

nation of Patterson function and Fourier differences. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were defined between 0.58 and 0.33 e Å⁻³ and refined isotropically. The weighting scheme used was $w = 1/\sigma(F_o)^2 = [\sigma^2(I) + (0.04F_o^2)^2]^{1/2}$. The best full-matrix least-squares refinement of the structure³⁰ (x, y, z, β_{ij} for non-hydrogen atoms and x, y, z for

(30) All calculations were performed by using the SDP package provided by Enraf-Nonius.

hydrogen atoms) gave $R_w = 0.035$ (goodness of fit $S_w = 1.42$). See Table I for full details of the analysis. Positional parameters are given in Table II, and bond lengths and angles are provided in Table III.

Supplementary Material Available: Tables of general temperature factor expressions, torsional angles, hydrogen positional parameters, and C–H bond distances (5 pages); a table of observed and calculated structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

Synthesis, Characterization, and X-ray Studies of Nonplanar Mesogens: Carboxylato-Bridged Orthopalladated Azine Complexes

P. Espinet* and J. Perez

Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47005 Valladolid, Spain

M. Marcos, M. B. Ros, and J. L. Serrano*

Química Orgánica, Instituto de Ciencia de Materiales de Aragón, Facultad de Ciencias, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain

J. Barberá and A. M. Levelut*

Laboratoire de Physique des Solides, Bâtiment 510, Université Paris-Sud, 91405 Orsay Cedex, France

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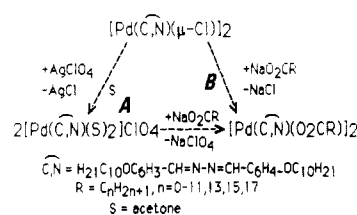
The family of book-shaped orthopalladated dimers $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CC}_n\text{H}_{2n+1})]_2$ ($n = 0-11, 13, 15, 17$), which show mesogenic behavior influenced by the length of the bridging carboxylate, have been prepared. The shortest ($n = 1-3$) and longest ($n \geq 10$) carboxylates give rise to more ordered mesophases and wider ranges of mesogenic behavior than the carboxylates of medium length. This is interpreted as a consequence of the molecular packing being disturbed on changing from short to medium chains and facilitated again when the carboxylate chains are long enough to situate themselves parallel to the azine chains. X-ray diffraction studies on monodomains give evidence of a peculiar molecular packing in these mesophases: some palladium–palladium correlations are found, which indicate the tendency to both a lateral association and a longitudinal shifting between neighboring molecules.

Introduction

Rodlike molecules containing rigid cores have traditionally been regarded as having the most suitable geometry to give rise to mesogenic behavior.^{1,2} In 1977, a new type of thermotropic compound, based on disklike molecules, was discovered³ and since then other molecular shapes described as cone-shaped,⁴ lamellar,^{5,6} phasmids,⁷ and sandwich-shaped⁸ have been reported to give mesogens.

The synthesis of liquid crystals based on organometallic or coordination compounds opens new perspectives in the design of mesogenic molecules. In this respect we have recently reported the unexpected finding of mesogenic behavior in the book-shaped orthopalladated dimers

Scheme I



$[\text{Pd}(\text{R}'\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OR}')(\mu\text{-O}_2\text{C-CH}_3)]_2$ ($\text{R}' = n\text{-C}_n\text{H}_{2n+1}$; $n = 6-10, 12, 14$).⁹

The presence of a metal atom, in addition, makes it possible to synthesize related derivatives by means of very simple coordination chemistry, which can be advantageous in comparison with the usually more tedious procedures when a series of related molecules is needed. Thus, we have shown how optical activity can easily be introduced in the above-mentioned complexes simply by replacing the bridging acetate with (*R*)-2-chloropropionate.¹⁰

We were intrigued by the possibility of using the bridging system in our open-book-shaped molecules as a tuner of their thermotropic properties. Changing the

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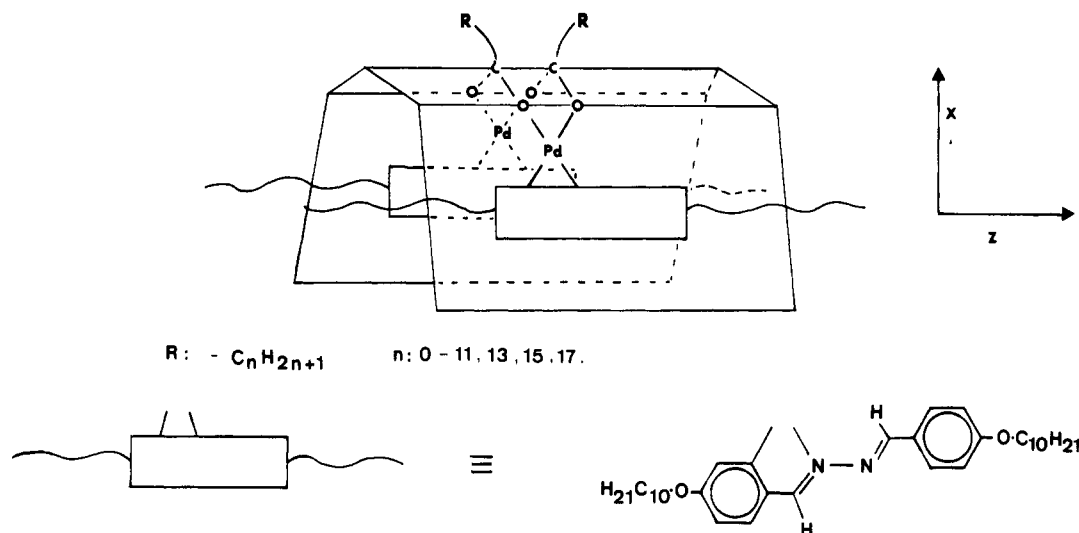


Figure 1. Schematic representation of the book-shaped derivatives $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CC}_n\text{H}_{2n+1})_2]$.

length of an alkyl chain is a common strategy in rodlike- or disklike-based mesogens, and this approach was used in our previous paper,⁹ where we studied the influence of the alkoxy chains in the azines, which directly define the maximum length of the molecule. However, what the effect of changing the length of the bridging carboxylates should be is less obvious, since these carboxylates span out of the main molecular dimension (*Z*); although at first sight this should disturb the easy packing of molecules leading to mesogenic properties, we felt that the carboxylic chains could eventually align themselves along the main molecular direction (*Z*) and allow mesogenic behavior, thus providing a second tuner of properties. In order to check this idea, we have prepared the series of book-shaped derivatives $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CC}_n\text{H}_{2n+1})_2]$ ($n = 0-11, 13, 15, 17$) and studied their thermotropic behavior by hot-stage optical microscopy, differential scanning calorimetry, and X-ray diffraction on the mesophases (Figure 1).

Results and Discussion

Synthesis and Characterization of the Complexes.

The family of complexes $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C-C}_n\text{H}_{2n+1})_2]$ is straightforwardly obtained by exchange reactions in one (method B) or two steps (method A) as shown in Scheme I.

Thus, the preparation of a series of related complexes in order to study the influence of the alkyl chain on their mesogenic properties is achieved very easily compared to the usually lengthy and tedious methods that are needed when the alkyl chain to be varied is linked to an organic substrate.

The analytical results, yields, and molecular weights of the complexes are collected in Table I. The molecular weights of the complexes in solution show that they are dimeric for the entire range of bridging carboxylates investigated.

It is inferred from crystallographic studies on related complexes¹¹⁻¹³ that these carboxylato-bridged dimers have the structure of an open book (Figure 1) with a dihedral angle between the covers of about 30°, and we have previously shown^{9,10,14} that this structure does not undergo

Table I. Analytical Data, Yields, and Molecular Weights for $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CC}_n\text{H}_{2n+1})_2]$ (Calculated Values in Parentheses)

<i>n</i>	anal.			yield, %	mol wt
	C	H	N		
0	62.50 (62.63)	7.71 (7.81)	4.23 (4.17)	55	1321 (1342.4)
1	62.99 (63.10)	7.70 (7.94)	4.16 (4.09)	50	1397 (1370.5)
2	63.20 (63.55)	7.99 (8.07)	4.10 (4.00)	73	1369 (1398.6)
3	63.93 (63.99)	8.42 (8.20)	3.79 (3.93)	75	1412 (1426.6)
4	64.51 (64.40)	8.20 (8.31)	3.80 (3.85)	78	1432 (1454.7)
5	65.02 (64.80)	8.74 (8.43)	3.76 (3.78)	72	1451 (1482.7)
6	65.32 (65.19)	8.61 (8.54)	3.75 (3.71)	76	1493 (1510.8)
7	65.76 (65.57)	8.70 (8.65)	3.46 (3.64)	78	1526 (1538.8)
8	66.12 (65.93)	8.60 (8.75)	3.50 (3.58)	73	1532 (1566.9)
9	65.99 (66.27)	8.75 (8.85)	3.40 (3.51)	71	1575 (1594.9)
10	66.60 (66.60)	9.03 (8.94)	3.35 (3.45)	80	1635 (1623.0)
11	66.53 (66.93)	9.20 (9.04)	3.41 (3.39)	75	1630 (1651.0)
13	67.39 (67.54)	9.10 (9.21)	3.14 (3.28)	71	1691 (1707.1)
15	69.39 (69.22)	9.60 (9.52)	3.14 (3.23)	73	1698 (1735.2)
17	70.45 (70.85)	9.95 (9.83)	3.15 (3.18)	77	1740 (1763.2)

easy inversion in solution for orthopalladated derivatives. This kind of rigid nonplanar structure makes pairs of hydrogens diastereotopic in some methylene groups. This is the case with the methylene groups of the alkoxy chains for both the *cis* and the *trans* isomers; this is also the case with the methylene groups of the carboxylate bridges in the *trans* isomers. In the *cis* isomers, a symmetry plane makes the two hydrogens in each methylene group of the carboxylate chains enantiotopic, but the two bridges are inequivalent (see below and Table II).

¹H NMR parameters for the complexes are collected in Table II. All the compounds consist of a mixture within a range of 23 ± 2% of the *cis* isomer and 77 ± 2% of the *trans* isomer. The parameters of the azine moiety are the same for all the complexes within less than ±0.03 ppm for the chemical shifts and less than ±0.2 Hz for the coupling constants and are given in parts A and B, respectively, Table II; only H_α for the formato-bridged complex shows a greater variation, appearing at 8.44 (*trans*) and 8.52 (*cis*) ppm.

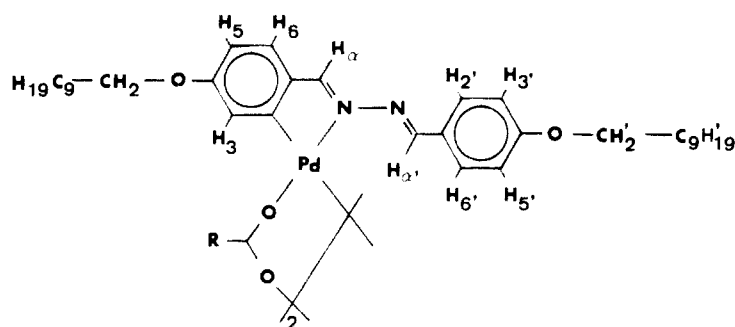
The methyl and most of the methylene groups of the alkoxy and carboxylate chains overlap in the range 0.8–1.9 ppm. Only the methylene groups directly linked to the oxygen atom (in the alkoxy chains) or the CO₂ group (in

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Table II. ^1H NMR Parameters^a for the Complexes(A) Chemical Shifts (δ) for the Azine Moieties (See Text)

isomer	δ /ppm (multiplicities)							
	H ₆	H ₅	H ₃	H ₂ , H _{6'}	H _{3'} , H _{5'}	H _α	H _{α'}	CH ₂
trans	7.05 (d)	6.47 (d, d)	6.27 (d)	7.52 (d)	6.86 (d)	7.68 (s)	8.50 (s)	3.70–3.50 (m) 3.40–3.20 (m)
cis	<i>b</i>	<i>b</i>	<i>b</i>	7.32 (d)	6.67 (d)	7.95 (s)	8.58 (s)	3.95–3.75 (m)

(B) Coupling Constants (Hz) for the Azine Moieties

isomer	$J(\text{H}_{5,6})$	$J(\text{H}_{5,3})$	$J(\text{H}_{2,3'})$
trans	8.4	2.3	8.9
cis	<i>b</i>	<i>b</i>	8.8

(C) Chemical Shifts of the Distinct Protons for Some Carboxylic Bridges

R	δ /ppm (multiplicities)	
	trans	cis
H	8.17 (s)	8.08 (s), 8.21 (s)
CH ₃	2.09 (s)	2.34 (s), <i>b</i>
CH ₂ CH ₃	2.31 (m)	2.49 (q), 2.06 (q)
CH ₂ R'	2.29 (m)	2.49 (t), 2.04 (t)

^a In CDCl₃, recorded at 200 MHz. ^b Cis signal overlapped by other signals.

the carboxylate chains) can be observed separately and are reported in parts A and C of Table II. It can be noted that in the trans isomers the two bridges are equivalent (through a C_2 axis) whereas in the cis isomers they are inequivalent and give rise to different signals. Moreover, in the propionate complex, for example (Table IIC), the methylene signals in the cis isomer are simple quartets as expected for the A part of an A_2X_3 system; the trans isomer, however, produces a multiplet consistent with the AB part of the expected ABX_3 system.

Mesogenic Behavior. All the complexes show liquid crystalline properties (enantiotropic or monotropic), and the mesophases were identified by their optical textures as nematic and smectic C phases. The transition temperatures and enthalpies were determined by DSC and are summarized in Table III.

The complex with $n = 0$ shows a smectic C phase, which is observed by optical microscopy, but decomposes just after melting. When the chain length of the carboxylate group is increased to $n = 1$, the complex melts to an anisotropic liquid, which was identified as a smectic C phase, with a range of stability of 19.3 °C.

For $n = 2$ two enantiotropic phases are found (nematic and smectic C). For $n = 3$ a monotropic smectic C phase and an enantiotropic nematic phase are observed. The homologues with $n = 4$ –9 exhibit only a nematic phase (enantiotropic for $n = 4$ –6 and monotropic for $n = 7$ –9). For the higher homologues ($n = 10, 11, 13, 15, 17$), two mesophases are again observed (monotropic smectic C and enantiotropic nematic for $n = 10, 13, 17$ and both monotropic for $n = 11, 15$).

The transition temperatures of the compounds versus the alkyl lengths of the central carboxylate are displayed in Figure 2. As can be seen, the melting temperatures

change quite irregularly within a short range of temperatures (90–132 °C). The clearing temperatures decrease with increasing length of the bridging carboxylate up to $n = 7$, and then the temperatures are practically similar, with a variation in a range of 7 °C (between 103.3 °C ($n = 15$) and 110.5 °C ($n = 9$)).

It is remarkable that, in contrast to what happens in typical rodlike molecules, where the smectic phases are suppressed by lateral branches,^{15,16} the complexes described here show smectic phases for the shortest ($n = 1$ –3) and for the longest chains ($n \geq 10$) but not for intermediate lengths; furthermore, carboxylates of intermediate length ($n = 3$ –9) produce a pronounced decrease in the nematic–isotropic transition temperatures. In other words, small increases in the length of the carboxylate chain make the molecular ordering in the mesophase more difficult, whereas sufficiently long carboxylates again facilitate this molecular arrangement. This behavior can be easily understood by the intuitive model shown in Figure 3. When the length of the carboxylate bridges is increased from short to medium, the lateral size x increases and the z/x ratio decreases since the molecular length z is constant, thus reducing the tendency for ordered molecular packing. After a few more carbons are added, however, the flexible alkyl chains in the carboxylate will be able to orient themselves along the z axis without further increase of the lateral size x and contribute to the intermolecular interactions, and the smectic properties appear again. Eventually, a sufficiently long carboxylate may produce an increase in the z dimension and consequently begin to pro-

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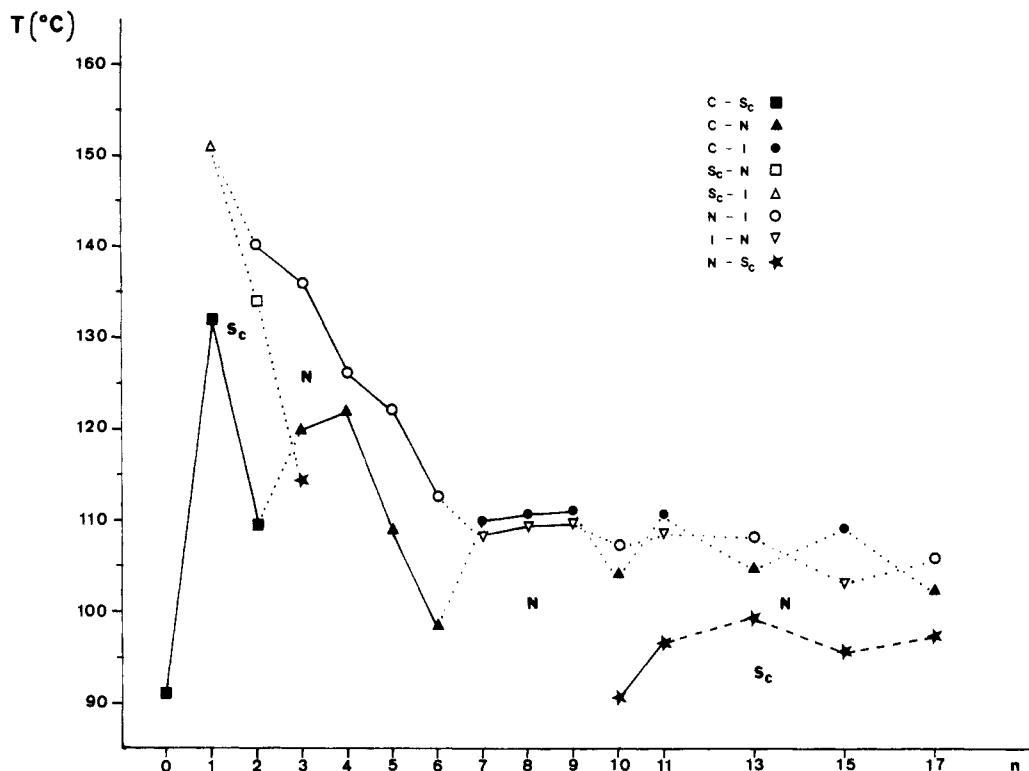


Figure 2. Transition temperatures as a function of the bridging carboxylate length of the complexes.

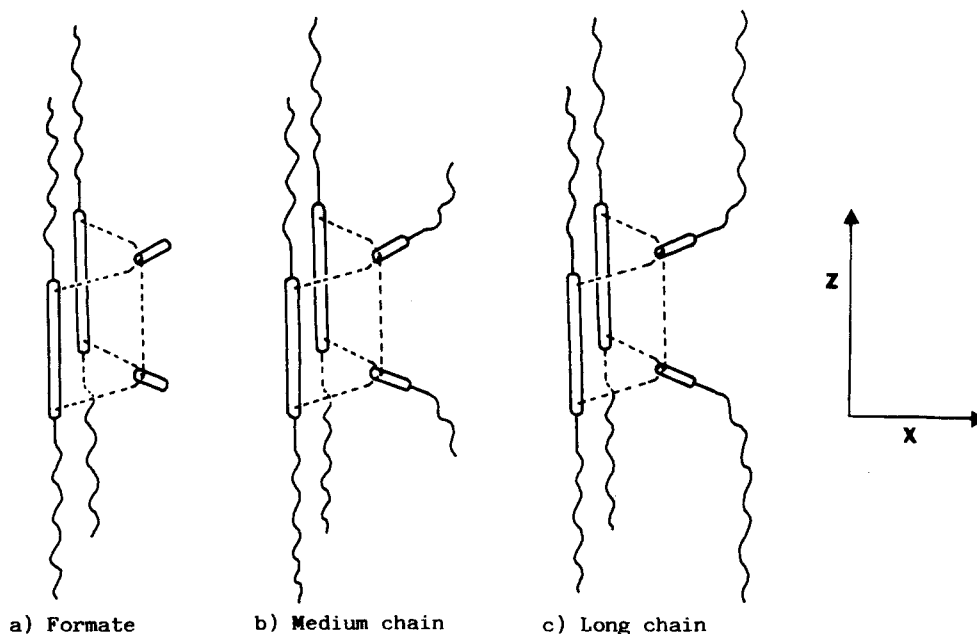


Figure 3. Model for the carboxylate chain arrangements.

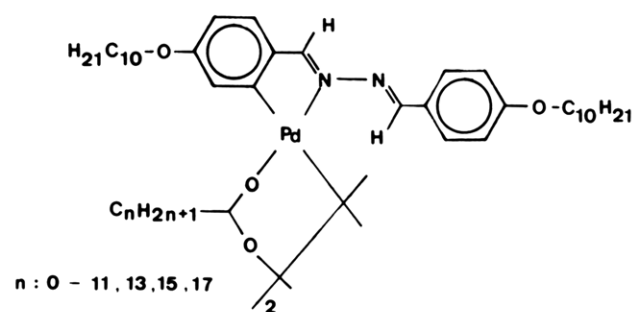
duce a recovery of the z/x ratio.

X-ray Diffraction Study. In order to confirm our intuitive ideas about the molecular packing in the mesophase by some quantitative measurements, we have performed X-ray diffraction experiments on magnetically aligned samples. Three compounds have been studied, those with central alkyl carboxylate chains containing 3, 4, and 16 carbon atoms ($n = 2, 3, 15$).

Figure 4 shows that all these samples orient easily in the nematic state. The director is parallel to the magnetic field, and the pattern is very similar to that of a rodlike nematic phase. The proximity of the smectic phase induces smectic C like fluctuations, indicated by the four-point pattern at small angles (2θ about 2.8 – 3.0°), at least for the two short-length derivatives ($n = 2, 3$). This value

gives a layer spacing of about 28 – 29 Å for the short homologues ($n = 2, 3$) and 30 – 31 Å for the long homologue ($n = 15$). The apparent molecular length calculated from the X-ray data is about 34 – 35 Å for $n = 2, 3$ and 37 Å for $n = 15$. The apparent length is smaller than the length of the ligand in a fully extended conformation (42 Å, calculated from Dreiding stereomodels). The chains are in fact rather disordered, but with a denser packing in the case of the $n = 15$ compound. From the layer spacing and apparent molecular length data we obtain a tilt angle of 35 – 36° for the three complexes studied.

The large-angle diffuse crescents take place at a scattering angle 2θ of about 19 – 20° , corresponding to a distance perpendicular to the director of about 4.2 Å for $n = 2, 3$ and 4.5 Å for $n = 15$. The angular extension of these

Table III. Optical, Thermal, and Thermodynamic Data for the Complexes

<i>n</i>	transition	temp, °C	ΔH , kJ/mol
0	C-S _C	90.9 ^b	78.8
1	C-S _C	131.8	71.6
	S _C -I	151.1	5.7
2	C-S _C	109.5	56.2
	S _C -N	133.8	3.9
	N-I	140.2	2.7
3	C-C'	88.6	42.9
	C'-N	119.9	18.5
	N-I	135.8	2.0
	N-S _C ^a	114.6	1.7
4	C-C'	85.2	25.4
	C'-N	122.2	31.1
	N-I	126.3	2.5
5	C-N	108.7	53.7
	N-I	121.8	1.9
6	C-N	98.4	71.2
	N-I	112.6	1.8
7	C-I	109.5	52.9
	I-N ^a	108.8	1.7
8	C-C'	67.5	9.2
	C'-I	110.6	56.1
	I-N ^a	109.9	2.3
9	C-C'	80.9	38.9
	C'-I	110.8	55.5
	I-N ^a	110.5	1.9
10	C-N	104.0	80.8
	N-I	106.9	2.3
	I-S _C	90.6	1.8
11	C-I	110.3	95.2
	I-N ^a	108.4	2.1
	N-S _C ^a	96.5	1.9
13	C-N	104.5	77.1
	N-I	108.2	2.2
	N-S _C ^a	98.9	2.4
15	C-I	109.3	80.5
	I-N ^a	103.3	1.5
	N-S _C ^a	95.6	2.9
17	C-N	102.1	75.6
	N-I	105.6	2.6
	N-S _C ^a	96.9	3.3

^a Monotropic transition. ^b The complex decomposes just after melting.

crescents has the usual value for a nematic phase. A slight difference in the maximum intensity position cannot be related to any change in the lateral size of molecules, since very complex pair correlation functions have to be taken into account in any prediction of the diffraction pattern. However, if some features of the diffraction pattern can be unambiguously assigned to Pd-Pd interferences, a better view of the organization of the complexes can be obtained.

In fact, the difference between the pattern of the nematic phase of this series and that of the usual rodlike

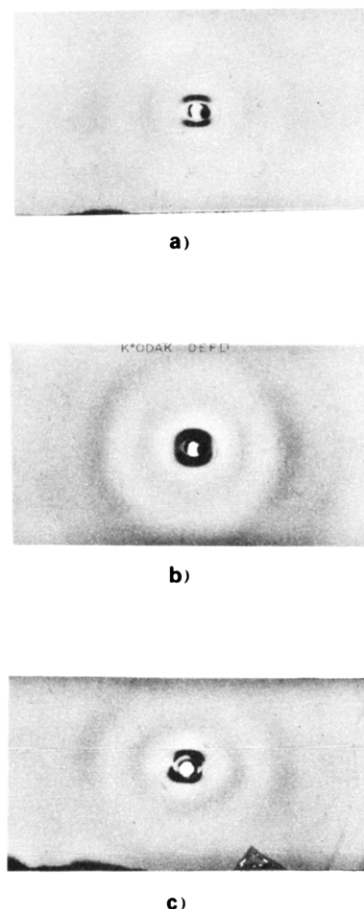


Figure 4. X-ray diffraction patterns of samples aligned by a magnetic field of 1.7 T (X-ray wavelength λ (Cu K α), cylindrical film, Sample-film distance 60 mm): (a) $n = 3$, $T = 126^\circ\text{C}$, nematic phase, exposure time 30 min; (b) $n = 15$, $T = 100^\circ\text{C}$, nematic phase, exposure time 2 h; (c) $n = 2$, $T = 130^\circ\text{C}$, smectic C phase, exposure time 30 min.

nematic phase is clearly seen in the pattern of high exposure times (Figure 4b). A diffuse shell with an ellipsoid shape is seen with scattering angles 2θ of about $9-10^\circ$. The ellipsoids have the same shape and size in the three compounds studied. The shortest axis of the ellipsoid is parallel to the director. In the equatorial plane the maximum corresponds to a mean distance between atoms of about $8.5-8.7 \text{ \AA}$. This distance is probably related to the distance between two molecules put side by side (Figure 5A shows one of the possible arrangements), and the scattered intensity is due to Pd-Pd interference. A similar feature was seen with a weaker intensity in the case of some copper complexes in a S_A phase.¹⁷ In the case of the Pd complexes the intensities of the inner equatorial crescent (at $2\theta = 10^\circ$) and of the outer one (at $2\theta = 19-20^\circ$) are nearly the same, while the ratio between the intensity of the inner and the outer maxima is less than 1/10 for the previously mentioned copper complexes. Even if we take the Pd/Cu structure factor ratio into account, it seems that the possibility of a side-by-side array is higher for this series than for the Cu complexes. Therefore, the idea of a local ribbon array induced by the book shape appears to be confirmed by the X-ray data. However, the real proof can only be obtained by a comparison between the number of Pd-Pd pairs of $8.5-8.7$ - and $4.2-4.5$ - $\text{\AA}$ separation. Information of this type requires the use of other diffraction

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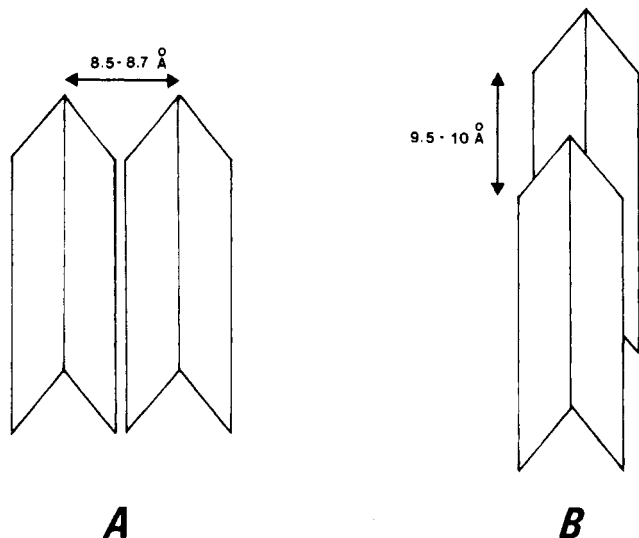


Figure 5. Possible local molecular arrangements of the book-shaped orthopalladated dimers in the mesophase.

techniques, such as anomalous X-ray scattering or neutron diffraction.

The existence of a maximum along the meridian parallel to the director at a scattering angle 2θ of about $9-9.2^\circ$ is more surprising. The corresponding mean distance of about $9.5-10 \text{ \AA}$ cannot be accounted for by the existence of a local S_C array with a tilt angle of $35-36^\circ$. This makes us think that the adjacent complex molecules are parallel but that the central parts of the complexes tend to lie at a distance of $9.5-10 \text{ \AA}$ parallel to the director (Figure 5B). However, this relative translation of two adjacent molecules is not correlated at a long distance.

We had difficulty in obtaining X-ray patterns of the S_C phase. Figure 4c presents one of the patterns obtained. It is clear that this pattern confirms the S_C symmetry. Nevertheless, the local order of the Pd atoms characterized by the inner ellipsoid scattered surface does not change when the sample is cooled from the nematic to the smectic C phase.

Experimental Section

General Considerations. ^1H NMR spectra were recorded on a Varian XL-200 spectrometer. IR spectra were obtained on a Perkin-Elmer 599 spectrometer. Microanalyses were performed with a Perkin-Elmer 240 B microanalyzer. Molecular weights were measured in CHCl_3 solution with a Knauer apparatus (isopiestic method).

The textures of the mesophases were studied with a Meiji polarizing microscope equipped with a Mettler FP82 hot stage and FP80 central processor.

Transition temperatures were measured by differential scanning calorimetry with a Perkin-Elmer DSC-2 instrument operated at a scanning rate of 5 K/min on heating. The apparatus was calibrated with indium (429.6 K ; 28.4 J/g) and tin (505.06 K ; 60.46 J/g) as standards.

X-ray diffraction experiments were carried out with use of a monochromatic $\text{Cu K}\alpha$ X-ray beam issued from a double bent pyrolytic graphite monochromator. The samples, held in a Lindemann glass tube ($\phi = 0.5 \text{ mm}$), were aligned by a magnetic field perpendicular to the X-ray beam. The temperature of the sample was constant within $\pm 1 \text{ K}$. The diffraction pattern was collected on a photographic film.

Synthesis of the Precursors. The synthesis of the azine was described in a previous paper.¹⁸ $[\text{Pd}(\text{C}_{10}\text{H}_{21}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-X})_2]$ ($\text{X} = \text{OAc}, \text{Cl}$) were prepared as reported before.⁹

Synthesis of the Complexes. All the complexes can be prepared by either of the two methods described below with similar yields.

Caution! Method A, which avoids wasting large amounts of sodium carboxylate, involves the use of AgClO_4 . It is known that perchlorates are potentially explosive and great care should be exercised when handling them.

Method A. $[\text{Pd}(\text{C}_{10}\text{H}_{21}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-Cl})_2]$ (200 mg) in acetone (40 mL) was stirred for 10 h with the stoichiometric amount of AgClO_4 ($\text{Pd/Ag} = 1/1$), shielded from the light. The white precipitate (AgCl) was filtered off, and the corresponding $\text{NaO}_2\text{CC}_n\text{H}_{2n+1}$ ($\text{Pd/carboxylate} = 1/2$) was added to the orange solution, whereupon a color change to yellow occurred and a yellow precipitate began to appear slowly. After the mixture was stirred for 24 h, the solvent was evaporated off, the yellow residue was extracted into CH_2Cl_2 , the extract was filtered to remove NaClO_4 , and the compound was crystallized by evaporation and the addition of ethanol.

Method B. $[\text{Pd}(\text{C}_{10}\text{H}_{21}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-Cl})_2]$ (200 mg) and a large excess of the corresponding $\text{NaO}_2\text{CC}_n\text{H}_{2n+1}$ ($\text{Pd/carboxylate} = 1/15$) in acetone (40 mL) were refluxed for 14 h. The solvent was evaporated off, and the yellow residue was worked up as in method A.

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Registry No. $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CH})_2]$, 127421-22-1; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CCH}_3)_2]$, 127421-23-2; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{CCH}_2\text{CH}_3)_2]$, 127421-24-3; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_2\text{CH}_3)_2]$, 127421-25-4; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_3\text{CH}_3)_2]$, 127421-26-5; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_4\text{CH}_3)_2]$, 127421-27-6; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_5\text{CH}_3)_2]$, 127421-28-7; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_6\text{CH}_3)_2]$, 127421-29-8; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_7\text{CH}_3)_2]$, 127421-30-1; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_8\text{CH}_3)_2]$, 127421-31-2; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_9\text{CH}_3)_2]$, 127421-32-3; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_{10}\text{CH}_3)_2]$, 127421-33-4; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_{12}\text{CH}_3)_2]$, 127421-34-5; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_{14}\text{CH}_3)_2]$, 127421-35-6; $[\text{Pd}(\text{H}_{21}\text{C}_{10}\text{OC}_6\text{H}_3\text{CH}=\text{NN}=\text{CHC}_6\text{H}_4\text{OC}_{10}\text{H}_{21})(\mu\text{-O}_2\text{C}(\text{CH}_2)_{16}\text{CH}_3)_2]$, 127421-36-7.

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