Metallomesogens. Synthesis and Mesomorphic Properties of 2-Hydroxy-4-*n*-Alkoxy-4′-*n*-Alkylazobenzenes Palladium(II) Complexes

Mauro Ghedini[*] and Stefania Morrone

Dipartimento di Chimica, Università della Calabria, I-87030 Arcavacata (CS), Italy

Oriano Francescangeli

Dipartimento di Scienze dei Materiali e della Terra, Università di Ancona,
Via Brecce Bianche, I-60131 Ancona, Italy

Roberto Bartolino

Dipartimento di Fisica, Università della Calabria, I-87030 Arcavacata (CS), Italy

Received July 12, 1994. Revised Manuscript Received July 12, 1994[⊗]

The synthesis and characterization of *o*-hydroxyazobenzene mesogens [$HL_n(m)$] which form the two different homologous series $HL_n(12)$ (2-hydroxy-4-*n*-dodecyloxy-4′-*n*-C_nH_{2n+1}-azobenzenes, $n = 1-4, 6, 8$) and $HL_1(m)$ (2-hydroxy-4-*n*-C_nH_{2n+1}-*O*-4′-methylazobenzenes, $m = 7, 9, 12, 14$) are reported. They form N and/or S_C mesophases at quite low temperatures. These ligands react with [$Pd(PhCN)_2Cl_2$] or Pd[(Azoxy-6)Pd(MeCN)$_2$]BF$_4$ giving rise to the corresponding [$L_n(m)]_2$Pd and {(Azoxy-6)Pd[$L_n(m)$]} species [Azoxy-6 is the deprotonated form of 4,4′-bis(hexyloxy)azoxybenzene]. The [$L_n(m)]_2$Pd compounds are not mesogenic. On the contrary, the cyclopalladated mixed-ligand complexes, {(Azoxy-6)Pd[$L_n(m)$]}, are prevalently nematogenic as optical, DSC, and X-ray analysis evidence. The {(Azoxy-6)Pd[$L_n(12)$]} compounds show enantiotropic nematic ($n = 1$), monotropic nematic ($n = 2-4, 6$) and monotropic nematic and S_c mesophases ($n = 8$). The {(Azoxy-6)Pd[$L_1(m)$]} species form monotropic ($m = 7, 9$) and enantiotropic ($m = 12, 14$) nematic mesophases. A comparison between the thermal behavior displayed by [$L_n(m)]_2$Pd and {(Azoxy-6)Pd[$L_n(m)$]} complexes seems to explain the role played by the respective rigid molecular cores. The electronic and/or structural modifications induced by the azoxy group are discussed.

Introduction

Metal-containing liquid-crystal compounds are currently under investigation as new materials.[1] Therefore, to be of use for practical applications, the chemical stability of the complexes is a requirement not to be ignored.

Salicylideneamines are common ligands for transition metals.[2] Taking advantage of this simple chemistry, several copper,[3−11] palladium,[8a−c,9a,11] nickel,[6a,b,9a,10b,c] vanadyl,[13−18] and iron[19] mesogenic complexes have been prepared. Unfortunately, despite such versatility, it

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[*] To whom correspondence should be addressed.

[⊗] Abstract published in *Advance ACS Abstracts,* September 1, 1994.

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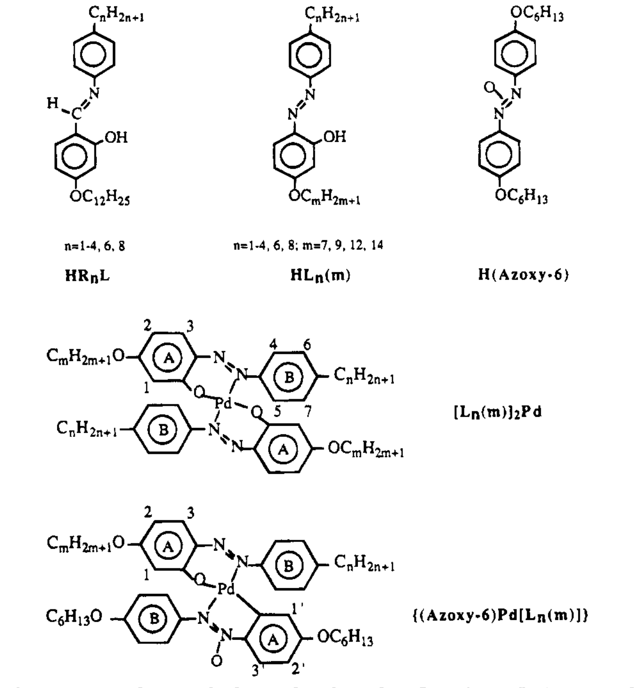


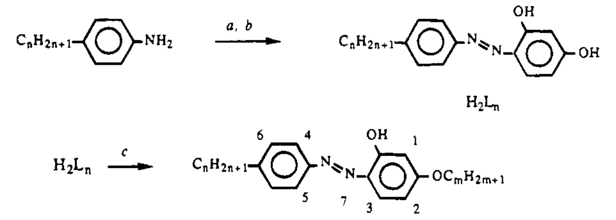
Figure 1. General formula for the HR_nL, $HL_n(m)$, and H(Azoxy-6) ligands and for the $[L_n(m)]_2Pd$ and {(Azoxy-6)Pd-$[L_n(m)]$} complexes. The proton numbering schemes of the palladium species are shown.

must be pointed out that the C=N group of these ligands should become more polarized upon metal complexation. Consequently a greater vulnerability to nucleophilic attack at the carbon atom and a diminished stability toward hydrolysis must be expected.[2a]

A possible approach to overcome this limitation is the replacement of the azomethine for the azo group. Accordingly, 2-hydroxyazobenzenes can be a substitute for salicylideneanilines since they exhibit similar complexation properties.[19−24]

In previous papers we described the preparation of palladium−mesogens of general formula $(R_nL)_2Pd$[12] or $[(Azoxy\text{-}6)Pd(R_nL)]$[25] [H(Azoxy-6) is 4,4′-bis(hexyloxy)-azoxybenzene] obtained by reacting HR_nL (Figure 1) with $[Pd(PhCN)_2Cl_2]$ or $[(Azoxy\text{-}6)Pd(MeCN)_2][BF_4]$, respectively. The work reported herein focuses on the preparation of new metallomesogens prepared by reaction of 2-hydroxy-4-*n*-alkoxy-4′-*n*-alkylazobenzenes, $HL_n(m)$ in Figure 1, with the same palladium(II) species.

Scheme 1. Synthesis and Proton Numbering Scheme for the $HL_n(m)$ Compounds



[a] HCl, $NaNO_2$, 0 °C.[b] Resorcinol, KOH.[c] $C_mH_{2m+1}Br$, EtOH, KOH.

The present paper reports the synthesis, characterization, and the mesomorphic properties of both the ligands and the corresponding complexes (Figure 1).

Experimental Section

General Procedures. The commercially available standard chemicals 4-substituted anilines, 1-bromododecane, 1-bromotetradecane, 1-bromononane, 1-bromoheptane, and resorcinol were used as supplied. $Pd(PhCN)_2Cl_2$ was prepared by literature methods.[26] The standard chemicals 4,4′-bis(hexyloxy)azoxybenzene, H(Azoxy-6) (Eastman Kodak Co.), and $AgBF_4$ (Fluka A.G.) were used as supplied. The palladium complexes $[(Azoxy\text{-}6)Pd(\mu\text{-}Cl)]_2$ and $[(Azoxy\text{-}6)Pd(MeCN)_2]BF_4$ were synthesized according to previously described procedures.[25]

The IR spectra (KBr) were recorded on a Perkin-Elmer 1330 spectrophotometer and ^1H NMR spectra ($CDCl_3$, standard $SiMe_4$) on Bruker AW 80 and AW 300 spectrometers.

Elemental analyses were carried out by the Microanalysis Laboratory of the Dipartimento di Chimica, Università della Calabria.

The thermal behavior was monitored by means of a Perkin-Elmer DSC 7 at a heating rate of 5 °C min^{-1}. The apparatus was calibrated with indium (156.6 °C, 28.4 J/g) as standard.

The textures of the mesophases were observed with a Zeiss Axioscope polarizing microscope coupled with a Linkam CO 600 heating stage.

The X-ray diffraction measurements were performed with the INEL CPS-120 powder diffractometer, equipped with a position-sensitive detector covering 120° in 2θ. Monochromatized Cu Kα radiation (λ = 1.54 Å) was used. The samples, about 1 mm thick, were placed between two thin Al sheets, fixed to a circular hole (1 cm diameter) in an Al matrix. Heating was achieved by a hot-stage containing electric resistors and the temperature of the sample was controlled by a temperature regulator to ±0.3 °C. Oriented nematic mesophases were produced by applying an external magnetic field of intensity B = 0.1 T normally directed to the incident X-ray beam and lying in the plane of the X-ray beam and of the position-sensitive detector (the horizontal plane).

Synthesis of the Ligands. The ligands have been prepared according to Scheme 1.

Preparation of 2,4-Dihydroxy-4′-n-alkylazobenzenes (H_2L_n). A typical preparation is described for $\mathbf{H_2L_1}$. To *p*-toluidine (1 g, 9.3 mmol) were added 10 mL of distilled water containing hydrochloridic acid (12 M, 2.3 mL, 27.9 mmol). To the resulting stirred mixture cooled at 0 °C was added, dropwise, a solution of sodium nitrite (640 mg, 9.3 mmol) in 10 mL of water. The resulting diazonium chloride was consecutively coupled with an alkaline solution of resorcinol (1.024 g, 9.3 mmol) in 10 mL of water containing 18.6 mmol of potassium hydroxide. The red precipitate which forms immediately was filtered, washed several times with water, and dissolved in chloroform or diethyl ether, and the resulting organic solution dried over anhydrous sodium sulfate. The crude product obtained after removal of the solvent under reduced pressure was purified by recrystallization form cold diethyl ether; yield

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70%. Anal. Calcd for $C_{13}H_{12}N_2O_2$: C, 68.41%; H, 5.29%; N, 12.27%. Found: C, 68.41%; H, 5.30%; N, 12.32%. ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.7 (m, H_3, H_4, H_5), 7.2 (m, H_6, H_7), 6.5 (dd, H_2, $J(H_2,H_3)$ = 8 Hz, $J(H_2,H_1)$ = 3 Hz), 6.4 (d, H_1, $J(H_1,H_2)$ = 3 Hz); 2.6 (s, Ar CH_3).

The homologous H_2L_n compounds were prepared in the same way. Their ^{1}H NMR data are strictly similar to those reported for H_2L_1 while purifications, yields, and analytical data are as follows:

H_2L_2. Crystallization from cold diethyl ether; yield 72%. Anal. Calcd for $C_{14}H_{14}N_2O_2$: C, 69.40%; H, 5.82%; N, 11.56%. Found: C, 69.37%; H, 5.80%; N, 11.61%.

H_2L_3. Crystallization from cold diethyl ether; yield 56%. Anal. Calcd for $C_{15}H_{16}N_2O_2$: C, 70.29%; H, 6.29%; N, 10.93%. Found: C, 70.30%; H, 6.23%; N, 11.08%.

H_2L_4. Chromatography on a silica gel column eluted with a mixture of hexane and diethyl ether (60/40, v/v); yield 48%. Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09%; H, 6.71%; N, 10.36%. Found: C, 71.40%; H, 6.71%; N, 10.03%.

H_2L_6. Chromatography on a silica gel column eluted with a mixture of hexane and diethyl ether (60/40, v/v); yield 70%. Anal. Calcd for $C_{18}H_{22}N_2O_2$: C, 72.46%; H, 7.43%; N, 9.39%. Found: C, 72.59%; H, 7.42%; N, 9.21%.

H_2L_8. Chromatography on a silica gel column eluted with a mixture of hexane and diethyl ether (60/40, v/v); yield 65%. Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59%; H, 8.03%; N, 8.58%. Found: C, 73.27%; H, 8.12%; N, 8.51%.

Preparation of 2-Hydroxy-(4-n-dodecyloxy)-4'-n-alkylazobenzenes, $HL_n(12)$, and 2-Hydroxy-4-n-alkoxy-4'-methylazobenzenes, $HL_1(m)$. **$HL_1(12)$.** To a suspension of H_2L_1 (1 g, 4.4 mmol) in absolute ethanol (20 mL) were added an ethanolic solution (20 mL) of potassium hydroxide (246 mg, 4.4 mmol) and 1-bromododecane (2.11 mL, 8.8 mmol). The resulting mixture was stirred under reflux for 18 h. After this time the suspension was filtered off, and the orange solution cooled. The orange solid which precipitated on cooling was collected by filtration and finally purified by chromatography on a silica gel column eluted with a mixture of hexane and diethyl ether (95:5, v/v); yield 20%. Anal. Calcd for $C_{25}H_{36}N_2O_2$: C, 75.72%; H, 9.15%; N, 7.06%. Found: C, 75.92%; H, 9.31%; N, 6.86%. ^{1}H NMR (80 MHz, $CDCl_3$) δ 7.7 (m, H_3, H_4, H_5), 7.2 (m, H_6, H_7), 6.5 (dd, H_2, $J(H_2,H_3)$ = 8. Hz, $J(H_2,H_1)$ = 2 Hz); 6.4 (d, H_1, $J(H_1,H_2)$ = 3 Hz), 3.9 (t, Ar O–CH_2–), 2.4 (s, Ar CH_3), 0.9(t, CH_3–CH_2–), 13.8 (s, OH).

All analogous compounds were prepared as described for $HL_1(12)$. No significant differences were observed in the ^{1}H NMR spectra. Yields and analytical data are as follows:

$HL_2(12)$. Yield 37%. Anal. Calcd for $C_{26}H_{38}N_2O_2$: C, 76.06%; H, 9.33%, N, 6.82%. Found: C, 76.09%; H, 9.45%; N, 6.73%.

$HL_3(12)$. Yield 40%. Anal. Calcd for $C_{27}H_{40}N_2O_2$: C, 76.37%; H, 9.49%; N, 6.60%. Found: C, 76.53%; H, 9.60%; N, 6.25%.

$HL_4(12)$. Yield 42%. Anal. Calcd for $C_{28}H_{42}N_2O_2$: C, 76.67%; H, 9.65%; N, 6.39%. Found: C, 76.95%; H, 9.76%; N, 6.82%.

$HL_6(12)$. Yield 36%. Anal. Calcd for $C_{30}H_{46}N_2O_2$: C, 77.21%; H, 9.93%; N, 6.00%. Found: C, 76.98%; H, 9.87%; N, 5.93%.

$HL_8(12)$. Yield 32%. Anal. Calcd for $C_{30}H_{50}N_2O_2$: C, 77.68%; H, 10.18%; N, 5.66%. Found: C, 78.01%; H, 10.62%; N, 5.70%.

$HL_1(7)$. Yield 37%. Anal. Calcd for $C_{20}H_{26}N_2O_2$: C, 73.59%; H, 8.03%; N, 8.58%. Found: C, 73.53%; H, 8.08%; N, 8.61%.

$HL_1(9)$. Yield 33%. Anal. Calcd for $C_{22}H_{30}N_2O_2$: C, 74.54%; H, 8.53%; N, 7.90%. Found: C, 74.63%; H, 8.65%; N, 7.97%.

$HL_1(14)$. Yield 40%. Anal. Calcd for $C_{27}H_{40}N_2O_2$: C, 76.37%; H, 9.49%; N, 6.60%. Found: C, 76.18%; H, 9.97%; N, 5.97%.

Synthesis of $[L_n(m)]_2Pd$ Complexes. $[L_1(12)]_2Pd$. To a suspension of $HL_1(12)$ (100 mg, 0.252 mmol) in absolute ethanol (5 mL) were added 3 mL of an ethanolic solution of potassium hydroxide (14 mg, 0.252 mmol) and $Pd(PhCN)_2Cl_2$ (48 mg, 0.126 mmol). The mixture was stirred at room temperature for 5 h; the dark red solid formed during this period was filtered, recrystallized from chloroform–ethanol, and dried under vacuum; yield 70 mg (62%). Anal. Calcd for $C_{50}H_{70}N_4O_4Pd$: C, 66.89%; H, 7.86%; N, 6.27%. Found: C, 66.77%; H, 7.78%; N, 5.97%. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (m, H_3, H_4, H_5), 7.25 (m, H_6, H_7), 6.34 (dd, H_2, $J(H_2,H_3)$ = 8.5 Hz, $J(H_2,H_1)$ = 2.6 Hz), 5.85 (d, H_1, $J(H_1,H_2)$ = 2.6 Hz), 3.94 (t, Ar OCH_2–), 2.33 (s, Ar CH_3), 0.95(t, CH_3–).

All homologous complexes were synthetized following the procedure described for $[L_1(12)]_2Pd$ and give similar ^{1}H NMR spectra. Yields and analytical data are as follows:

$[L_2(12)]_2Pd$. Yield (86%). Anal. Calcd for $C_{52}H_{74}N_4O_4Pd$: C, 67.46%; H, 8.06%; N, 6.07%. Found: C, 67.22%; H, 7.65; N, 6.56%.

$[L_3(12)]_2Pd$. Yield (51%). Anal. Calcd for $C_{54}H_{78}N_4O_4Pd$: C, 67.99%; H, 8.24%; N, 5.90%. Found: C, 67.53%; H, 8.13%; N, 5.97%.

$[L_4(12)]_2Pd$, 4. Yield (65%). Anal. Calcd for $C_{56}H_{82}N_4O_4Pd$: C, 68.50%; H, 8.42%; N, 5.73%. Found: C, 68.65%; H, 8.45%; N, 5.43%.

$[L_6(12)]_2Pd$. Yield (72%). Anal. Calcd for $C_{60}H_{90}N_4O_4Pd$: C, 69.44%; H, 8.74%; N, 5.40%. Found: C, 69.03%; H, 8.71%; N, 5.25%.

$[L_8(12)]_2Pd$. Yield (65%). Anal. Calcd for $C_{64}H_{98}N_4O_4Pd$: C, 70.13%; H, 9.01%; N, 5.13%. Found: C, 70.11%; H, 9.16%; N, 5.15%.

$[L_1(7)]_2Pd$. Yield (63%). Anal. Calcd for $C_{40}H_{50}N_4O_4Pd$: C, 63.44%; H, 6.65%; N, 7.40%. Found: C, 63.50%; H, 6.72%; N, 7.12%.

$[L_1(9)]_2Pd$. Yield (67%). Anal. Calcd for $C_{44}H_{58}N_4O_4Pd$: C, 64.95%; H, 7.18%; N, 6.91%. Found: C, 65.15%; H, 7.16%; N, 6.86%.

$[L_1(14)]_2Pd$. Yield (52%). Anal. Calcd for $C_{54}H_{78}N_4O_4Pd$: C, 67.99%; H, 8.24%; N, 5.90%. Found: C, 67.63%; H, 8.00%; N, 5.57%.

Synthesis of {(Azoxy-6)Pd[$L_n(m)$]} Complexes. A typical preparation for the {(Azoxy-6)Pd[$L_n(m)$]} complexes is as follows:

To a suspension of complex $[(Azoxy\text{-}6)Pd(MeCN)_2]BF_4$ (0.100 g, 0.148 mmol) in absolute ethanol (10 mL) was added a stoichiometric amount of the appropriate $HL_n(m)$ ligand. The mixture was stirred for 5 h at room temperature. The resulting bright orange precipitate was filtered off and recrystallized from diethyl ether–ethanol to give the product as a microcrystalline solid.

Yields and elemental analyses are as follows:

{(Azoxy-6)Pd[$L_1(12)$]}. Yield 75%. Anal. Calcd for $C_{49}H_{68}N_4O_5Pd$: C, 65.41%; H, 7.62%; N, 6.25%. Found: C, 65.20%; H, 7.63%; N, 6.09%.

{(Azoxy-6)Pd[$L_2(12)$]}. Yield 80%. Anal. Calcd for $C_{50}H_{70}N_4O_5Pd$: C, 65.72%; H, 7.72%; N, 6.16%. Found: C, 66.15%; H, 7.81%; N, 5.88%.

{(Azoxy-6)Pd[$L_3(12)$]}. Yield 72%. Anal. Calcd for $C_{51}H_{72}N_4O_5Pd$: C, 66.02; H, 7.82%; N, 6.06%. Found: C, 66.06%; H, 7.84%; N, 5.98%.

{(Azoxy-6)Pd[$L_4(12)$]}. Yield 77%. Anal. Calcd for $C_{52}H_{74}N_4O_5Pd$: C, 66.31%; H, 7.92%; N, 5.97%. Found: C, 66.15%; H, 7.91%; N, 6.33%.

{(Azoxy-6)Pd[$L_6(12)$]}. Yield 73%. Anal. Calcd for $C_{54}H_{78}N_4O_5Pd$: C, 66.87%; H, 8.10%; N, 5.80%. Found: C, 66.86%; H, 8.20%; N, 5.83%.

{(Azoxy-6)Pd[$L_8(12)$]}. Yield 74%. Anal. Calcd for $C_{56}H_{82}N_4O_5Pd$: C, 67.40%; H, 8.28%; N, 5.64%. Found: C, 67.28%; H, 8.24%; N, 5.49%.

{(Azoxy-6)Pd[$L_1(7)$]}. Yield 76%. Anal. Calcd for $C_{44}H_{58}N_4O_5Pd$: C, 63.70%; H, 7.05%; N, 6.78. Found: C, 63.94%; H, 7.15%; N, 6.83%.

{(Azoxy-6)Pd[$L_1(9)$]}. Yield 79%. Anal. Calcd for $C_{46}H_{62}N_4O_5Pd$: C, 64.42%; H, 7.29%; N, 6.56%. Found: C, 63.92%; H, 7.21%; N, 6.55%.

{(Azoxy-6)Pd[$L_1(14)$]}. Yield 80%. Anal. Calcd for $C_{51}H_{68}N_4O_5Pd$: C, 65.51%; H, 8.12%; N, 5.56%. Found: C, 66.03%; H, 7.71%; N, 6.06%.

As a representative example of the whole series, selected ^{1}H NMR data (300 MHz, $CDCl_3$) cocerning {(Azoxy-6)Pd[L_1(12)]} are reported: δ 6.04 [d, H_1, $J(H_1H_2)$ = 2.60 Hz], 6.33

[dd, H$_2$, J(H$_2$H$_1$) = 2.59 Hz, J(H$_2$H$_3$) = 9.14 Hz], 7.50 (m, H$_3$), 5.64 [d, H$_{1'}$, J(H$_{1'}$H$_{2'}$) = 2.44 Hz], 6.52 [dd, H$_{2'}$, J(H$_{2'}$H$_{1'}$) = 2.44 Hz, J(H$_{2'}$H$_{3'}$) = 8.87 Hz], 7.50 (m, H$_{3'}$), 2.38 (s, Ar CH_3).

Results and Discussion

Synthesis of the Compounds. The HL$_n$(m) ligands were synthesized in a two-step process as shown in Scheme 1. The first step consists of the diazotization of a 4-substituted primary aromatic amine followed by the coupling reaction with an alkaline solution of resorcinol to obtain the 2,4-dihydroxy-4′-n-alkylazobenzenes (H$_2$L$_n$). Thereafter, the H$_2$L$_n$ products were reacted with the appropriate alkyl bromide and the HL$_n$(m) compounds are obtained. All the HL$_n$(m) products give elemental analysis and ^{1}H NMR spectra that agree with the expected formula (Experimental Section).

Two molecules of the HL$_n$(m) ligands react with [Pd(PhCN)$_2$Cl$_2$] to give [L$_n$(m)]$_2$Pd complexes (Experimental Section) whose formula is sketched in Figure 1. The stoichiometry of the synthesized complexes was confirmed by elemental analysis and evidence for the proposed N,N trans structure were provided by ^{1}H NMR spectroscopy. Indeed the spectra of the [L$_n$(m)]$_2$Pd compounds account for the presence of only one species whose H$_1$ proton (Figure 1) resonates about 0.6 ppm upfield with reference to the uncomplexed HL$_n$(m) parent (Experimental Section). Since such a shift can be the result of the shielding exerted by the freely rotating phenyl group (B in Figure 1), we suggest that these molecules adopt a trans arrangement of N (and O) donor atoms.

The synthesis of the {(Azoxy-6)Pd[L$_n$(m)]} compounds is achieved according to the reaction scheme previously tested for the synthesis of mixed-ligand compounds containing the palladated 4,4′-dialkoxyazoxybenzene fragments and salicylideneanilines.[25,27] In the present case the compounds were obtained by mixing the [(Azoxy-6)Pd(MeCN)$_2$]BF$_4$ salt and the HL$_n$(m) ligands in equimolar amount (Experimental Section). The {(Azoxy-6)Pd[L$_n$(m)]} products were characterized by elemental analyses and ^{1}H NMR spectroscopy (Experimental Section). These experimental data were in agreement with the expected stoichiometry.

As far as the stereochemistry of the complexes is concerned, anions such as L$_n$(m) could bind the [(Azoxy-6)Pd] group giving rise to N,N cis and/or N,N trans isomers. Actually for the similar [(Azoxy-6)Pd(R$_n$L)] series an isomeric mixture, in a 1:5 cis-to-trans ratio was detected by ^{1}H NMR spectroscopy.[25] In contrast, the ^{1}H NMR spectra of the {(Azoxy-6)Pd[L$_n$(m)]} species indicate pure compounds. In particular all the spectra show a doublet at about δ 5.7 attributable to the proton H$_{1'}$ of the cyclopalladated ring close to a freely rotating phenyl ring (B in Figure 1). According to this finding these new complexes are assigned the trans structure.[27]

Mesomorphic Properties. With reference to the molecular structure, the HL$_n$(m) compounds are distinguished by a variable length of either the alkyl or the alkoxy chain. Therefore, to best discuss the mesogenic properties, two different homologous series can be considered. In particular we define one series as compounds bearing the same alkoxy chain (i.e., C$_{12}$H$_{25}$O) and the other as those having the same alkyl chain (i.e., CH$_3$). These series will be thereafter referred to as HL$_n$(12) and HL$_1$(m), respectively. We will similarly designate the palladium complexes formed from these ligands.

Table 1. Transition Temperatures (°C), Enthalpies (ΔH), and Mesophases[a] for HL$_n$(12) Ligands

n	transition	T (°C)	ΔH (J/g)
1	K–N	62.1	70.52
	N–I	70.6	2.36
	I–N	70.0	4.85
	N–K	48.0	57.60
2	K–N	64.2	96.98
	N–I	74.2	2.54
	I–N	70.5	4.13
	N–K[b]	30.0	
3	K–N	43.7	89.44
	N–I	81.0	2.79
	I–N	80.6	3.80
	N–S$_C$	37.2	0.21
	S$_C$–K[b]	30.0	
4	K–S$_C$	37.9	55.49
	S$_C$–N	48.0	0.25
	N–I	77.6	4.47
	I–N	76.0	4.55
	N–S$_C$	48.0	0.34
	S$_C$–K[c]		
6	K–S$_C$	40.6	57.38
	S$_C$–N	64.6	0.09
	N–I	79.8	2.61
	I–N	77.9	3.70
	N–S$_C$	63.3	0.43
	S$_C$–K[c]		
8	K–S$_C$	41.1	81.24
	S$_C$–I	86.4	4.66
	I–S$_C$	86.0	4.78
	S$_C$–K[c]		

[a] K = solid phase, N = nematic phase, S$_A$ = smectic A phase, S$_C$ =smectic C phase. [b] Observed by optical microscopy only. [c] The crystallization process does not take place until room temperature.

Table 2. Transition Temperatures (°C), Enthalpies (ΔH), and Mesophases[a] for HL$_1$(m) Ligands

m	transition	T (°C)	ΔH (J/g)
7	K–N	63.1	75.56
	N–I	80.3	3.21
	I–N	75.5	2.45
	N–K	54.3	64.78
9	K–N	65.1	102.27
	N–I	82.6	2.39
	I–N	78.8	2.67
	N–K	51.2	73.48
12	n = 1 in Table 1		
14	K–N	64.8	97.28
	N–I	69.0	2.20
	I–N	67.1	6.36
	N–K[b]	33.0	

[a] K = solid phase, N = nematic phase, I = isotropic phase. [b] Observed by optical microscopy only.

The different mesophases were identified by combined optical microscopy and X-ray diffraction analysis on powder samples. The transition temperatures were determined by differential scanning calorimetry and confirmed by X-ray diffraction.

Mesogenic Behavior of the Ligands. All the HL$_n$(12) and HL$_1$(m) species are low melting mesogens which exhibit good thermal stability. Their transition temperatures and ΔH values are summarized in Tables 1 and 2, respectively. The nematic, N, and the smectic C, S$_C$, phases were both recognized by their optical textures.[28] In particular the N phase displays schlieren or marbled texture, while the S$_C$ phase is readily

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(27) Ghedini, M.; Morrone, S.; De Munno, G.; Crispini, A. *J. Organomet. Chem.* **1991**, *415*, 281.

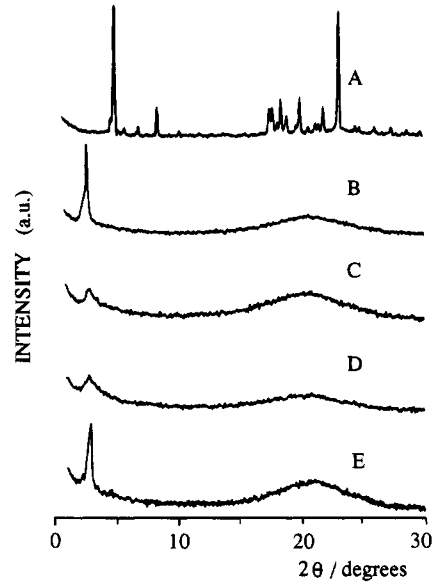

Figure 2. X-ray powder diffraction patterns of $HL_4(12)$ recorded at different temperatures during a complete thermal cycle. Heating cycle: (A) room temperature; (B) $T = 41$ °C; (C) $T = 55$ °C. Cooling cycle: (D) $T = 60$ °C, (E) $T = 40$ °C.

identified from the characteristic schlieren texture which exhibits only centers with four brushes.

The nature of the different mesophases was confirmed by X-ray diffraction analysis. The unambiguous identification of the nematic mesophase for some of the compunds required the performing of the measurement on oriented specimens. This was achieved by applying an external magnetic field to the sample. In these cases, the orientation of the directors of the nematic microdomains along the direction of the magnetic field was revealed by a considerable growth in the intensity of the diffuse reflection characterizing the small-angle region of the spectrum. As an example of the results of the X-ray measurements, Figure 2 reports the diffraction spectra of unoriented $HL_4(12)$, measured at different temperatures, from room temperature up to the isotropization point, during a heating–cooling thermal cycle.

The spectra of the smectic mesophases clearly display the sharp peak in the low-scattering-angle region associated with the Bragg reflection of the smectic layers, while the spectra recorded in the nematic phase exhibit the characteristic small-angle weak diffuse peak. The position of the sharp peak gives, according to the Bragg law, the smectic layer spacing, d, whereas the center of the diffuse signal in the spectra of the nematic mesophases gives the apparent molecular length, l. For all samples a good agreement has been found between the l values in the nematic mesophases and the length of the molecule, L, calculated on the basis of a model where the chains are in the fully extended conformation. Table 3 reports the measured d values and the molecular lengths L for all the samples which exhibits the S_C mesophase [$HL_3(12)$–$HL_8(12)$]. The d values are taken from the spectra measured at temperatures corresponding to the center of the mesophase range. For all the samples the layer spacing d was found to be temperature independent throughout the whole mesophase thermal stability region.

Table 3. Periodicities (d),[a] Theoretical Molecular Lengths (L),[b] and Tilt Angle (β) for the S_C Phase of $HL_n(12)$ Ligands

n	d (Å)	L (Å)	β (deg)
3	29.1	29.2	5.5
4	30.1	30.4	8.0
6	32.2	32.9	12.6
8	33.5	35.5	19.3

[a] Layer spacing derived from diffraction patterns (in the central region of phases stability). [b] Molecular length determined by molecular modeling (alkyl chains in all-trans conformation).

From the ratio between d and L the apparent tilt angles β of the director with respect to the layer normal have been evaluated and the values are also reported in Table 3. A progressive increase with the length n of the alkyl chain following an almost linear behavior is observed for β, which varies from $\beta = 5.5°$ ($n = 3$) to $\beta = 19.3°$ ($n = 8$).

The mesogenic behavior exhibited throughout the series by the two families of ligands, $HL_n(12)$ and $HL_1(m)$, is quite different. In the $HL_n(12)$ compounds only a nematic phase is present for the samples with $n = 1$ and $n = 2$, whereas $HL_3(12)$, $HL_4(12)$, and $HL_6(12)$ display, in addition to the nematic phase, a smectic C phase which is monotropic for the shortest compound [$HL_3(12)$] and enantiotropic for $HL_4(12)$ and $HL_6(12)$. Finally, $HL_8(12)$ shows only an enantiotropic S_C phase. Therefore, on increasing the molecular length the mesophase turns from nematic to smectic, thus paralleling the trend usually observed.[29] In the $HL_1(m)$ series, as previously reported by Hegge and van der Veen[30] about very similar mesogens (i.e., 2-hydroxy-4-n-alkoxy-4′-n-butylazobenzenes) only nematic phases are present.

The molecular structure of the $HL_n(12)$ compounds and that of the previously investigated N-(4-(dodecyloxy)salicylidene)-4′-alkylanilines,[7d,e] HR_nL (Figure 1), differs solely in the nature of the group bridging the two phenyl rings: —N=N— instead of —CH=N—. Accordingly, a meaningful comparison between the two series can be done. While for the $HL_n(12)$ compounds only nematic and S_C phases are observed (Table 1), the HR_nL series shows N and S_A phases for shortest terms of the series ($1 < n < 3$) and S_A and S_C phases for the longest one ($n > 4$).[7d,e] Moreover, the HR_nL clearing temperatures are 10–15 °C higher than the homologous $HL_n(12)$ terms.

In rodlike mesogens the azo group is usually considered a better linking group than the imine one because it induces a planar configuration in the molecule, and consequently a better conjugation associated with a good thermal stability.[29] In addition, when in these molecules a hydroxy group occurs as in HR_nL or $HL_n(m)$ (Figure 1), a strong intramolecular hydrogen bond forms and the temperatures of both the solid–nematic and nematic–isotropic transitions rise.[30] Therefore, in the present case the effect of the linking group on the thermal stability of the mesophases should be dominated by the OH group which, allowing a more planar

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(28) (a) Demus, D.; Richter, L. *Texture of Liquid Crystals*; Verlag Chemie: Wenheim, 1980. (b) Gray, G. W.; Goodby, J. W. *Smectic Liquid Crystals, Textures and Structures*; Leonard Hill: Glasgow, 1984.

(29) Kelker, H.; Hatz, R. *Handbook of Liquid Crystals*; Verlag Chemie: Wenheim, 1980.

(30) Van der Veen, J.; Hegge, T. C. J. M. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 344.

Table 4. Transition Temperatures (°C), Enthalpies (ΔH), and Mesophases[a] for {(Azoxy-6)Pd[L_n(12)]} Complexes

n	transition	T (°C)	ΔH (J/g)
1	K–N	103.1	46.31
	N–I	107.1	0.39
	I–N	106.1	0.79
	N–K	75.0	
2	K–I	113.4	47.29
	I–N	102.4	0.88
	N–K	60.0	
3	K–I	116.5	48.18
	I–N	106.1	0.87
	N–K	77.5	1.57
4	K–I	116.2	20.52
	I–N	104.8	1.08
	N–K	72.6	1.79
6	K–I	132.3	40.47
	I–N	108.4	1.41
	N–K	74.4	0.30
8	K–I	128.8	43.49
	I–N	111.3	2.06
	N–S_C	91.3	0.06
	S_C–K	87.4	0.05

[a] K = solid phase, N = nematic phase, S_C = smectic C phase, I = isotropic phase.

Table 5. Transition Temperatures (°C), Enthalpies (ΔH), and Mesophase[a] for {(Azoxy-6)Pd[L_1(m)]} Complexes

m	transition	T (°C)	ΔH (J/g)
7	K–I	146.8	57.32
	I–N	111.4	0.77
	N–K[b]		
9	K–I	153.2	80.58
	I–N	109.6	0.83
	N–K[b]		
12	n = 1 in Table 4		
14	K–N	96.9	48.11
	N–I	105.6	0.94
	I–N	103.1	0.76
	N–K[b]		

[a] K = solid phase, N = nematic phase, I = isotropic phase. [b] The crystallization process does not take place until room temperature.

configuration, makes the HR_nL and the HL_n(12) ligands structurally very similar. These structural characteristics reflect into the quite similar transition temperatures displayed by the two series.

Mesogenic Behavior of the Complexes. The [L_n(m)]$_2$-Pd molecules did not show any mesomorphic behavior (melting points in the range 165–187 °C) while the homologous series of mixed-ligand complexes {(Azoxy-6)Pd[L_n(12)]} and {(Azoxy-6)Pd[L_1(m)]} display highly viscous nematic phases (n = 1–4, 6, 8) and in one case (n = 8) a smectic C phase. The nematic phases have been recognized by the characteristic marbled or threaded textures while the smectic C phases by the broken focal conic texture.

The mesomogenic behavior of {(Azoxy-6)Pd[Ln(12)]} and {(Azoxy-6)Pd[L_1(m)]} complexes is reported in Tables 4 and 5 respectively. With reference to the {(Azoxy-6)Pd[L_n(12)]} complexes, the shortest chain derivative gives rise to an enantiotropic nematic phase; for n = 2 to n = 6 the nematic phase becomes monotropic and for the octyl derivative even a monotropic smectic C phase has been observed. The last Sc phase on further cooling is transformed into a highly viscous birefringent phase. The X-ray analysis performed on this sample clearly indicated that the highly viscous phase is not an ordered liquid-crystalline phase but a solid one. The diffraction spectrum of this phase is in fact characterized by several reflections which are distributed throughout the whole range of scattering angles investigated (Figure 3F).

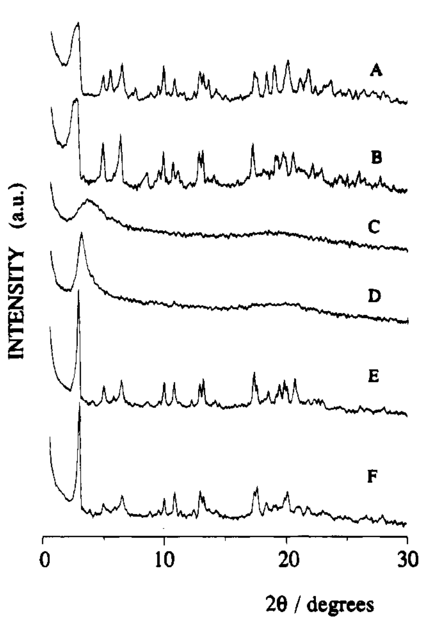

Figure 3. X-ray diffraction patterns of the {(Azoxy-6)Pd[L_8-(12)]} complex recorded at different temperatures in a thermal cycle. Heating cycle: (A) room temperature; (B) T = 120 °C. Cooling cycle: (C) T = 105 °C; (D) T = 90 °C; (E) T = 80 °C; (F) room temperature. Spectra A, B, D–F were obtained on an unoriented specimen, whereas the spectrum C of the nematic mesophase was obtained with the sample oriented in an external magnetic field (B = 0.1 T) normal to the incident X-ray beam and lying in the plane of the X-ray beam and of the detector (horizontal plane).

The maximum periodicity, corresponding to the reflection with the dominant intensity, is coincident with the layer spacing of the higher temperature mesophase ($d \sim 28$ Å). In addition, most of the reflections are characterized by weak and diffuse peaks, thus indicating a relatively poor crystalline nature of the solid phase which, on the other hand, possesses a strong lamellar nature as indicated by the sharp intense small-angle reflection). This could be the reason for the relatively low value measured for the enthalpy corresponding to the Sc–K transition.

Comparing the thermotropic behavior of the {(Azoxy-6)Pd[L_n(12)]} compounds with the HL_n(12) parents it is apparent that the complexation of the L_n(12) anions to the (Azoxy-6)Pd fragment produces an increase of the transition temperatures of about 30 °C. Regarding to the nature of the mesophases, the nematic one is preserved throughout the homologous series of complexes and the smectic one is retained only in the derivative with the longest alkyl chain (n = 8).

The {(Azoxy-6)Pd[L_1(m)]} series is featured by the lengthening of the alkoxy terminal chain. These compounds form a nematic phase, monotropic (m = 7 and 9) or enantiotropic (m = 12 and 14). Remarkably, such a phase is characterized by a wide range of stability in the cooling cycle (Table 5) and the N–K transition is not observed until room temperature.

Within the homologous series, as far as the enantiotropic transitions are concerned, it should be pointed out that the coordination of HL_1(m) to the cyclopalladated species produces a narrowing of the nematic range.

Comparing the two series of complexes {(Azoxy-6)-Pd[L_n(12)]} and {(Azoxy-6)Pd[L_1(m)]} it seems that the different length of the aliphatic chains is a crucial point in obtaining stable mesophases. In fact, enantiotropic nematic phases were detected for [(Azoxy-6)Pd[L_1(12)]} and {(Azoxy-6)Pd[L_1(14)]}; otherwise {(Azoxy-6)Pd-[L_n(12)]} ($n = 2-4, 6, 8$) and {(Azoxy-6)Pd[L_1(m)]} ($m = 7, 9$) show only mesophases with a monotropic behavior.

The calorimeter behavior of the complexes {(Azoxy-6)Pd[L_n(12)]} ($n = 1, 2$) deserves a comment. In the first cooling cycle the crystallization process is never detected by DSC. The optical observations are in agreement with these data since the liquid-crystalline phase transforms into a plastic phase which preserves the optical textures of the previous mesophase. In the second heating cycle the crystallization process is observed and the DSC trace displays a large exothermic peak. This effect is probably related to the relatively slow kinetics of crystallization if compared to the cooling rate involved in the DSC and optical investigations. A similar behavior has been observed, in fact, also in the X-ray diffraction measurements when the same rate involved in the DSC and optical measurements was used to cool the sample to room temperature. The room-temperature X-ray diffraction spectra recorded just after the cooling process were found to be characteristic of the higher temperature mesophase (nematic). Only after times of the order of an hour at room temperature or after a heating treatment at temperatures varying between 60 and 70 °C, we observed the X-ray diffraction spectra of the solid phase. A different behavior was observed when the temperature was lowered by intermediate steps, each temperature of the step sequence being maintained constant for the time necessary to the X-ray data acquisition (about 20 min). In this case, in fact, we could observe the formation of the low-temperature solid phase during the first cooling cycle. The N–K transition temperatures reported in Table 4 correspond to the transition temperatures as obtained from the X-ray measurements in these conditions.

As an example of the results of the X-ray diffraction measurements of the complexes, Figure 3 shows the diffraction patterns obtained for {(Azoxy-6)Pd[L_8(12)]} at different temperatures between room temperatures and the clearing temperature in a thermal cycle. The spectrum of the nematic phase (Figure 3C) was obtained when the sample is put into the magnetic field. The position of the small angle sharp peak in the spectrum of the S_C mesophase (Figure 3D) corresponds to a layer spacing of 28.0 Å. With the calculated value $L = 35$ Å of the molecular length, this gives an apparent tilt angle $\beta = 36.7°$.

Mixing Experiments. The mixing of a metallomesogen with an organic compound having similar mesogenic behavior is a useful method for lowering the melting temperature with a consequent increase of the mesomorphic range. Thus, to perform mixing experiments we selected the palladium complex which revealed the best mesomorphic properties within the whole series of compounds, {(Azoxy-6)Pd[L_1(14)]} (Table 5) and its parents, HL_1(14) (Table 3) and H(Azoxy-6) [K $\rightarrow$ (80 °C) N $\rightarrow$ (126 °C) I]. Equimolar solution of the different compounds were prepared and mixed together. The solvent was successively evaporated to leave a solid mixture. In the first experiment we mixed {(Azoxy-6)Pd[L_1(14)]} and HL_1(14). The crystal-to-nematic transition was lowered from 97 to 52 °C, and the clearing point was lowered from 105 to 89 °C. Thus the nematic range of the mixture was about 37 °C while in the pure complex it was only about 8 °C. In the second experiment {(Azoxy-6)Pd[L_1(14)]} was added to H(Azoxy-6). In this case the melting point was observed at 67 °C, while the clearing point was 110 °C. The nematic range of such a mixture was about 43 °C, even larger than the previous one.

Concluding Remarks

The complexation of palladium(II) to the same mesogenic ligands, HL_n(m), or to different calamitic moieties, H(Azoxy-6) and HL_n(m), allows the synthesis of [L_n(m)]$_2$Pd homoligand and {(Azoxy-6)Pd[L_n(m)]} mixed-ligand complexes. Even if both the *o*-hydroxyazobenzenes and 4,4′-bis(hexyloxy)azoxybenzene are mesogenic, the different combination in palladium complexes of these two ligands induces a dissimilar thermal behavior. In fact, the homoligand complexes did not show any mesomorphic properties, whereas the mixed-ligand ones are nematogenic.

These species display similar molecular shapes and comparable alkyl chain lengths whereas the rigid molecular cores significantly differ both in nature and symmetry (by effect of the N–O group that features the azoxy complexes, Figure 1). In particular, the molecular core is symmetric and apolar in [L_n(m)]$_2$Pd whereas it is asymmetric and polar in {(Azoxy-6)Pd[L_n(m)]}. Consequently, intermolecular interactions should be mainly attributable to weak dispersion forces in the former species and to comparatively stronger dipole–dipole interactions in the latter one. Moreover, it should be considered that the local order in the mesophase is imposed by the elongated shape of molecules which are probably not free to rotate around their longest molecular axis owing to their H-like structure. Therefore, the molecular dipoles of the azoxy compounds can be thought randomly oriented and giving rise to either dipole–dipole attractions or repulsions.

To bring about a mesophase a proper balance between intermolecular attractions and thermal disorder is required. Usually in mesogens as those reported herein these roles are played by the rigid molecular core and by the alkyl chains respectively. Despite the fact that the alkyl chains are similar in length, the experimental data show that the [L_n(m)$_2$Pd species lack mesomorphism, whereas the {(Azoxy-6)Pd[L_n(m)]} ones are liquid crystals. Therefore, we conclude that the observed behavior may be mainly attributable to the increased entropy which results from the electronic and/or structural modifications induced by the azoxy group onto the rigid part of the molecules.

Finally, with reference to the potential applications of metal-containing liquid-crystalline materials, worthy of note is the strong enlargement of the nematic range obtained on mixing the {(Azoxy-6)Pd[L_1(14)]} complex with the corresponding mesomorphic ligands.

Acknowledgment. This work was supported by the Ministero dell'Universita' e della Ricerca Scientifica e Tecnologica (MURST) under the cover of "Chimica dei Materiali". We thank Johnson Matthey, Ltd., for a generous loan of $PdCl_2$. We are also grateful to Dr. F. Neve for NMR experiments.