Substituted Aza and Aza-Thia Macrocycles: An Example of a Calamitic Macrocyclic Metallomesogen

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Abstract. The new bis-4-(hexyloxy)benzamide and bis-4-(dodecyloxy)benzamide derivatives of macrocyclic ligands [18]aneN$_2$O$_4$ (**L$_1$** and **L$_2$**) and [18]aneN$_2$S$_4$ (**L$_3$** and **L$_4$**) have been prepared and characterized by ^{1}H and ^{13}C NMR spectroscopy, differential scanning calorimetry and optical microscopy. The nonmesogenic ligands **L$_3$** and **L$_4$** react with [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ to give the cationic complexes [Pd(L$_3$)][BF$_4$]$_2$ and [Pd(L$_4$)][BF$_4$]$_2$. [Pd(L$_4$)][BF$_4$]$_2$ shows mesomorphic behaviour affording a smectic mesophase.

1. Introduction

The challenge of making metal complexes with mesogenic properties is often doubled by the need for appropriate new ligands. Although thermotropic liquid crystallinity is not a necessary requirement for ligands to be used in complexation experiments, some conditions must be fulfilled in order to get metallomesogens [1].

The induction of new mesomorphic phases in saturated macrocyclic ligands was realized by Lehn *et al.* [2] by the introduction of long lateral chains into macrocyclic polyamines. *N*-Acylated hexacyclene derivatives with one-chain substituents were found to exhibit mesogenic behaviour and the mesophase structure was described either as 'tubular' *columnar discotic* [2–4] or *smectic* [5], and more recently as *hexagonal columnar* [6]. The same approach was followed to prepare acylated [3, 4, 7, 8] and sulfonated [3] derivatives of cyclic tri- and tetramines, which sometimes displayed discotic mesophases [7, 8]. Metal ion complexation by *N*-substituted non-mesogenic polyamines has been proved to be another important way to induce mesophase formation [9, 10].

If one wants to pursue the formation of prolate instead of flat, plate-like molecules (either ligands or complexes), bibracchial lariat ethers [11] and their analogues are a good starting point. Substitution at the secondary nitrogen sites of the appropriate diazacrown ether can indeed afford molecules which, in principle,

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could show mesomorphic behaviour depending on the length, flexibility, and tail structure. With this objective in mind we proceeded to synthesize some bis{p-(alkyloxy)benzoyl} derivatives of the mixed-donor macrocycle [18]aneN$_2$O$_4$ (**1**).
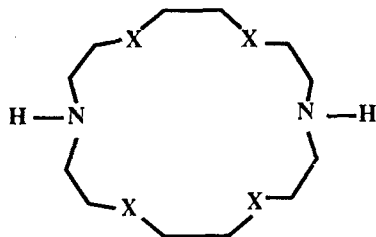
1, X = O; 2, X = S

Our strategy was to take advantage of the well-documented reactivity of aza-crown compounds [12] to build up functionalized macrocycles with an elongated shape. Subsequent extension of the synthetic scheme to the diazatetrathia macrocycle 18[ane]N$_2$S$_4$ (**2**) would result in the formation of ligands with potentially good ability for complexation of d-block elements. In the present study we report on the synthesis of the acylated derivatives of **1** and **2**. Complexation studies with the nonmesogenic thioether macrocycles also demonstrate that liquid crystallinity can be achieved through molecular recognition.

2. Experimental

All reactions were performed under a dry argon atmosphere in freshly distilled solvents. Anhydrous N, N-dimethylacetamide (DMA, Aldrich), 4-(dimethylamino)-pyridine (DMAP, Aldrich), 4-(hexyloxy)benzoyl chloride (Aldrich), and 1,10-diaza-4,7,13,16-tetrathiacyclooctadecane (**2**, [18]aneN$_2$S$_4$) (Lancaster) were used as received. 1,10-Diaza-4,7,13,16-tetraoxacyclooctadecane (**1**, [18]aneN$_2$O$_4$) [13], 4-(dodecyloxy)benzoyl chloride [4], and [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ [14] were synthesized according to the literature.

^{1}H and ^{13}C NMR spectra were recorded on a Bruker WH 300 spectrometer with internal tetramethylsilane as reference. IR spectra were recorded on a Perkin-Elmer 1330 spectrometer. Conductivity measuremens were carried out using an LKB 5300 B Conductolyser conductivity bridge. Elemental analyses were performed at the Microanalytical Laboratory of our department

X-ray diffraction measurements were performed with an INEL CPS 120 powder diffractometer using Ni filtered CuK$_\alpha$ radiation (λ = 1.54 Å) strongly collimated with an appropriate slit system. Heating was achieved by a hot stage whose accuracy and stability were $\pm$ 0.5°C and $\pm$ 0.1°C, respectively.

Optical textures were observed with a Zeiss Axioskop polarizing microscope equipped with a Linkam CO 600 heating stage and temperature control. Transition temperatures were measured by differential scanning calorimetry (DSC) with a Perkin Elmer DSC-7 instrument operating at a scanning rate of 10°C/min.

2.1 General Procedure for Acylation Reactions

As preparations of the acylated ligands L_{1-4} are similar a typical procedure is reported only for L_2.

2.1.1. *1,10-Bis[(4-dodecyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (L₂)*

DMAP (0.184 g, 1.51 mmol) and **1** (0.17 g, 0.68 mmol) were dissolved in dry DMA (10 mL) and the reaction vessel cooled to 0°C. A solution of 4-(dodecyloxy)benzoyl chloride (0.460 g, 1.42 mmol) in dichloromethane (10 mL) was then added dropwise over 30 min. The formation of white solid was observed during the addition. After addition the reaction mixture was heated at reflux temperature for 72 h. The mixture was then allowed to cool, filtered and concentrated *in vacuo*. The residue was taken up with chloroform (30 mL), extracted twice with saturated NaCl solution, dried over anhydrous Na_2SO_4 and evaporated to a viscous yellowish oil which solidified on standing. Purification of the product was achieved by silica gel chromatography using 1% methanol/dichloromethane as eluent and recrystallization from dichloromethane/*n*-hexane (2 : 10) at –20°C. Yield 60%. *Anal. Found:* C, 71.40; H, 9.72; N, 3.50. *Calc.* for $C_{50}H_{82}N_2O_8$: C, 71.66; H, 9.85; N, 3.34. IR (KBr): 2910(s), 2844(s), 1612(s), 1506(m), 1460(s), 1426(s), 1279(m), 1236(s), 1132(s), 1032(s), 830(s), 761(m), 624(m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.92 (t, 6 H, CH_3), 1.29 (m, 36 H, $(CH_2)_9$), 1.60 (m, 4 H, O—CH_2—CH_2), 3.28 (br s, 8 H, N—CH_2—CH_2), 3.59 (t, 4 H, O—CH_2), 3.56–3.66 (m, 16 H, CH_2—O—CH_2), 6.78 (d, 4 H, arom. 3,5), 7.49 (d, 4 H, arom. 2,6). ^{13}C{^{1}H} NMR (75.47, C_6D_6, 298 K): δ 14.97, 23.74, 27.08, 30.25, 30.44, 30.69, 30.74, 32.97, 49.71 (br), 68.74, 71.03, 71.62, 115.06, 130.05, 130.06, 161.11, 172.26. In $CDCl_3$ the carbon resonance which can be assigned to N—CH_2 appears as two distinct broad signals at 48.60 and 49.92 ppm.

2.1.2. *1,10-Bis[(4-hexyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetraoxacyclooctadecane (L₁)*

Reflux time: 72 h. Yield 58%. *Anal. Found:* C, 68.30; H, 8.83; N, 4.05. *Calc.* for $C_{38}H_{58}N_2O_8$: C, 68.30; H, 8.71; N, 4.18. IR (neat): 2930(s), 2858(m), 1610(s br), 1508(m), 1453(s), 1410(s), 1285(s), 1240(s), 1122(s), 1074(s), 1008(s), 840(s), 760(m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 333 K): δ 0.87 (t, 6H, CH_3), 1.18–1.29 (m, 12 H, $(CH_2)_3$), 1.56 (m, 4 H, O—CH_2—CH_2), 3.32 (s, 8 H, N—CH_2—CH_2), 3.64 (t, 4 H, O—CH_2), 3.59–3.69 (m, 16 H, CH_2—O—CH_2), 6.77 (d, 4 H, arom. 3,5), 7.50 (d, 4H, arom. 2,6). ^{13}C{^{1}H} NMR (75.47, C_6D_6, 298 K): δ 14.82, 23.57, 26.67, 30.14, 32.51, 49.50 (br), 68.71, 71.04, 71.62, 115.06, 130.04, 130.60, 161.11, 172.26.

2.1.3. *1,10-Bis[(4-hexyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane* (**L₃**)

Reflux time: 24 h. Yield 53%. *Anal. Found:* C, 61.93; H, 7.96; N, 3.84. *Calc.* for $C_{38}H_{58}N_2O_4S_4$: C, 62.09; H, 7.96; N, 3.81. IR (neat): 2930(s), 2862(m), 1610(s), 1592(s), 1501(m), 1454(s), 1412(s), 1342(m), 1288(s), 1241(s), 1168(s), 1018(s), 840(s), 762(m) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.91 (t, 6 H, CH_3), 1.20–1.36 (m, 12 H, $(CH_2)_3$), 1.61 (m, 4 H, O—CH_2—CH_2), 2.67 (v br s, 16 H, CH_2—S—CH_2), 3.60 (v br s, 8 H, N—CH_2—CH_2), 3.63 (t, 4 H, O—CH_2), 6.83 (d, 4 H, arom. 3,5), 7.49 (d, 4 H, arom. 2,6). $^{13}C\{^1H\}$ NMR (75.47, C_6D_6, 298 K): δ 14.63, 23.36, 26.47, 29.94, 31.68 (br), 32.32, 33.67, 49.50 (br), 68.63, 115.05, 129.76, 129.84, 161.17, 172.10.

2.1.4. *1,10-Bis[(4-dodecyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane* (**L₄**)

Reflux time: 20 h. Yield 64%. *Anal. Found:* C, 66.15; H, 9.14; N, 3.17. *Calc.* for $C_{50}H_{82}N_2O_4S_4$: C, 66.47; H, 9.15; N, 3.10. IR (KBr): 2916(s), 2851(s), 1612(s), 1594(m), 1500(m), 1458(s), 1402(m), 1341(m), 1294(s), 1243(s), 1234(m), 1166 (s), 1017(s), 839(s) cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6, 298 K): δ 0.96 (t, 6 H, CH_3), 1.33 (m, 36 H, $(CH_2)_9$), 1.65 (m, 4 H, O—CH_2—CH_2), 2.68 (v br s, 16 H, CH_2—S—CH_2), 3.63 (v br s, 8 H, N—CH_2—CH_2), 3.65 (t, 4 H, O—CH_2), 6.84 (d, 4 H, arom. 3,5), 7.48 (d, 4 H, arom. 2,6). $^{13}C\{^1H\}$ NMR (75.47, C_6D_6, 298 K): δ 14.99, 23.74, 27.08, 30.24, 30.45, 30.68, 30.70, 30.74, 31.82 (br), 32.98, 33.83, 49.8 (v br), 68.83, 115.22, 129.94, 130.06, 161.36, 172.32.

2.1.5. *{1,10-Bis[(4-hexyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetrathiacyclooctadecane} palladium(II)tetrafluoroborate* [Pd(**L₃**)][BF₄]₂

[Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ (0.07 g, 0.16 mmol) was dissolved in acetonitrile (4 mL) and the solution was added by cannula to a stirring solution of **L₃** (0.117 g, 0.16 mmol) in dichloromethane (3 mL). Instantly the colourless solution turned yellow. The solution was allowed to stir for 1 h. Then the solvent was partially removed and diethyl ether added dropwise to give a pale yellow solid which was recrystallized from nitromethane-diethyl ether. Yield 65%. *Anal. Found:* C, 45.45; H, 5.75; N, 2.98. *Calc.* for $C_{38}H_{58}B_2F_8N_2O_4PdS_4$: C, 44.96; H, 5.76; N, 2.76. $\Lambda_M(9 \times 10^{-4}$ M in acetone) 264.9 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1604 (C=O), 1045 cm^{-1} (BF$_4^-$). ^{1}H NMR (300 MHz, CD$_3$NO$_2$, 298 K): δ 0.87 (t, 6 H, CH_3), 1.31–1.47 (m, 12 H, $(CH_2)_3$), 1.77 (m, 4 H, O—CH_2—CH_2), 3.47 (br m, 16 H), 3.80 (br m, 4 H), 4.04 (t, 4 H, O—CH_2), 4.32 (br, obscured by solvent peak), 7.03 (d, 4 H, arom. 3,5), 7.60 (br d, 4 H, arom. 2,6). $^{13}C\{^1H\}$ NMR (75.47, CD$_3$NO$_2$, 298 K): δ 14.50, 23.72, 26.83, 30.29, 32.76, 39.24 (br, CH_2—S—CH_2), 46.61 (br, N—CH_2), 69.89 (O—CH_2), 116.29 (arom. $C_{3,5}$), 128.10 (arom. C_1), 130.73 (arom. $C_{2,6}$), 162.94 (arom C_4), 174.58 (C=O).

2.1.6. {1,10-Bis[(4-dodecyloxy)benzoyl]-1,10-diaza-4,7,13,16-tetrathiacyclo-octadecane} palladium(II)tetrafluoroborate [Pd(L$_4$)][BF$_4$]$_2$

A solution of [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ (0.08 g, 0.18 mmol) in acetonitrile (5 mL) was added to a solution of L$_4$ (0.160 g, 0.18 mmol) in dichloromethane (10 mL). A bright yellow solution was immediately obtained. After 1.5 h stirring the solvent was removed and the greenish yellow solid residue was washed with diethyl ether, filtered off, and vacuum dried. Recrystallization from acetonitrile-diethyl ether afforded the product in 76% yield. *Anal. Found:* C, 50.60; H, 6.90; N, 2.46. *Calc.* for C$_{50}$H$_{82}$B$_2$F$_8$N$_2$O$_4$PdS$_4$: C, 50.75; H, 6.98; N, 2.37. Λ_M (8.5 × 10^{-4} M in acetone) 275.1 Ω^{-1} mol^{-1} cm^2. IR (KBr): 1615 (C=O), 1050 cm^{-1} (BF$_4^-$). ^{1}H NMR (300 MHz, CD$_3$CN, 298 K): δ 0.89 (*t*, 6 H, CH$_3$), 1.25–1.47 (*m*, 36 H, (CH$_2$)$_9$), 1.81 (*m*, 4 H, O—CH$_2$—*CH$_2$*), 3.35 (br *m*, 16 H), 3.78 (br *m*, 8 H), 4.03 (*t*, 4 H, O—CH$_2$), 4.06 (br *m*), 7.01 (*d*, 4 H, arom. 3,5), 7.57 (br *d*, 4 H, arom. 2,6). ^{13}C{^{1}H} NMR (75.47, CD$_3$NO$_2$, 298 K): δ 13.50, 22.69, 26.06, 29.21, 29.43, 29.48, 29.68 (br), 31.98, 38.23 (br, CH$_2$—S—CH$_2$), 45.45 (br, N—CH$_2$), 68.76 (O—CH$_2$), 115.15 (arom. C$_{3,5}$), 126.93 (arom. C$_1$), 129.64 (arom. C$_{2,6}$), 161.78 (arom C$_4$). The C=O resonance was not resolved.

3. Discussion

3.1 LIGAND SYNTHESIS

Derivatives of [18]-aneN$_2$O$_4$ (**1**) with two appended sidearms have been prepared by several different methods [15]. Direct acylation of **1** in dichloromethane dimethylacetamide (DMA) in the presence of 4-(dimethylamino)pyridine (DMAP) affords the bis(amides) **L$_1$** and **L$_2$** (Scheme I).

Due to the possibility of inversion of the nitrogen atoms, **L$_1$** and **L$_2$** should be highly flexible ligands. The ^{1}H NMR spectra of **L$_1$** and **L$_2$** show a temperature dependence which may be attributed to conformational changes of the macrocycles in solution. Figure 1 shows the spectrum of **L$_1$** in benzene-d_6. The presence of sharp signals for the aromatic protons indicates that rotation about the amide N—C(O) bonds is fast on the NMR time scale over the whole temperature range. The absence of a restricted rotation about the amide C—N bonds [4, 9, 16] is confirmed by ^{13}C{^{1}H} NMR spectroscopy. The ^{13}C{^{1}H} NMR spectra of **L$_1$** and **L$_2$** in C$_6$D$_6$ at 298 K show a single sharp signal at about 130 ppm which can be assigned to the aromatic carbon atoms *ortho* to the amide function (C$_{2,6}$). Moreover, the ^{13}C{^{1}H} NMR spectrum of **L$_1$** (wherein assignment is much easier than for **L$_2$**) includes a broad signal at 49.50 ppm, assigned to the α-carbon atoms, and two sharp signals at 71.04 and 71.62 ppm which are assignable to the β and γ pairs of carbon atoms. Noteworthy, the inequivalence of the α and α' carbons is observed in the ^{13}C{^{1}H} NMR spectrum of **L$_2$** in CDCl$_3$ at 298 K with no other consequence on the remaining carbon resonances (see Experimental section).

Compounds **L$_1$** and **L$_2$** had no detectable mesophases as shown by DSC and

$$X = O; \quad n = 5 \ (\mathbf{L_1}), \quad 11 \ (\mathbf{L_2})$$
$$X = S; \quad n = 5 \ (\mathbf{L_3}), \quad 11 \ (\mathbf{L_4})$$
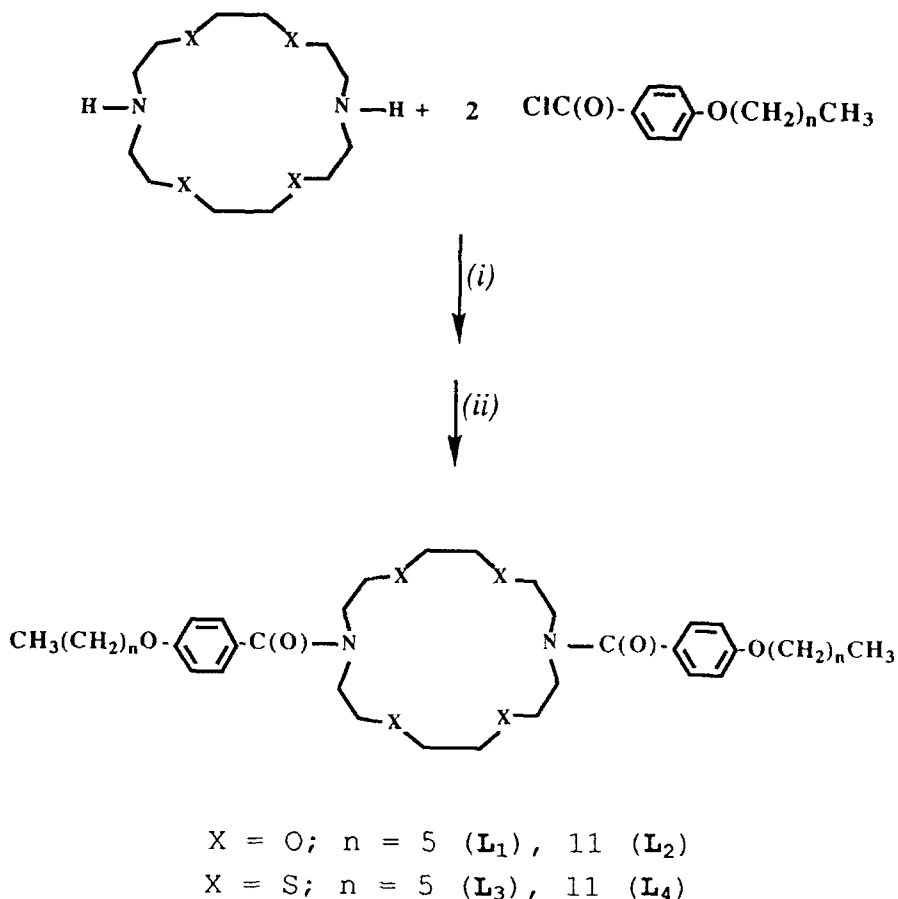
Scheme I. *(i)* CH_2Cl_2/DMA, DMAP, 0°C; *(ii)* reflux.

polarizing microscopy. Amide L_1 shows a crystal-isotropic transition at 86°C (ΔH = 72.74 kJ mol^{-1}), while the higher homologue L_2 has a melting temperature of 86–87°C (ΔH = 85.27 kJ mol^{-1}).

Macrocycles L_1 and L_2 are of course of no use for coordination of transition metals and could be viewed as prototypical models for more versatile ligands.

Substitution of oxygen for sulfur in the cycle backbone of **1** gives the mixed S- and N-donor macrocycle [18]aneN_2S_4 (**2**) and its N, N'-disubstituted derivatives are very effective in binding soft transition metal ions [18]. Reported side arms range from simple alkyl or acyl substituents [19], to ferrocenylmethyl [20] or diphenylphosphinomethyl [21].

The novel ligands L_3 and L_4 were prepared using the same experimental procedure followed for L_1 and L_2. NMR characterization showed that in solution L_3 and L_4 behave in a similar way to the corresponding N, O mixed-donors L_1 and L_2. The only appreciable difference is that both α and β-carbon atoms of the macro-
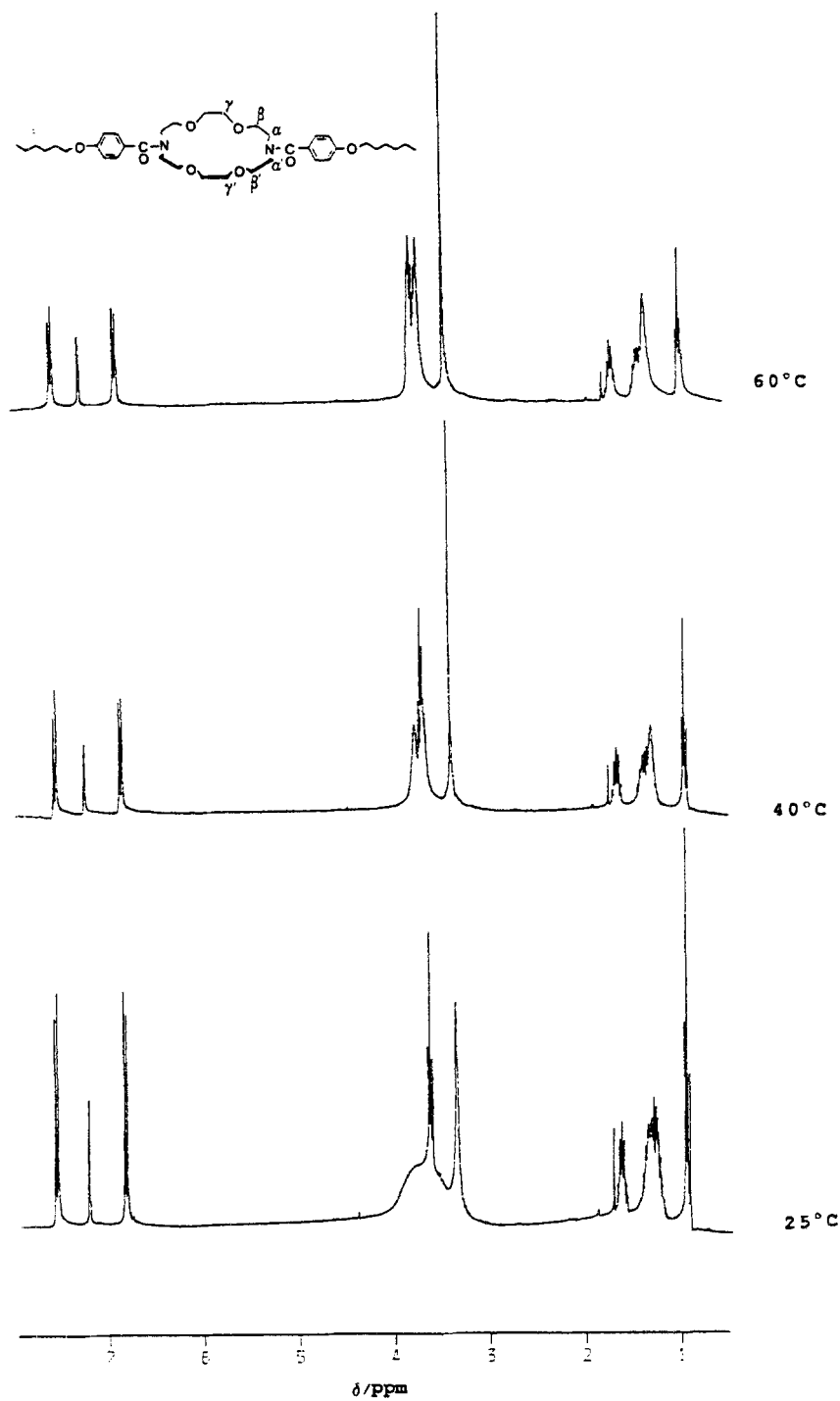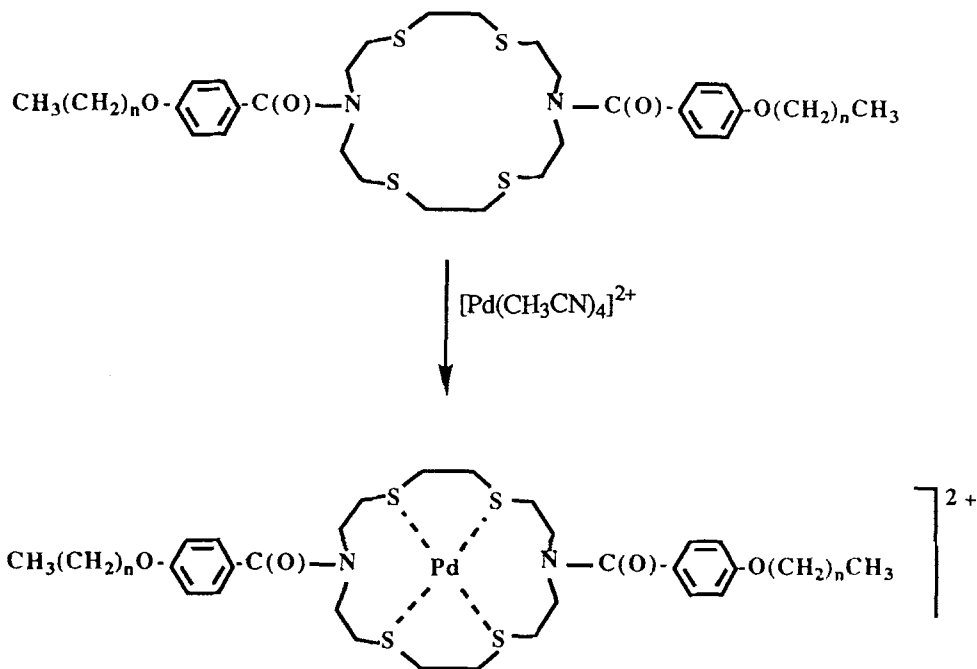
Fig. 1.   Variable-temperature 300 MHz ^{1}H NMR spectra of **L**$_1$ in benzene-d_6.

Scheme II.

cycle give rise to broad signals in the room temperature $^{13}C\{^1H\}$ NMR spectra of L_3 and L_4.

Both L_3 and L_4 did not show mesomorphic behaviour. L_3 has a melting point of 76°C (ΔH = 50.88 kJ mol^{-1}) and goes from the isotropic phase to a glassy room temperature phase. L_4 shows a crystal-isotropic transition at 72°C (ΔH = 28.68 kJ mol^{-1}).

3.2   COORDINATION STUDIES

Testing the coordination chemistry of the potentially hexadentate ligands L_3 and L_4 was the next step of our study. Our interest was in metal complexes with four-coordination geometry, which could be obtained for example with Pd(II) and Pt(II) metal centres. The reaction of either L_3 or L_4 with one equivalent of [Pd(CH$_3$CN)$_4$][BF$_4$]$_2$ in dichloromethane-acetonitrile (Scheme II) affords yellow solutions of products which were formulated as [Pd(L$_3$)][BF$_4$]$_2$ or [Pd(L$_4$)][BF$_4$]$_2$ on the basis of elemental analysis, conductivity, and spectroscopic characterization. Conductivity data are consistent with the presence in solution of 1 : 2 electrolytes [22].

Schröder and coworkers [23] have clearly established that while [18]aneN$_2$S$_4$

binds the Pd(II) ion in a distorted octahedral geometry, its N, N'-disubstituted derivative $Me_2[18]aneN_2S_4$ affords a Pd(II) complex with square-planar coordination at the metal ion. This stereochemical diversity arises from the steric hindrance of the NMe groups which does not allow N-coordination. Therefore, as in the case of $[Pd(Me_2[18]aneN_2S_4)][PF_6]_2$ [23], the palladium ion in $[Pd(L_3)][BF_4]_2$ and $[Pd(L_4)][BF_4]_2$ is tentatively assigned a square-planar geometry with the four S atoms of the macrocycle bound to the metal centre. The $^{13}C\{^1H\}$ NMR spectrum of $[Pd(L_3)][BF_4]_2$ in CD_3NO_2 at 298 K exhibits only two resonances at 46.61 and 39.24 ppm assignable to methylene carbons of the eighteen-member ring of L_3 (Figure 2). Both signals are broad suggesting some degree of fluxionality in solution. All other carbon resonances of L_3 however do not show broadening on complexation.

The ^1H NMR spectrum of $[Pd(L_3)][BF_4]_2$ measured in CD_3NO_2 is characterized by very broad signals at δ 3.47–4.32 ppm, assigned to the macrocyclic methylene protons. Interestingly, the signal assigned to the protons *ortho* to the amide function is broader than in the free ligand, thus suggesting some stiffening of the ligand upon complexation. ^1H and ^{13}C NMR features for $[Pd(L_4)][BF_4]_2$ are very similar to those discussed above for $[Pd(L_3)][BF_4]_2$.

The thermal behaviour of complexes $[Pd(L_3)][BF_4]_2$ and $[Pd(L_4)][BF_4]_2$ was studied by optical microscopy and differential calorimetry. For $[Pd(L_3)][BF_4]_2$ no mesogenic behaviour was detected. No birefringence or optical textures were indeed observed on heating or cooling. The DSC thermogram of the sample shows a very broad peak centered at 171.5°C (ΔH = 51.47 kJ mol^{-1}) corresponding to the transition to an isotropic liquid melt. Optical microscopy gives a transition temperature of 170°C.

$[Pd(L_4)][BF_4]_2$ has a more interesting (but not completely understood) thermal behaviour. On heating the formation of a highly viscous birefringent phase (Figure 3a) was observed at 140°C which increases in mobility at 161°C. Clearing was observed at 188°C. On cooling from the isotropic melt bâtonnets [24] began to form at 180°C (Figure 3b). An ill defined texture was obtained after annealing for about 1 h at 170°C (Figure 3c).

The DSC curve corresponding to the first heating shows a broad peak at 165°C (ΔH = 1.7 kJ mol^{-1}), followed by a strong broad peak at 191°C (ΔH = 26.3 kJ mol^{-1}) (Figure 4a). Cooling the isotropic melt led to a small exotherm at 151°C (ΔH = –0.3 kJ mol^{-1}) (Figure 4b). The second heating, performed after a 24 h wait, afforded a featureless DSC curve (Figure 4c), while a small broad peak at 138°C (ΔH = –0.1 kJ mol^{-1}) again was detected on cooling (Figure 4d). The absence of a recrystallization process is a plausible explanation for the unusual DSC curves. Thermal instability at the clearing point (partial decomposition was observed after two heating cycles) is another possible cause of abnormal behaviour.

X-ray scattering is the most powerful method of mesophase identification [25]. Thus, low resolution X-ray diffraction studies on $[Pd(L_4)][BF_4]_2$ indicate a solid-mesophase transition at 163°C. The presence of a disordered lamellar mesophase
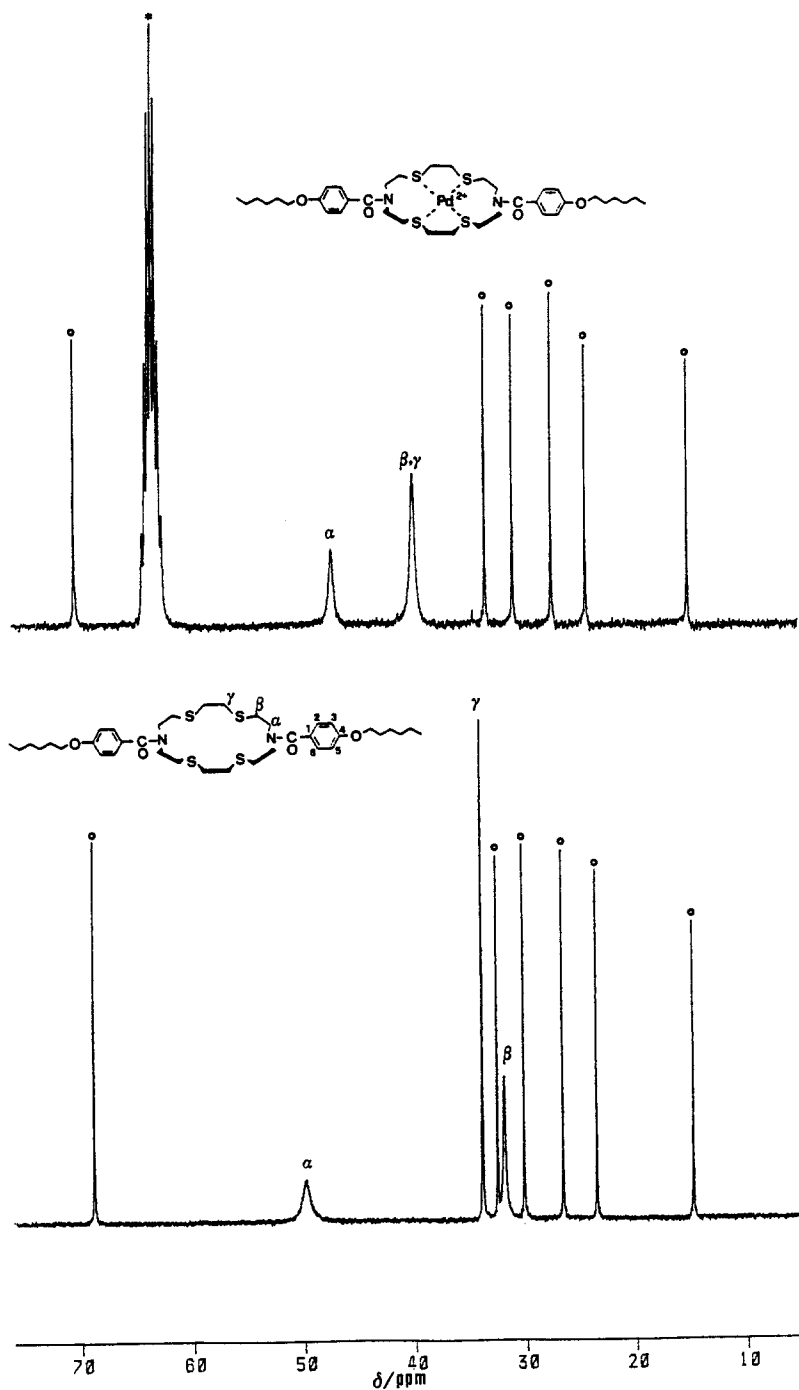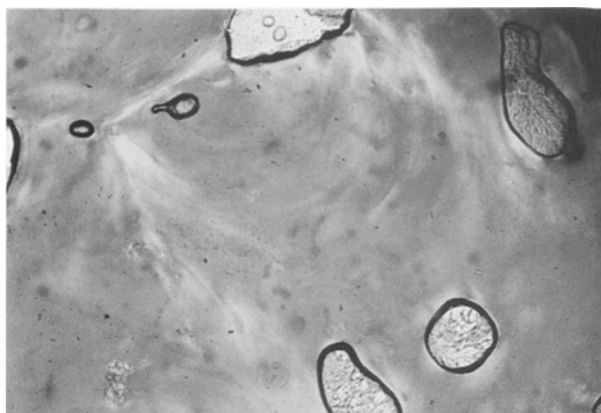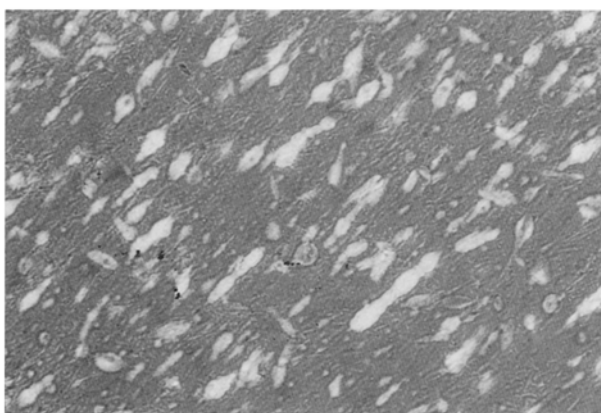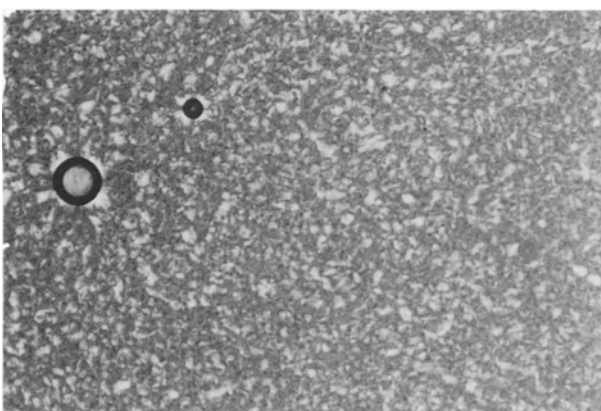
Fig. 2. 75.5 MHz ^{13}C{^{1}H} NMR spectra of (a) L$_3$ (in CDCl$_3$) and (b) [Pd(L$_3$)][BF$_4$]$_2$ (in CD$_3$NO$_2$/CD$_3$CN) in the region of aliphatic carbons at room temperature. * Solvent peak. ° Aliphatic tail carbons.

(a)

(b)

(c)

Fig. 3. Optical textures of [Pd(L$_4$)][BF$_4$]$_2$ between crossed polarizers: (a) on heating the solid, 140°C, × 100; (b) on cooling from the isotropic melt, 175°C, × 320; (c) after annealing for 1 h, 170°C, × 160.
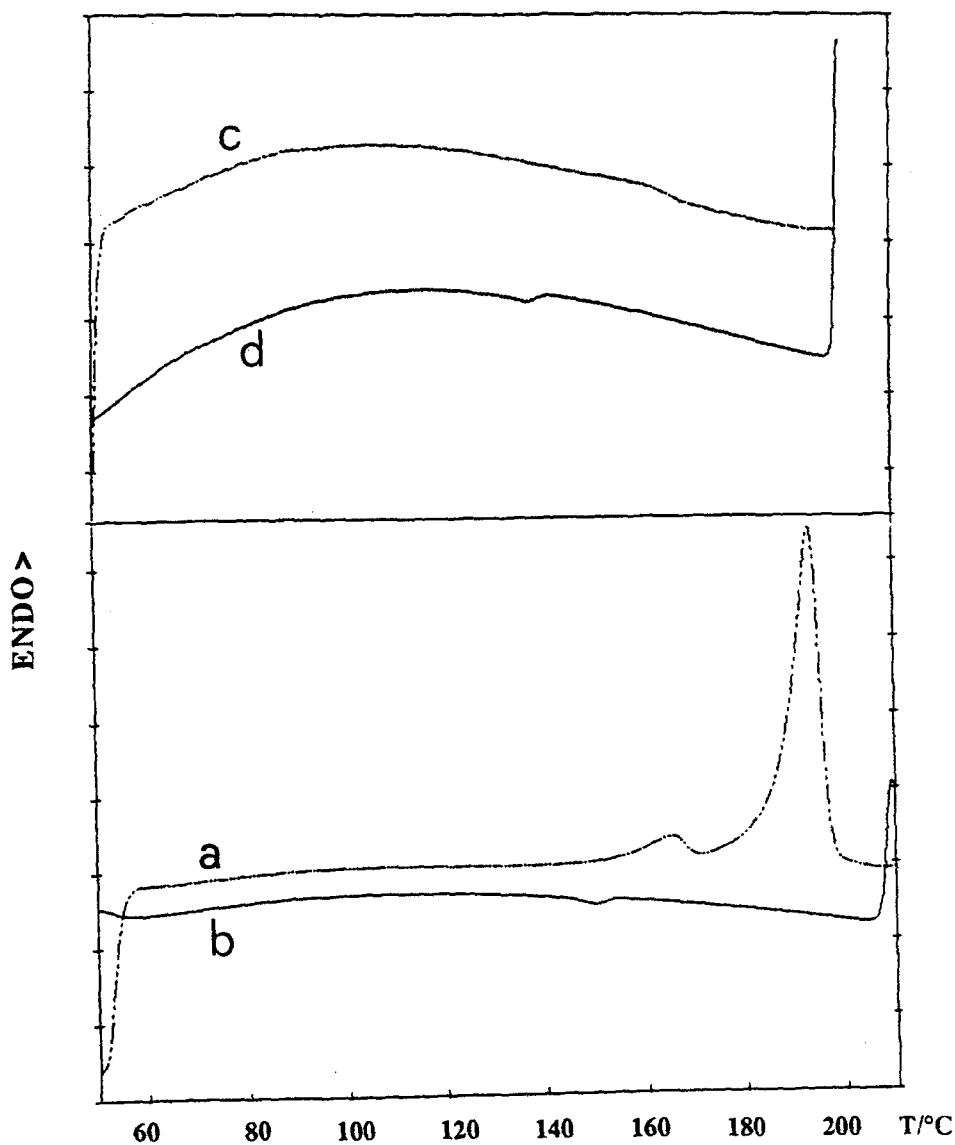
Fig. 4.   DSC thermograms for [Pd(L$_4$)][BF$_4$]$_2$: (a) first heating; (b) first cooling; (c) second heating; (d) second cooling.

was established by inspection of the diffraction pattern. The only feature is a rather diffuse peak at low θ values which corresponds to a main periodicity of ≈ 53 Å.

4. Conclusions

The absence of mesomorphic behaviour for ligands L_{1-4} is not entirely unexpected. Whereas the choice of the right length/diameter ratio seems to be critical, some considerations to the molecular geometry of the ligands can be given. Although the amide bonds increase the rigidity of the molecule over simple methylene units, both the presence of only one aromatic group on each side of the molecule and the inherent conformational flexibility of the central ring probably contribute to prevent mesophase formation. The possibility of multiple conformational structures is likely to be a less important factor, as new liquid crystals based on the same N_2O_4 macrocyclic backbone as in 1 have been reported [26, 27]. The need for different side groups is therefore apparent.

The formation of complexes derived from L_3 and L_4 is certainly a way of achieving conformational rigidification of the ligands. The exclusive appearance of mesomorphism for $[Pd(L_4)][BF_4]_2$ indicates that, provided the geometrical requirements are fulfilled, the metal ion is the determining factor for both a rigid-core organization (short-range order) and stronger intermolecular interaction (long-range order). Assuming that the mesophase is a calamitic layered one and considering that the approximate length of L_4 along its molecular long axis is of the order of 50–52 Å, the layer thickness of 53 Å is consistent with a molecular packing characteristic of smectic A phases. Based upon these observations, we can also rule out the possibility of interpenetration of smectic layers or chain melting [28].

Preliminary results show that $Cu(I)/L_4$ (1 : 1) ionic complexes seem to exhibit a clear mesogenic behaviour and the occurrence of smectic phases is supported by experimental evidence.

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