Liquid Crystals

Publication details, including instructions for authors and subscription information:
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Urszula Jarek-Mikulska[a]; Zbigniew Galewski[a]
[a] Department of Chemistry, University of Wroclaw, Wroclaw, Poland

To cite this Article Jarek-Mikulska, Urszula and Galewski, Zbigniew(2009) 'Influence of substituting thioester for ester group and alkyloxy for alkyl chain on liquid-crystalline polymorphism of certain azobenzene derivatives', Liquid Crystals, 36: 2, 187 — 195

To link to this Article: DOI: 10.1080/02678290902759228

URL: http://dx.doi.org/10.1080/02678290902759228

Liquid Crystals,
Vol. 36, No. 2, February 2009, 187–195

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Influence of substituting thioester for ester group and alkyloxy for alkyl chain on liquid-crystalline polymorphism of certain azobenzene derivatives

Urszula Jarek-Mikulska* and Zbigniew Galewski

Department of Chemistry, University of Wroclaw, Joliot-Curie, 14 50-383, Wroclaw, Poland

(Received 15 October 2008; final form 19 January 2009)

In this paper we report on a synthesis and basic characterisation (polarising optical microscopy, differential scanning calorimetry, thermo-optical analysis) of four new liquid-crystalline compounds. These are 4”-heptylphenyl 4-[(4’-nonyloxyphenyl)diazenyl]benzoate and its three derivatives differentiating from the parent compound either by having a sulphur atom in the ester group or an oxygen atom in the heptyl chain or both these features, thus constituting a cross-section of four new groups of derivatives. We describe and compare their liquid-crystalline polymorphism and comment on the effect such structure changes have on appearing mesophases, and their temperature range.

Keywords: azobenzene; thioester; structural modifications; thiophenol

1. Introduction

Today the synthesis of new materials does not only occur randomly. Obviously, for some compounds, totally unexpected properties are found. But parallel to this there is another route, which tries to predict theoretically how a certain compound will behave, what properties it will have and whether they would be adequate for a certain need before attempting to synthesise it. Within the field of liquid crystals, there is a quantum method (*1*) that allows prediction of the temperature of the nematic–isotropic transition, vital for various applications. This is derived from parameters obtained by the semi-empirical PM3 method – surface area, molecular volume, ovality, HOMO and LUMO energies, dipole moment and atomic charge. There is also a comparative method for predicting temperatures of liquid-crystalline phase transitions (*2*) based on empirical parameters describing the quality of the temperature change upon substitution of one group of atoms with another.

However, these methods both work well only for compounds similar to those already known. There seems therefore to be a need for analysis of the influence of various structural changes on liquid-crystalline properties – not only would this help to develop prediction methods for molecular design, but it would also enhance the general understanding of rules governing liquid-crystallinity. This is the field our article contributes to.

This paper deals mostly with the influence of a sulphur atom on liquid-crystalline properties of a chosen compound, in particular determining the effect of substituting an ester group with a thioester group.

In our previous paper (*3*) we described the liquid-crystalline properties of the homologous series of 4”-alkylphenyl 4-[(4’-alkyloxyphenyl)diazenyl]benzoates. We supposed that the sulphur atom in such compounds would increase polarity and polarisability and thus enhance liquid-crystalline properties. Unfortunately we had nothing to compare them with, as the oxygen analogues had not been described; in addition, from analysis of data in the literature, the effect of sulphur insertion is not always predictable. For example, the liquid crystal database (*4*) finds 459 pairs of compounds differing only in their thioester/ester. For some of them (e.g. 4-cyanobenzoic acid 4-pentylphenyl ester and its sulphur analogue (*5*)) on going from ester to thioester a monotropic phase changes into enantiotropic; for some (e.g. 4-butylsulfanylbenzoic acid 4-isothiocyanatophenyl ester (*7*), 4-decylbenzoic acid 4-hexylphenyl ester (*8*), 4-octyloxybenzoic acid 4-pentylphenyl ester (*9*) and their thioester analogues) additional phases appear; for some (e.g. 4-heptyloxybenzoic acid 4-decylphenyl ester and its thioester analogue (*8b*, *10*)) one mesophase is substituted with another; for some (e.g. 4-ethoxybenzoic acid 4-ethylphenyl ester and its sulphur analogue (*5*, *11*)) only the thioester is liquid-crystalline; for some (e.g. 4-decyloxybenzoic acid 4-fluorophenyl ester and corresponding thioester (*12*)) the mesophase range of thioester is narrower; for some (e.g. 4-(5-pentyl-[1,3]dioxan-2-yl)-benzoic acid 4-heptylphenyl ester and the thioester analogue (*13*)) there are less mesophases in the sulphur compound; and finally, in some rare cases the sulphur can even totally eliminate liquid-crystallinity (e.g. 4-pentylcyclohexanecarboxylic acid 4-nitrophenyl ester and corresponding thioester (*14*)).

For our present study we chose four compounds, shown in Figure 1, that differ from one another in ester/thioester and heptyl/hexyloxy fragments (these

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*Corresponding author. Email: ulajarek@wcheto.chem.uni.wroc.pl

ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290902759228
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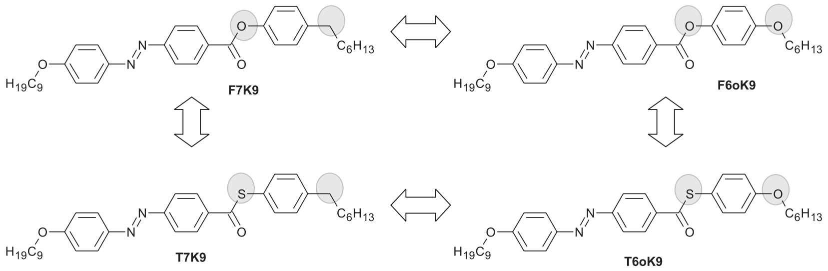

Figure 1. Structures of the four compounds described in this paper together with their acronyms. The structural differences between compounds are highlighted.

differences are highlighted in Figure 1 for convenience; also acronyms used throughout the paper are included).

The presence of azo group not only makes the compounds orange (and thus easy to work with) but also photosensitive. They might therefore be suitable candidates for some opto-electronic applications such as optical memories (as side chains of polymers) (*15*), optically tunable cholesterics (as dopants) (*16*) or other dye-doped LC systems. The presence of room-temperature G phase in sulphur compounds suggest the application as helical pitch modifiers for FLC (*17*). Also some further structure modifications of these compounds may lead to interesting properties e.g. inserting a chiral alkyl chain might result in the formation of FLC materials, and side-ring substituents should reduce the temperature range of liquid-crystallinity. However, they make an excellent material to study the influence of the sulphur atom on optical properties of azo compounds, which is our future goal. For now, the aim of this paper is to systematically study how the above-described structural changes influence mesomorphism.

2. Experimental

2.1. Synthesis

2.1.1. 4-[(4'-nonyloxyphenyl)diazenyl]benzoic acid (K9)

The synthesis of acid K9 is shown in Figure 2. Although the procedure is almost exactly as described in the literature (*18*), we present it here for convenience.

K0 (*4-[(4'-hydroxyphenyl)diazenyl]benzoic acid*): 25 g (0.18 mol) of 4-aminobenzoic acid (commercial) was dissolved in about 40 ml of concentrated hydrochloric acid and 200 ml of water and cooled to 0°C in an ice bath while stirred mechanically. 13 g (0.56 mol) of $NaNO_2$ in saturated water solution was added slowly dropwise so as the temperature did not exceed 5°C. The mixture was cooled in a fridge and added in portions to a stirred ice-cold solution of 17 g (0.18 mol) of phenol and 20 g (0.20 mol) of sodium carbonate in water. The reaction mixture was then stirred for 20 more minutes and immediately afterwards the orange precipitate was filtered off, washed with water and dried in air. The product (**K0**) was used without further purification. Yield: 31 g (70%).

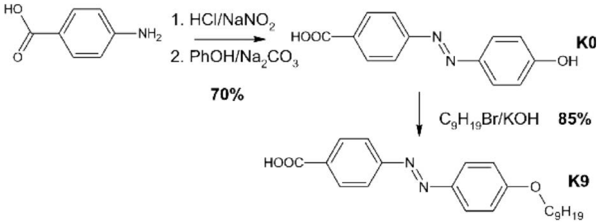

Figure 2. Synthesis outline of 4-[(4'-nonyloxyphenyl) diazenyl]benzoic acid (K9).

K9: 5 g (21 mmol) of K0 and 15 g (0.27 mol) of KOH were refluxed in 200 ml of ethanol until all solid dissolved, then cooled to room temperature. 52 g (0.25 mol) of 1-bromononane was added dropwise and the reaction mixture refluxed for a further 20 hours. After cooling down to room temperature, orange precipitate was filtered off and recrystallised twice from concentrated acetic acid. Yield: 6.46 g (85%) of **K9**.

2.1.2. 4''-heptylphenyl 4-[(4'-nonyloxyphenyl)diazenyl] benzoate (F7K9)

150 mg (0.78 mmol) of 4-heptylphenol (Eastman Kodak), 180 mg (0.49 mmol) of K9 and 150 mg (0.73 mmol) of *N,N'*-dicyclohexylcarbodiimide (DCC) (see Figure 3) were dissolved in tetrahydrofuran (THF) and left overnight (the progress was monitored by TLC in chloroform; if necessary the mixture was left for additional time until reaction was completed). Afterwards the solvent was removed under vacuum, the crude product dissolved in dichloromethane (DCM) and filtered on a silica gel column (also *N,N'*-dicyclohexylurea was easily removed in this step). F7K9 was then recrystallised from hexane. Yield: 95mg (36%). ^{1}H NMR (500MHz, $CDCl_3$):

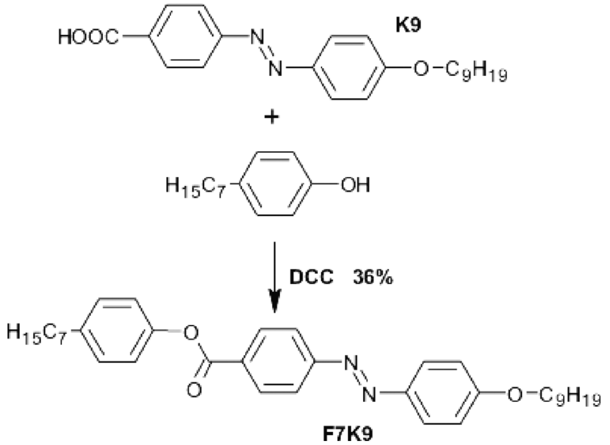

Figure 3. Synthesis outline of 4''-heptylphenyl 4-[(4'-nonyloxyphenyl)diazenyl]benzoate (F7K9).

δ 8.32 (d, 8.4Hz, 2H), 7.96 (2 × d, 4H), ab. 7.24 (d, 2H), 7.14 (d, 8.4Hz, 2H), 7.02 (d, 8.9Hz, 2H), 4.06 (t, 6.5Hz, 2H), 2.63 (t, 7.5 Hz, 2H), 1.83 (q$^{1\cdot}$, 2H), 1.63 (q,2H), 1.49 (q, 2H), 1.30 (b, 18H), 0.89 (2 × t, 6H); ^{13}C NMR (500 MHz, $CDCl_3$): δ 164.9, 162.5, 155.8, 148.8, 146.9, 140.7, 131.2, 130.6, 129.4, 125.3, 122.5, 121.3, 114.8, 68.5, 35.4, 31.9, 31.8, 31.5, 29.5, 29.4, 29.3, 29.2, 26.0, 22.7, 14.1; comb. analysis: calc. %C 77.45, %H 8.54, %N 5.16, found %C 77.17 (Δ0.28), %H 8.76 (Δ0.22), %N 5.36 (Δ0.2).

2.1.3. *4''-hexyloxyphenyl 4-[(4'-nonyloxyphenyl) diazenyl]benzoate (**F6oK9**)*

4-hexyloxyphenol necessary for this synthesis is easily available by monoetherification of hydroquinone (*19*). The esterification is shown in Figure 4.

200 mg (103 mmol) of freshly recrystallised (ethanol) 4-hexyloxyphenol, 200mg (0.54mmol) of K9 and 150mg (0.73mmol) of DCC were dissolved in THF. The procedure is then exactly the same as described above for F7K9. Yield: 102mg (33%). ^{1}H NMR (500MHz, $CDCl_3$): δ 8.32 (d, 8.6Hz, 2H), 7.96 (2 × d, 4H), 7.14 (d, 9.0Hz, 2H), 7.02 (d, 9.0Hz, 2H), 6.94 (d, 9.0Hz, 2H), 4.06 (t, 6.5Hz, 2H), 3.97 (t, 6.7Hz, 2H), 1.8 (m, 4H), 1.47 (q, 2H) 1.32 (b, 16H), 0.92 and 0.89 (2 × t, 6H); ^{13}C NMR (500MHz, $CDCl_3$): δ 165.1, 162.5, 157.0, 155.7, 146.9, 144.2, 131.2, 130.6, 125.3, 122.5, 122.4, 115.1,114.8, 68.49, 68.46, 31.9, 31.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.7, 22.7, 22.6, 14.1, 14.0; comb. analysis: calc. %C 74.97, %H 8.14, %N 5.14, found %C 74.75 (Δ0.22), %H 8.22 (Δ0.08), %N 5.01 (Δ0.13).

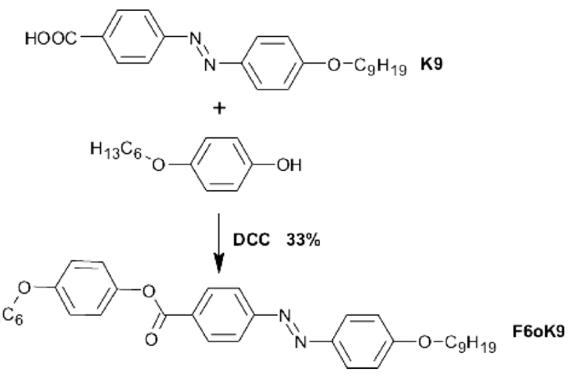

Figure 4. Synthesis outline of 4''-hexyloxyphenyl 4-[(4'-nonyloxyphenyl)diazenyl]benzoate (F6oK9).

2.1.4. *4''-heptylphenyl 4-[(4'-nonyloxyphenyl)diazenyl] thiobenzoate (**T7K9**)*

T7K9 was synthesised as shown in Figure 5. This synthesis has already been described by the authors (*3*), but we repeat it here for a complete picture. The method of thiol synthesis results from combining and modifying two synthesis strategies described previously (*20*, *21*).

Potassium 4-heptyphenylsulphonylate: 5g (28 mmol) of heptylbenzene (Sigma-Aldrich) and 7.5 ml of concentrated sulphuric acid were stirred vigorously for an hour in an oil bath of temperature 70 to 80°C (the colourless mixture turns brownish), then the reaction mixture was cooled and poured slowly with stirring into 50ml ice-cold 25% KOH solution; more 25% KOH solution was then added to just obtain an alkaline mixture. The white sediment was filtered off, washed with a small amount of ice-cold water, recrystallised from water and dried under vacuum.

Due to difficulties with separating the product from K_2SO_4 (both compounds dissolve comparably well in water), the yield of reaction was not measured as the presence of K_2SO_4 is not problematic for the next step and is afterwards removed. NMR proved that only 4-substituted product was obtained under these conditions (*20*).

4-heptylphenylsulphonic chloride: Into potassium 4-heptylphenylsulphonylate obtained in the previous step $POCl_3$ was added while hand stirring in an amount enough to obtain a fairly wet mixture, which was then slowly warmed in an oil bath to 170°C and kept at this temperature for one hour. The hot mixture was then transferred in portions into a small amount of ice-cold water, extracted with chloroform, washed well with water, dried over $MgSO_4$ and chloroform removed under vacuum. Distillation is avoided through careful extraction. A brownish oil was thus obtained with yield 6.23g (80%).

T7 *(4-heptylthiophenol)*: Into 700 mg (18 mmol) of $LiAlH_4$ in 50ml of dry THF cooled to 0°C the solution of 2.5g (9.1 mmol) of 4-(n-heptyl)-phenylsulphonic chloride in a small amount of dry THF was added dropwise under nitrogen. The mixture was then refluxed overnight, cooled, the reaction quenched by

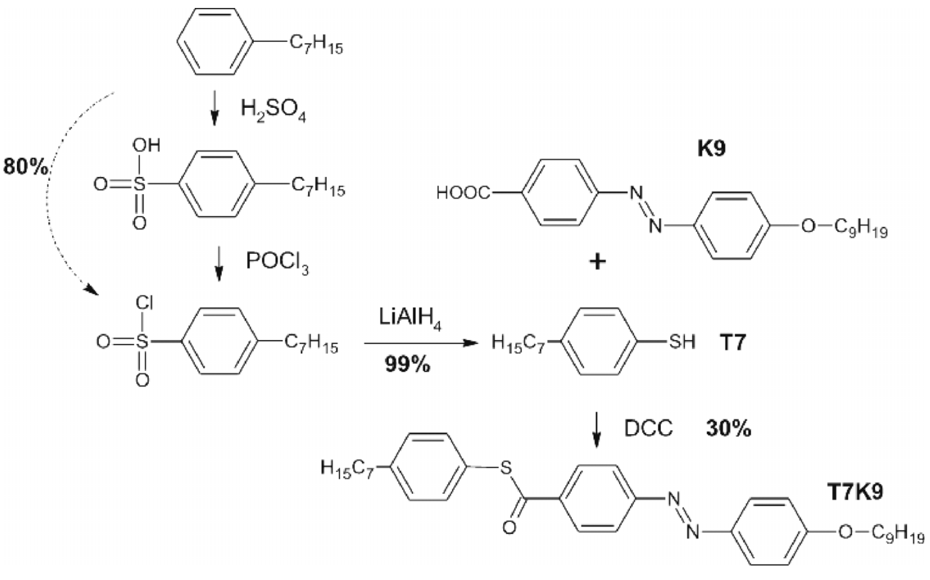

Figure 5. Synthesis outline of 4''-heptylphenyl 4-[(4'-nonyloxyphenyl)diazenyl]thiobenzoate (T7K9).

careful addition of water and 20% HCl. Sufficient amount of 20% HCl was then added to dissolve all jelly mass that had been produced, and THF was removed. The thiophenol was extracted with hexane, the organic layer well washed with water, dried, and the hexane removed. The yellowish oil of thiophenol was obtained. Yield: 1.88g (99%).

T7K9: 150 mg (0.72 mmol) of T7, 180 mg (0.49 mmol) of K9 and 150 mg (0.73 mmol) of DCC were dissolved in THF and prepared exactly as F7K9. In this case additional chromatography was necessary with a mixture of toluene and DCM of 1:3 volume ratio. The product was then recrystallised from hexane. Yield: 82mg (30%). ^{1}H NMR (300MHz, $CDCl_3$): δ 8.16 (d, 8.5Hz, 2H), 7.95 (2 × d, 4H), 7.43 (d, 8.0Hz, 2H), 7.29 (d, 8.0Hz, 2 H), 7.02 (d, 8.5Hz, 2H), 4.02 (t, 6.7Hz, 2H), 2.67 (t, 8.0Hz, 2H), 1.87 (q, 2H), 1.65 (q, 2H), 1.31 (b, 20H), 0.89 (2 × t, 6H); ^{13}C NMR (500MHz, $CDCl_3$): δ 190.0, 162.5, 155.7, 146.9, 144.9, 137.4, 135.0, 129.5, 128.5, 125.3, 123.8, 122.7, 114.8, 68.5, 35.8, 31.9, 31.8, 31.7 31.3, 29.5, 29.4, 29.3, 29.2, 29.15, 29.1, 26.0, 22.7, 22.6, 14.1; comb. analysis: calc. %C 75.23, %H 8.30, %N 5.01, %S 5.74 found %C 75.07 (Δ0.16), %H 8.57 (Δ0.27), %N 4.86 (Δ0.15), %S 5.43 (Δ0.31).

*2.1.5. 4''-hexyloxyphenyl 4-[(4'-nonyloxyphenyl) diazenyl]thiobenzoate (**T6oK9**)*

The procedure leading to T6oK9 is presented in Figure 6. The starting hexyloxybenzene may be easily prepared by Williamson etherification of phenol (*22*).

4-hexyloxyphenylsulphonic chloride: 10 g (56 mmol) of hexyloxybenzene was dissolved in 100 ml of dry chloroform and cooled under a condenser to −10°C. While stirring, 13 ml of chlorosulphonic acid was added dropwise slowly enough to maintain −10°C in the reaction mixture. The reaction was left overnight, poured into ice, extracted with chloroform, dried over

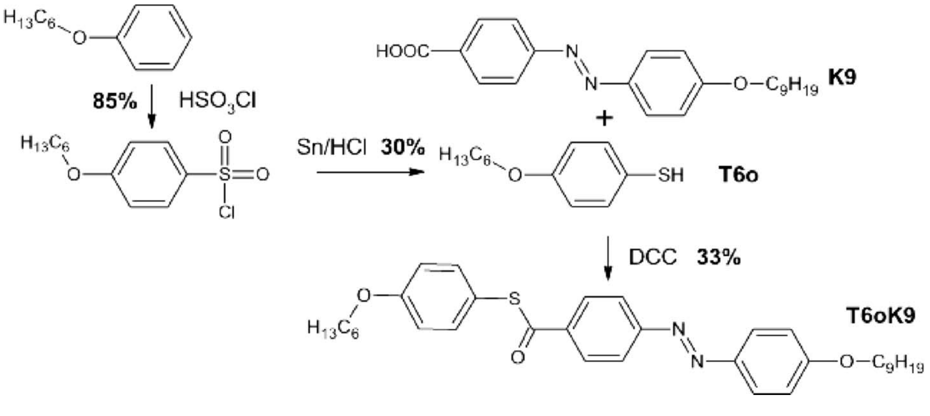

Figure 6. Synthesis outline of 4''-hexyloxyphenyl 4-[(4'-nonyloxyphenyl)diazenyl]thiobenzoate (T6oK9).

$CaCl_2$, filtered and the solvent removed under vacuum. Yield: 9 g (58%).

T6o (*4-hexyloxythiophenol)*: 1.78g (6.4mmol) of 4-hexyloxyphenylsulphonic chloride was added to 4.5 ml of concentrated HCl in dioxane. 1.85 g (15 mmol) of Sn was added and the reaction refluxed with stirring for 3 hours. The mixture was then poured into ice, extracted three times with chloroform, dried over $MgSO_4$ and the solvent removed under vacuum. Yield: 0.40 g (30%).

T6oK9: 150 mg (0.71 mmol) of T6o, 180 mg (0.49 mmol) of K9 and 150 mg (0.73 mg) of DCC were dissolved in THF and prepared exactly as F7K9. Yield: 82 mg (30%). ^1H NMR (300 MHz, $CDCl_3$): δ 8.14 (d, 8.4Hz, 2H), 7.9 (2 × d, 4H), 7.4 (d, 8.4Hz, 2H), 7.0 (2 × d, 4H), 4.05 (t, 6.1Hz, 2H), 4.0 (t, 6.6Hz, 2H), 1.8 (m, 4H), 1.46 and 1.28 (b, 18H), 0.88 (2 × t, 6H); ^{13}C NMR (500MHz, $CDCl_3$): δ 190.5, 162.5, 160.5, 155.7, 146.9, 137.4, 136.6, 128.5, 125.4, 122.7, 117.4, 115.4,114.8, 68.5, 68.2, 31.9, 31.6, 29.5, 29.4, 29.3, 29.2, 26.0, 25.7, 22.8, 22.6, 14.1, 14.0; comb. analysis: calc. %C 72.82, %H 7.91, %N 5.0, %S 5.72 found %C 72.52 (Δ0.3), %H 8.19 (Δ0.28), %N 4.90 (Δ0.10), %S 5.47 (Δ0.25).

2.2. *Setup for physical measurements*

The NMR spectra were recorded on Bruker 300 MHz or Bruker 500 MHz spectrometers. The purity of products was checked by TLC, combustion analysis and indirectly proven by clean NMR spectra. Polarisation microscopy observations (POM) and thermal optical analysis (TOA) were both performed on Olympus BX60 with the thermostating device Linkam TNS 93 and Linkam LNP cooling system. Differential scanning calorimetry (DSC) was carried out on a Perkin-Elmer DSC7. The assignment of types of mesophases to all detected mesophases is based on POM texture observations only, while the temperatures are derived from DSC and TOA results.

3. Results and discussion

The liquid-crystalline properties of compounds studied are presented in Table 1 for readers' convenience. In this section, before any conclusions will be made, we will describe in more detail the important aspects of each.

We would like to stress that because the assignment of mesophases has been done on the basis of POM observations only, it should be treated as probable and not final. It is especially the case with difficult-to-differentiate smectic I and smectic F phases (apart from the case of T7K9, where both phases are present and the sequence establishes identity). For three other compounds the smectic I phase assignation has been based on a schlieren texture difficult to bring into microscope focus (*23*).

3.1. *Liquid-crystallinity of F7K9*

F7K9 shows on cooling four mesophases: nematic, SmA, SmC and SmI. The first three are clearly visible both on DSC and TOA scans (Figure 7). In Figure 8(a), the nematic texture is shown, in 8(b) the smectic A texture, and in Figure 8(c) the schlieren texture of smectic C phases – this is the same fragment of the sample as in Figure 8(b). The SmI phase is monotropic and it appears on cooling when the crystallisation starts. Its presence is visible in the DSC plot as a bump on the crystallisation peak. The texture of the simultaneously present SmI and crystalline state are shown in Figure 8(d). On heating we observed two additional solid-state transitions for this compound.

3.2. *Liquid-crystallinity of F6oK9*

F6oK9 is similar to F7K9 apart from having no smectic A phase. Again the smectic I phase is monotropic, this time it appears just before the crystallisation starts. DSC and TOA plots are shown in Figure 9. Figure 10(a) shows nematic texture, 10(b) smectic C, 10(c) smectic I and 10(d) crystalline state texture. For

Table 1. LC phases of compounds described in this paper. ◆ means a mesophase was detected for a compound. The values describing phase transitions are, from top to bottom: temperature of transition in °C, enthalpy of transition in kJ mol^{-1}.

	Cr		G gl.		G		F		I		C		A		N		is
F7K9	◆	96							◆	72	◆	150	◆	170	◆	194	◆
		33.0								–		–		*0.42*		*1.28*	
F6oK9	◆	106							◆	84	◆			170	◆	216	◆
		42.7								–				*0.23*		*1.36*	
T7K9	◆	90	◆	–	◆	78	◆	104	◆	110	◆			179	◆	217	◆
		35.3		–		*9.15*		–		*1.69*				*0.79*		*1.40*	
T6oK9	◆	92	◆	88	◆	92			◆	106	◆			182	◆	234	◆
		24.6		–		*11.2*				*1.27*				*1.47*		*1.38*	

Note: Apart from monotropic transitions all parameters are collected from heating mode. '–' means the value could not be derived from DSC scan, 'gl.' means glass. 'Sm' for smectics is omitted for clarity.

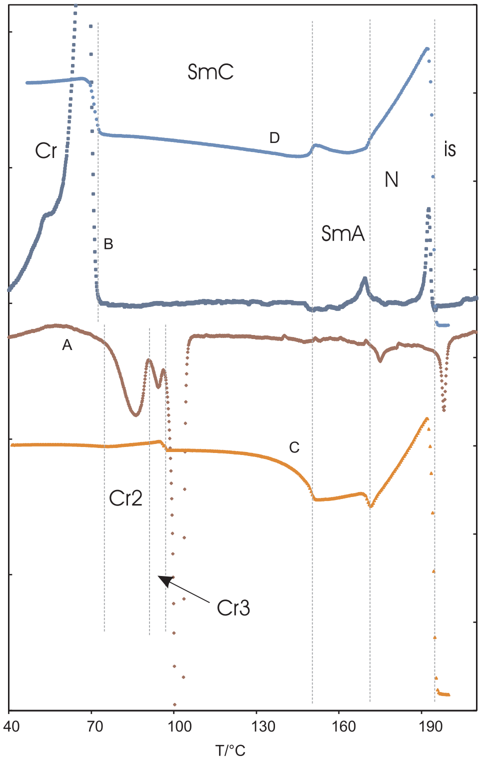

Figure 7. DSC (A – heating, B – cooling) and TOA (C – heating, D – cooling) plots for F7K9.

F6oK9 we do not detect any solid-state transitions in studied temperature range (down to 0°C).

3.3. *Liquid-crystallinity of T7K9*

T7K9 has the richest polymorphism of all compounds described here. It has five mesophases: nematic, SmC, SmI, SmF and SmG. Their identity is most conclusively established since all of them are present and can only appear in this order. In Figure 11 we present DSC and TOA plots for this compound. Of the most interesting textures, smectic I is shown in Figure 12(a), smectic F in Figure 12(b)

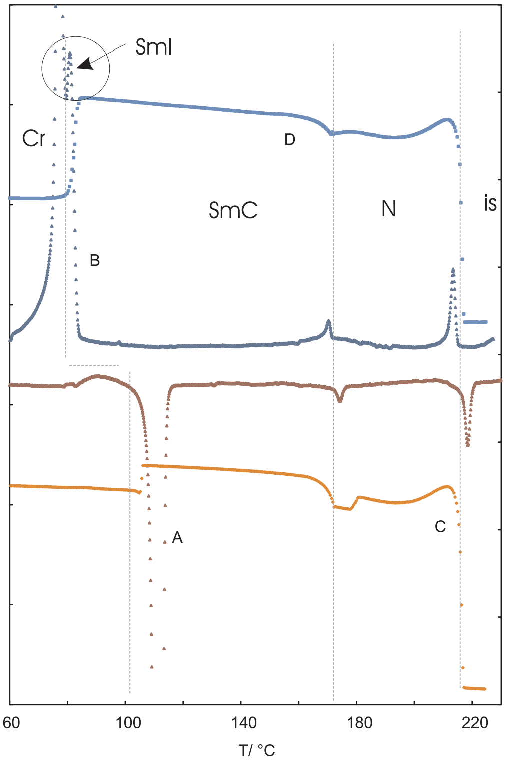

Figure 9. DSC (A – heating, B – cooling) and TOA (C – heating, D – cooling) plots for F6oK9.

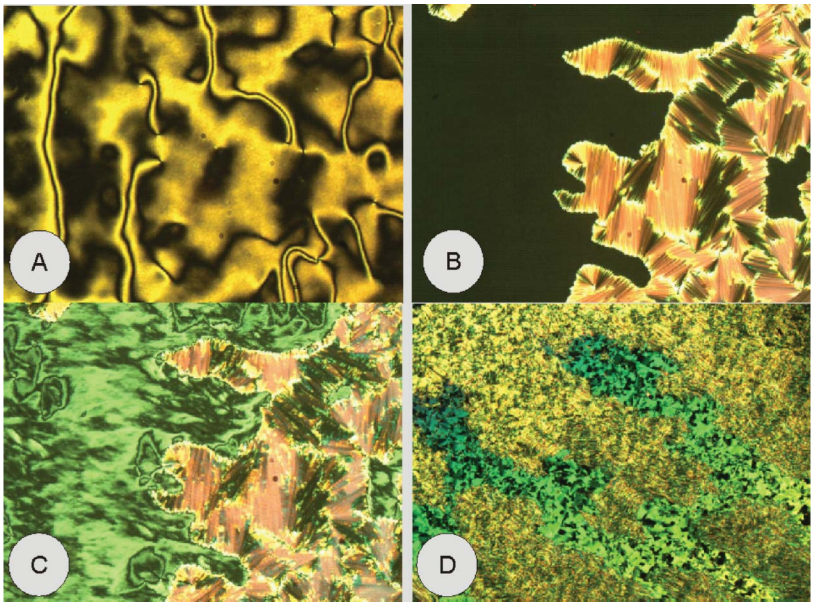

Figure 8. POM textures of F7K9 on cooling (a) nematic, (b) smectic A, (c) smectic C, (d) smectic I and crystalline state.

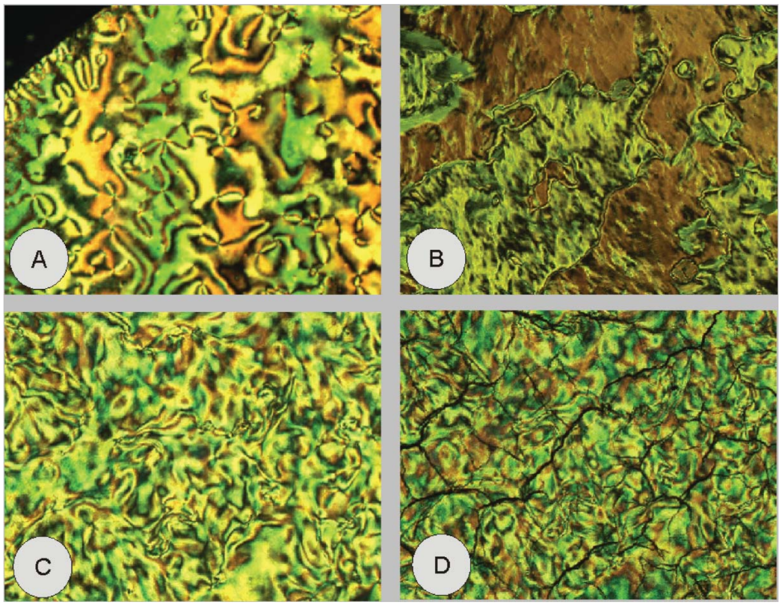

Figure 10. POM textures of F6oK9 on cooling (a) nematic, (b) smectic C, (c) smectic I, (d) crystalline state.

and smectic G in glassy state in Figure 12(c). We obtained this compound in a synthesis in its crystalline state. However, after heating it above the melting temperature (90°C) it does not crystallise again, but the smectic G goes into a glassy state around 75°C (no crystallisation was observed under POM down to 0°C); moreover the last peak on DSC is too small to represent crystallisation – this energy effect has far lower enthalpy than the enthalpy of melting, and is therefore ascribed to F-G transition.

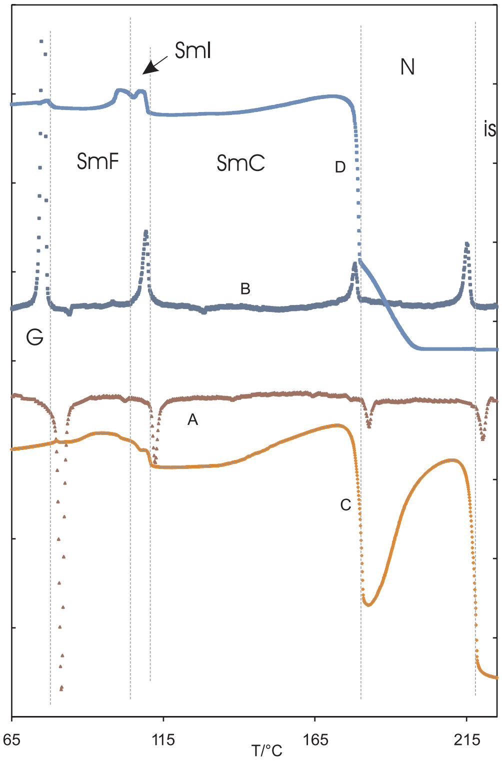

Figure 11. DSC (A – heating, B – cooling) and TOA (C – heating, D – cooling) plots for T7K9.

3.4. *Liquid-crystallinity of T6oK9*

The liquid-crystalline properties of this compound are similar to those of T6oK9, the difference being that there is no smectic F in this case. Again the smectic G turns into a glassy state and the crystalline state does not reappear after the first melting. DSC and TOA plots are shown in Figure 13. Textures of smectic C, I and G are shown in Figure 14.

3.5. *Comparison of liquid-crystalline behaviour of the described compounds*

In Figure 15 we directly compare the liquid-crystalline polymorphism of the four compounds described above.

As regards the influence of sulphur atom we can certainly say that the thioester group, compared with the ester group, enriches liquid-crystalline polymorphism of the studied compounds and also broadens the temperature range in both directions. For both thioesters high-ordered smectics appear and they are enantiotropic, while in esters we have only monotropic smectic I in an extremely narrow temperature range. Also, the presence of the smectic G phase seems to inhibit crystallisation and for both thioesters we have glass transitions and smectic G ‘frozen’ down to at least 0°C. We attribute these effects to greater core interaction due to additional electrons of the sulphur atom (compared with oxygen).

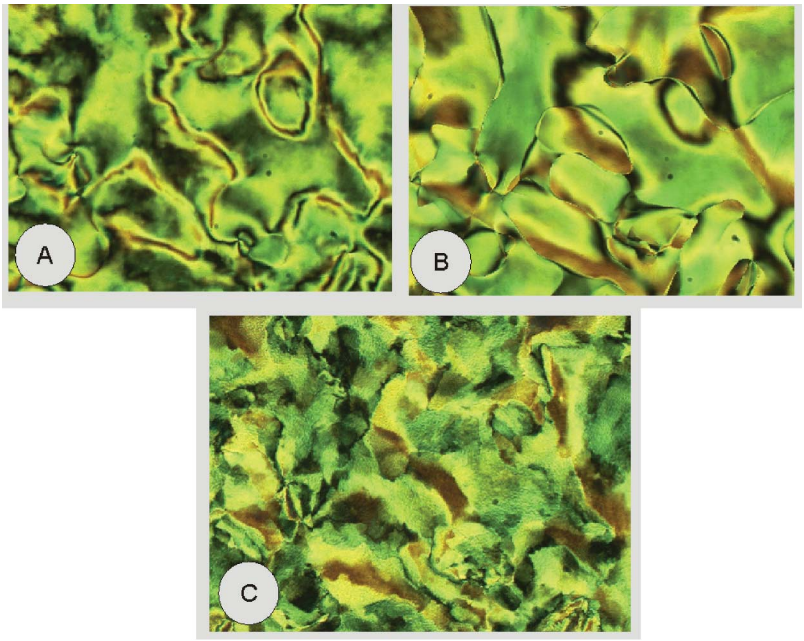

Figure 12. POM textures of T7K9 on cooling (a) smectic I, (b) smectic F, (c) smectic G.

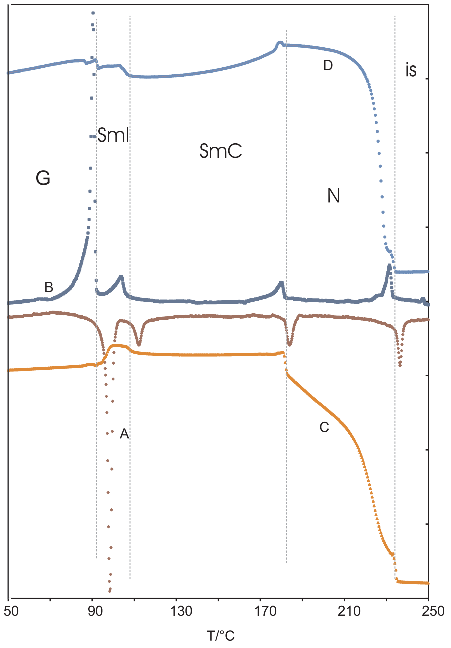

Figure 13. DSC (A – heating, B – cooling) and TOA (C – heating, D – cooling) plots for T6oK9.

The substitution of the alkyl chain by an alkyloxy chain of comparable length impoverishes liquid-crystalline polymorphism – some of the mesophases disappear, ordering seems to be more direct (e.g. nematic turns immediately into smectic C, omitting smectic A in case of F6oK9). The temperature effect is typical – it raises the isotropisation temperature.

4. Conclusions

To sum up, we have worked out synthetic routes towards four new types of calamitic liquid-crystalline compounds. Four comparable representatives of these groups have been synthesised and their liquid-crystalline behaviour studied. We compared the effect that the sulphur atom in a core fragment and the oxygen atom in a side chain have on liquid-crystalline properties of these compounds. Insertion of the sulphur atom allows in this case to broaden temperature range of liquid-crystallinity and results in more complex mesophases.

All of compounds were found to be liquid-crystalline and all exhibit more than two mesophases. Their synthesis is easy and cheap, they are thermally stable and liquid-crystalline in a broad range of temperatures. These features, together with the presence of the azo group, make them promising materials for further studies towards applications.

Note

[1] We would like to emphasise that signals assigned for practical purposes as quintets are truly triplets of triplets with coupling constants so similar to one another that they appear as quintets on spectra; therefore no coupling constants are given.

Acknowledgments

The authors would like to thank Professor Dabrowski from the Military University of Technology, Warsaw, Poland for

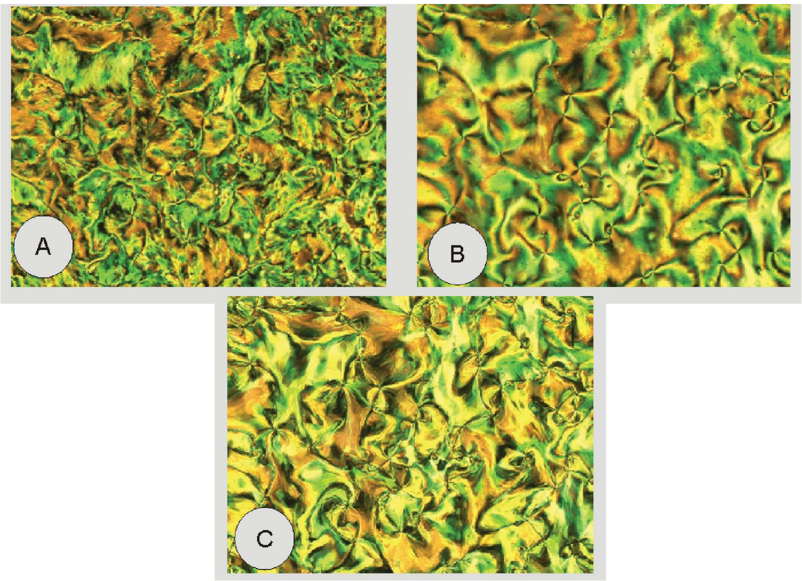

Figure 14. POM textures of T6oK9 on cooling (a) smectic C, (b) smectic I, (c) smectic G.

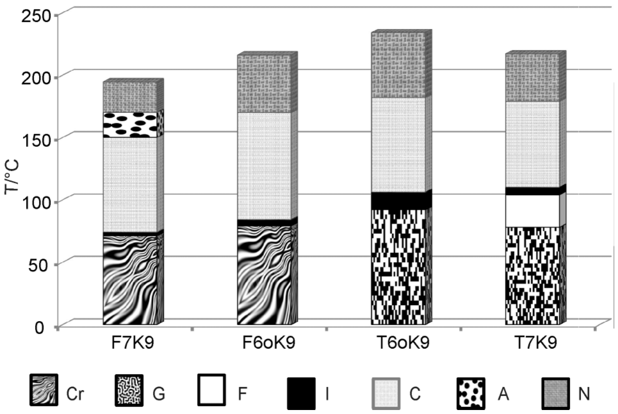

Figure 15. Comparison of liquid-crystalline properties of F7K9, F6oK9, T7K9 and T6oK9.

supplying them with 1g of 4-heptylphenol. We particularly thank Joanna Godzwon for her expert opinion in the identification of mesophases of the described compounds.

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