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New liquid-crystalline materials containing a five-membered heteroalicycle: trans-2,4-disubstituted 1,3-oxathiolanes

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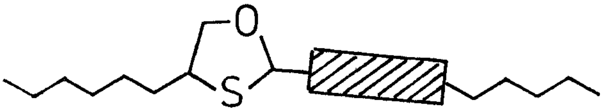
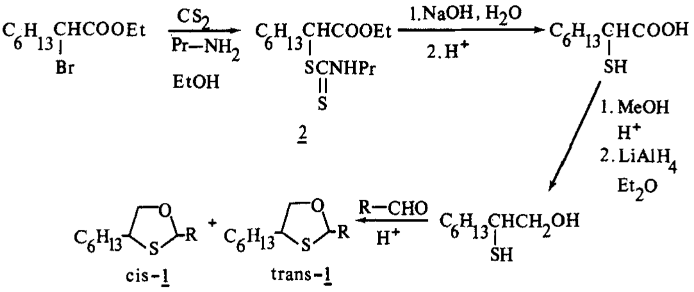
The synthesis of new liquid-crystalline materials containing a five membered heteroalicyclic ring is described. The trans 2,4-disubstituted 1,3-oxathiolane derivatives exhibit lower clearing temperatures and melting points than the analogous six membered 1,3-oxathiane compounds. However the mesophase stability of the 1,3-oxathiolane derivatives is superior to that of comparable cyclopentane derivatives.

1. Introduction

It is well known, that heteroalicyclic compounds are a valuable source of liquid-crystalline materials [1–10]. However until now, only a few attempts have been made to incorporate five-membered heteroalicyclic rings in the principal structure of calamitic mesogens [11, 12]. Here we report new liquid-crystalline materials which include the 2,4-disubstituted 1,3-oxathiolane ring:



The synthesis of these compounds started with ethyl 2-bromooctanoate. Nucleophilic displacement of the bromine was achieved with carbon disulphide in the presence of *n*-propylamine [13]. The resulting dithiocarbamate **2** was hydrolysed to the 2-mercaptooctanoic acid, which was esterified and afterwards reduced with lithium aluminium hydride. Acetalization of the resulting 2-mercaptooctanol with appropriate aldehydes afforded mixtures of cis- and trans-2,4-disubstituted 1,3-oxathiolanes **1**, from which the pure trans isomers were isolated by repeated crystallization from methanol or acetone.



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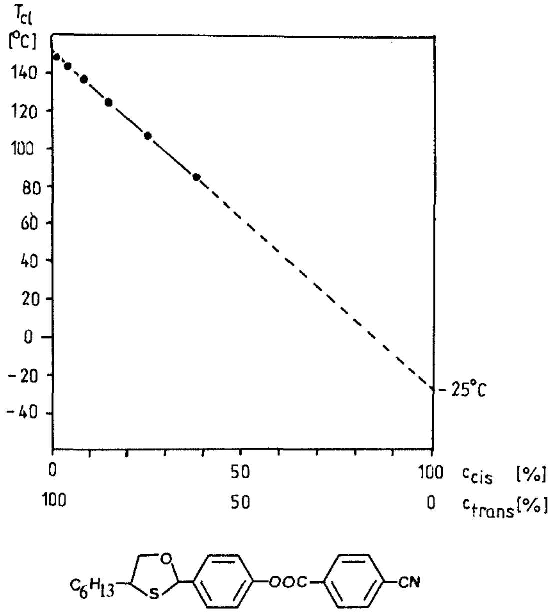


Figure 1. Dependence of the clearing temperatures of **1.1** on the cis/trans ratio.

After each recrystallization step, the cis/trans ratios of the mixtures were easily obtained from peak area integration of the well separated 2–H signals (cis-**1.1**: 6·08 ppm; trans-**1.1**: 6·15 ppm; cis-**1.9**: 4·84 ppm; trans-**1.9**: 4·91 ppm; measured in $CDCl_3$). As shown in figure 1 there is a strictly linear dependence of the clearing temperatures on the cis/trans ratios. Extrapolation to $c_{cis} = 100$ per cent gave the virtual clearing temperature of cis-**1.1** as -25°C. There is a large difference between the clearing temperatures of cis-**1.1** and trans-**1.1** ($\Delta T_{cl} = 176$ K), indicating the very different molecular geometry of these two isomers. The liquid-crystalline properties of the trans-2,4-disubstituted 1,3-oxathiolanes **1.1**–**1.11** are collected in the table. All of the compounds investigated exhibit enantiotropic liquid-crystalline phases. The nematic mesophase is predominant for the aromatic derivatives, whereas the pure aliphatic compounds **1.7** and **1.9**–**1.11** exhibit only the smectic B phase.

Comparison with the related six-membered trans-2,5-disubstituted 1,3-oxathianes **3** (see the table) indicates, that the 1,3-oxathiolane derivatives generally exhibit lower clearing temperatures and melting points. The depression of the mesophase stability could be caused by at least two reasons. First, the five-membered ring causes a bent molecular structure which disfavours liquid crystal formation. Secondly, it is well known that five-membered (hetero)alicycles are much more flexible than six-membered ones [14]. Figure 2 represents the molecular geometry of the 1,3-oxathiolane-ring. It is evident that there is a steric interaction only between the axial C–2 substituent and the axial hydrogen atom at C–5 (there are two of these interactions in 1,3-oxathianes). Furthermore, this interaction should be very weak, since the axial C–2-substituent is tilted away from the H–5 hydrogen. Thus, the energy difference between the diaxial and diequatorial conformers of the trans-2,4-disubstituted 1,3-oxathiolanes should be low and gives rise to an enhanced population of the more spherical (and therefore less mesogenic) diaxial conformer. Inspection of the table also indicates, that the clearing temperature differences between 2-phenyl

Comparison of the transition temperatures (°C) of the trans-2,4-disubstituted oxathiolanes **1.1–1.11** and trans-2,5-disubstituted oxathianes **3.1–3.6**.

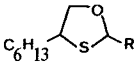
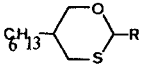
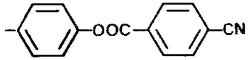
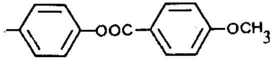
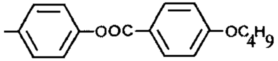
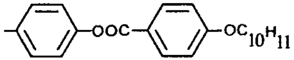
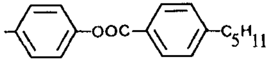
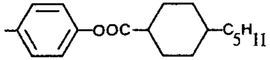
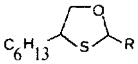
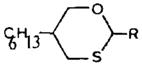
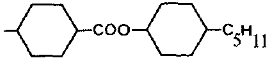
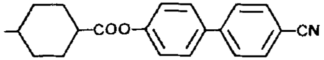
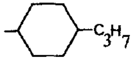
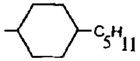
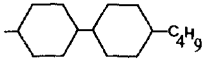
R																					
	Compound	C		S_B		S_A		N		I	Compound	C		S_B		S_A		N		I	$(T_{c13}-T_{c11})$/K
	**1.1**	●	85	—	—	—	—	●	151	●	**3.1**	●	108	—	—	●	111	●	224	●	73
	**1.2**	●	76	—	—	—	—	●	114	●											
	**1.3**	●	69	—	—	—	—	●	117	●	**3.2**	●	82	—	—	—	—	●	184	●	67
	**1.4**	●	57	—	—	—	—	●	109	●											
	**1.5**	●	53	—	—	●	55	●	89	●											
	**1.6**	●	85	—	—	—	—	●	106	●	**3.3**	●	119	—	—	—	—	●	171	●	65

Table (*continued*)

R																					
	Compound	C		S_B		S_A		N		I	Compound	C		S_B		S_A		N		I	$(T_{c13}-T_{c11})$/K
	**1.7**	●	28	●	110	—	—	—	—	●	**3.4**	●	82	●	138	—	—	●	163	●	53
	**1.8**	●	82	—	—	—	—	●	265	●											
	**1.9**	●	20	●	23	—	—	—	—	●											
	**1.10**	●	37	●	45	—	—	—	—	●	**3.5†**	●	75	●	99	—	—	—	—	●	54
	**1.11**	●	42	●	180	—	—	—	—	●	**3.6**	●	75	●	223	—	—	—	—	●	43

† [4].

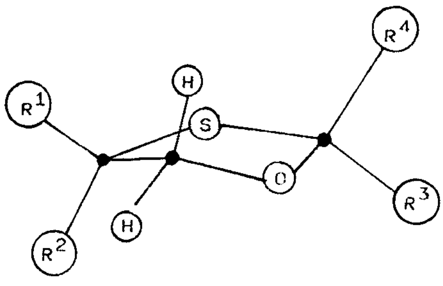
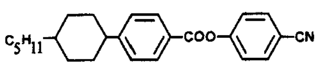


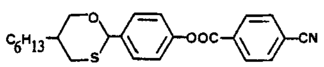
Figure 2. The molecular geometry of the 1,3-oxathiolane ring, drawn by means of a PASCAL-program [15] using the X-ray data of cholestan-4-one-3-spiro-(2,5-oxathiolane) [16]. trans-**1**: R^2, $R^4=H$ (diequatorial conformer), R^1, $R^3=H$ (diaxial conformer). cis-**1**: R^1, $R^4=H$ or R^2, $R^3=H$.

substituted 1,3-oxathiolanes and 1,3-oxathianes is larger than that of the 2-cyclohexyl derivatives. This should be due to the additional stabilization of axially phenyl substituted conformers by the anomeric effect between the heteroatoms and the 2-phenyl substituent [17]. This stereoelectronic effect only destabilizes the mesophases of the 2-phenyl-1,3-oxathiolanes **1.1**–**1.6**. In the 2-phenyl-1,3-oxathianes **3.1**–**3.3** the influence of this effect is largely suppressed by the strong 1,3-diaxial steric interactions of the axial 2-substituent [18]. Since the magnitude of the anomeric effect increases with growing electron withdrawing properties of the substituent attached to the phenyl group, the clearing temperature difference between the 4-cyanobenzoates **1.1** and **3.1** is larger than that of the 4-alkoxy derivatives **1.2** and **3.2**.

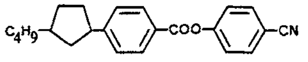
These differences are, however, small, if compared with those between the cyclohexane and cyclopentane derivatives **4** [19] and **5** [20, 21].



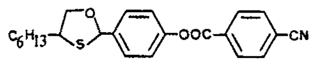
C 111°C N 225°C I **4**



C 108°C S_A 111°C N 224°C I **3.1**



C 58°C N 85°C I **5**



C 85°C N 151°C I **1.1**

Furthermore, the clearing temperatures of the cyclopentane derivative **5** is largely increased by the replacement of two methylene groups by O and S, because this leads to a more linear molecular structure. Therefrom we must conclude, that the trans-2,4-disubstituted 1,3-oxathiolane ring is a valuable new structural unit for calamitic mesogens.

2. Experimental

Melting points and transition temperatures were determined using a Boetius polarizing microscope; ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker WP 200 spectrometer. All new compounds have satisfactory IR, ^1H NMR and ^{13}C NMR spectra and elemental analysis.

2,5-Disubstituted 1,3-oxathiane derivatives (compounds **3.1**–**3.3** and **3.6**) were synthesized as described previously [4].

2.1. *Methyl 2-mercaptooctanoate*

0·50 mol (29·6 g) *n*-propylamine was added carefully to a solution of 0·2 mol (50·2 g) ethyl 2-bromooctanoate and 0·25 mol (19·5 g) carbon disulphide in 300 ml methanol at 20–30°C. This mixture was stirred for 12 hours. Afterwards 1000 ml water and 200 ml diethyl ether were added. The organic layer was separated and the aqueous layer was extracted twice with ethyl ether. The combined organic layers were dried over sodium sulphate and the solvent was evaporated. A solution of 2·0 mol (80 g) sodium hydroxide in a mixture of 300 ml water and 100 ml ethanol was added to the residue. After refluxing for 2 hours, the solvent was evaporated and the residue was dissolved in 300 ml water. After acidification the organic layer was separated, the aqueous layer was extracted twice with diethyl ether and the combined organic layers were evaporated after drying over sodium sulphate. The 2-mercaptooctanoic acid, obtained in this way, was esterified by refluxing with 300 ml dry methanol and 10 ml sulphuric acid for 4 hours. After the usual work-up procedure and vacuum distillation 22·1 g (58 per cent) methyl 2-mercaptooctanoate (b.p.: 76°C/0·1 Torr) was obtained.

2.2. *2-Mercaptooctanol*

A solution of 0·1 mol (19·0 g) methyl 2-mercaptooctanoate in 50 ml dry diethyl ether was added dropwise to a stirred suspension of 0·1 mol (3·8 g) lithium aluminium hydride in 250 ml dry diethyl ether. The mixture was stirred fro 2 hours at room temperature and afterwards carefully hydrolysed by the dropwise addition of 20 ml water. The resulting suspension was filtered through a Celite pad; this was washed twice with 100 ml diethyl ether. After evaporation of the solvent, the residue was distilled in vacuum (b.p.: 86–90°C/0·2 Torr) giving 11·9 g (73 per cent) 2-mercaptooctanol.

2.3. *Cycloacetalization*

A mixture of 0·01 mol 2-mercaptooctanol, 0·009 mol of the appropriate aldehyde, 100 mg *p*-toluene sulphonic acid and 100 ml benzene was refluxed in a water separator. After cooling the mixture was washed with sodium bicarbonate solution (5 per cent) and water, then dried over sodium sulphate and the solvent was evaporated. The residue was purified by fractionated recrystallization from methanol or acetone until constant transition temperatures were obtained. The yields were 10–30 per cent. The transition temperatures of these compounds are summarized in the table.

The structures of the products and their isomeric purities were checked using ^{1}H and ^{13}C NMR as well as IR spectroscopy. The ^{1}H and ^{13}C NMR spectra of compound **1.2** gave the analyses:

> ^{1}H NMR (200 MHz, $CDCl_3$): 8·13 (d, $J = 8{\cdot}9$ Hz, 2 H, CH–arom.), 7·50 (d, $J = 8{\cdot}6$ Hz, 2 H, CH–arom.), 7·17 (d, $J = 8{\cdot}6$ Hz, 2 H, CH–arom.), 6·95 (d, $J = 8{\cdot}9$ Hz, 2 H, CH–arom.), 6·13 (s, 1 H, H–2), 4·48 (dd, $J = 8{\cdot}9$ Hz, $J = 5{\cdot}7$ Hz, 1 H, H–5equ), 3·86 (s, 3 H, $-OCH_3$), 3·78 (m, 1 H, H–4), 3·59 (*t*, $J = 8{\cdot}6$ Hz, 1 H, H–5ax), 1·69 (m, 2 H, $=CH-CH_2-$), 1·4–1·2 (broad, 8 H, $-(CH_2)_4-$), 0·88 (t, $J = 6{\cdot}4$ Hz, 3H, $-CH_3$).

> ^{13}C MNR (50 MHz, $CDCl_3$): 164·5 (C = O), 163·9, 151·1, 137·0 (C–quart.), 132·2 (2 C, CH–arom.), 127·8 (2 C, CH–arom), 121·8 (C–quart.), 121·6 (2 C, CH–arom.), 113·8 (2 C, CH–arom.), 86·4 (C–2), 76·9 (C–5), 55·4 (OCH_3), 51·5 (C–4), 34·3, 31·6, 29·1, 29·0, 22·5 ($-CH_2-$), 14·0 ($-CH_3$).

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