Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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To cite this Article Moutloali, Richard M. , Darkwa, James and Marfo-Owusu, Emmanuel(2006) 'Mesogenic behaviour of (4-alkoxybenzylideneamino)bromobenzene, (4-alkoxybenzylideneamino)benzenethiols, and thiolatonickel complexes of the thiols', Liquid Crystals, 33: 3, 321 — 326

To link to this Article: DOI: 10.1080/02678290500502475

URL: http://dx.doi.org/10.1080/02678290500502475

Liquid Crystals, Vol. 33, No. 3, March 2006, 321–326

Mesogenic behaviour of (4-alkoxybenzylideneamino)bromobenzene, (4-alkoxybenzylideneamino)benzenethiols, and thiolatonickel complexes of the thiols

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(*Received 19 July 2005; in final form 19 October 2005; accepted 29 October 2005*)

The synthesis, characterization and mesogenic properties of Schiff base compounds arising from the reaction of 4-alkoxybenzaldehydes with 4-aminothiophenol or 4-bromoaniline are described. Whereas the Schiff base thiol with two benzene rings in the molecule, $HSC_6H_4NC(H)C_6H_4OC_{16}H_{33}$ (**2**), is non-mesogenic, the bromo analogue, $BrC_6H_4NC(H)C_6H_4OC_{16}H_{33}$ (**3**), is mesogenic. The introduction of a third benzene ring into the molecular architecture of **2** and **3** produced thiol- and bromo-Schiff base compounds, $HSC_6H_4NC(H)C_6H_4OC(O)C_6H_4OC_{16}H_{33}$ and $BrC_6H_4NC(H)C_6H_4OC(O)C_6H_4OC_{16}H_{33}$, respectively, that are both mesogenic. The thiol compounds react with nickelocene to form $[(\eta^5\text{-}C_5H_5)Ni(\mu_2\text{-}SC_6H_4NC(H)C_6H_4OC_{16}H_{33})]_2$ and $[(\eta^5\text{-}C_5H_5)Ni(\mu_2\text{-}SC_6H_4NC(H)C_6H_4OC(O)\text{-}C_6H_4OC_{16}H_{33})]_2$, but the nickel complexes are not mesogenic.

1. Introduction

One of the synthetic strategies for making metallomesogens is to react metal fragments with either mesogenic or pro-mesogenic compounds as ligands [1–6]. In producing metallomesogens, donor properties in the coordinating atom in the ligand is essential in producing complexes that are stable to air and moisture. Typically sulphur-containing ligands satisfy this requirement, but to date very few metallomesogens containing sulphur ligands are known. These include Ni and Pt dithiolene complexes [7] and Ni and Pd dithiocarboxylate complexes [8] that have bidentate sulphur binding ligands. Monodentate sulphur donor ligands in metallomesogens would thus represent a new dimension in molecular design of metal-containing liquid crystals. Such ligands would have donor atom(s) linked to a ring, which in turn would be attached to other rings via linkers such as –N=N–, –HC=N– or $–CO_2–$; and finally have an alkyl or alkoxy end group. In adopting this design, we chose sulphur donor atoms that are attached to a phenyl ring, an imine linker and a second phenyl ring that has alkoxy end groups. A modification of this design, in which a carboxylic group is linked to a third phenyl ring, was also used. This report presents our attempt to prepare mesogenic thiols that can be used as ligands in preparing metallomesogens. Our results show a ligand design that gives mesogens when hydrogen bonding is not a factor.

2. Experimental

2.1. *Materials and instrumentation*

All the reactions were performed under a nitrogen atmosphere in Schlenk tubes, but the work-up of the compounds was done in air; see schemes 1 and 2. Commercially available compounds were obtained from Sigma-Aldrich and were used as received. Solvents were dried by literature methods and used as fresh distillates.

2.2. *Synthesis of $OHCC_6H_4OC(O)C_6H_4OC_{16}H_{33}$ (1)*

1,3-Dicyclohexylcarbodiimide (6.06 g, 32.8 mmol), 4-hydroxybenzaldehyde (2.00 g, 16.4 mmol), 4-hexadecyloxybenzoic acid (5.94 g, 16.4 mmol) and dimethylaminopyridine (0.1 g) were suspended in CH_2Cl_2 (60 ml) and stirred at room temperature for 8 h. The ensuing white solid was filtered off to give a clear filtrate. The solvent was removed from the filtrate to leave a white residue, which was crystallized from a mixture of

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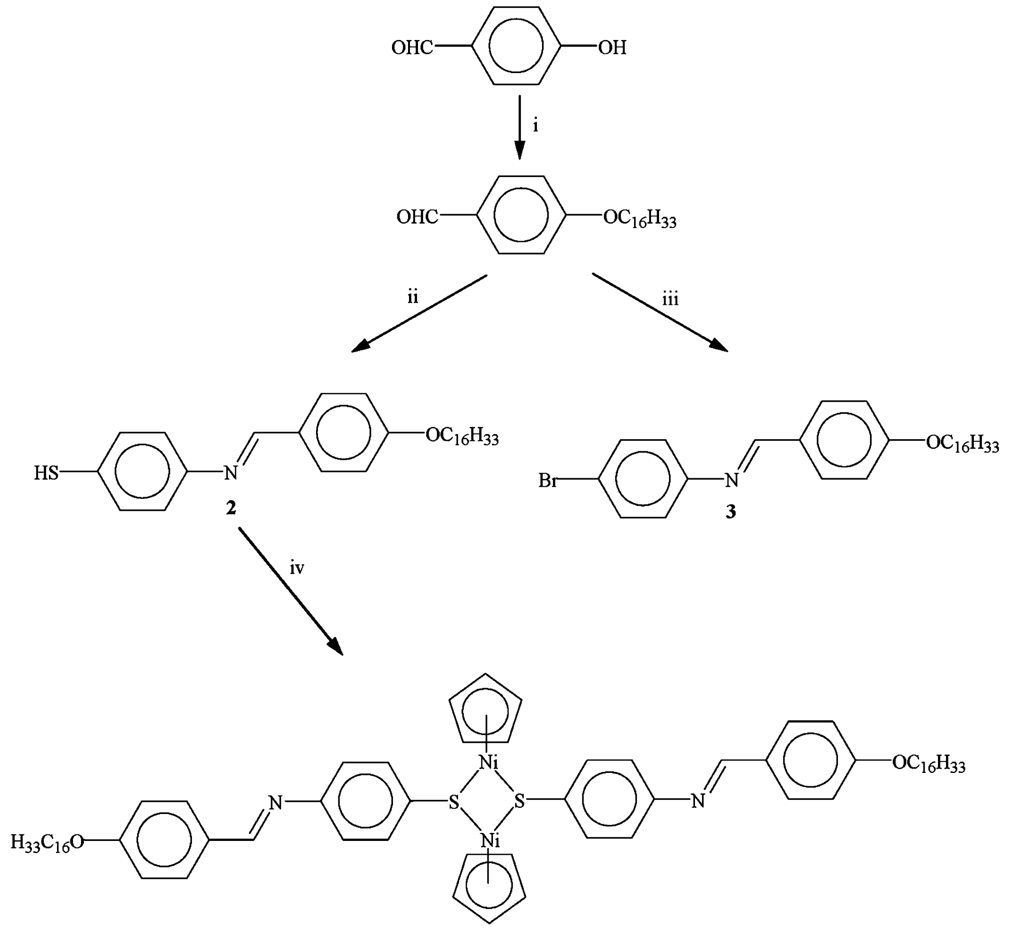
Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2006 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500502475



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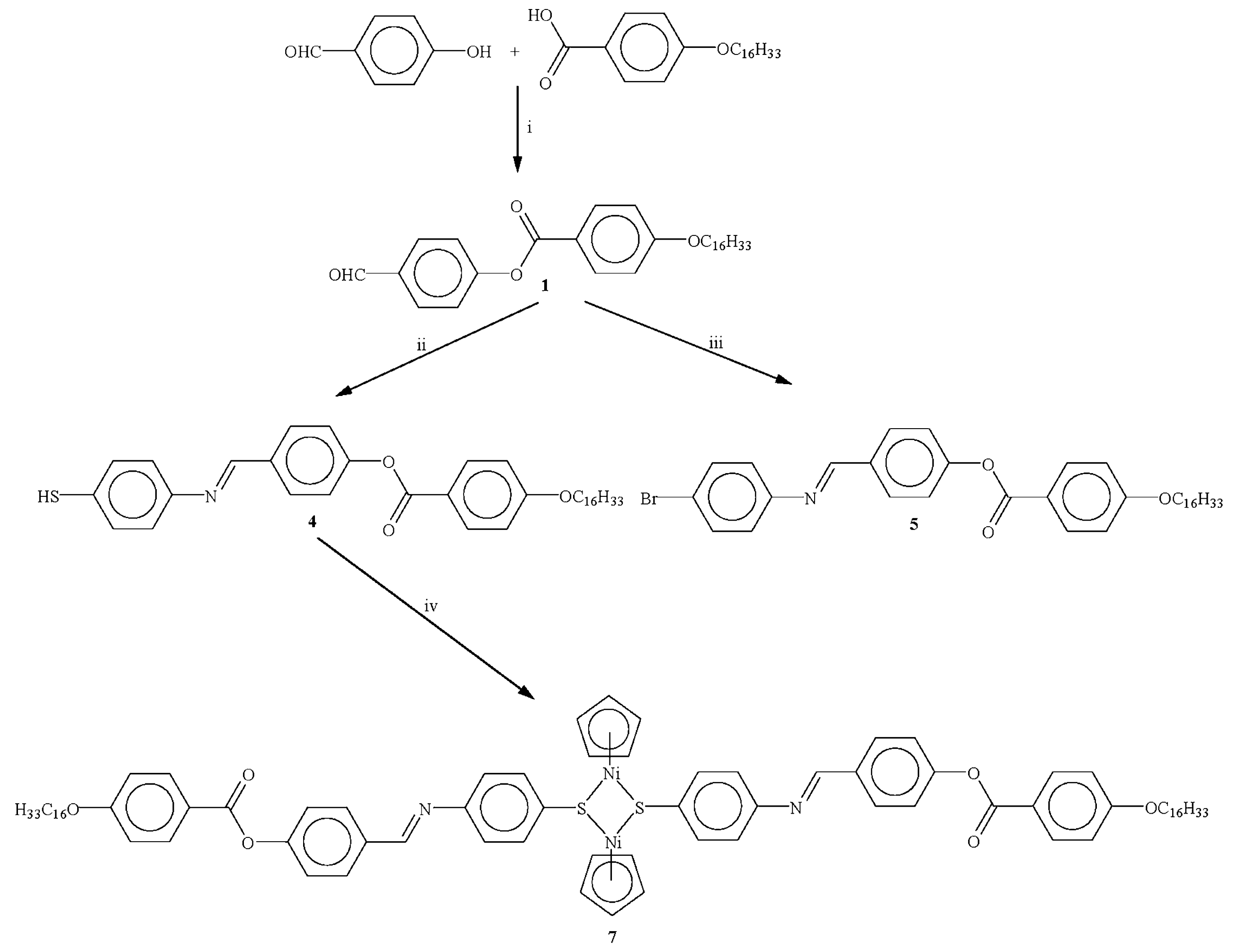
Scheme 1. Synthetic route to compounds with two phenyl rings, and nickel complex of compound **2**. (i) K_2CO_3, bromoalkane, acetone, reflux, 48 h; (ii) 4-aminothiophenol, EtOH, acetic acid, r.t., 18 h; (iii) 4-bromoaniline, EtOH, acetic acid; (iv) nickelocene, toluene, r.t., 18 h.

CH_2Cl_2/hexane (1/1) at −15°C to give analytically pure white powder **1**; yield 5.98 g (78%). ^1H NMR ($CDCl_3$): δ 10.02 (s, 1H, CHO), 8.13 (d, 2H, J_{HH}=9.20 Hz, $C(O)C_6H_4$), 7.96 (d, 2H, J_{HH}=8.4 Hz, $OHCC_6H_4$), 7.40 (d, 2H, J_{HH}=8.80 Hz, $C(O)OC_6H_4$), 6.98 (d, 2H, J_{HH}=9.20 Hz, OC_6H_4), 4.05 (t, 2H, OCH_2), 1.84 (q, 2H, OCH_2CH_2), 1.26 (br s, 26H, $(CH_2)_{13}$), 0.88 (t, 3H, CH_3). Anal: calcd for $C_{30}H_{42}O_4$: C 77.22, H 9.07; found C 77. 40, H 9. 00%.

2.3. *Synthesis of Schiff base compounds*

2.3.1. $HSC_6H_4NC(H)C_6H_4OC_{16}H_{33}$ (2). A mixture of 4-hexadecyloxybenzaldehyde (3.00 g, 6.42 mmol) and 4-aminothiophenol (0.80 g, 6.42 mmol) was dissolved in toluene (60 ml). Five drops of acetic acid was added to this solution and the mixture stirred at room temperature for 18 h. After evaporating the solvent, the pale yellow residue obtained was crystallized from CH_2Cl_2/hexane (1/1) at −15°C to obtain analytically pure **2**; yield 2.70 g, (93%). ^1H NMR ($CDCl_3$): 8.36 (s, 1H, C(H)N), 7.82 (d, 2H, J_{HH}=8.8 Hz, $C(H)C_6H_4$), 7.30 (d, 2H, J_{HH}=8.4 Hz, NC_6H_4), 7.10 (d, 2H, J_{HH}=8.4 Hz, OC_6H_4), 6.96 (d, 2H, J_{HH}=8.8 Hz, SC_6H_4), 4.02 (t, 2H, OCH_2), 3.47 (s, 1H, SH), 1.79 (q, 2H, OCH_2CH_2), 1.45–1.23 (br s, 26H, $(CH_2)_{13}$), 0.88 (t, 3H, CH_3). Anal: calcd for $C_{29}H_{43}NOS$ C 70.08, H 8.72, N 2.82; found C 69.55, H 8.65, N 3.04%.

2.3.2. $BrC_6H_4NC(H)C_6H_4OC_{16}H_{33}$ (3). Compound **3** was prepared in a similar manner to **2**, using 4-hexadecyloxybenzaldehyde (3.0 g, 8.66 mmol) and 4-bromoaniline (1.49 g, 8.66 mmol); yield 3.60 g (83%). ^1H NMR ($CDCl_3$): δ 8.34 (s, 1H, C(H)N), 7.82 (d, 2H, J_{HH}=8.4 Hz, $C(H)C_6H_4$), 7.49 (d, 2H, J_{HH}=8.8 Hz, NC_6H_4), 7.06 (d, 2H, J_{HH}=8.6 Hz, OC_6H_4), 6.96



Scheme 2. Synthetic route to compounds with three phenyl rings, and nickel complex of compound **4**. (i) DCC, DMAP, CH_2Cl_2, r.t., 6 h; (ii) 4-aminothiophenol, acetic acid, EtOH, r.t., 18 h; (iii) 4-bromoaniline, acetic acid, EtOH, r.t., 18 h; (iv) nickelocene, toluene, r.t., 18 h.

(d, 2H, J_{HH}=8.8 Hz, SC_6H_4), 4.02 (t, 2H, OCH_2), 1.80 (q, 2H, OCH_2CH_2), 1.56–1.26 (br s, 26H, $(CH_2)_{13}$), 0.92 (t, 3H, CH_3). Anal: calcd for $C_{29}H_{42}BrNO$ C 69.58, H 8.46, N 2.80; found C 69.60, H 8.35, N 2.83%.

2.3.3. $HSC_6H_4NC(H)C_6H_4OC(O)C_6H_4OC_{16}H_{33}$ (4).

The preparation of **4** followed the same procedure used to prepare **2** from compound **1** (2.50 g, 5.36 mmol) and 4-aminothiophenol (0.66 g, 5.27 mmol); yield 2.40 g (79%). ^{1}H NMR ($CDCl_3$): δ 8.45 (s, 1H, C(H)N), 8.10 (d, 2H, J_{HH}=8.8 Hz, $C(O)C_6H_4$), 7.95 (d, 2H, J_{HH}=8.0 Hz, $C(H)C_6H_4$), 7.32 (m, 4H, J_{HH}=$C(O)OC_6H_4$, NC_6H_4), 7.12 (d, 2H, J_{HH}=8.4 Hz, OC_6H_4), 6.97 (d, 2H, J_{HH}=8.8 Hz, SC_6H_4), 4.05 (t, 2H, OCH_2), 1.82 (q, 2H, OCH_2CH_2), 1.60–1.25 (br s, $(CH_2)_{13}$), 0.88 (t, 3H, CH_3). Anal: calcd for $C_{36}H_{47}NO_3S$ C 75.35, H 8.25, N 2.44; found C 75.53, H 8.14, N 2.40%.

2.3.4. $BrC_6H_4NC(H)C_6H_4OC(O)C_6H_4OC_{16}H_{33}$ (5).

Compound **5** was prepared from **1** (2.00 g, 4.29 mmol) and 4-bromoaniline (0.94 g, 5.50 mmol) in a similar manner as described for **2**; yield 2.23 g (84%). ^{1}H NMR ($CDCl_3$): δ 8.40 (s, 1H, C(H)N), 8.10 (d, 2H, J_{HH}=8.8 Hz, $C(O)C_6H_4$), 7.92 (d, 2H, J_{HH}=8.4 Hz, $C(H)C_6H_4$), 7.47 (d, 2H, J_{HH}=8.4 Hz, $C(O)OC_6H_4$), 7.29 (d, 2H, J_{HH}=8.6 Hz, NC_6H_4), 7.06 (d, 2H, J_{HH}=8.4 Hz, OC_6H_4), 6.94 (d, 2H, J_{HH}=8.8 Hz,

SC_6H_4). Anal: calcd for $C_{36}H_{46}BrNO_3$ C 69.66, H 7.47, N 2.26; found C 69.74, H 7.40, N 2.25%.

2.4. *Synthesis of cyclopentadienylnickel thiolato Schiff base complexes*

2.4.1. $[(\eta^5\text{-}C_5H_5)Ni(\mu_2\text{-}SC_6H_4NC(H)C_6H_4OC_{16}H_{33})]_2$ (6). Nickelocene (0.25 g, 1.32 mmol) and $HSC_6H_4NC(H)C_6H_4OC_{16}H_{33}$ (0.60 g, 1.32 mmol) were dissolved in toluene and the resultant green solution stirred at room temperature for 18 h. The colour gradually turned brown–black. The mixture was filtered and the solvent removed from the filtrate to leave a brown residue which was recrystallized from CH_2Cl_2/hexane (1/1) mixture at −15°C; yield 0.60 g, (79%). ^1H NMR ($CDCl_3$): δ 8.40 (s, 2H, C(H)N), 8.08 (d, 4H, $J_{HH}=8.6$ Hz, $C(H)C_6H_4$), 7.83 (d, 4H, $J_{HH}=8.4$ Hz, NC_6H_4), 7.05 (d, 4H, $J_{HH}=8.4$ Hz, OC_6H_4), 6.97 (d, 4H, $J_{HH}=8.8$ Hz, SC_6H_4), 4.63 (s, 10H, C_5H_5), 4.03 (t, 4H, $J_{HH}=6.6$ Hz, OCH_2), 1.80 (q, 4H, $J_{HH}=7.8$ Hz, OCH_2CH_2), 1.26 (br s, 52H, $(CH_2)_{26}$), 0.88 (t, 6H, CH_3). Anal: calcd for $C_{68}H_{94}N_2S_2Ni_2$ C 70.84, H 8.22, N 2.43; found C 70.61, H 8.48, N 2.48%.

2.4.2. $[(\eta^5\text{-}C_5H_5)Ni(\mu_2\text{-}SC_6H_4NC(H)C_6H_4OC(O)C_6H_4OC_{16}H_{33})]_2$ (7). Complex **7** was prepared from nickelocene (0.25 g, 1.32 mmol) and **4** (0.76 g, 1.32 mmol) as described for **6**; yield 0.58 g (32%). ^1H NMR ($CDCl_3$): δ 8.49 (s, 2H, C(H)N), 8.13 (m, 8H, $C(O)C_6H_4$, $C(H)C_6H_4$), 7.97 (d, 4H, $J_{HH}=8.0$ Hz, $C(O)OC_6H_4$), 7.34 (d, 4H, $J_{HH}=8.6$ Hz, NC_6H_4), 7.08 (d, 4H, $J_{HH}=8.0$ Hz, OC_6H_4, 6.98 (d, 4H, $J_{HH}=8.8$ Hz, SC_6H_4), 4.65 (s, 10H, C_5H_5), 4.05 (t, 4H, OCH_3), 1.83 (q, 4H, OCH_2CH_2), 1.60–1.28 (br s, 52H, $(CH_2)_{26}$), 0.89 (t, 6H, CH_3). Anal: calcd for $C_{82}H_{102}N_2O_6S_2Ni_2$ C 73.66, H 7.69, N 2.09; found C 73.55, H 7.43, N 2.21%.

2.5. *Characterization of phase behaviour*

The phase behaviour of the compounds was determined by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). DSC measurements were performed with a Mettler DSC 30 instrument. Heating and cooling rates were 5°C min^{-1} in all cases. Transition temperatures were taken at the maximum of the transition peaks. A polarizing microscope, Olympus BH2, equipped with a Mettler FP82HT hot stage was used for texture studies and phase transitions were identified by POM in conjunction with DSC measurements. The phase transition temperatures of the compounds are shown in table 1.

Table 1. Phase transition temperatures of compounds **2**, **3**, **4** and **5** by DSC: Cr=crystal, N=nematic phase, SmA=smectic A phase, E=E phase, I=isotropic liquid.

	Phase transition temperature/°C	
Compound	Heating	Cooling
2	Cr 97 I	I 86 Cr
3	Cr 88 I	I 87 SmA 76 Cr
4	—	I 125 N 114.3 SmA
5	—	I 203 SmA 119.6 E

3. Results and discussion

3.1. *Synthesis of Schiff base compounds*

The starting aldehydes for the Schiff base compounds were prepared using the Williamson ether synthesis by reacting 1-bromohexadecane with 4-hydroxybenzaldehyde (scheme 1), or by the esterification of hexadecaloxybenzoic acid with 4-hydroxybenzaldehyde (scheme 2). The Schiff base thiols (**2** and **4**) were then synthesized by condensation of the appropriate aldehyde with 4-aminothiophenol (schemes 1 and 2). The yellow powders obtained from the condensation reactions had the characteristic imine proton signal at 8.36 ppm (**2**) and 8.45 ppm (**4**) and no sign of the aldehyde from which they were prepared. The bromo analogues, on the other hand, were isolated as white powders via condensation reactions between 4-bromoaniline and the appropriate aldehyde. The absence of the resonance due to the aldehyde proton, and the appearance of the resonance due to the imine proton, in the ^1H NMR spectra of the products confirmed that condensation was complete in each reaction.

3.2. *Mesogenic behaviour*

First, we tested the ability of compound **2** to behave as a mesogen. Both the DSC and hotstage POM experiments showed this compound to be non-mesogenic (table 1). However, in similar experiments, the bromo analogue **3** exhibited the smetic A (SmA) phase (table 1) on cooling from the isotropic liquid. This suggests that the polarity and size of the terminal functional group (HS or Br) play important roles in determining the liquid crystalline behaviour of the molecule. The POM photomicrograph texture in figure 1 shows the smectic A phase and homeotropic textures for **3** taken at 75°C. Compound **3** remains liquid crystalline between 87 and 75°C, which is reminiscent of mesogenic changes found in the bromo Schiff base compounds reported by Galweski [9].

It is possible that the non-mesogenic behaviour of **2** results from hydrogen bonding between the thiol

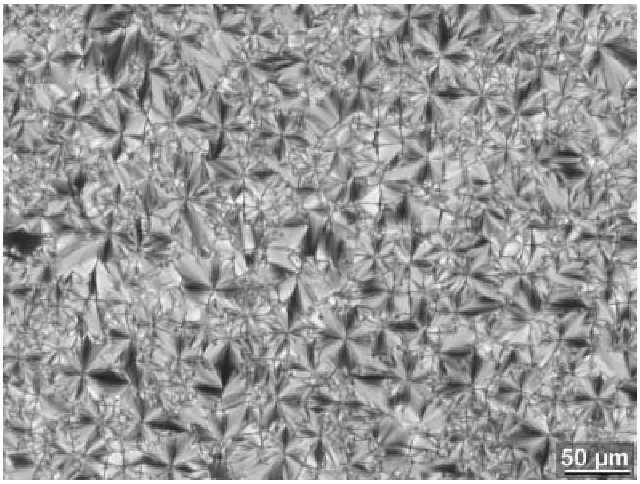


Figure 1. Optical microscopic texture observed on cooling compound **3** from the isotropic meltte 75°C; SmA, focal-conic, fan homeotropic textures.

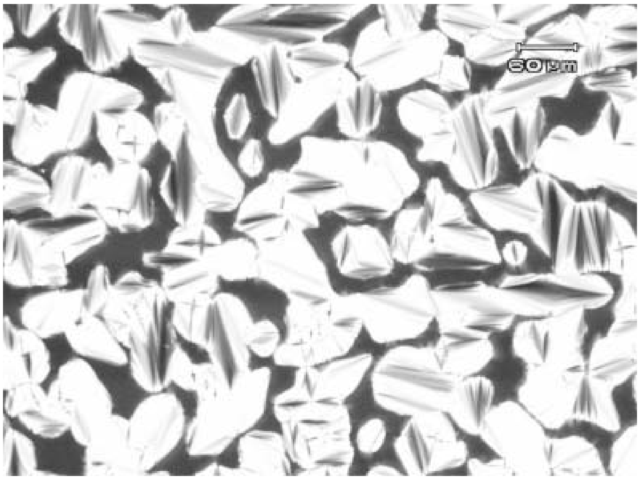


Figure 2. Optical microscopic texture showing the SmA phase (at 100°C) of compound **4**.

hydrogen of one molecule and an oxygen atom of the alkoxy chain of an adjacent molecule, thereby disrupting the molecular alignment necessary for mesogenic behaviour. It is also possible that electronic effects within the central and terminal groups in **2** do not produce the anisotropy necessary for mesogenic behaviour, as suggested by Nessim [10]. To test the proposal that hydrogen bonding might be responsible for the non-mesogenic behaviour of **2**, we modified the molecular design to include a second alkoxy chain to prepare the dialkoxy compound **2a**. DSC experiments on **2a** resulted in multiple endotherms when the compound was heated, and on cooling there were multiple exotherms to show that **2a** is a mesogen. It is therefore likely that the presence of the second alkoxy chain disrupts any hydrogen bonding that could arise in **2a**.

A second modification of **2** was the inclusion of a second linker (–CO_2–) and a third phenyl ring to form compound **4**. The bromo analogue of **4** was also prepared. From DSC measurements mesophase transitions associated with **4** and **5** were determined (table 1). The data of table 1 show that the exchange of terminal substituents (HS/Br) results in a subtle change in the phase sequences (I–N–SmA and I–SmA–E for **4** and **5**, respectively). This change suggests that the polarity and size of the terminal group as well as the second linker (–CO_2–) and a third phenyl ring are very important in determining the phase transitions and liquid crystalline behaviour in **4** and **5**. The relative position of the ester unit (–CO_2–), with respect to the terminal alkoxy group, is an additional factor that enhances the smectic properties of the liquid crystals cores of **4** and **5**. The presence of the ester unit results in an increase in flexibility of the core, and its electron-withdrawing

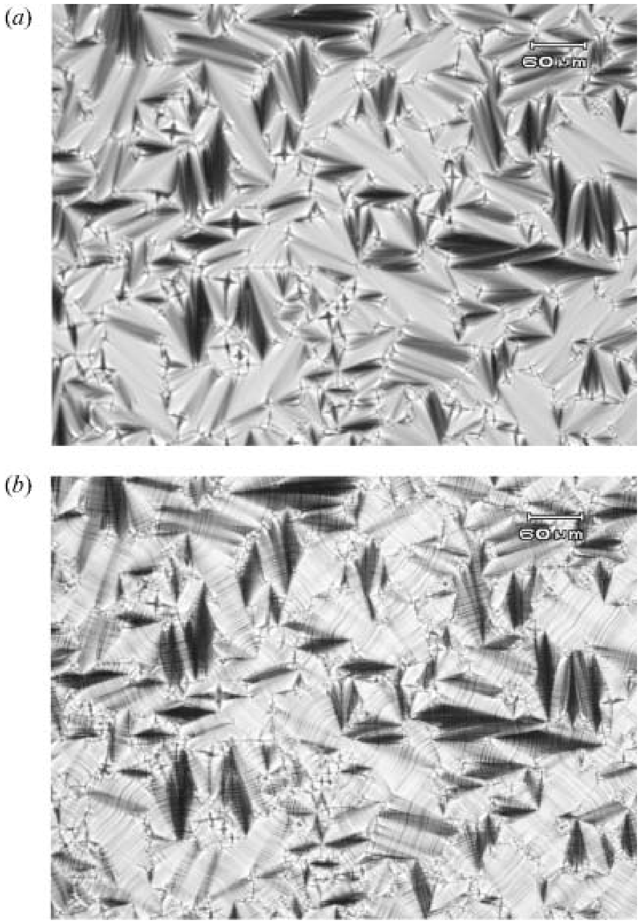
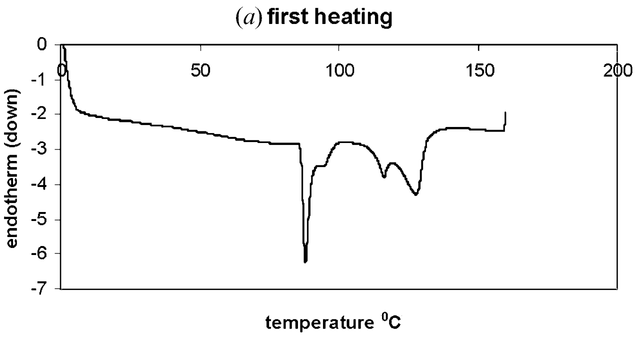


Figure 3. (*a*) Optical microscopic texture showing the SmA phase (at 200°C) of compound **5**; (*b*) the E phase (at 100°C) of compound **5**.



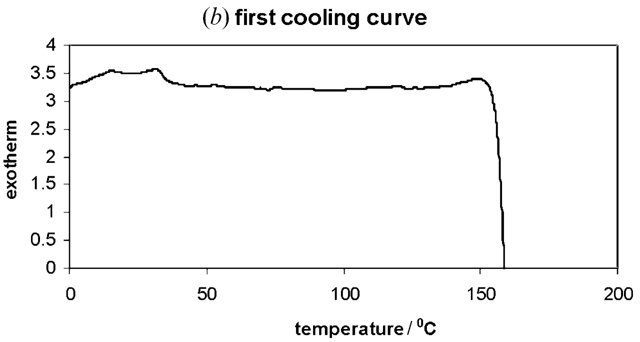


Figure 4. DSC thermograms for complex **6** on (*a*) first heating, (*b*) first cooling.

nature increases the core polarity. The ester unit contributes to the formation of the SmA phase in **4** and **5**, as well as the N phase in **5**; this behaviour is observed in many liquid crystals having an ester linkage. The characteristic textures of the SmA phase for **4**, and SmA and E phases for **5** are shown in figures 2, 3 (*a*) and 3 (*b*), respectively. It is clear that the increase in rigid core length in **4** produces mesogenic behaviour in **4** as compared with **2**; probably because no hydrogen bonding is involved in compound **4**.

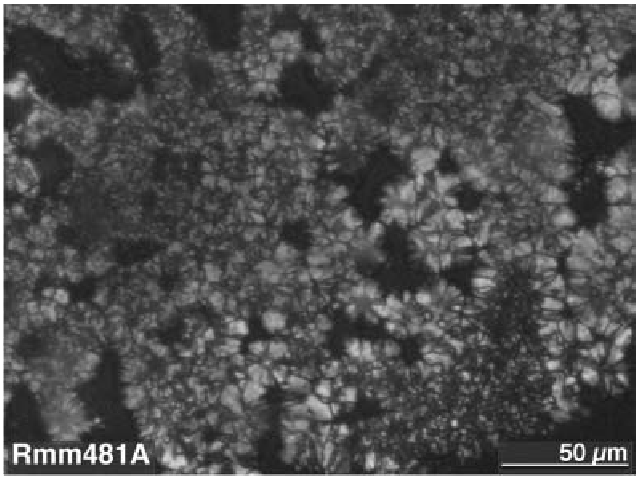


Figure 5. Texture observed at 122°C for nickel complex **6** on annealing the melt.

Compounds **2** and **4** react with $[Ni(\eta^5\text{-}C_5H_5)_2]$ to form the bridging thiolato complexes $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}SC_6H_4NC(H)C_6H_4OC_{16}H_{33})]_2$ (**6**) and $[Ni(\eta^5\text{-}C_5H_5)(\mu\text{-}SC_6H_4NC(H)C_6H_4OC(O)C_6H_4OC_{16}H_{33})]_2$ (**7**), respectively. The mesogenic behaviour of these nickel complexes was investigated. Complex **6** showed multiple endotherms, but on cooling no exotherms were found (figure 4). No texture associated with mesophase changes could be observed on gradual heating of **6** on a hot stage. However, when samples were rapidly heated with a gas burner followed by annealing, textures with bright zones were observed, see figure 5. DSC experiments showed that **7** decomposed before melting; we were therefore unable to demonstrate the effect of a longer rigid core in **4** on the mesophase behaviour of **7**. Nonetheless, the increased rigid core length in **4** produces mesogenic behaviour. Although we did not find **6** to exhibit stable mesophases on heating (probably due to the orientation of the cyclopentadienylnickel moiety in the complexes), we envisage that with the appropriate metal framework, the Schiff base thiols **2** and **4** should be able to form metallomesogens, and thus represent new ligands that could be used to prepare a new class of thiolato-metallomesogens.

Acknowledgements

We thank Dr W. A. Ddamba, University of Botswana for some of the DSC data. We also thank the National Research Foundation (South Africa) for a postgraduate bursary (R.M.M.) and the University of the Western Cape (J.D.) for funding.

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