

This article was downloaded by:

On: 25 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Liquid Crystals

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713926090>

Bis(salicylaldiminate) copper(II) and palladium(II) complexes: towards columnar mesophases

Joaquín Barberá^a; Raquel Giménez^a; Nélida Gimeno^a; Mercedes Marcos^a; Maria Del Carmen Pina^b; José Luis Serrano^a

^a Química Orgánica, Facultad de Ciencias-Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009 Zaragoza, Spain, ^b Instituto de Materiales y Reactivos. Universidad de La Habana. Zapata y G, Vedado. 10400 La Habana, Cuba,

Online publication date: 11 November 2010

To cite this Article Barberá, Joaquín , Giménez, Raquel , Gimeno, Nélida , Marcos, Mercedes , Pina, Maria Del Carmen and Serrano, José Luis(2003) 'Bis(salicylaldiminate) copper(II) and palladium(II) complexes: towards columnar mesophases', *Liquid Crystals*, 30: 6, 651 – 661

To link to this Article: DOI: 10.1080/0267829031000099617

URL: <http://dx.doi.org/10.1080/0267829031000099617>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Bis(salicylaldiminate) copper(II) and palladium(II) complexes: towards columnar mesophases

JOAQUÍN BARBERÁ, RAQUEL GIMÉNEZ, NÉLIDA GIMENO,
MERCEDÉS MARCOS, MARIA DEL CARMEN PINA† and
JOSÉ LUIS SERRANO*

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

†Instituto de Materiales y Reactivos. Universidad de La Habana. Zapata y G,
Vedado. 10400 La Habana, Cuba

(Received 30 September 2002; in final form 20 January 2003; accepted 21 January 2003)

Copper and palladium complexes of new salicylaldimines derived from 3,4,5-tridecyloxyaniline, 2,3,4-tridecyloxyaniline and 4-decyloxyaniline have been synthesized and characterized. All the ligands bear four or more aliphatic chains with the aim of inducing columnar mesophases at low temperatures. In particular, metal complexes derived from 4-(3,4,5-tridecyloxybenzoyloxy)-salicyliden-3,4,5-tridecyloxyaniline display rectangular columnar mesophases at (or near) room temperature. These mesophase assignments have been confirmed by X-ray diffraction. A significant decrease of the melting points of the compounds is observed in the tridecyloxyaniline derivatives compared with those of similar complexes derived from mono- or di-decyloxyaniline.

1. Introduction

The incorporation of transition metals into liquid crystals has led to the study of interesting magnetic, electronic and optical properties in mesomorphic materials [1]. Moreover, this area of research has led to the discovery of new molecular structures capable of producing both known and new mesomorphic phases, and now the study of structure–property relationships is a major concern [2–5].

Salicylaldimines have been employed in the synthesis of metallomesogens due to their synthetic versatility and ability to coordinate metals [6]. In the literature many salicylaldiminate metal complexes are reported to exhibit lamellar or nematic phases. In particular, complexes of *N*-(4'-alkoxyphenyl)-4-alkoxysalicylaldimines (two-ring ligand systems with two flexible chains) have an overall brick-like shape leading to the formation of smectic phases [7]. Other complexes derived from *N*-(4'-alkoxyphenyl)-4-alkoxybenzoyloxysalicylaldimines (three-ring ligand systems with two flexible chains) have a higher length-to-breadth ratio and display nematic and/or smectic C phases depending on the length of the aliphatic chains [8]. Similar compounds with an additional alkoxy chain at the 2- or 3-position of the benzoyloxy moiety exhibit lower transition temperatures and display nematic and smectic phases, respectively [9].

On the other hand, only a few salicylaldiminate complexes display columnar phases [10]. Among these studies Lai *et al.* recently reported that an appropriate adjustment of the aspect ratio in the two-ring ligand system by introducing two alkoxy chains in the aniline leads to copper complexes with columnar mesophases [10c].

Following our work describing molecular structure and mesogenic properties using salicylaldimines, we are particularly interested in obtaining columnar phases with copper complexes for which paramagnetic properties are expected [11]. The design of ligands with four or more aliphatic chains should lead to complexes with columnar behaviour at low temperatures. Moreover, by modifying the shape of the ligand, their complexes may sit at the interface between uniaxial and biaxial behaviour. In the present paper we report the synthesis and characterization of new salicylaldimine ligands derived from 3,4,5-tri-decyloxyaniline (series **a** and **c**), 2,3,4-tridecyloxyaniline (series **b** and **d**) or 4-decyloxyaniline (series **e**) together with their copper and palladium complexes (figure 1); the study of their thermal properties will shed light on the limits of the mesomorphism of these systems when changing the position of the substituents.

2. Experimental

2.1. Characterization

Elemental analysis were performed using a Perkin-Elmer 240B microanalyser. Infrared spectra were obtained with

* Author for correspondence; e-mail: joseluis@posta.unizar.es

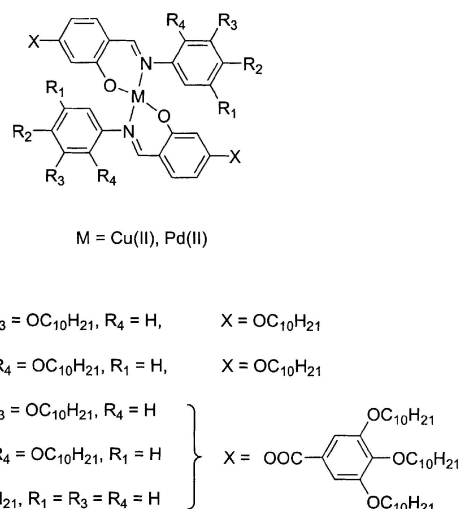


Figure 1. Structure of the metal complexes examined in this study.

a Mattson Genesis (FTIR) spectrophotometer in the range $\nu = 400\text{--}4000\text{ cm}^{-1}$; ^1H NMR and ^{13}C NMR spectra were recorded on a Varian Unity 300 MHz spectrometer in CDCl_3 solutions. The optical textures of the mesophases were studied with an Olympus polarizing microscope equipped with a Linkam THMS600 hot stage and a CS196 cooling system. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a Perkin-Elmer DSC-7 or TA Instruments

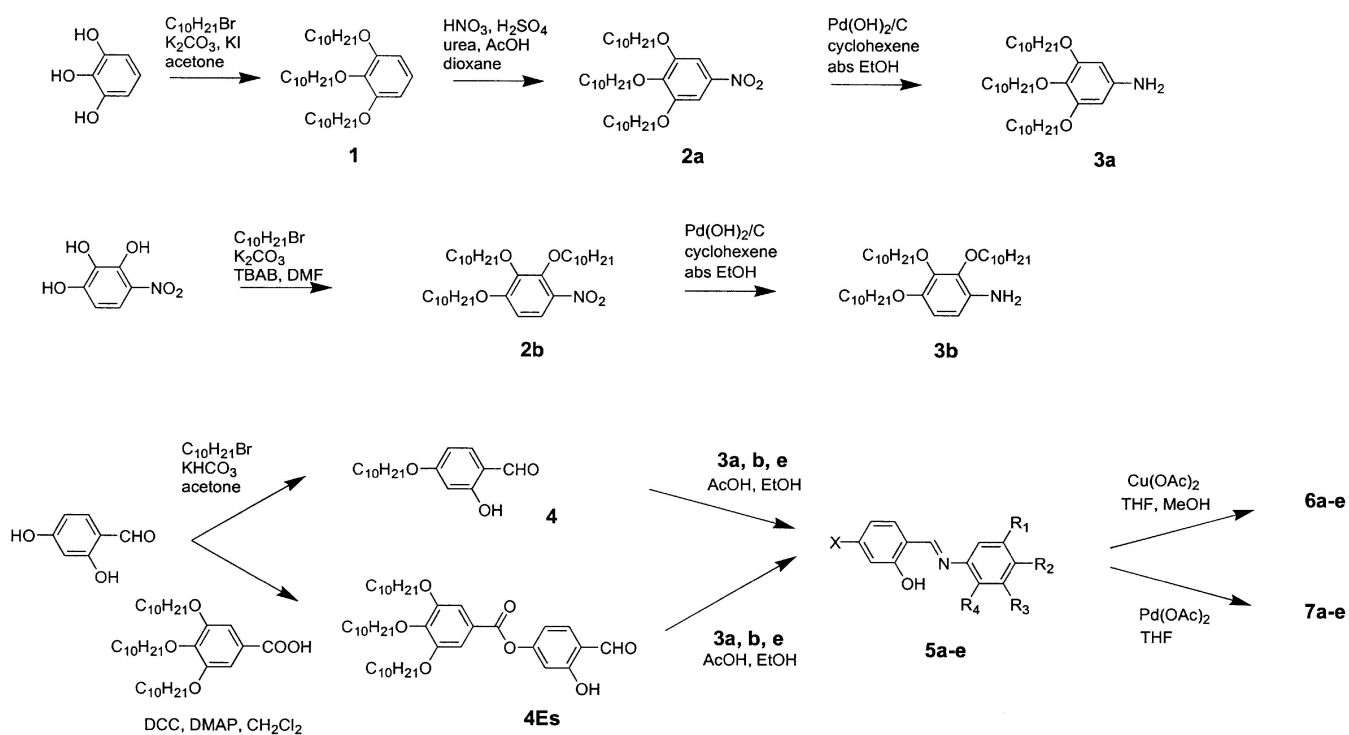
calorimeter operated at a scanning rate of $10^\circ\text{C min}^{-1}$ on heating. The apparatus were calibrated with indium (156.6°C ; 28.4 J g^{-1}) as standard. X-ray diffraction (XRD) measurements were performed with a Pinhole camera (Anton-Paar) operating with a point-focused Ni-filtered Cu-K_α beam. The sample was held in Lindemann glass capillaries (1 mm diameter) and heated, when necessary, with a variable temperature attachment. The patterns were collected on flat photographic film. The capillary axis and the film were perpendicular to the X-ray beam. Spacings were obtained via Bragg's law.

2.2 Synthesis

p-Decyloxyaniline (**3e**) was prepared as previously described [12]. The new compounds were obtained following the synthetic pathways shown in the scheme.

2.2.1. 1,2,3-Tridecyloxybenzene (**1**)

To a stirred solution of 5.00 g (0.04 mol) of 1,2,3-trihydroxybenzene, 24.84 g (0.18 mol) of K_2CO_3 and 0.008 mol of KI in 300 ml of dry acetone, was added dropwise 28.28 g (0.128 mol) of bromodecane; the mixture was heated at reflux and stirred for 48 h under an argon atmosphere. The precipitate was filtered off and the solvent removed from the filtrate under vacuum. The product was purified by flash chromatography using 1/1 hexane/dichloromethane as eluent. A white solid was obtained; yield 70%. IR (Nujol, cm^{-1}) ν 1595 (C-C_{Ar}), 1252 (C-O).



^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.0$ Hz, 9H), 1.23–1.54 (m, 42H), 1.72–1.79 (m, 6H), 3.93–4.01 (m, 6H), 6.5 (d, $J = 8.4$ Hz, 2H), 6.8 (t, $J = 8.4$ Hz, 1H).

2.2.2. 1,2,3-Tridecyloxy-5-nitrobenzene (**2a**)

To a mixture of 0.1 g of urea, 2 ml of acetic acid, 0.3 ml of nitric acid and 0.4 ml of sulphuric acid at 0°C was added a solution of 1.00 g (1.83 mmol) of 3,4,5-tridecyloxybenzene in 5 ml of 1,4-dioxane to give a dark red solution. The mixture was stirred at room temperature for 4 h. The reaction mixture was added to distilled water (50 ml) and extracted into diethyl ether; this extract was washed with saturated NaHCO_3 , dried over MgSO_4 and evaporated under vacuum. The product was recrystallized from ethanol; yield 45%, m.p. 42°C . IR (Nujol, cm^{-1}) ν 1510 (NO_2), 1344 (NO_2), 1321 (NO_2), 1236 (C–O). ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 9H), 1.23–1.52 (m, 42H), 1.7 (m, 6H), 4.03 (m, 6H), 7.4 (s, 2H).

2.2.3. 1,2,3-Tridecyloxy-4-nitrobenzene (**2b**)

To a mixture of 1 g (5.55 mmol) of 1,2,3-trihydroxy-4-nitrobenzene and 8 g (57.97 mmol) of K_2CO_3 in 20 ml of *N,N*-dimethylformamide (DMF) were added, first 3.69 g (16.65 mmol) of bromodecane dropwise and then 0.1 g of tetrabutylammonium bromide (TBAB). The mixture was stirred at 60°C for 4 h under an argon atmosphere. The reaction mixture was added carefully to 50 ml of distilled water. After acidifying with dilute hydrochloric acid, the product was extracted into diethyl ether. The crude product was purified by flash chromatography using 100/3 hexane/ethyl acetate as eluent; yield 66%. IR (Nujol, cm^{-1}) ν 1521 (NO_2), 1348 (NO_2), 1290 (C–O). ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.8$ Hz, 9H), 1.25–1.53 (m, 42H), 1.69–1.85 (m, 6H), 3.93 (t, $J = 6.4$ Hz, 2H), 4.01 (t, $J = 6.4$ Hz, 2H), 4.11 (t, $J = 6.4$ Hz, 2H), 6.62 (d, $J = 8.8$ Hz, 1H), 7.63 (d, $J = 8.8$ Hz, 1H).

2.2.4. Synthesis of the anilines (**3a**, **b**)

To a solution of 620 mg (1.04 mmol) of the nitro derivative **2a** or **2b** in absolute ethanol (20 ml) and cyclohexene (10 ml) was added, 93.2 mg of 20% palladium hydroxide on carbon (15% w/w catalyst/substrate), and the mixture was heated under reflux for 18 h. The catalyst was removed by filtration through celite and the solvent was then removed using a rotary evaporator. The crude product was recrystallized from ethanol to obtain the compounds as white solids.

3a: IR (Nujol, cm^{-1}) ν 3300 (N–H), 1211 (C–O). ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6$ Hz, 9H), 1.24–1.58 (m, 42H), 1.7 (m, 6H), 3.5 (br s, 2H), 3.9 (m, 6H), 5.9 (s, 2H).

3b: IR (Nujol, cm^{-1}) ν 3300 (N–H), 1266 (C–O). ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 9H), 1.25–1.53 (m, 42H), 1.69–1.85 (m, 6H), 3.12 (br s,

2H) 3.85 (t, $J = 6.4$ Hz, 2H), 3.96 (t, $J = 6.4$ Hz, 2H), 4.01 (t, $J = 6.4$ Hz, 2H), 6.35 (d, $J = 8.2$ Hz, 1H), 6.46 (d, $J = 8.2$ Hz, 1H).

2.2.5. 4-Decyloxy-2-hydroxybenzaldehyde (**4**)

To a solution of 10.00 g (0.072 mol) of 2,4-dihydroxybenzaldehyde and 7.24 g (0.072 mol) of KHCO_3 in 400 ml of dry acetone, was added 15.91 g (0.072 mol) of bromodecane, dropwise, and the mixture was heated under reflux for 24 h. The precipitate was filtered off and the solvent was removed from the filtrate under vacuum. The crude product was purified by flash chromatography using first 3/1 and then 1/1 hexane/toluene as eluent; yield 52%, m.p. 32°C . IR (Nujol, cm^{-1}) ν 1644 (C=O), 1220 (C–O). ^1H NMR (300 MHz, CDCl_3) δ 0.84 (t, $J = 6.5$ Hz, 3H), 1.26–1.81 (m, 16H), 4.01 (t, $J = 6.5$ Hz, 2H), 6.40 (d, $J = 2$ Hz, 1H), 6.52 (dd, $J = 2$ Hz, $J = 8.8$ Hz, 1H), 7.41 (d, $J = 8.8$ Hz, 1H), 10.31 (s, 1H), 11.30 (s, 1H).

2.2.6. 4-(3',4',5'-Tridecyloxybenzoyloxy)-2-hydroxybenzaldehyde (**4Es**)

A solution was prepared containing 540 mg (0.913 mmol) of 3,4,5-tridecyloxybenzoic acid, 126 mg (0.913 mmol) of 2,4-dihydroxybenzaldehyde and 188 mg (0.913 mmol) of *N,N'*-dicyclohexylcarbodiimide in 20 ml of dry dichloromethane. Then 11 mg (0.0913 mmol) of 4-dimethylaminopyridine were added and the mixture was stirred at room temperature for 3 h under an argon atmosphere. The mixture was filtered and the solvent removed from the filtrate under vacuum. The crude product was purified by flash chromatography using 10/1 hexane/ethyl acetate as eluent; yield 82% m.p. 46°C . IR (Nujol, cm^{-1}) ν 1726 (C=O), 1660 (C=O), 1192 (C–O). ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 9H), 1.25–1.85 (m, 48H), 4.02 (t, $J = 6.4$ Hz, 6H), 6.84 (d, $J = 2.2$ Hz, 1H), 6.88 (dd, $J = 2.2$ Hz, $J = 8.4$ Hz, 1H), 7.35 (s, 2H), 7.61 (d, $J = 8.4$ Hz, 1H), 9.87 (s, 1H), 11.24 (s, 1H).

2.2.7. General procedure for the synthesis of the Schiff bases (**5a–e**)

To a solution of 0.98 mmol of the aniline **3a**, **3b** or **3c** in 45 ml absolute ethanol was added one equivalent of the aldehyde **4** or **4Es** plus a drop of acetic acid. The mixture was heated at reflux for 24 h. The solvent was removed on a rotary evaporator and the residue dissolved in hexane and washed with water. After removing the solvent, products were obtained as yellow oils. Purification and characterization data for each imine are given below; yields 75–82%.

5a was purified by flash chromatography using neutral alumina (previously washed with methanol and dried under vacuum) and 7/3 hexane/ethyl acetate as eluent. IR (Nujol, cm^{-1}) ν 1617 (C=N), 1229 (C–O). Anal: calcd for $\text{C}_{53}\text{H}_{91}\text{NO}_5$ C 77.41, H 11.15, N 1.70; found C 77.38,

H 11.10, N 1.71%. ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 12H), 1.25–1.84 (m, 64H), 3.98 (m, 8H), 6.40 (m, 4H), 7.21 (d, $J = 8.4$ Hz, 1H), 8.44 (s, 1H), 13.8 (s, 1H).

5b was purified by flash chromatography using neutral alumina (previously washed with methanol and dried under vacuum) and 7/3 hexane/ethyl acetate as eluent. IR (Nujol, cm^{-1}) ν 1616 (C=N), 1228 (C=O). Anal: calcd for $\text{C}_{33}\text{H}_{91}\text{NO}_5$ C 77.41, H 11.15, N 1.70; found C 77.43, H 11.13, N 1.70%. ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 12H), 1.25–1.84 (m, 64H), 3.98 (m, 8H), 6.39 (d, $J = 3$ Hz, 1H), 6.43 (dd, $J = 3$ Hz, $J = 9$ Hz, 1H), 6.63 (d, $J = 9$ Hz, 1H), 6.86 (d, $J = 9$ Hz, 1H), 7.17 (d, $J = 9$ Hz, 1H), 8.51 (s, 1H), 14.22 (s, 1H).

5c was purified using flash chromatography on neutral alumina with 1/1 hexane/ethyl acetate as eluent. IR (Nujol, cm^{-1}) ν 1736 (C=O), 1619 (C=N), 1191 (C=O). Anal: calcd for $\text{C}_{81}\text{H}_{137}\text{NO}_9$ C 76.67, H 10.88, N 1.10; found C 76.70, H 10.85, N 1.11%. ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 18H), 1.25–1.84 (m, 96H), 3.89–4.04 (m, 12H), 6.49 (s, 2H), 6.77 (d, $J = 7.5$ Hz, 1H), 6.85 (s, 1H), 7.32 (s, 2H), 7.38 (d, $J = 7.5$ Hz, 1H), 8.57 (s, 1H), 13.4 (br s, 1H).

5d was recrystallized from an ethanol/dichloromethane mixture. IR (Nujol, cm^{-1}) ν 1726 (C=O), 1617 (C=N), 1201 (C=O). Anal: calcd for $\text{C}_{81}\text{H}_{137}\text{NO}_9$ C 76.67, H 10.88, N 1.10; found C 76.64, H 10.90, N 1.09%. ^1H NMR (300 MHz, CDCl_3) δ 0.86 (t, $J = 6.4$ Hz, 18H), 1.25–1.86 (m, 96H), 3.95–4.06 (m, 12H), 6.65 (d, $J = 9$ Hz, 1H), 6.75 (dd, $J = 9$ Hz, $J = 3$ Hz, 1H), 6.83 (d, $J = 3$ Hz, 1H), 6.91 (d, $J = 9$ Hz, 1H), 7.36 (d, $J = 9$ Hz, 1H), 7.38 (s, 2H), 8.66 (s, 1H), 14.11 (s, 1H).

5e was recrystallized from an ethanol/dichloromethane mixture. IR (Nujol, cm^{-1}) ν 1732 (C=O), 1620 (C=N), 1251 (C=O). Anal: calcd for $\text{C}_{60}\text{H}_{95}\text{NO}_7$ C 76.47, H 10.16, N 1.49; found C 76.44, H 10.18, N 1.48%. ^1H NMR (300 MHz, CDCl_3) δ 0.86 (m, 12H), 1.20–1.49 (m, 56H), 1.70–1.90 (m, 8H), 3.92–4.07 (m, 8H), 6.77 (dd, $J = 8.7$ Hz, $J = 2.3$ Hz, 1H), 6.83 (d, $J = 2.3$ Hz, 1H), 6.92 (d, $J = 8.7$ Hz, 2H), 6.91 (d, $J = 9$ Hz, 1H); 7.25 (d, $J = 8.7$ Hz, 2H), 7.38–7.40 (s, 3H), 8.60 (s, 1H), 13.82 (s, 1H).

2.2.8. General procedure for the synthesis of the copper complexes (**6a–e**)

To a solution 0.12 mmol of the imine in distilled tetrahydrofuran, was added 0.06 mmol of copper(II) acetate monohydrate in hot absolute ethanol, and the mixture was heated under reflux for 2 h. The solvent was removed and the crude product dissolved in dichloromethane and filtered through celite. The solvent was removed under vacuum to yield brown solids or oils; yield 82–87%.

6a: IR (Nujol, cm^{-1}) ν 1609 (C=N), 1216 (C=O), 1117 (C=O). Anal: calcd for $\text{C}_{106}\text{H}_{180}\text{N}_2\text{O}_{10}\text{Cu}$ C 74.62,

H 10.63, N 1.64; found C 74.55, H 10.66, N 1.64%. MS, FAB^+ : 1705 $[\text{M} + 1]^+$.

6b: IR (Nujol) ν (cm^{-1}): 1607 (C=N), 1214 (C=O), 1121 (C=O). Anal: calcd for $\text{C}_{106}\text{H}_{180}\text{N}_2\text{O}_{10}\text{Cu}$ C 74.62, H 10.63, N 1.64; found C 74.58, H 10.67, N 1.63%. MS, FAB^+ : 1705 $[\text{M} + 1]^+$.

6c: IR (Nujol, cm^{-1}) ν 1726 (C=O), 1609 (C=N), 1228 (C=O), 1114 (C=O). Anal: calcd for $\text{C}_{160}\text{H}_{268}\text{N}_2\text{O}_{18}\text{Cu}$ C 74.73, H 10.51, N 1.09; found C 74.69, H 10.59, N 1.10%. MS, FAB^+ : 1255 $[\mathbf{5c} + 2]^+$.

6d: IR (Nujol, cm^{-1}) ν 1735 (C=O), 1611 (C=N), 1192 (C=O), 1117 (C=O). Anal: calcd for $\text{C}_{160}\text{H}_{268}\text{N}_2\text{O}_{18}\text{Cu}$ C 74.73, H 10.51, N 1.09; found C 74.57, H 10.48, N 1.12%. MS, FAB^+ : 1255 $[\mathbf{5d} + 2]^+$.

6e: IR (Nujol, cm^{-1}) ν 1739 (C=O), 1615 (C=N). Anal: calcd for $\text{C}_{120}\text{H}_{188}\text{N}_2\text{O}_{14}\text{Cu}$ C 74.05, H 9.74, N 1.44; found C 74.10, H 9.80, N 1.41%. MS, FAB^+ : molecular peak not detected.

2.2.9. General procedure for the synthesis of the palladium complexes (**7a–e**)

A solution of 0.15 mmol of the requisite imine **5a–e** was dissolved in 10 ml of distilled THF and deoxygenated several times. Afterwards, 0.075 mmol of palladium acetate was added and the mixture was stirred at room temperature for 24 h. The solution was filtered through a pad of celite and the solvent evaporated under vacuum. An orange oil was obtained in all cases; yield 84–88%.

7a: IR (Nujol, cm^{-1}) ν 1600 (C=N), 1216 (C=O), 1117 (C=O). Anal: calcd for $\text{C}_{106}\text{H}_{180}\text{N}_2\text{O}_{10}\text{Pd}$ C 72.79, H 10.37, N 1.60; found C 72.71, H 10.03, N 1.70%. MS, FAB^+ : 1749 $[\text{M}^+]$. ^1H NMR (300 MHz, CDCl_3) δ 0.84–0.86 (m, 24H), 1.24–1.75 (m, 128H), 3.74 (t, $J = 6.4$ Hz, 4H), 3.94 (t, $J = 6.4$ Hz, 12H), 5.65 (d, $J = 2.1$ Hz, 2H), 6.12 (dd, $J = 2.1$ Hz, $J = 8.8$ Hz, 2H), 6.50 (s, 4H), 7.02 (d, $J = 8.8$ Hz, 2H), 7.56 (s, 2H).

7b: IR (Nujol, cm^{-1}) ν 1605 (C=N), 1212 (C=O), 1093 (C=O). Anal: calcd for $\text{C}_{106}\text{H}_{180}\text{N}_2\text{O}_{10}\text{Pd}$ C 72.79, H 10.37, N 1.60; found C 72.79, H 10.37, N 1.57%. MS, FAB^+ : molecular peak not detected. ^1H NMR (300 MHz, CDCl_3) δ 0.81–0.86 (m, 24H), 1.06–2.07 (m, 128H), 3.71 (t, $J = 6.6$ Hz, 4H), 3.94–4.09 (m, 12H), 5.50 (d, $J = 2.2$ Hz, 2H), 6.04 (dd, $J = 2.2$ Hz, $J = 8.7$ Hz, 2H), 6.61 (d, $J = 9$ Hz, 2H), 6.93 (d, $J = 9$ Hz, 2H), 6.96 (d, $J = 8.7$ Hz, 2H), 7.45 (s, 2H).

7c: IR (Nujol, cm^{-1}) ν 1725 (C=O), 1608 (C=N), 1226 (C=O), 1114 (C=O). Anal: calcd for $\text{C}_{160}\text{H}_{268}\text{N}_2\text{O}_{18}\text{Pd}$ C 73.51, H 10.33, N 1.07; found C 73.62, H 10.29, N 1.08%. MS, FAB^+ : 2614 $[\text{M}^+]$. ^1H NMR (300 MHz, CDCl_3) δ 0.71–0.86 (m, 36H), 1.25–1.83 (m, 192H), 3.89–4.03 (m, 24H), 6.06 (s, 4H), 6.36 (d, $J = 8.2$ Hz, 2H), 6.49 (s, 2H), 7.31 (s, 4H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.70 (s, 2H).

7d: IR (Nujol, cm^{-1}) ν 1734 (C=O), 1610 (C=N), 1192 (C=O). Anal: calcd for $\text{C}_{160}\text{H}_{268}\text{N}_2\text{O}_{18}\text{Pd}$ C 73.51,

H 10.33, N 1.07; found C 73.26, H 10.20, N 1.11%. MS, FAB⁺: molecular peak not detected. ¹H NMR (300 MHz, CDCl₃) δ 0.84–0.88 (m, 36H), 1.14–2.10 (m, 194H), 3.92–4.11 (m, 24H), 5.93 (d, *J* = 3 Hz, 2H), 6.29 (dd, *J* = 3 Hz, *J* = 9 Hz, 2H), 6.64 (d, *J* = 9 Hz, 2H), 6.95 (d, 2H, *J* = 9 Hz, 2H), 7.13 (d, *J* = 9 Hz, 2H), 7.33 (s, 4H), 7.60 (s, 2H).

7e: IR (Nujol, cm⁻¹) ν 1732 (C=O), 1605 (C=N), 1232, 1192 (C–O). Anal: calcd for C₁₂₀H₁₈₈N₂O₁₄Pd C 72.46, H 9.53, N 1.41; found C 72.41, H 9.56, N 1.39%. MS, FAB⁺: 1987 [M⁺]. ¹H NMR (300 MHz, CDCl₃) δ 0.86 (m, 24H), 1.20–1.90 (m, 128H), 3.93–4.07 (m, 16H), 6.05 (d, *J* = 2.4 Hz, 2H), 6.35 (dd, *J* = 8.8 Hz, *J* = 2.4 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 4H), 7.16 (d, *J* = 8.8 Hz, 2H), 7.20 (d, *J* = 8.8 Hz, 4H), 7.34 (s, 4H), 7.67 (s, 2H).

3. Results and discussion

3.1. Synthesis and characterization

Known synthetic procedures were adapted for the preparation of the compounds (see the scheme). In particular, the synthesis of 1,2,3-tridecyloxy-5-nitrobenzene was successfully accomplished by the nitration of 1,2,3-tridecyloxybenzene. Steric hindrance avoids nitration in the more electronically favoured 4-position [13]. The isomer 1,2,3-tridecyloxy-4-nitrobenzene was obtained by alkylation of 4-nitropyrogallol. The anilines were prepared in a straightforward manner from the nitro compounds by reduction with palladium hydroxide on carbon and cyclohexene.

The Schiff's bases were prepared by condensation of the aldehyde with the corresponding aniline in ethanol with acid catalysis. The compounds derived from tridecyloxyaniline (**5a–d**) have low melting points and were obtained from the reaction mixture as oils, which prevented their purification by recrystallization. Thus, these imines had to be purified by column chromatography using neutral alumina. The chromatographic technique proved to be a reproducible procedure if the alumina was washed with methanol and dried in an oven prior use.

Copper complexes were obtained by mixing a solution of the corresponding imine with a solution of copper(II) acetate. An immediate change of colour indicated complex formation; however the mixture was heated at reflux for 2 h to ensure completion of the reaction. Palladium complexes were prepared at room temperature to prevent decomposition of the palladium(II) acetate.

Attempts to obtain nickel and oxovanadium complexes with Schiff's bases **5a–d** proved unsuccessful. This may be due to the steric effects of the three long chains in the aniline fragment.

Complex formation was confirmed by IR spectroscopy; specifically, the C=N stretching vibration in the ligands is located in the 1616–1619 cm⁻¹ region and shifts to lower wavenumbers (1611–1607 cm⁻¹ in the copper com-

plexes and 1608–1600 cm⁻¹ in the palladium complexes), indicating that the azomethine N atom is involved in a metal–nitrogen bond. In addition, for the palladium complexes, the ¹H NMR spectrum shows a substantial shift for the aromatic protons to higher field with respect to the ligand. Figure 2 displays the assignment of the protons in the aromatic region for compounds **5d** and **7d**.

3.2. Mesomorphic properties

All the salicylaldimine ligands and their metal complexes have been studied by polarizing optical microscopy (POM) and DSC. The data are gathered in tables 1 and 2.

3.2.1. The Schiff's bases

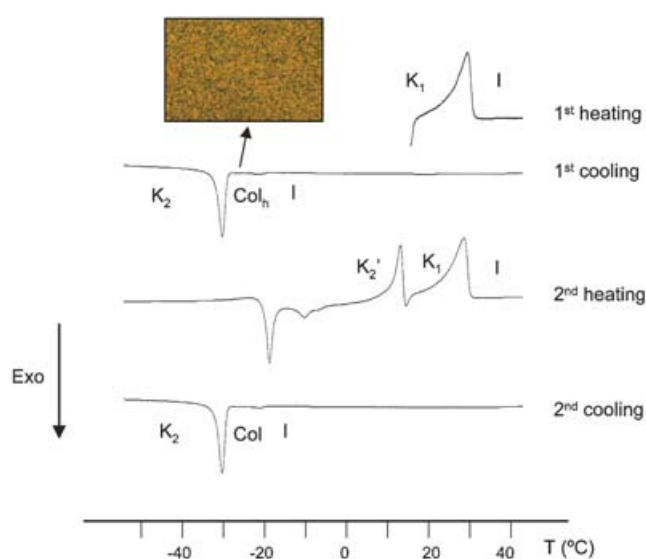
The Schiff's bases were obtained in pure form as yellow oils which crystallize over time. All of them melt directly to the isotropic liquid in the first heating cycle with a high associated enthalpy change. Successive thermal cycles are in some cases more complex and deserve comment. For imine **5a**, crystallization occurs at –26°C and the compound solidifies into a different crystalline form, as observed in the second heating cycle in which the compound shows double melting behaviour. On cooling compound **5b**, two peaks can be seen: the first at –18°C corresponds to the appearance of a mesophase (figure 3) with a texture characteristic of a columnar hexagonal phase; a second peak at –29°C corresponds to crystallization. The second heating cycle shows a recrystallization process and double melting behaviour like **5a**.

Table 1. Temperatures (°C) and enthalpies (kJ mol⁻¹, in brackets) for the phase transitions of the Schiff's bases.

Compound		<i>T</i> _{onset} (Δ <i>H</i>)
5a	1st heating	Cr ₁ 39.3 (63.9) I
	1st cooling	I –26.2 (–20.2) Cr ₂
	2nd heating	Cr ₂ –13.8 (26.1) I Cr ₁ 37.4 (63.8) I
5b	1st heating	Cr ₁ 29.5 (43.9) I
	1st cooling	I –18.4 (–0.4) Col _h –28.7 (–17.4) Cr ₂
	2nd heating	Cr ₂ 15.2 (14.3) I Cr ₁ 28.5 (35.5) I
5c	1st heating	Cr 33.1 (85.6) I
	1st cooling	I 5.0 (–4.2) Φ
	2nd heating	Φ 8.9 (8.4) I
5d	1st heating	Cr 37.0 (41.4) I
	1st cooling	I 4.0 (–21.5) Cr
	2nd heating	Cr 34.4 (51.0) I
5e	1st heating	Cr ₁ 33.3 (2.0) Cr ₂ 53.0 Cr ₃ 55.5 (51.4) I
	1st cooling	I 28.1 (52.5) Cr ₂
	2nd heating	Cr ₂ 50.5 Cr ₃ 55.3 (55.1) I

Table 2. Temperatures ($^{\circ}\text{C}$) and enthalpies (kJ mol^{-1} , in brackets) for the phase transitions of the metal complexes.

Compound		$T_{\text{onset}} (\Delta H)$
6a	1st heating	—
	1st cooling	g -69.5 I
6b	1st heating	Cr 46.3 (14.8) I
	1st cooling	—
6c	1st heating	Cr 1.8 (21.1) Col _r 55.1 (6.4) I
	1st cooling	I 54.6 (-9.7) Col _r
	2nd heating	Cr 0.7 (20.5) Col _r 56.7 (7.8) I
6d	1st heating	Cr 33 I
	1st cooling	—
6e	1st heating	Cr ₁ 68.1 (76.5) I
	1st cooling	I 40.2 g
	2nd heating	Cr ₂ 38.0 (4.1) I
7a	1st heating	Cr 33.5 (24.7) I
	1st cooling	I -27.9 g
7b	1st heating	Cr ₁ 66.0 (14.8) I Cr ₂ 81.0 (38.8) I
	1st cooling	I 3.6 Cr ₃ -3.5 (-16.5) Cr ₄
	2nd heating	Cr ₁ 65.2 (20.4) I Cr ₂ 79.0 (37.9) I
7c	1st heating	Cr ₁ 45.9 (30.5) Col _r 65.3 (3.3) I
	1st cooling	I 59.3 (-4.8) Col _r
	2nd heating	Col _r 65.3 (4.6) I
7d	1st heating	Cr 33.9 (77.4) I
	1st cooling	I 28.2 (-2.3) Col
	2nd heating	Cr + Col 37.9 (4.6) I
7e	1st heating	Cr ₁ 81.5 (82.6) I
	1st cooling	I 28.4 g
	2nd heating	Cr ₂ 56.1 (4.8) I

Figure 3. DSC thermogram and mesophase texture of compound **5b**.

Compounds **5a** and **5b** both have two aromatic rings and differ only in the position of one alkoxy chain. It is interesting to note the lower melting point and induction of a mesophase when the alkoxy chain is in the 2-position of the aniline ring (**5b**); that is, when there is the possibility of distribution of the aliphatic chains around one half of the molecule (figure 4).

Compound **5c** shows a monotropic mesophase on cooling; the texture is displayed in figure 5 and it could be assigned as a phasmidic mesophase on the basis of its molecular shape [10d]. The low temperatures at which these mesophases occur and their monotropic character precluded their study by XRD.

For compound **5d** there is no evidence of the presence of a mesophase. 2,3,4-Substitution in the aniline disturbs the phasmidic shape of the compound with respect to **5c** and prevents the appearance of mesomorphism. Imine **5e**, with only one decyloxy chain on the aniline fragment, is not mesomorphic and shows higher melting points than the other imines of the ester series, **5c** and **5d**.

3.2.2. The copper complexes

Complexes **6a** and **6b**, derived from imines with only two aromatic rings, are not mesomorphic. **6a** was obtained as a brown isotropic liquid that vitrifies at -69.5°C and does not crystallize over time. Compound **6b** was obtained as a partially crystalline brown solid that melts directly to the isotropic liquid. The enthalpy of this transition does not correspond to the total mass of the sample. Under the microscope it can be observed that crystallization occurs slowly at room temperature.

A dramatic lowering of the melting point, produced by the grafting of three decyloxy chains in the aniline fragment, can be observed if we compare them with a similar compound containing only two decyloxy chains previously reported by Lai *et al.* [10c] In the latter case, the copper complex melts at 166°C to a columnar phase that persists until 313°C . Thus, the presence of an extra chain at the 2- or 5-position of the aniline moiety impedes the packing of the molecules, probably as a result of a higher twist of this ring with respect to the mean molecular plane in order to accommodate all the substituents.

In the ester series (imines with three aromatic rings), compound **6c** displays an enantiotropic mesophase at room temperature, which has been characterized as a columnar rectangular phase (*vide infra*). The texture is shown in figure 6. On cooling, this mesophase supercools to under -20°C and crystallizes on the second heating cycle at -8°C .

However the isomeric compound **6d** is not mesomorphic. It was obtained as an isotropic liquid which

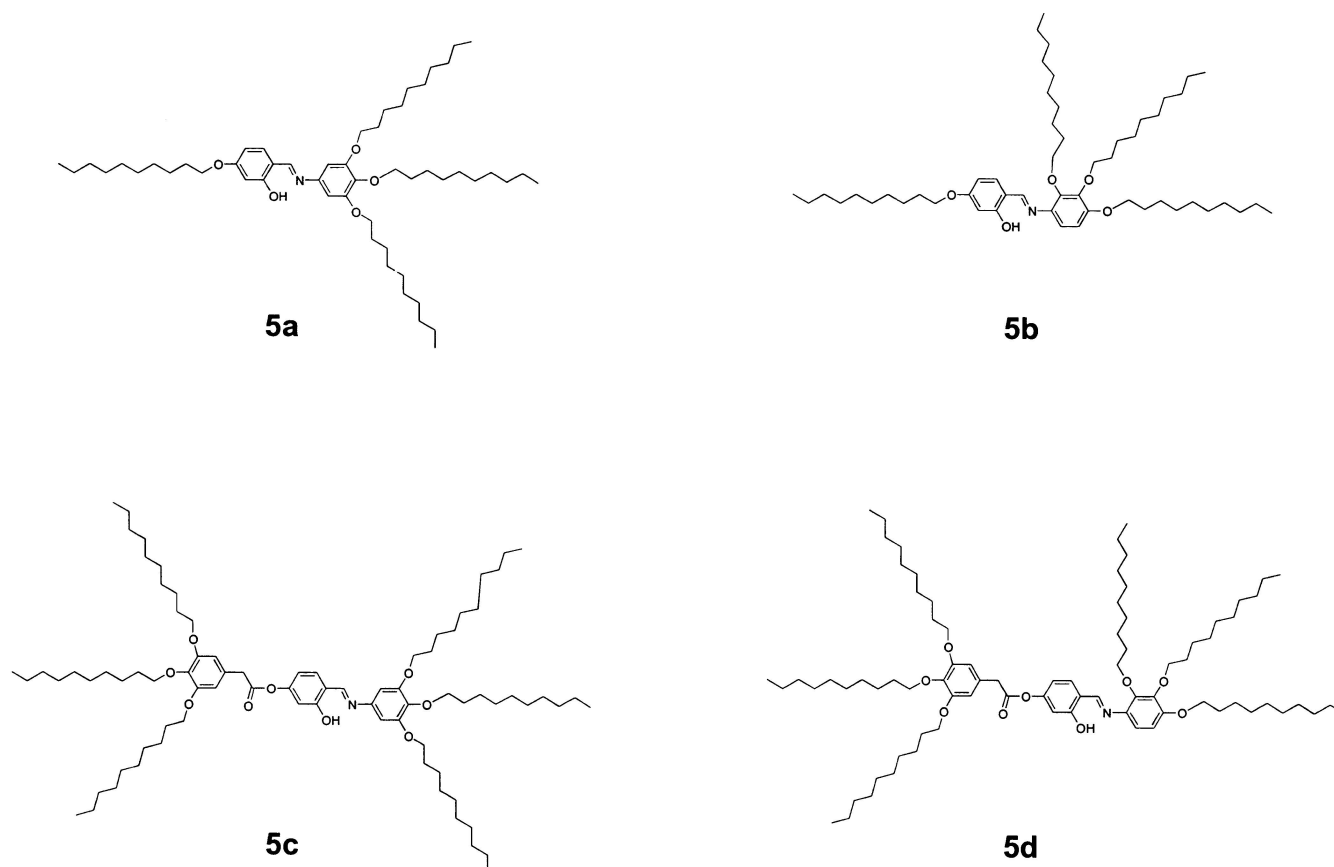
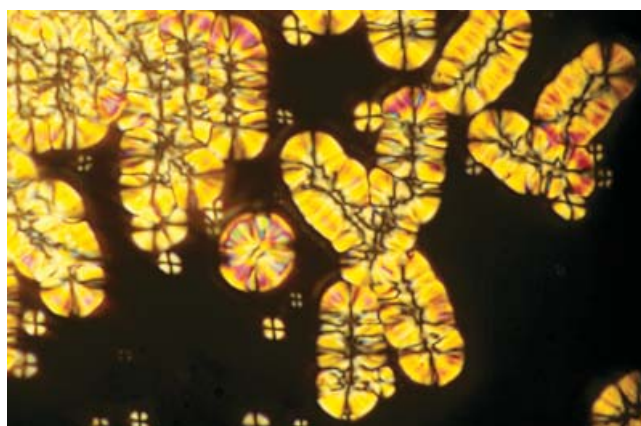
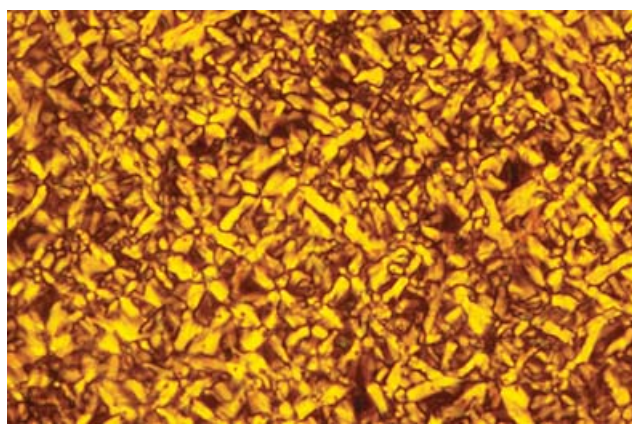


Figure 4. Comparative structures of the salicylaldimines.

Figure 5. Mesophase texture of compound **5c**.Figure 6. Mesophase texture of compound **6c**.

crystallizes over time. Under the optical microscope these crystals melt at 33°C. On successive cooling and heating cycles there are no transitions in the DSC traces.

The presence of the benzoyloxy group in these copper complexes only induces mesomorphic properties in **6c**, showing the importance of the three lateral alkoxy chains in the aniline moiety. Again, lateral substitution in these

complexes plays an important role, as has already been reported in calamitic systems where substitution at the 2-position tends to reduce intermolecular interactions and depress the transition temperatures [9]. Compound **6e**, with only one aliphatic chain in the aniline, should preclude steric hindrance in packing but this is insufficient to generate columnar phases.

3.2.3. The palladium complexes

Palladium complexes show, in general higher transition temperatures than their copper analogues but follow the same trend in behaviour. Compound **7a** melts to an isotropic liquid, and on cooling vitrifies showing no mesomorphic behaviour. Compound **7b** shows a double melting behaviour and partial crystallization on cooling with no liquid crystal properties. As with the copper complexes, the presence of the alkoxy chain in the *ortho* position of the aniline raises the melting point.

The presence of the benzoyloxy moiety induces mesomorphism in compound **7c**, which displays an enantiotropic mesophase characterized as columnar rectangular by XRD (*vide infra*). The texture is displayed in figure 7. This mesophase supercools to below room temperature (-20°C in the DSC). In the second heating only the columnar-to-isotropic liquid transition appears.

Compound **7d** is an orange solid at room temperature which melts at a lower temperature than **7c** and shows a monotropic columnar mesophase on cooling. Palladium complex **7e** derived from 4-decyloxyaniline has the highest melting point and is not mesomorphic. On cooling it vitrifies and on second heating, recrystallizes to a different crystal phase with a lower melting point than that of the fresh sample.

3.3. X-ray diffraction studies

The phase behaviour of the three mesomorphic complexes in these series (**6c**, **7c** and **7d**) was investigated by XRD. Experiments were performed at room temperature, both on fresh samples and on samples previously heated to the isotropic phase, as well as at high temperatures. An X-ray study of the mesomorphic ligands **5b** and **5c** was not possible, as our apparatus is not equipped with a low temperature attachment. In fact, the study of **7d** was also very difficult due to the monotropic nature of its mesophase and its strong tendency to recrystallize below the temperature of transition from isotropic liquid

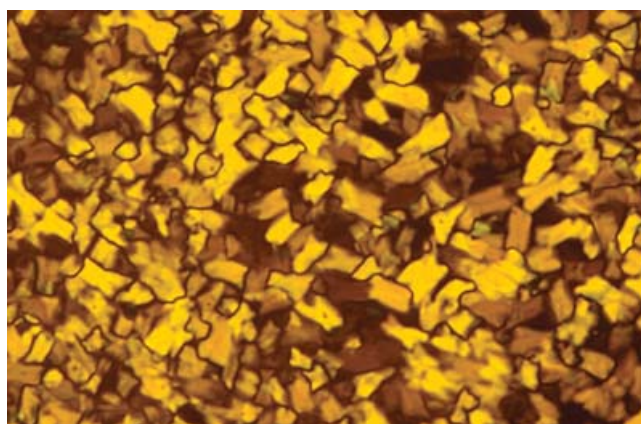


Figure 7. Mesophase texture of compound **7c**.

to the mesophase. Therefore high quality patterns could not be obtained and only short exposure time patterns were obtained which did not allow for an unambiguous classification of the mesophase type.

On the other hand, the mesophases of **6c** and **7c** are enantiotropic and we were able to characterize their structures. Both compounds were studied mainly at room temperature, as under these conditions **6c** exhibits a thermodynamically stable mesophase and **7c** a metastable mesophase that can be kept for long periods of time after the compound has been heated to the isotropic liquid and then cooled to room temperature.

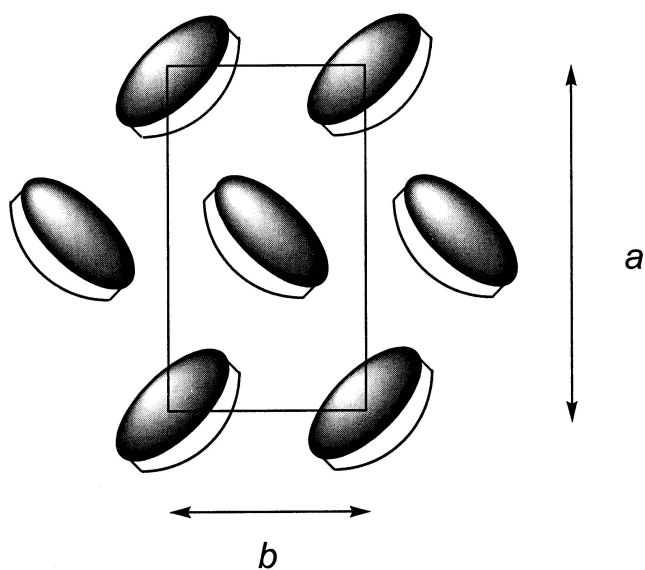
Powder patterns as well as oriented patterns were recorded. The oriented X-ray patterns were obtained from samples aligned by shearing with a metal or glass rod on the inner wall of the capillary in which the sample is held, at a temperature just below the clearing point. Using this technique, we obtained fibre patterns with the fibre axis parallel to the shear direction. The patterns revealed that the columns are oriented parallel to the capillary axis and hence perpendicular to the X-ray beam. In the oriented patterns a number of spots are observed at low angles, the intensity of which is a maximum in the equator (plane perpendicular to the capillary axis). These maxima are related to a two-dimensional (2D) array of columns. This array is better characterized from the powder patterns, from which more accurate spacings can be measured, which can be indexed in a 2D rectangular lattice ($h k 0$ spots). A list of the reflections observed, together with the proposed indices, is given in table 3. It is interesting to note that most of the spacings are in a reciprocal ratio typical of a hexagonal symmetry (i.e. $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, etc.). However, the presence of the reflection indexed as $(2\ 1\ 0)$ is inconsistent with a two-dimensional hexagonal lattice and indicates that the symmetry is in fact rectangular (Col_r mesophase). The lattice constants of this rectangular lattice are $a = 57\ \text{\AA}$, $b = 33\ \text{\AA}$ for **6c**, and $a = 54\ \text{\AA}$, $b = 31\ \text{\AA}$ for **7c**.

In the high angle region we find a diffuse ring corresponding to a mean distance of $4.4\ \text{\AA}$, characteristic of the liquid-like order between the conformationally disordered aliphatic chains. Moreover, in the case of **6c** several additional reflections are observed that cannot be assigned to the two-dimensional array of columns. Most probably, these reflections are due to some amount of a coexisting crystalline phase that persists up to the transition to the isotropic liquid. This indicates a biphasic region over all the thermal range studied.

From density considerations, it may be deduced that the 2D unit cell contains two columns, located at the centre and at the corner of the rectangle (figure 8). Although no reflection corresponding to the stacking distance is observed, if we assume a reasonable density value of about $1\ \text{g cm}^{-3}$, it may be shown that the molecules

Table 3. X-ray results for the Col_r mesophase of **6c** and **7c** measured at room temperature. The table lists, the compound code, the proposed indexing, the observed and calculated spacings and the rectangular lattice constants.

Compound	<i>h k l</i>	<i>d</i> _{obs} /Å	<i>d</i> _{calc} /Å	Lattice constants/Å
6c	1 1 0, 2 0 0	28.7	28.5	<i>a</i> = 57
	2 1 0	21.5	21.6	<i>b</i> = 33
	0 2 0, 3 1 0	16.4	16.5	
	2 2 0, 4 0 0	14.2	14.3	
	1 3 0, 4 2 0, 5 1 0	10.9	10.8	
		4.4 (diffuse)		
7c	1 1 0, 2 0 0	27.0	27.0	<i>a</i> = 54
	2 1 0	20.0	20.4	<i>b</i> = 31.2
	0 2 0, 3 1 0	15.6	15.6	
	2 2 0, 4 0 0	13.4	13.5	
	5 0 0	10.7	10.8	
	1 3 0, 4 2 0, 5 1 0	10.0	10.2	
	3 3 0, 6 0 0	9.2	9.0	
		4.4 (diffuse)		

Figure 8. Two-dimensional unit cell of the columnar rectangular mesophase for compounds **6c** and **7c**.

must be stacked inside the columns at a mean distance of about 4.5 Å for **6c** and about 5.1 Å for **7c**. The greater stacking distance for **7c** can be accounted for by the larger size of the palladium atom compared with copper and/or by a higher tilt angle of the molecules with respect to the columnar axis.

It is interesting to note that the lattice constants *a* and *b* are in the ratio $\sqrt{3}$, which is characteristic of a hexagonal structure. However, and as mentioned previously, the presence of the reflection indexed as (2 1 0) is inconsistent with a hexagonal lattice and indicates a columnar phase with a p_{2gg} rectangular symmetry. The same kind of *pseudohexagonal* arrangement has been found in a number of non-chiral [14] and chiral [15]

columnar mesophases. In a rectangular columnar mesophase with p_{2gg} symmetry the molecular cores are not perpendicular to the column axes and their tilt direction is different for the two columns of the same unit cell. This means that the director (axis perpendicular to the molecular planes) has a fixed direction in each column and the mutual orientation of the director of neighbouring columns is defined by the symmetry of the lattice, and in particular by the two-fold helical axis.

X-ray patterns were also taken at high temperatures. The structure of the mesophase of the two compounds at 55°C is the same as that at room temperature, except for a slight decrease in the lattice parameters of **7c** (*a* = 52 Å, *b* = 30 Å).

4. Conclusions

Bis(salicylaldimine) copper and palladium complexes exhibiting columnar mesophases at low temperatures can be prepared via a suitable adjustment of the aspect ratio of the ligands. The number of decyloxy chains in the aniline moiety plays an important role in inducing mesomorphism.

For series **a** and **b** a significant decrease in the melting point is observed compared with those of similar compounds bearing only two alkoxy chains in the *meta*- and *para*-positions of the aniline fragment. Indeed, the presence of an extra chain in the *meta*- (series **a**) or *ortho*- (series **b**) positions proved detrimental to columnar packing and none of the complexes were mesomorphic.

By using salicylaldimines with three aromatic rings and six decyloxy terminal chains, it is possible to generate rectangular columnar phases in complexes with a symmetric substitution (series **c**) at (or near) room temperature. In these mesophases the molecules are in a pseudohexagonal arrangement but their cores are not perpendicular to the column axes.

A reduction of the number of alkoxy chains in the aniline fragment from three to one (series e) leads to the disappearance of liquid crystallinity which indicates the subtle limits of mesomorphism in these polycatenar salicylaldimine complexes placed at the interface of calamitic and columnar mesomorphism.

This work has been supported by the Comisión Interministerial de Ciencia y Tecnología (Spain) (Projects MAT1999-1009-CO2-02 and MAT2000-1293-CO2-01). M.C.P. thanks the AECI (Spain) for funding her visits.

References

- [1] Several reviews of metallomesogens have been published: (a) GIROUD-GODQUIN, A. M., and MAITLIS, P. M., 1991, *Angew. Chem. Ed. Eng.*, **30**, 375; (b) ESPINET, P., ESTERUELAS, M. A., ORO, L. A., SERRANO, J. L., and SOLA, E., 1992, *Coord. Chem. Rev.*, **117**, 215; (c) POLISHCHUK, A. P., and TIMOFEEVA, T. V., 1993, *Russ. Chem. Rev.*, **62**, 291; (d) HUDSON, S. A., and MAITLIS, P. M., 1993, *Chem. Rev.*, **93**, 861; (e) SERRANO, J. L. (editor), 1996, *Metallomesogens: Synthesis, Properties and Applications* (Weinheim: Wiley-VCH); (f) BRUCE, D. W., 1996, *Inorganic Materials*, edited by D. W. Bruce and D. O'Hare, 2nd Edn (Chichester: Wiley), p. 429-522; (g) GIROUD-GODQUIN, A. M., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H. W. Spiess and V. Vill (Weinheim: Wiley-VCH), Chap. XIV; (h) DONNIO, B., and BRUCE, D. W., 1999, *Struct. Bonding*, **95**, 193.
- [2] COLLINSON, S. R., and BRUCE, D. W., 1999, *Transition Metals in Supramolecular Chemistry*, Vol. 5, edited by J.-P. Sauvage (Wiley), p. 285.
- [3] TSCHERSKE, C., 2001, *J. mater. Chem.*, **11**, 2647.
- [4] OHTA, K., YAMAGUCHI, N., and YAMAMOTO, I., 1998, *J. mater. Chem.*, **8**, 2637.
- [5] ZHENG, H., and SWAGER, T. M., 1994, *J. Am. chem. Soc.*, **116**, 761.
- [6] HOSHINO, N., 1998, *Coord. Chem. Rev.*, **174**, 77.
- [7] (a) OVCHINNIKOV, I. V., GALYAMETDINOV, Y. G., IVANOVA, G. I., and YAGRAFOVA, L. M., 1984, *Dokl. Akad. Nauk SSSR*, **276**, 126; (b) CAFARGNA, C., CARUSO, U., ROVIELLO, A., and SIRIGU, A., 1987, *Macromol. Chem. rapid Commun.*, **8**, 345; (c) MARCOS, M., ROMERO, P., SERRANO, J. L., BUENO, C., CABEZA, J. A., and ORO, L. A., 1989, *Mol. Cryst. liq. Cryst.*, **167**, 123; (d) ALONSO, P. J., MARCOS, M., MARTÍNEZ, J. I., ORERA, V. M., SANJUAN, M. L., and SERRANO, J. L., 1993, *Liq. Cryst.*, **13**, 585; (e) HOSHINO, N., TAKAHASHI, K., SEKIUCHI, T., TANAKA, H., and MATSUNAGA, Y., 1998, *Inorg. Chem.*, **37**, 882; (f) DIAZ, F. R., VALDEBENITO, N., SERRANO, J. L., MARCOS, M., MARTÍNEZ, J. I., and ALONSO, P. J., 1998, *Liq. Cryst.*, **25**, 217.
- [8] (a) HOSHINO, N., MURAKAMI, H., MATSUNAGA, Y., INABE, T., and MARUYAMA, Y., 1990, *Inorg. Chem.*, **29**, 1177; (b) MARCOS, M., ROMERO, P., and SERRANO, J. L., 1990, *Chem. Mater.*, **2**, 495; (c) SERRANO, J. L., ROMERO, P., MARCOS, M., and ALONSO, P. J., 1990, *Chem. Commun.*, 859; (d) MARCOS, M., SERRANO, J. L., ALONSO, P. J., and MARTÍNEZ, J. I., 1995, *Adv. Mater.*, **7**, 173; (e) CAMPILLOS, E., MARCOS, M., SERRANO, J. L., BARBERÁ, J., ALONSO, P., and MARTÍNEZ, J. I., 1993, *Chem. Mater.*, **5**, 1518; (f) CAMPILLOS, E., MARCOS, M., ORIOL, L. T., and SERRANO, J. L., 1992, *Mol. Cryst. liq. Cryst.*, **215**, 127; (g) CAMPILLOS, E., MARCOS, M., OMENAT, A., and SERRANO, J. L., 1996, *J. mater. Chem.*, **6**, 349.
- [9] BERDAGUÉ, P., PÉREZ, F., COURTIEU, J., and BAYLE, J.-P., 1994, *Bull. Soc. Chim. Fr.*, **35**, 131.
- [10] (a) SERRETTE, A. G., and SWAGER, T. M., 1993, *J. Am. chem. Soc.*, **115**, 8879; (b) KILIAN, D., KNAWBY, D., ATHANASSOPOULOU, M. A., TRZASKA, S. T., SWAGER, T. M., WROBEL, S., and HAASE, W., 2000, *Liq. Cryst.*, **27**, 509; (c) LAI, C. K., CHANG, C.-H., and TSAI, C.-H., 1998, *J. mater. Chem.*, **8**, 599; (d) NGUYEN, H.-T., DESTRADE, C., and MALTHETE, J., 1997, *Adv. Mater.*, **9**, 375; (e) BRUCE, D. W., and DATE, R. W., 1999, Oral Communication, 6th International Symposium on Metallomesogens, Rotenburg a. d. Fulda, Germany, 1999; (f) MARTIN, F., COLLINSON, S. R., and BRUCE, D. W., 2000, *Liq. Cryst.*, **27**, 859.
- [11] BODEN, N., and MOVAGHAR, B., 1998, *Handbook of Liquid Crystals*, Vol. 2B, edited by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess and V. Vill (Weinheim: Wiley-VCH), Chap. IX.
- [12] KELLER, P., and LIEBERT, L., 1978, *Solid State Phys. Suppl.*, **14**, 19.
- [13] XU, B., and SWAGER, T. M., 1993, *J. Am. chem. Soc.*, **115**, 1159.
- [14] (a) WEBER, P., GUILLON, D., and SKOULIOS, A., 1991, *Liq. Cryst.*, **9**, 369; (b) ECKERT, J. F., NICOU, J. F., GUILLON, D., and NIERENGARTEN, J. F., 2000, *Tetrahedron Lett.*, **41**, 6411.
- [15] BARBERÁ, J., IGLESIAS, R., SERRANO, J. L., SIERRA, T., DE LA FUENTE, M. R., PALACIOS, B., PÉREZ-JUBINDO, M. A., and VÁZQUEZ, J. T., 1998, *J. Am. chem. Soc.*, **120**, 2908.