Liquid Crystals

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

New liquid-crystalline heteroalicyclic compounds

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To cite this Article Tschierske, C. , Joachimi, D. , Vorbrodt, H-M. , Zaschke, H. , Wiegeleben, A. , Hauser, A. and Demus, D.(1989) 'New liquid-crystalline heteroalicyclic compounds', Liquid Crystals, 5: 1, 177 — 190
To link to this Article: DOI: 10.1080/02678298908026361
URL: http://dx.doi.org/10.1080/02678298908026361

LIQUID CRYSTALS, 1989, VOL. 5, NO. 1, 177–190

New liquid-crystalline heteroalicyclic compounds

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A wide variety of new sulphur-containing heteroalicyclic liquid-crystalline compounds have been synthesized. Special attention has thus been focussed on the influence of the heteroatoms on the mesomorphic behaviour. 2-Cyclohexyl substituted 1,3-dithianes and 1,3-oxathianes have been found to be superior to those with 2-phenyl substituents. The clearing temperatures of the 2-phenyl-1,3-dithianes depend on the electron donating or electron accepting properties of the substituents attached to the phenyl group. The mesophase stability of the 2-cyclohexyl substituted (hetero)alicycles increases in the order: 1,3-dioxane < 1,3-oxathiane < cyclohexane < 1,3-dithiane. This order is partly reversed for the cyclohexane annulated compounds: 1-oxa-3-thiadecalin < 1,3-dioxadecalin < decalin < 1,3-dithiadecalin. Selected values of the birefrigence and some melting enthalpies have been measured.

1. Introduction

In previous papers [1–3] we have reported the mesogenic properties of various heteroalicyclic compounds like 1,3-dioxanes and 1,3-dioxadecalins. These compounds exhibit useful liquid-crystalline properties. The basic structural unit is an acetalic one, which enables the rather simple synthesis of a great variety of differently substituted compounds. In this way these species are very useful for the investigation of the influence of structural variations upon mesogenic behaviour. Recently we have focussed our attention on the question of to what extent different heteroatoms, incorporated in alicyclic structural units, influence liquid-crystalline properties.

For this reason we have synthesized differently substituted 1,3-oxathianes, 1,3-dithianes, 1-oxa-3-thiadecalins and 1,3-dithiadecalins. Although 2-aryl-substituted 1,3-dithianes and 1,3-oxathianes have also been described by Haramoto and co-workers [4–11] and others [12], only a few 2-cyclohexyl-substituted 1,3-dithianes have been reported by us [13]. The 1,3-dithiadecalins and 1-oxa-3-thiadecalins are new structural units in liquid crystal chemistry.

2. Experimental

All compounds were synthesized by acid catalysed acetalization using boron trifluoride etherate as a catalyst (table 1). A mixture of stereoisomers results, from which the desired *trans*-isomers were separated by repeated recrystallization from methanol. The *cis*-isomers were enriched in the mother liquour, and were equilibrated to the *trans*-isomers using boron trifluoride etherate. In this way we obtained high yields of the stereoisomerically pure compounds **1–8**.

The synthesis of the aldehydes has been described recently [3]. The differently substituted 3-mercaptopropanols and 1,3-dimercaptopropanes have been prepared

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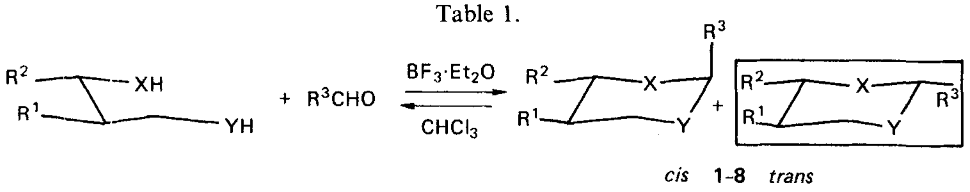
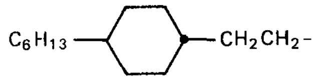
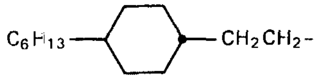
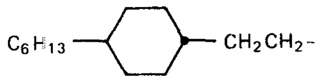
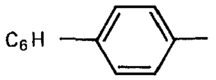
Table 1.



R^1	R^2	X	Y	Compound
	H	O	O	**1**
C_6H_{13}-	H	O	S	**2**
	H	O	S	**3**
-$(CH_2)_4$-		O	S	**4**
n-alkyl-	H	S	S	**5**
	H	S	S	**6**
	H	S	S	**7**
-$(CH_2)_4$-		S	S	**8**

using procedures from the literature. Details of the synthetic procedures for these compounds will be reported elsewhere.

The ethylene bridged compounds **1**, **3** and **6** were prepared according to the scheme given in figure 1. The *trans*-4-(*trans*-5-*n*-hexyl-1,3-oxathian-2-yl)-cyclohexanecarboxylates **2.4–2.12** and *trans*-4-(*trans*-5-*n*-hexyl-1,3-dithian-2-yl)-cyclohexanecarboxylates **5.17–5.33** were synthesized as shown in figure 2. Thus, the simple alkyl-*trans*-4-(*trans*-5-*n*-hexyl-1,3-diheterocyclohexan-2-yl)-cyclohexanecarboxylates **2.3** and **5.16** were prepared as described previously. These compounds were then saponified with potassium hydroxide in wet methanol and the free acids **2.2** and **5.15** were liberated by careful acidification and were extracted with ethyl acetate. These acids were esterified with different alcohols, cyclohexanols and phenols using 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide-methiodide as condensing agent in the presence of catalytic amounts of 4-dimethylaminopyridine [14] to give the desired compounds **2.4–2.12** and **5.17–5.33**.

3. Results and discussion

The mesomorphic properties of the new compounds are summarized in tables 2–8. We shall now make various comparisons of these compounds with each other or with

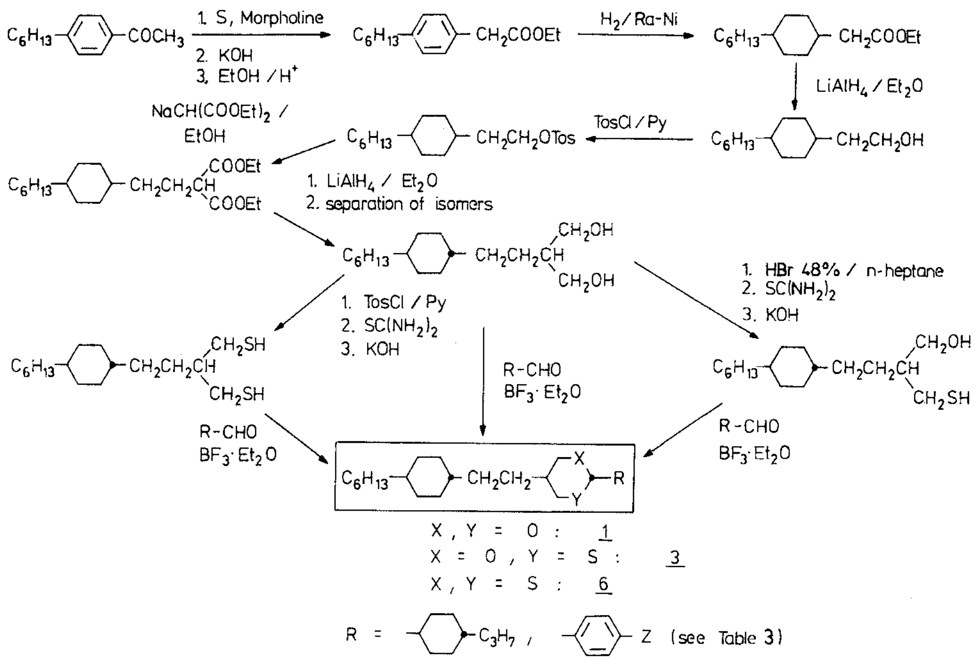


Figure 1. Synthesis of the 5-(*trans*-4-hexylcyclohexane-ethyl)-2-substituted 1,3-diheterocyclohexanes **1**, **3** and **6**.

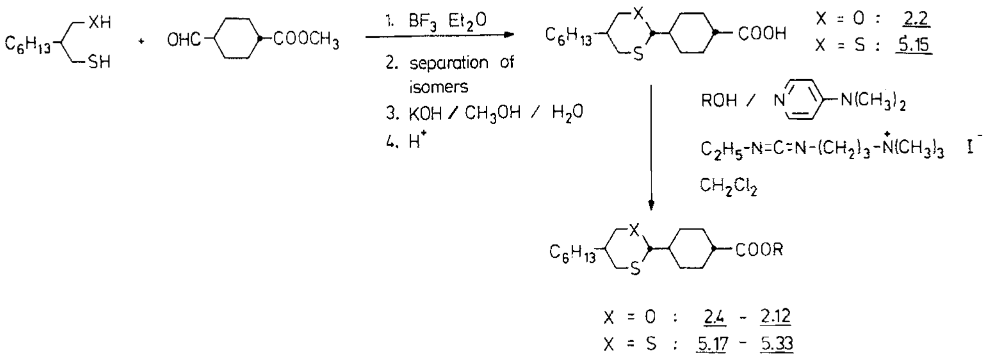


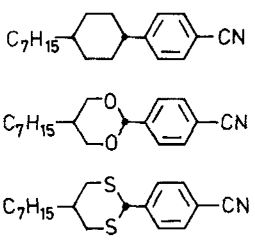
Figure 2. Synthesis of the *trans*-4-(*trans*-5-*n*-hexyl-1,3-diheterocyclohexan-2-yl)-cyclohexanecarboxylates **2.4–2.12** and **5.17–5.33**.

relevant analogues in order to estimate the influence exerted by different structural parameters on the transition temperatures.

3.1. *5-Substituted 2-phenyl-1,3-dithianes*

In the 5-alkyl-2-(4-cyanophenyl)-1,3-dithianes, contrary to the majority of analogous cyclohexane and 1,3-dioxane derivatives no mesomorphic behaviour was observed (scheme 1).

We synthesized different three ring compounds incorporating the 2-phenyl-1,3-dithiane structural unit (tables 2 and 3) and we have found that the nematic–isotropic



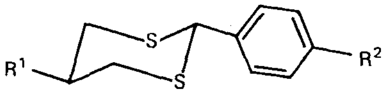
C 30 (S 17) N 59 I [15]

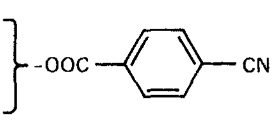
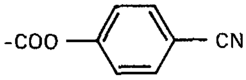
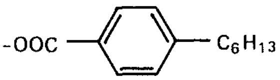
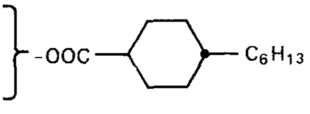
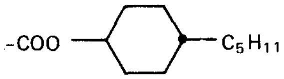
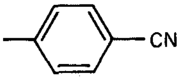
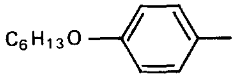
C 59 (N 56) I [1]

C 99 I [13]

Scheme 1.

Table 2. Mesomorphic properties of the 2-phenyl-1,3-dithiane derivatives **5.1**–**5.10** and **7.1**.

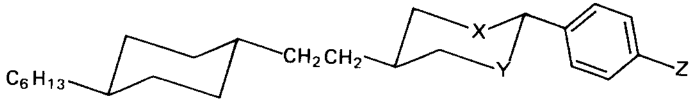


Compound	R^1	R^2	C		S		N		I
5.1	C_5H_{11}-		●	160	–	–	●	251	●
5.2	C_6H_{13}-		●	156	–	–	●	245	●
5.3	C_7H_{15}-		●	155	–	–	●	232	●
5.4	C_7H_{15}		●	127	–	–	●	215	●
5.5	C_6H_{13}-		●	111	–	–	●	164	●
5.6	C_6H_{13}-		●	140	–	–	●	184	●
5.7	C_7H_{15}-		●	134	–	–	●	178	●
5.8	C_6H_{13}-		●	115	–	–	●	155	●
5.9	C_5H_{11}-		●	134	–	–	●	222	●
5.10	C_6H_{13}-	$-COOC_2H_5$	●	90	(●	50)	–	–	●
7.1		-CN	●	128	–	–	●	182	●

transition temperatures of the 1,3-dithianes are always somewhat higher than those reported for the cyclohexane and 1,3-dioxane derivatives.

In order to obtain more information about the relationship between structure and liquid-crystalline properties we investigated the properties of some 5-(*trans*-4-hexylcyclohexane-ethyl)-2-phenyl-1,3-dioxanes **1.1**–**1.7** and 5-(*trans*-4-hexylcyclohexane-ethyl)-2-phenyl-1,3-dithianes **6.1**–**6.7** with different substituents attached to the 2-phenyl ring (table 3). Two 2-phenyl-1,3-oxathianes, **3.1** and **3.2**, are also included

Table 3. Comparison of the liquid-crystalline properties of the 5-(*trans*-4-hexylcyclohexane-ethyl)-2-phenyl-1,3-diheterocyclohexane derivatives **1.1–1.7**, **3.1**, **3.2** and **6.1–6.7**.



	X, *Y* = O										*X* = O, *Y* = S								*X*, *Y* = S							
Z	Compound	C		S_B		S_A		N		I	Compound	C		S_B		N		I	Compound	C		S_B		N		I
NO_2	**1.1**	●	99	-	-	●	103	●	158	●									**6.1**	●	135	-	-	●	162	●
CN	**1.2**	●	93	-	-	●	113	●	172	●	**3.1**	●	76	-	-	●	171	●	**6.2**	●	136	-	-	●	181	●
Cl	**1.3**	●	77	-	-	-	-	●	142	●									**6.3**	●	120	-	-	●	154	●
H	**1.4**	●	75	-	-	-	-	(●	74)	●									**6.4**	●	137	-	-	-	-	●
C_4H_9	**1.5**	●	40	●	153	-	-	-	-	●									**6.5**	●	60	●	206	-	-	●
OC_2H_5	**1.6**	●	61	-	-	●	140	●	163	●	**3.2**	●	76	●	150	●	161	●	**6.6**	●	82	●	196	-	-	●
$N(CH_3)C_2H_5$	**1.7**	●	<20	●	101	-	-	-	-	●									**6.7**	●	<20	●	147	-	-	●

in this comparison. This shows that the clearing temperatures of the 1,3-dithiane derivatives are always significantly higher than those of the corresponding 1,3-dioxane compounds. It is also evident from these values that strongly electron attracting substituents such as –CN, –Cl and $-NO_2$ give rise to rather small clearing temperature differences between dioxane and dithiane derivatives, whereas these differences are much more significant for compounds with electron donating substituents such as *n*-butyl, –OEt, –N(Me)Et at the 2-phenyl ring. Furthermore, these differences increase with increasing electron donating properties of the substituent *Z*. The Hammet substituent constants are empirical values for the quantitative evaluation of the electron donating and electron accepting properties of different substituents at the aromatic ring [16]. A plot of the clearing point differences between dioxanes and dithianes against the Hammet constants σ_p gives a rather good linear relationship, as shown in figure 3.

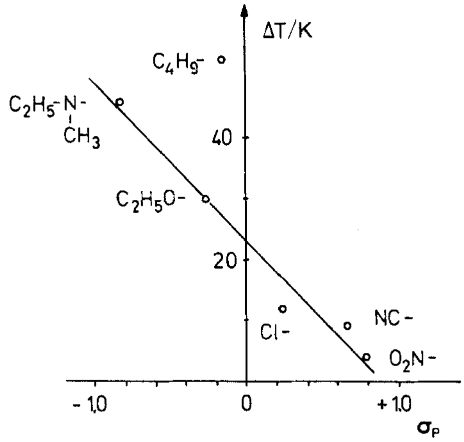
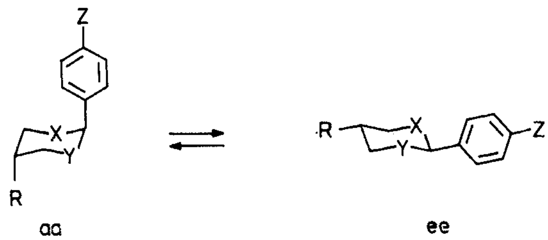


Figure 3. Plot of the clearing point differences $\Delta T = T_{cl.6} - T_{cl.1}$ against the σ_p values of the substituents *Z* in the phenyl ring.

This dependence of the clearing temperature differences on the kind of substituent attached to the aromatic ring should, at least partly, be due to conformational effects, which influence the conformational equilibria aa $\rightleftharpoons$ ee of the 1,3-dioxanes and 1,3-dithianes to a different extent (scheme 2). Although the 2-phenyl group strongly prefers the equatorial position in 1,3-dioxanes, the equatorial preference is much less significant in 1,3-dithianes, due to different ring geometries [17]. In this way the conformational equilibrium aa $\rightleftharpoons$ ee in 1,3-dithianes is more sensitive to conformational effects, caused by the different electron accepting properties of the 2-phenyl ring. Indeed, we have recently found from N.M.R. investigations that for the 1,3-dithianes the equilibrium aa $\rightleftharpoons$ ee depends on the electron accepting properties of the substituent *Z* [18]. As a result strong electron acceptors give rise to a slightly enhanced proportion of the aa conformer in the equilibrium aa $\rightleftharpoons$ ee. Because an increased amount of the more spherical conformer, aa, should lower the clearing temperature, this observation is in agreement with the liquid-crystalline behavior of the 1,3-dithiane derivatives investigated.

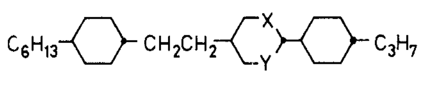
The mesophase types are essentially the same for 1,3-dioxane, 1,3-dithiane and the parent cyclohexane derivatives.



Scheme 2.

3.2. *5-Substituted 2-cyclohexyl-1,3-dithianes*

As we have described, the mesomorphic properties of the 1,3-dithiane derivatives depend upon the kind of substituent attached to the anomeric C-2 atom. Since the cyclohexyl moiety has a large equatorial preference in the axial–equatorial conformational equilibrium [17], the 2-cyclohexyl-substituted 1,3-dithianes should exhibit broad mesomorphic ranges. Indeed, the 1,3-dithiane **6.8** has a significantly higher clearing temperature than the 1,3-oxathiane **3.3** and the 1,3-dioxane **1.8** (scheme 3).



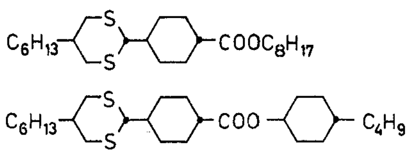
Comp.	*X*	*Y*	*C*		S_B		I
1.8	O	O	●	<25	●	188	●
3.3	O	S	●	<25	●	202	●
6.8	S	S	●	67	●	249	●

Scheme 3.

We synthesized a large number of differently substituted 2-cyclohexyl-1,3-dithianes, which are summarized in tables 4 and 5. All of these 1,3-dithiane derivatives have broad mesomorphic ranges. Indeed, the two ring 2-cyclohexyl-1,3-dithianes **5.12–5.14** exhibit S_B phases with surprisingly high clearing temperatures.

The esterification of the *trans*-4-(*trans*-5-hexyl-1,3-dithian-2-yl)-cyclohexane carboxylic acid **5.15** gave a wide variety of different carboxylates **5.17–5.33**. The simple alkyl carboxylates **5.16–5.19** exhibit only S_B phases. Surprisingly, the introduction of a cyclohexane ring into the alkyloxy group of these carboxylates does not influence their mesomorphic properties (scheme 4). The various phenyl carboxylates also exhibit nematic and S_A phases.

The birefringence of compounds **5.16** and **5.20** have been determined by extrapolation from their binary mixtures and have been found to be rather low ($\Delta n_{20^\circ C} = 0{\cdot}04$ and $\Delta n_{30^\circ C} = 0{\cdot}11$ respectively).

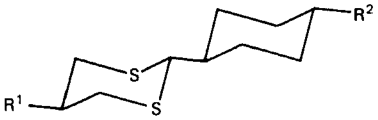


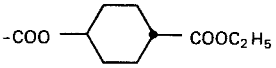
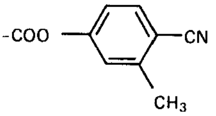
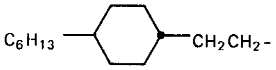
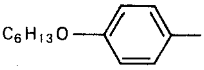
C 54 S_B 116 I

C 55 S_B 120 I

Scheme 4.

Table 4. Mesomorphic properties of the 2-cyclohexyl-1,3-dithiane derivatives **5.12–5.24**, **6.8** and **7.2–7.6**.

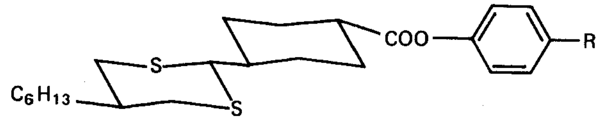


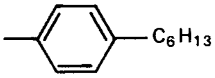
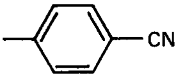
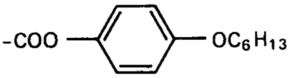
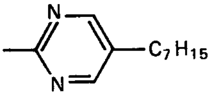
Compound	R^1	R^2	C		S_B		S_A		N		I
5.12	C_6H_{13}-	$-C_3H_7$	●	44	●	132	–	–	–	–	●
5.13		$-C_6H_{13}$	●	57	●	146	–	–	–	–	●
5.14		$-C_7H_{15}$	●	62	●	138	–	–	–	–	●
5.15		-COOH	●	220	–	–	–	–	●	230	●
5.16		$-COOC_2H_5$	●	61	●	136	–	–	–	–	●
5.17		$-COOC_4H_9$	●	50	●	122	–	–	–	–	●
5.18		$-COOC_8H_{17}$	●	54	●	116	–	–	–	–	●
5.19		$-COOCH(CH_3)C_6H_{13}$	●	60	●	123	–	–	–	–	●
5.20		$-COOCH_2CH_2CN$	●	85	●	126	–	–	–	–	●
5.21			●	55	●	120	–	–	–	–	●
5.22			●	64	●	118	–	–	–	–	●
5.23			●	60	●	121	–	–	–	–	●
5.24			●	100	–	–	●	118	●	174	●
6.8		$-C_3H_7$	●	67	●	249	–	–	–	–	●
7.2		$-C_3H_7$	●	104	●	211	–	–	–	–	●
7.3		$-C_4H_9$	●	110	●	215	–	–	–	–	●
7.4		$-C_5H_{11}$	●	105	●	217	–	–	–	–	●
7.5		$-C_7H_{15}$	●	100	●	211	–	–	–	–	●
7.6		$-C_8H_{17}$	●	94	●	207	–	–	–	–	●

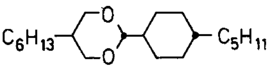
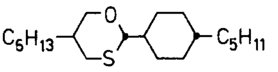
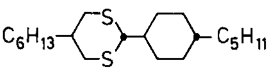
3.3. *1,3-Oxathiane derivatives*

The transition temperatures of the 5-substituted 2-cyclohexyl-1,3-oxathianes are given in table 6. There are many similarities between 1,3-dithaine and 1,3-oxathiane derivatives: e.g. the mesomorphic phase sequences are essentially the same in both cases. However, the clearing temperatures of the oxathiane compounds are significantly

Table 5. Mesomorphic properties of the 2-cyclohexyl-1,3-dithiane derivatives **5.25–5.33**.



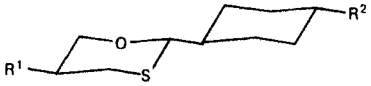
Compound	*R*	C		S_B		S_A		N		I
5.25	$-C_5H_{11}$	●	45	●	185	–	–	●	192	●
5.26	$-C_6H_{13}$	●	70	●	187	–	–	●	191	●
5.27	$-OC_4H_9$	●	85	●	186	–	–	●	219	●
5.28	$-OC_5H_{11}$	●	95	●	187	–	–	●	211	●
5.29	$-CN$	●	130	–	–	–	–	●	228	●
5.30		●	91	●	226	●	238	●	286	●
5.31		●	102	●	174	●	179	●	315	●
5.32		●	111	–	–	–	–	●	298	●
5.33		●	109	–	–	–	–	●	276	●

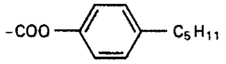
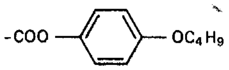
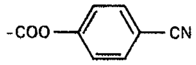
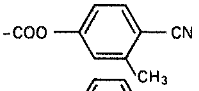
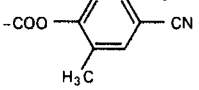
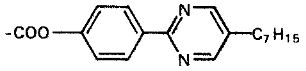
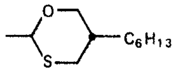
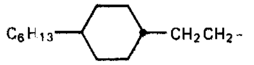
	C	20	S_B	98	I
	C	74	S_B	99,2	I
	C	57	S_B	146	I

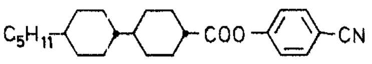
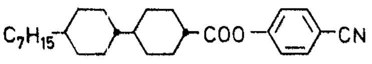
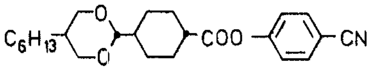
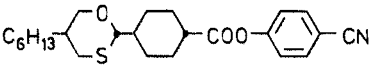
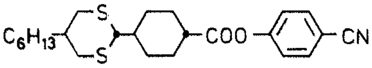
Scheme 5.

lower in most cases (schemes 5 and 6). This could be due to the different bond angles and bond lengths of the C–O and C–S bonds, which lead to some deviations from a linear molecular geometry. Generally the clearing temperatures of the 1,3-oxathianes are comparable with those of the corresponding 1,3-dioxane derivatives, although the transition temperatures of the former are slightly higher. This behaviour could, possibly, be caused by the enhanced polarizability of the sulphur-containing compounds. This reinforces the intermolecular attraction and overcompensates the disturbance caused by the deviation from linearity, leading to increased mesophase stability.

Table 6. Liquid-crystalline properties of the 2-cyclohexyl-1,3-oxathiane derivatives **2.1**–**2.13** and **3.3**.

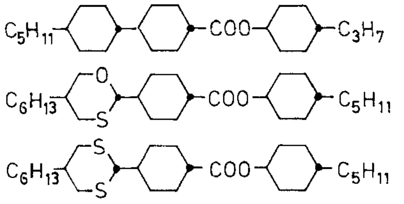


Compound	*R*¹	*R*²	C		S_B		S_A		N		I
2.1	C_6H_{13}	$-C_5H_{11}$	●	75	●	99	–	–	–	–	●
2.2		$-COOH$	●	179	–	–	–	–	●	201	●
2.3		$-COOCH_3$	●	82	(●	73)	–	–	–	–	●
2.4		$-COOC_9H_{19}$	●	56	(●	55)	–	–	–	–	●
2.5		$-COOCH_2CH_2CN$	●	90	(●	80)	–	–	–	–	●
2.6			●	82	●	138	–	–	●	163	●
2.7			●	55	●	123	–	–	●	157	●
2.8			●	74	●	141	–	–	●	185	●
2.9			●	103	–	–	(●	70)	●	205	●
2.10			●	86	–	–	(●	58)	●	137	●
2.11			●	116	–	–	–	–	●	185	●
2.12			●	118	–	–	–	–	●	256	●
2.13			●	140	●	166	–	–	●	186	●
3.3		$-C_3H_7$	●	<25	●	202	–	–	–	–	●

	C	92	N	232	I			[19]
	C	90	S	118	N	222	I	[19]
	C	96	N	191	I			
	C	103	(S_A	70)	N	205	I	**2.9**
	C	130	N	228	I			**5.29**

Scheme 6.

There is, however, one exception. The oxathiane derivative **2.6** has a much higher clearing temperature than the corresponding dithiane derivative **5.22** (scheme 7). We can find no simple explanation for this behaviour.



C	64	S	175	N	183	I	[19]
C	81	S	137	N	163	I	**2.6**
C	64	S	118	I			**5.22**

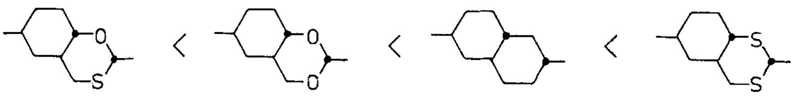
Scheme 7.

The birefringence of some representative oxathiane derivatives have been measured to 0·10, 0·075 and 0·12 for the compounds **2.1**, **2.6** and **2.8** respectively. The melting enthalpies of two representative compounds have been determined by differential scanning calorimetry; they are **2.1**, $\Delta_F H = 24{\cdot}1\,\mathrm{kJ\,mol^{-1}}$, **2.6**, $\Delta_F H = 25{\cdot}9\,\mathrm{kJ\,mol^{-1}}$. A value of $\eta_{20°C} = 36\,\mathrm{mm^2\,s^{-1}}$ has been found for the kinematic viscosity of compound **2.8**.

3.4. *1,3-Dithiadecalins and 1-oxa-3-thiadecalins*

The transition temperatures of the synthesized derivatives of 2-phenyl-1,3-dithiadecalin and 1-oxa-3-thiadecalin, together with the values of the 1,3-dioxadecalins [3] are compared in table 7. We see that the 1,3-dithiadecalin derivatives exhibit clearing temperatures enhanced by approximately 60–70 K compared with the analogous 1,3-dioxadecalins. Surprisingly, the nematic–isotropic transition temperatures of the 1-oxa-3-thiadecalins are considerably lower (by 20 K) than those of the corresponding 1,3-dioxadecalins. At the same time the melting points of the 1-oxa-3-thiadecalins are generally higher. Therefore only monotropic mesophases have been observed for compounds **4.1**–**4.4**.

In this way the order of mesophase stability shown in scheme 8 results.



Scheme 8.

All synthesized compounds **4**, **8** and **9** exhibit only nematic phases. This is also true for the 2-cyclohexyl substituted 1,3-dithiadecalins **8.10**–**8.16** with the exception of compound **8.16**, which exhibits a narrow S_A phase region. These compounds are summarized in table 8.

4. Concluding remarks

A wide variety of different substituted sulphur-containing heteroalicyclic compounds have been synthesized. From the behaviour of these the following conclusions can be drawn.

The mesophase stability of the 1,3-dithiane derivatives depends upon the kind of substituent attached to the anomeric C-2 atom.

Table 7. Comparison of the liquid-crystalline behaviour of the 1,3-dioxadecalin [3], 1-oxa-3-thiadecalin and 1,3-dithiadecalin derivatives **9.1–9.9**, **4.1–4.5** and **8.1–8.9**.

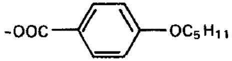
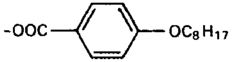
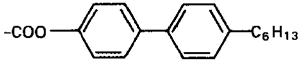
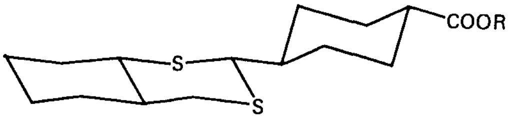
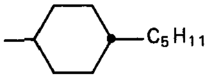
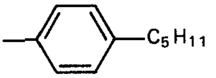
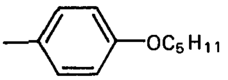
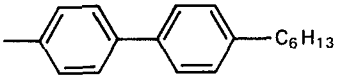
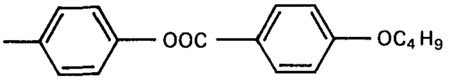
	X, *Y* = O						*X* = O, *Y* = S						*X*, *Y* = S					
R	Compound	C		N		I	Compound	C		N		I	Compound	C		N		I
	**9.1**	●	102	(●	74)	●							**8.1**	●	133	●	145	●
	**9.2**	●	95	(●	84)	●							**8.2**	●	112	●	145	●
	**9.3**	●	113	(●	66)	●							**8.3**	●	111	●	128	●
	**9.4**	●	112	●	135	●	**4.1**	●	137	(●	115)	●	**8.4**	●	155	●	204	●
	**9.5**	●	113	(●	112)	●	**4.2**	●	135	(●	94)	●	**8.5**	●	170	●	185	●
	**9.6**	●	94	●	115	●	**4.3**	●	119	(●	100)	●	**8.6**	●	133	●	181	●
	**9.7**	●	96	●	99	●	**4.4**	●	107	(●	84)	●	**8.7**	●	110	●	165	●
	**9.8**	●	68	●	97	●							**8.8**	●	112	●	143	●
	**9.9**	●	97	●	214	●	**4.5**	●	142	●	206	●	**8.9**	●	150	●	254	●

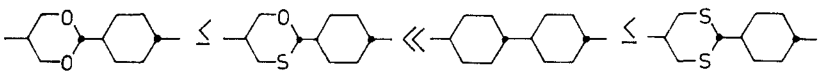
Table 8. Mesomorphic properties of the 2-cyclohexyl-1,3-dithiadecalin derivatives **8.10–8.16**.



Compound	*R*	C		S_A		N		I
8.10	-H	●	203	-	-	-	-	●
8.11	$-C_2H_5$	●	78	-	-	-	-	●
8.12		●	128	-	-	●	149	●
8.13		●	83	-	-	●	143	●
8.14		●	105	-	-	●	162	●
8.15		●	141	-	-	●	277	●
8.16		●	133	●	145	●	310	●

2-Phenyl substituted 1,3-dithiane compounds have a lower mesophase stability than the comparable 2-cyclohexyl substituted ones.

The clearing temperatures depend on the kind of substituent attached to the phenyl ring, electron acceptors decrease and electron donators increase the mesophase stability.



Scheme 9.

The 1,3-oxathianes have lower clearing temperatures than the corresponding 1,3-dithianes, but higher clearing temperatures than the 1,3-dioxanes.

The order of mesophase stability shown in scheme 9 results.

The kind of mesophases formed by the different heteroalicycles and the parent cyclohexane derivatives are essentially the same.

The order of mesophase stability is reversed for the cyclohexane annulated compounds: 1-oxa-3-thiadecalins < 1,3-dioxadecalins < 1,3-dithiadecalins.

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