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Synthesis and liquid crystalline properties of monothio- and dithioimides with chiral *N*-substituents

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Two compounds *i.e.* (*S*)-*N*-(2-methylbutyl)-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimide and (*S*)-*N*-(1-methylpropyl)-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimide were synthesised from chiral components (*S*)-2-methylbutan-1-ol and (*S*)-2-aminobutane, respectively. Then, the obtained ester imides were treated with Lawesson's reagent yielding monothio- and dithioimides. Liquid crystalline smectic C* phases occurred in all imides and thioimides studied.

Liquid crystalline thioimides were synthesised and described for the first time in our previous publication.[1] We found that biphenyl esters of *N*-alkyltrimellitimides† could be easily converted into mono- and dithioimides by means of Lawesson's reagent. In contrast to other types of thiocarbonyl compounds, thioimides are very stable compounds and these newly synthesised materials show interesting liquid crystalline properties. 4′-Substituted biphenyl esters of *N*-alkyltrimellitimides of the formula shown in Fig. 1 exhibit smectic and nematic or nematic phases. The presence of sulfur atoms changes the polarity of thioimides, in comparison with the corresponding imides. As expected, an abatement of polarity in sulfur-containing compounds involved a decrease in both clearing temperatures and melting points.

Our other studies indicated that *N*-substituents in ester imides play an important role in mesophase formation.[2] The presence of chiral carbon atoms in such moieties induced various smectic phases. For instance, the use of L-alanine methyl ester as *N*-substituents, in ester imides showed a transition from the SmA_1 to the ribbon $Sm\tilde{C}^*$ phase *via* an intermediate SmC_1^* phase, which have layered structures with chiral molecules tilted to the layer planes. During the last decade, the ferroelectric and antiferroelectric properties of liquid crystalline materials with chiral smectic C* phases have attracted increasing interest due to their potential applications in materials science.[3–5] A possibility of very fast switching (within the microsecond range) has interesting applications in display technology.

In this paper we present the synthesis and describe mesogenic properties of 4′-undecyloxybiphenyl esters of *N*-alkyltrimellitimides with chiral *N*-substituents. The synthetic pathways employed are presented in Schemes 1 and 2.

It should be noticed that all monothio- and dithioimides showed absorption bands in the visible range, forming a new class of colour (red and yellow) mesogenic materials.

Experimental

Instrumentation

All product structures were confirmed in the same way as described in the previous paper by elemental analysis, FT-IR, ^1H NMR and ^{13}C NMR spectroscopy.[1,2] In this paper only the data essential for identification are presented. The infrared spectra [in CH_2Cl_2] were recorded on a Perkin-Elmer 2000 apparatus equipped with Pegrams 2000 software, and the NMR spectra [in $CDCl_3$] were recorded using a Varian Gemini 200 MHz spectrometer. UV–Vis spectra [in $CHCl_3$] were made with a Perkin-Elmer λ11 apparatus. The phase transitions were observed using a polarising microscope BIOLAR equipped with a LINKAM heating stage THMs 600. Temperatures and enthalpies were measured by means of a DSC 141 SETARAM microcalorimeter. The measurements were made in both cycles – heating and cooling – at the rate of 1 K min^{-1}. The sample quantity was about 30 mg and special aluminium crucibles, with good thermal contact, were used. The hermetically sealed crucible with a sample was heated to the clearing temperature of the sample and then cooled to the crystallisation temperature. After this procedure, DSC measurement was started. The values of temperature and enthalpy were read directly from the calorimeter integration curves after preliminary calibration using standards (gallium of 99.99% purity; 6CHBT of 99.95% purity; indium of 99.999% purity; tin of 99.999% purity). The accuracy of the phase transition temperature measurements was about ±0.1 K. The measurement uncertainty of enthalpy value of phase transition was ±1%.

Synthesis

All the chemicals used were analytical grade commercial products and were applied without further purification.

4-Undecyloxy-4′-hydroxybiphenyl (**1**) was obtained as described previously; mp 153 °C.[2,7]

4-[(4′-Undecyloxybiphenyl-4-yl)oxycarbonyl]phthalic anhydride (2)

To 10 mmol of **1** (3.4 g) dissolved in 40 cm^3 of dry pyridine 10 mmol (2.1 g) of trimellitic anhydride chloride was slowly

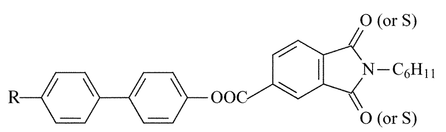

Fig. 1

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†The IUPAC name for trimellitimide is 5-carboxy-2,3-dihydro-1*H*-isoindole-1,3-dione.

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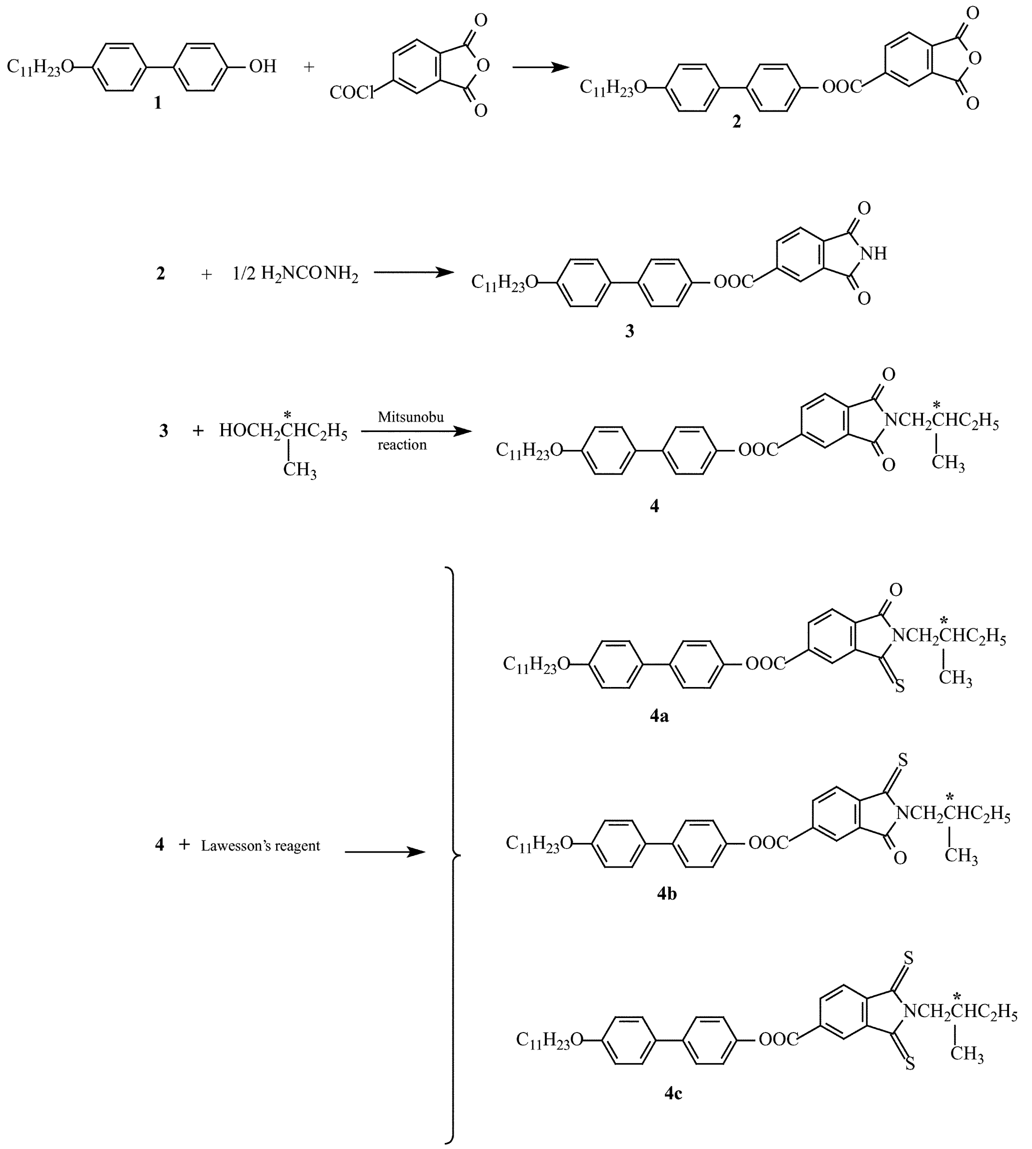


Scheme 1

added. The reaction mixture was stirred for 1 h at room temperature and then pyridine was evaporated to dryness under reduced pressure. The deposit was dissolved in boiling dry toluene and filtered off to remove pyridine hydrochloride. After cooling, white crystals of **2** were separated. Yield 58% (3 g); FT-IR (cm^{-1}) 1862 (C=O$_{anh}$), 1785 (C=O$_{anh}$), 1743 (C=O$_{ester}$); mp 172–174 °C.

4-[(4′-Undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimide (3)

A mixture of 2 mmol (1.28 g) of **2** and 1 mmol (60 mg) of urea was carefully melted for 5 minutes. Next, the alloy was powdered and crystallised from THF. Yield 79% (1 g); FT-IR (cm^{-1}) 3685 (N–H), 1743 (C=O$_{imide}$), 1740 (C=O$_{ester}$), 1703 (C=O$_{imide}$); mp 245 °C.

(*S*)-*N*-(2-Methylbutyl)-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimide (4)

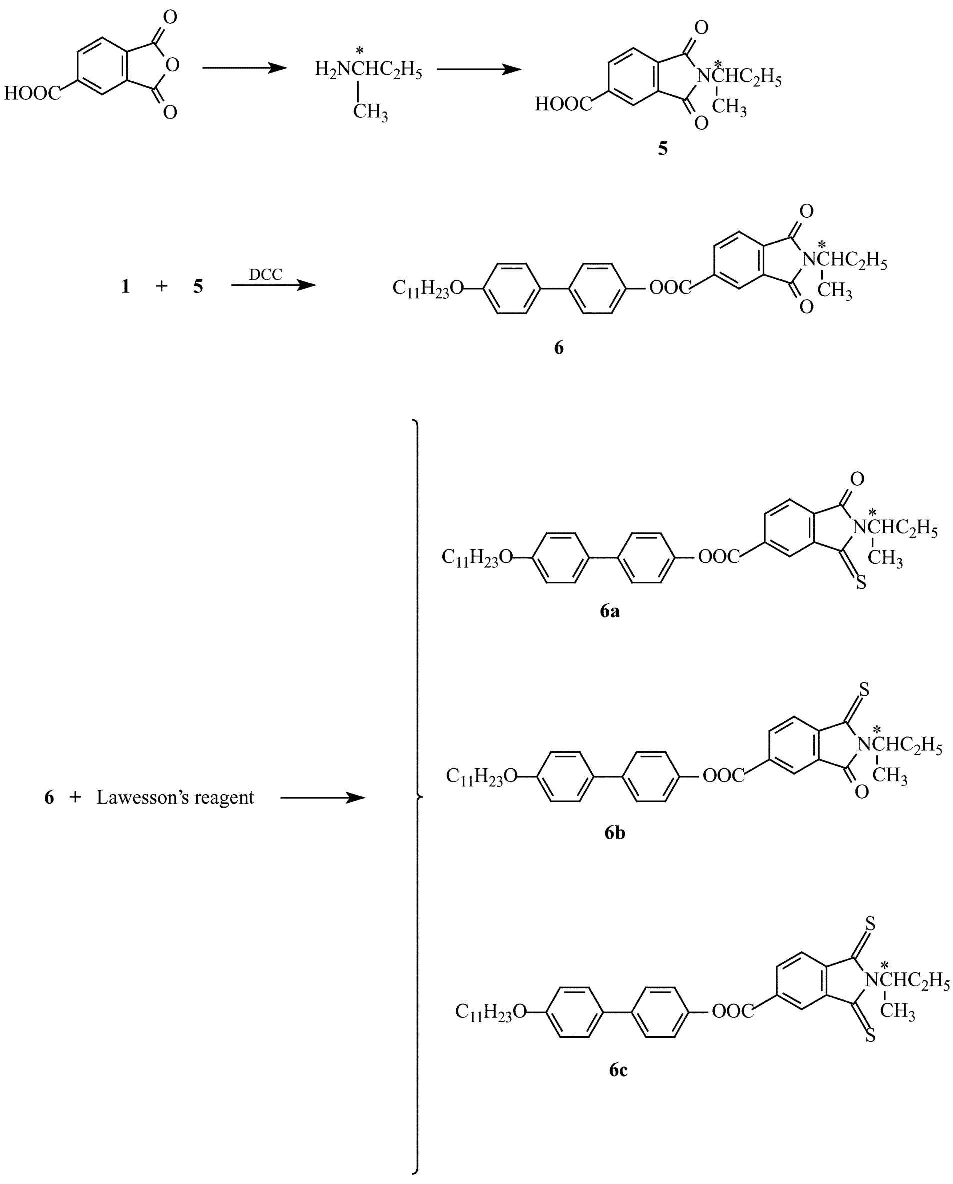
Equimolar amounts (2 mmol) of **3**, (*S*)-2-methylbutan-1-ol, triphenylphosphine and diethyl azodicarboxylate were dissolved in 25 cm^3 of pyridine. The mixture was stirred over 12 h. Then pyridine was evaporated and the deposit was washed with methanol. Purification of the crude product was performed by means of flash column chromatography [SiO$_2$] using chloroform as an eluent. Yield 57% (0.59 g); FT-IR (cm^{-1}) 1781 (C=O$_{imide}$), 1736 (C=O$_{ester}$), 1717 (C=O$_{imide}$); ^{1}H NMR (ppm) 1.24–2.25 (m, 30H), 3.96 (m, 2H N-CH$_2$), 4.36 (t, 2H CH$_2$O), 7.15 (m, 2H), 7.60–7.95 (m, 6H), 8.36 (dd, 1H$_{imide}$), 8.92–9.03 (m, 2H$_{imide}$). Elemental analysis: calc. C 76.05; H 7.71; N 2.40; found C 76.09; H 7.66; N 2.44%.

(*S*)-*N*-(l-Methylpropyl)-5-carboxy-2,3-dihydro-1*H*-isoindole-1,3-dione (5)

To 10 mmol (0.73 g) of (*S*)-2-aminobutane dissolved in 20 cm^3 of DMA 10 mmol (1.92 g) of trimellitic anhydride was added. Then the solution was refluxed over 10 h and next poured into diluted HCl. The crude product was filtered off and crystallised from H$_2$O–EtOH (1 : 1). Yield 65%; FT-IR (cm^{-1}) 3600–2700 (HOOC), 1770 (C=O$_{imide}$), 1720 (C=O$_{acid,imide}$); mp 193 °C.

(*S*)-*N*-(l-Methylpropyl)-4-[(4′-undecyloxybiphenyl-4-yl)oxycarbonyl]phthalimide (6)

The condensation of 5 mmol (1.7 g) of **1** and 5 mmol (1.24 g) of **5** was performed according to the standard procedure in CH$_2$C1$_2$ using DCC.[1,2] The crude product was purified by flash column chromatography [SiO$_2$] using chloroform as an eluent. Yield 86% (2.5 g); FT-IR (cm^{-1}) 1778 (C=O$_{imide}$), 1744 (C=O$_{ester}$); ^{1}H NMR (ppm) 0.90–2.05 (m, 29H), 4.01 (t, 2H OCH$_2$), 4.32 (m, 1H, NCH), 6.96 (d, 2H), 7.27–7.55 (m, 6H),



Scheme 2

7.96 (d, 1H_{imide}), 8.56–8.65 (m, 2H_{imide}). Anal. calc. C 75.82; H 7.55; N 2.46; found C 75.79; H 7.56; N 2.54%.

Synthesis of monothioimides 4a–c and dithioimides 6a–c

The thionation procedure of **4** and **6** was the same as described previously.[1] Also the separation and identification of monothioimides **4a**, **b**, **6a**, **b**, as well as dithioimides **4c** and **6c** were identical.

4a. Yield 18%; FT-IR (cm^{-1}) 1742 ($C{=}O_{ester}$), 1740 ($C{=}O_{imide}$), 1268 (C=S); ^{1}H NMR (ppm) 0.81–2.14 (m, 30H), 3.93–4.04 (m, 4H), 6.96–7.01 (m, 2H), 7.30 (m, 2H), 7.50–7.64 (m, 4H), 8.01 (m, 1H_{imide}), 8.50–8.63 (m, 2H_{imide}). Visible λ/nm (ε/dm^{3} mol^{-1} cm^{-1}) 510 (22). Elemental analysis: calc. C 74.09; H 7.50; N 2.33; S 5.33; found C 74.12; H 7.52; N 2.36; S 5.45%.

4b. Yield 23%; FT-IR (cm^{-1}) 1745 ($C{=}O_{ester}$), 1742 ($C{=}O_{imide}$), 1243 (C=S); ^{1}H NMR (ppm) 0.84–2.20 (m, 30H), 3.95–4.01 (m, 4H), 6.98–7.02 (m, 2H), 7.30 (m, 2H), 7.53–7.64 (m, 4H), 8.03 (m,1H_{imide}), 8.50–8.66 (m, 2H_{imide}). Visible λ/nm (ε/dm^{3}mol^{-1} cm^{-1}) 509 (75). Elemental analysis: calc. C 74.09; H 7.50; N 2.33; S 5.33; found C 74.19; H 7.55; N 2.37; S 5.45%.

4c. Yield 19%; FT-IR (cm^{-1}) 1739 ($C{=}O_{ester}$), 1266 (C=S); ^{1}H NMR (ppm) 0.86–2.30 (m, 30H), 4.01 (t, 2H, OCH_2), 4.44 (d, 2H, NCH_2), 6.97–7.01 (m, 2H), 7.27–7.32 (m, 2H), 7.60 (m, 4H), 7.97 (m, 1H_{imide}), 8.51–8.63 (m, 2H_{imide}). ^{13}C NMR (ppm) 11.5, 14.2, 16.3, 18.7, 22.7, 25.9, 28.5, 28.6, 29.0, 29.2, 29.4, 29.7, 31.9, 33.7, 34.4, 51.0, 65.0, 121.7, 123.4, 124.6, 126.9, 127.8, 128.4, 128.6, 132.5, 134.7, 135.9, 139.9, 149.9, 160.1, 164.9, 195.8, 195.9. Visible λ/nm (ε/dm^{3} mol^{-1} cm^{-1}) 513 (225). Elemental analysis: calc. C 72.16; H 7.31; N 2.27; S 10.39; found C 72.19; H 7.35; N 2.30; S 10.55%.

6a. Yield 20%; FT-IR (cm^{-1}) 1741 ($C{=}O_{ester}$), 1740 ($C{=}O_{imide}$), 1261 (C=S); ^{1}H NMR (ppm) 0.87–2.25 (m, 29H), 4.02 (t, 2H, OCH_2), 5.02 (m, lH, NCH), 6.97 (m, 2H), 7.28–7.32 (m, 2H), 7.88 (m, 4H), 7.92 (m, 1H_{imide}), 8.53–8.73 (m, 2H_{imide}). Visible λ/nm (ε/dm^{3} mol^{-1} cm^{-1}) 507 (24). Elemental analysis: calc. C 73.74; H 7.34; N 2.39; S 5.46; found C 73.72; H 7.32; N 2.36; S 5.55%.

6b. Yield 17%; FT-IR (cm^{-1}) 1744 ($C{=}O_{ester}$), 1741 ($C{=}O_{imide}$), 1244 (C=S); ^{1}H NMR (ppm) 0.87–2.25 (m, 29H), 4.01 (t, 2H, OCH_2), 5.01 (m, lH, NCH), 6.96 (m, 2H), 7.27 (m, 2H), 7.60 (m, 4H), 8.05 (m, 1H_{imide}), 8.51–8.60 (m, 2H_{imide}). Visible λ/nm (ε/dm^{3} mol^{-1} cm^{-1}) 517 (22). Elemental analysis: calc. C 73.74; H 7.34; N 2.39; S 5.46; found C 73.73; H 7.32; N 2.39; S 5.59%.

Table 1 Temperature/°C and enthalpies/kJ mol^{-1} (italic text) of phase transitions for compounds of series **4** and **6** from DSC

No	Cr$_1$		Cr		SmC*		SmA		N*		Iso
4	–		*	443.8 *27.7*	*	615.1 *0.126*	*	750.3 *6.69*	–		*
4a	–		*	418.8 *26.3*	*	539.7 *0.243*	*	645.6 *4.77*	–		*
4b	*	402.8 *5.32*	*	437.5 *16.7*	*	597.9 *0.195*	*	730.0 *3.72*	–		*
4c	–		*	361.3 *24.6*	*	548.9 *0.126*	*	616.7 *1.25*	*	627.6 *2.17*	*
6	*	446.3 *7.53*	*	529.6 *20.6*	(*	471.0) *0.021*	*	570.6 *2.34*	–		*
6a	*	233.6 *2.22*	*	488.2 *26.2*	(*	463.5) *0.251*	*	517.9 *4.48*	–		*
6b	–		*	489.1 *36.7*	(*	478.9) *0.795*	*	505.8 *2.84*	–		*
6c	*	236.5 *14.4*	*	324.9 *19.5*	*	412.8 *0.795*	*	419.1 *1.51*	–		*

6c. Yield 22%; FT -IR (cm^{-1}) 1738 (C=O$_{ester}$), 1261 (C=S); ^{1}H NMR (ppm) 0.83–2.54 (m, 29H), 4.02 (t, 2H, OCH$_2$), 5.57 (m, 1H, NCH), 6.97–7.01 (m, 2H), 7.28 (m, 2H), 7.55–7.65 (m, 4H), 7.94 (m, 1H$_{imide}$), 8.53–8.66 (m, 2H$_{imide}$). ^{13}C NMR (ppm) 11.7, 14.0, 16.3, 18.3, 22.7, 26.0, 28.5, 28.6, 29.0, 29.2, 29.4, 29.8, 31.9, 34.4, 60.6, 65.0, 121.7, 123.4, 124.6, 126.9, 127.8, 128.4, 128.6, 132.5, 134.7, 135.9, 139.9, 148.9, 160.1, 164.7, 195.7, 195.8. Visible λ/nm (ε/dm^3 mol^{-1} cm^{-1}) 559 (60). Elemental analysis: calc. C 71.78; H 7.15; N 2.33; S 10.63; found C 71.72; H 7.12; N 2.36; S 10.55%.

Results and discussion

The synthesis of ester imide **4** was performed *via* Mitsunobu condensation.[6] It led to introduction of a chiral *N*-substituent using easily accessible optical active substrate (*S*)-2-methylbutan-1-ol. On the other hand, ester imide **6** was obtained by the conventional method from (*S*)-2-aminobutane and trimellitic anhydride followed by esterification of **1** using DCC. Then, the ester imides **4** and **6** were treated with Lawesson's reagent which led to the three main products. These compounds formed three colour spots on TLC and could be easily separated by column chromatography. In the same way, as comprehensively described previously, we found that compounds with the highest R_f values have two thiocarbonyl groups.[1] On the other hand, we assigned compounds of intermediate mobility spots to the structures "**b**" and monothioimides of low mobility spots to "**a**". A substitution of the carbonyl oxygen atoms in the imide rings for sulfur atoms resulted in coloured thioimides, whereas their parent imides were colourless. The spectroscopic studies in the visible region for thioimides studied revealed broad absorption bands [n → π*] of modest ε values (22–225 ε/dm^3 mol^{-1} cm^{-1}) in the range of 505–560 nm.

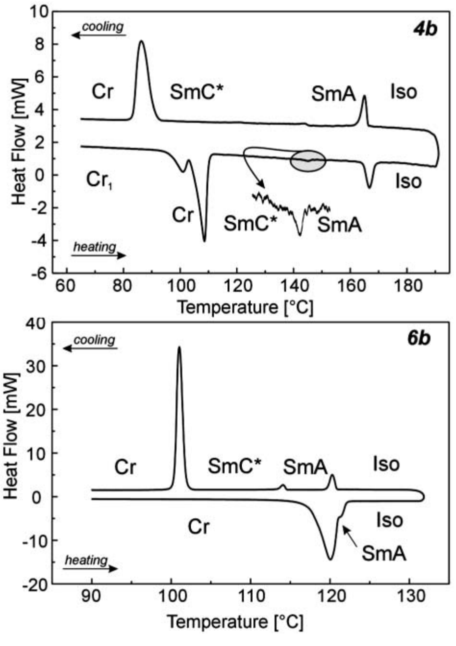


Fig. 2 Phase transitions for **4b** and **6b** as measured by DSC.

Using DSC analysis and polarised optical microscopy we found that all ester imides and their sulfur analogues have liquid crystalline properties. The transitional data for the compounds: **4**, **4a**, **4b**, **4c** and **6**, **6a**, **6b**, **6c** are presented in Table 1.

All the investigated compounds have smectic C* and A phases. They possess very typical microscopic texture and their miscibility with smectic C* and A phases of well-known (*S*)-4-(2-methylbutyl)phenyl 4-octylbiphenyl-4′-carboxylate makes it possible to identify them correctly.[8]

N-Substituted compounds with the 2-methylbutyl group (**4**, **4a**, **4b**, **4c**) have enantiotropic smectic C* phases, while compounds with the 1-methylpropyl group (**6**, **6a**, **6b**) have monotropic smectic C* phases excluding (**6c**) dithioimides. The phase difference results from reduction of the length of the substituent as well as shortening of the distance between the chiral centre and the imide ring. For both *N*-substituents, introduction of one or two sulfur atoms into an imide ring results in reduction of phase transition temperature values. This is a consequence of the considerable change of compound polarity and in the increase of the molecular breadth. In the case of **4c** dithioimides with a 2-methylbutyl constituent, a chiral nematic phase is observed in a short temperature range. Values of SmC*–SmA phase transition enthalpy are considerably smaller than clearing or SmA–N* phase transition (see Fig. 2). The only exception are compounds **6b** and **6c** where the enthalpy of SmC*–SmA transition is comparable with clearing enthalpy. Phase transition temperatures are the same for heating and cooling cycles; hysteresis is observed only for values of melting point (smectic C* phases over-cools substantially).

Conclusion

The compounds we have made are thermochemically stable. Heating them for several hours over the clearing temperature does not cause their decomposition and the temperatures of phase transitions do not alter. Occurrence of the smectic C* phases in all of the investigated compounds makes them good components for liquid crystalline mixtures with ferro- and antiferroelectric properties, however, high melting points limit their application as basic compounds of the mixtures. The distinct colour of mono and dithioimides is noteworthy. Hitherto known coloured liquid crystalline azo-compounds are less stable than the thioimides. Their presence in liquid crystalline mixtures makes control of spectral characteristics possible by cutting out the visible wavelength (red wavelength spectrum). This property can be employed in non-linear optics.

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