and the crystalline (inset) phases at 90°C and room temperature, respectively, of the bromo-bridged tetrapalladium compound **1 b**.

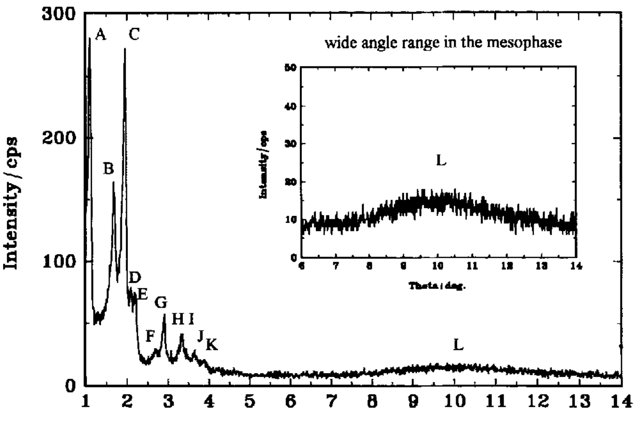


Figure 7. The X-ray pattern of the mesophase of the bromo-bridged tetrapalladium compound **2 b** at 150°C.

3.2. *The investigation of the mesophases*

The DSC measurements indicate several solid–solid transitions and, with the exception of the compounds **1 e** and **2 a**, only one mesophase each, with very high clearing temperatures and enthalpies; see these data in table 2. In the case of the azido-bridged **1 e**, the DSC curve exhibits the characteristic feature (cf. figure 3) found at the transition into the liquid crystalline phase. At 60°C a strong melting process appears which is followed by an additional transition at 87°C. The phase formed at the upper temperature could be characterized by X-ray studies to be a D_r phase. On the other hand, the X-ray pattern of the lower temperature phase does not allow any classification, since numerous weak reflections appear at Bragg angles below $\theta = 8{\cdot}0$ degrees. However, in the wide angle region around $\theta = 10$–11 degrees, a diffuse scattering can be observed simultaneously. On the basis of our DSC measurements (cf. table 2 and figure 3) and of the diffuse scattering observed in the X-ray pattern, as well as of our polarizing microscopic studies, this highly viscous phase of **1 e**, exhibiting a texture which we cannot interpret, is considered to be liquid crystalline.

The additional transition in the case of **2 a** could only be proved by DSC and polarizing microscopy, but not by X-ray methods, because of the decomposition in the D_2 phase. Whereas the clearing enthalpies decrease through series **1**, they increase through series **2**. Figure 4 shows the DSC trace for **2 c**.

Figure 5 displays the photomicrograph of the mesophase of **1 c**. Dendritic textures of this type were observed for most of these compounds after heating them above their clearing temperature and rapid cooling into their liquid crystalline phase; additionally, mosaic domains appeared after further cooling. In this connection, however, **1 d**, **1 e**, and **2 c** are exceptions since they decompose through this treatment.

The X-ray patterns of the mesophases of all members of the palladium organyl series **1**and **2** are characterized by a large number of sharp reflections in the small angle region together with diffuse scattering in the wide angle range—see figures 6 and 7. They are different from those obtained at room temperature, as shown for **1 b** in figure 6.

Schematic plots of the mesophase X-ray patterns obtained are presented in figure 8. Substances **1 a**, **1 b**, and **1 d** (X = Cl, Br or SCN, respectively) possess similar diffraction patterns which are different from that of **1 c** (X = I). This is also true for the compounds of the second series. With the exception of **1 c**, the reflections cannot be explained on the basis of a hexagonal or rectangular unit cell in the mesophase, but only on the assumption of an oblique cell. The pattern of **1 c** is, because of the small number of reflections, compatible with a rectangular as well as an oblique unit cell. The diffuse scattering of all

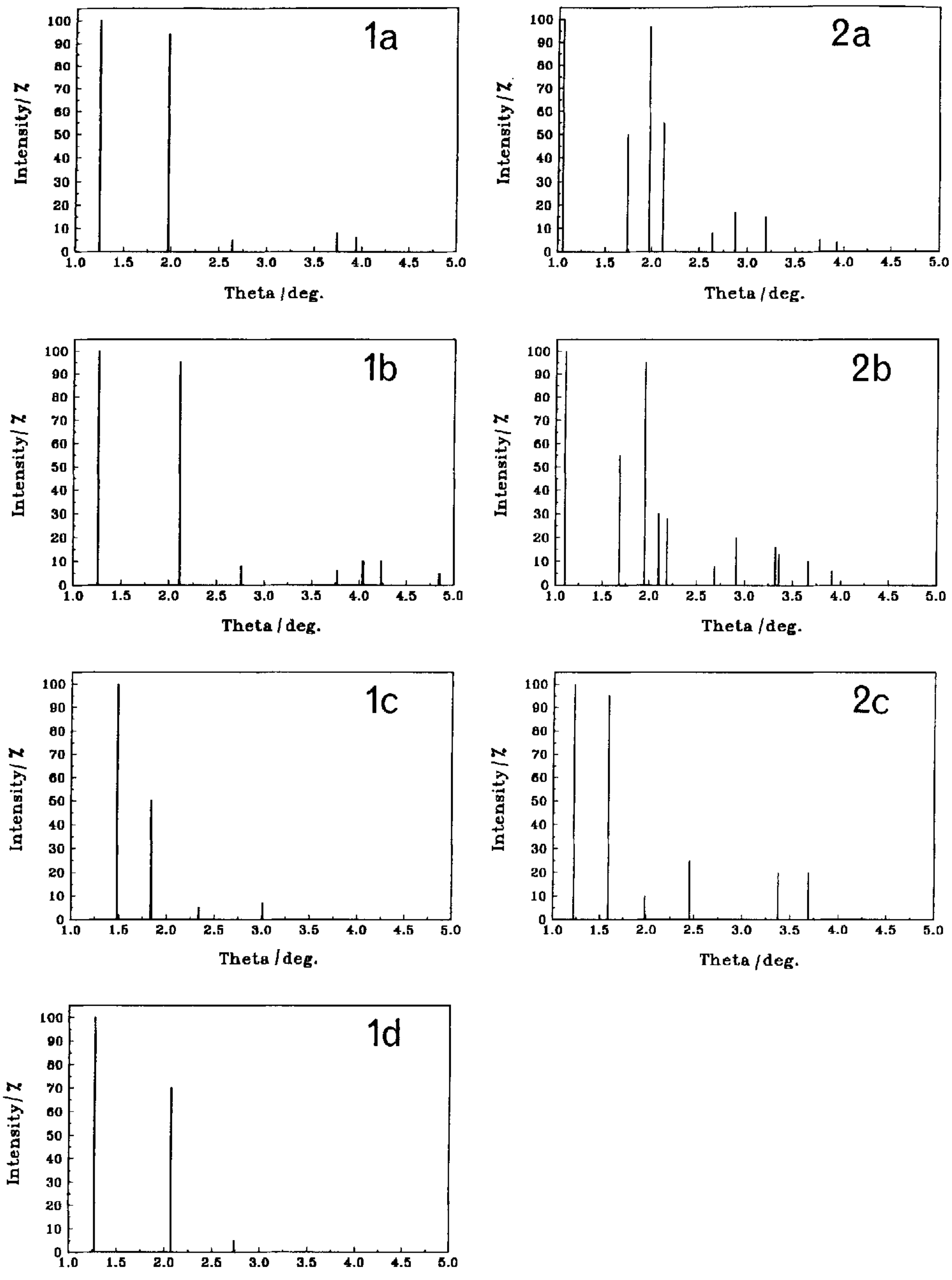


Figure 8. Schematic pictures of the positions and relative intensities of the observed reflections in the small angle range of the seven tetrapalladium liquid crystals **1 a–d** and **2 a–c** ($R = C_{12}H_{25}$).

compounds in the wide angle range stems from a disordered arrangement of the molecules mainly caused by their alkyl chains.

In the equation for the indexing of the oblique unit cell [18], three (unknown) cell parameters a, b, and γ exist. Three reflections are necessary to calculate these parameters; the others can be used as proof of the assumption. For **1 b** and **2 b** (see the diffraction patterns in figures 6 and 7); the observed and calculated θ-values are compared in table 3. They show only small deviations and should confirm the assumed oblique lattice type: D_{ob} mesophase.

The lattice parameters of the two-dimensional unit cells are listed in table 4. To compare the lattice size with the molecular parameters, we have estimated the packing coefficients $P = V_{mol}/V_{cell}$. The molecular volume V_{mol} has been calculated using the increment method [19], whereas V_{cell} was obtained from the X-ray data. Thus, in the case of compound **1 c′**, a value of $P = 0{\cdot}7$ results for the

Table 3. The X-ray data for the mesophases of the two bromo-bridged tetrapalladium compounds **1 b** and **2 b** ($R = C_{12}H_{25}$) obtained at 90°C and 150°C, respectively.

Liquid crystal	Reflexion	Θ_{measured}	d_{value}/nm	Indexing	$\Theta_{\text{calculated}}$/grd
1 b	A	1·26	3·50	(10)	—
	B	2·11	2·09	(11)	—
	C	2·76	1·60	(01)	—
	D	3·77	1·17	(30)	3·78
				(41)	3·75
	E	4·04	1·09	(32)	4·03
	F	4·23	1·04	(22)	4·22
				(42)	4·22
	G	4·85	0·91	(12)	4·75
	H	10·38	0·43	d_{halo}	—
2 b	A	1·10	4·01	(10)	—
	B	1·68	2·63	(11)	—
	C	1·95	2·26	(01)	—
	D	2·10	2·10	(21)	2·07
	E	2·19	2·02	(20)	2·20
	F	2·69	1·64	(− 11)	2·69
	G	2·91	1·52	(31)	2·85
	H	3·32	1·33	(30)	3·30
	I	3·36	1·31	(22)	3·36
	J	3·66	1·21	(32)	3·60
				(− 21)	3·61
	K	3·91	1·13	(02)	3·90
	L	10·09	0·44	d_{halo}	—

Table 4. The cell parameters of the liquid crystalline phases of the members **1 a–d** (cf. figure 9 (*a*)) and **2 a–c**, respectively, of the two series of palladomesogens **1** and **2** ($R = C_{12}H_{25}$).

Liquid crystal	T/°C	a/nm	b/nm	γ/°	Plane A/nm^2
1 a	90	4·81	2·19	47·8	7·81
b	90	4·79	2·19	46·9	7·66
c	90	3·79	2·40	51·8	7·15
d	70	4·79	2·23	46·2	7·71
2 a	150	4·77	2·54	61·8	10·68
b	150	4·66	2·63	59·3	10·54
c	125	4·51	2·78	53·4	10·07

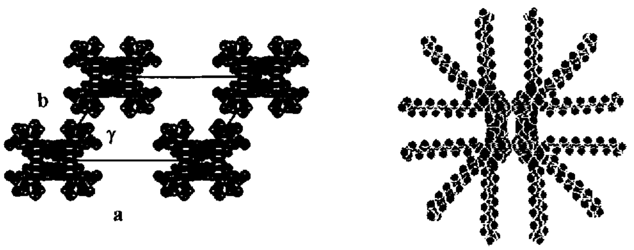
crystalline state, which seems to be reasonable according to reference [19]. In the unit cell of the crystal, the neighbouring molecules are separated by 0·86 nm in the *c*-direction. Upward and downward directed chains act as spacers. A corresponding value cannot be given by the X-ray studies of the liquid crystalline phase. To get the coefficient $P = 0{\cdot}7$ for the liquid crystalline phase, for example, in the case of substance **1 c**, the distance between neighbouring molecules perpendicular to the *a*–*b*-plane is calculated to be ~ 0·7 nm. This value is smaller than that for the crystalline state, which can be understood with respect to the higher flexibility of the chains, but it exceeds essentially the value observed for the so-called D_{ho} phase. It proves that the flexible chains must be directed out of the plane which is formed by the central core.

Figure 9, drawn to scale, displays the molecular space requirements within the two-dimensional unit cell. The parameters of the rigid core region from the single crystal structure analysis (O2 ··· O11 ≡ O5 ··· O8 = 1·35 nm and O8 ··· O11 ≡ O5 ··· O2 = 1·58 nm) were used for the schematic representation of the molecular arrangement plotted in figure 9 (*a*). The aliphatic chains (omitted in figure 9 (*a*) are disordered and fill out the rest of the cell.

According to this model there is only one molecule per unit cell. But oblique cells have also been described for other compounds [20, 21], for which the $P\bar{1}$ cell contains two molecules.

The X-ray measurements have been carried out at different temperatures, and the positions of the (10) and (11) reflections for the bromo-bridged mesogen **1 b** with increasing temperature are displayed in figure 10.

The calculated plane *A* of the unit cell increases with rising temperatures for all members of the



(*a*) (*b*)

Figure 9. (*a*) Our model of the oblique unit cell of the tetrapalladium liquid crystals **1 a–d** (without consideration of the whole lengths of their alkyl chains) and (*b*) a model of the molecular structure of all the members of series **1** with an all-*trans* arrangement of their alkyl chains $R = C_{12}H_{25}$.

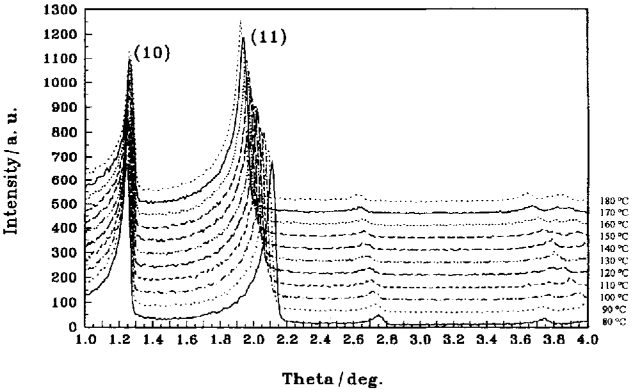


Figure 10. The graph of the temperature dependence of the positions of X-ray reflections of the mesophase of the bromo-bridged tetrapalladium compound **1 b** ($R = C_{12}H_{25}$).

palladomesogen series **1** and **2**. For **1 b** the parameters are: at 90°C $a = 4{\cdot}79$, $b = 2{\cdot}19$ nm, $\gamma = 46{\cdot}9°$, and $A = 7{\cdot}66\,\mathrm{nm}^2$, at 170°C $a = 56{\cdot}2$, $b = 2{\cdot}57$ nm, $\gamma = 38{\cdot}6°$, and $A = 9{\cdot}01\,\mathrm{nm}^2$.

This behaviour is due to an increasing mobility of the molecules at higher temperatures. The positions of the wide angle scattering maxima of all compounds show only a small influence of temperature on the positions.

In contrast to the other members of the palladium organyl series **1**, the azido bridged palladium homologue **1 e** exhibits two mesophases, cf. table 2. While the structure of the low temperature mesophase is still not fully clarified, the X-ray pattern of the high temperature mesophase may be explained on the basis of a rectangular unit cell. The parameters of this unit cell of **1 e** at 100°C are $a = 2{\cdot}94$ nm and $b = 2{\cdot}45$ nm.

4. Conclusions

A recent single crystal X-ray diffraction study on the dodeca*methoxy*, *bromo*-bridged example [9] of series **1** and our supplementary, analogous X-ray investigation of the dodeca*hexyloxy*, *iodo*-bridged homologue **1 c′** reported here concurrently prove the planarity of the macroheterocyclic core in this family of our liquid crystalline tetrapalladium complexes [4] independent of the kind of halogen bridging the four palladium atoms.

Investigations of all members of both series **1** and **2** by differential scanning calorimetry and polarizing microscopy show that columnar mesophases are exhibited over wide ranges of temperature.

With one exception (**1 e** and **2 a**) in both series the X-ray patterns of all other members are very similar within their mesophase. Many sharp reflections are visible in the small angle range and could be assigned only to an oblique unit cell. A diffuse scattering is observed in the wide angle range due to a disordered intracolumnar arrangement of the molecules. Temperature dependent X-ray measurements showed the two-dimensional cell to expand with temperature.

Finally, the examination of the constitution and shape of the macroheterocyclic molecular centre in the case of two compounds (see [9] and **1 c′**) by single crystal X-ray diffraction certainly justifies the assumption that the multiple ortho-metallation of bisimines seems to be a general principle for the 'dimer'-like macrocyclization of suitably bifunctionalized rod-shaped organic units of variable length [22]. For instance, this postulate should be applicable for the synthesis of numerous novel and large-sized disc-like metal containing liquid crystals with interesting thermo- and lyo-tropic [4 (*d*), (*e*), 22] or other fascinating properties.

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