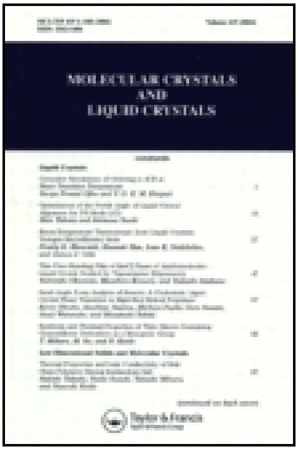

Molecular Crystals and Liquid Crystals

Sulphur-Containing Saturated Rings as Structural Fragments in Liquid Crystals

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Sulphur-Containing Saturated Rings as Structural Fragments in Liquid Crystals

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The effect on the physicochemical properties of liquid crystals of introducing sulphur-containing saturated fragments into their molecular structure is discussed and rationalized in terms of existing theories; a comparison is made with the other saturated derivatives.

Keywords: liquid crystals; physicochemical properties; sulphur

INTRODUCTION

In continuation of our study of the structure–property relationships in sulphur-containing liquid crystals (see, for example, the previous publications Refs. 1–3), we present here a review that examines in some detail the effect of the introduction of sulphur-containing saturated fragments into the molecular structure of liquid crystals on the appearance of the mesophases and their physicochemical properties. When possible, the physicochemical properties of the sulphur derivatives are compared with those of the corresponding saturated liquid crystals.

MESOMORPHIC PROPERTIES

The phase-transition temperatures of some sulphur-containing liquid crystals and the corresponding reference compounds are presented in Tables 1–4, where G, Cr, SmB, SmC*, SmA, N, Ch, and I are the glassy, crystalline, smectic B, smectic C*, smectic A, nematic, cholesteric, and isotropic phases, respectively; X is an uncharacterized

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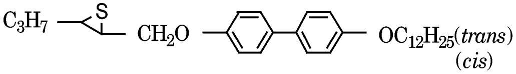
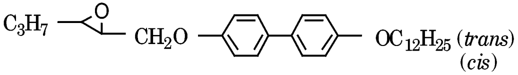
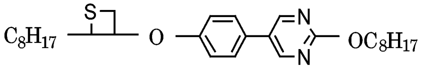
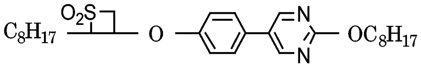
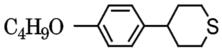
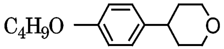
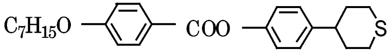
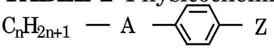
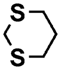
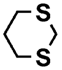
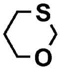
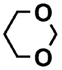
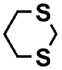
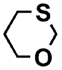
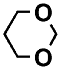
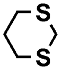
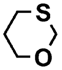
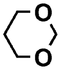
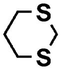
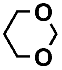
TABLE 1 Physicochemical Properties of Liquid Crystals

No.	Compound	Phase transitions, °C	Ps, $nCcm^{-2}$	Ref.
1-1	 (*trans*) (*cis*)	Cr 112 I Cr 84 I	$<0.3^a$ 15^a	[4]
1-2	 (*trans*) (*cis*)	Cr 118 SmB 124.7 SmA 128.5 I Cr 86 I	13^b 35^b	[4]
1-3		Cr 47 SmA 59.5 I	10^b	[5]
1-4		Cr 91.5 I	50^b	[5]Z
1-5		Cr 58 I		[6]
1-6		Cr 51 I		[5]
1-7		Cr 115 N (80) I		[6]
1-8		Cr 80 Sm 92 N 130 I		[6]
1-9		Cr 128 Sm 168 I		[6]

^{a,b}Extrapolated from the liquid-crystal mixture at 20°C and 30°C, respectively.

TABLE 2 Physicochemical Properties of Liquid Crystals:

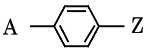


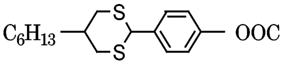
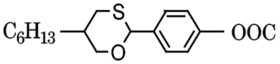
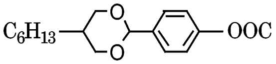
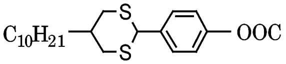
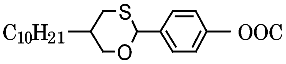
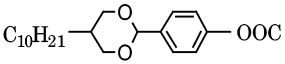
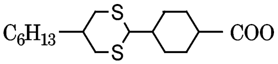
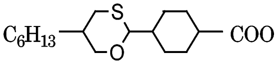
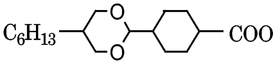
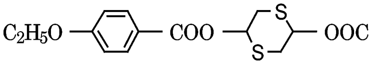
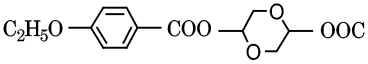
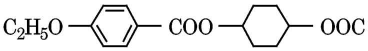
No.	n	A	Z	Phase transitions, °C	Δε[a]	Δn[a]	Ref.
2-1	6		OC_2H_5	Cr 58 SmA (27) N 46 I			[15]
2-2	6		OC_2H_5	Cr 61 N (43) I			[16]
2-3	6		OC_2H_5	Cr 58 N (32) I			[16]
2-4	6		OC_2H_5	Cr 48 SmA (34) N 48 I			[17]
2-5	4		OC_4H_9	Cr 68 I			[18]
2-6	4		OC_4H_9	Cr 37 N 45 I			[19]
2-7	4		OC_4H_9	Cr 44 N (40) I			[17]
2-8	4		OC_4H_9	Cr 42 X (30) I			[20]
2-9	6		CN	Cr 90 I			[16]
2-10	6		CN	Cr 73 N (17) I			[16]
2-11	6		CN	Cr 48 N (42) I			[17]
2-12	6		CN	Cr 42 N 47 I			[21]
2-13	3		SF_5	Cr 93 I	22.3	0.096	[22]
2-14	3		SF_5	Cr 69 I	20.3	0.091	[22]
2-15	3		SF_5	Cr 11 I	12	0.087	[22]

[a] Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.

mesophase. Values given in parentheses refer to monotropic phase transitions.

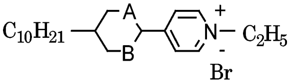
As is evident from Table 1, neither *trans* nor *cis* isomers of the thiirane derivative **1-1** are mesomorphic. The mesomorphic properties of

TABLE 3 Mesomorphic Properties of Liquid Crystals: 

No.	A	Z	Phase transitions, °C	Ref.
3-1		CN	Cr 156 N 245 I	[23]
3-2		CN	Cr 108 SmA 111 N 224 I	[24]
3-3		CN	Cr 135 Sm 170 N 232 I	[25]
3-4		R*	Cr 92 Sm (58) Ch 138 I	[26]
3-5		R*	Cr 88 Sm (47) Ch 122 I	[26]
3-6		R*	Cr 69 Sm (51) SmC* (58) Ch 123 I	[26]
3-7		CN	Cr 130 N 228 I	[23]
3-8		CN	Cr 103 SmA (70) N 205 I	[23]
3-9		CN	Cr 96 N 191 I	[27]
3-10		OC_2H_5	Cr 209 I	[28]
3-11		OC_2H_5	Cr 193 SmA (103) N (119) I	[28]
3-12		OC_2H_5	Cr 178.5 N 200.5 I	[28]

$R^* = OCH_2CH^*(CH_3)C_2H_5$.

TABLE 4 Physicochemical Properties of Liquid Crystals:



No.	A	B	Phase transitions, °C	d, Å	Ref.
4-1	S	S	G 5 SmA 188 I	39.4	[31]
4-2	S	O	G-7 SmA 166 I	38.9	[32]
4-3	O	O	G-24 SmA 152 I	38	[32]

the corresponding oxirane derivative **1-2** are more pronounced, with the smectic B and smectic A phases recorded for the *trans* isomer.

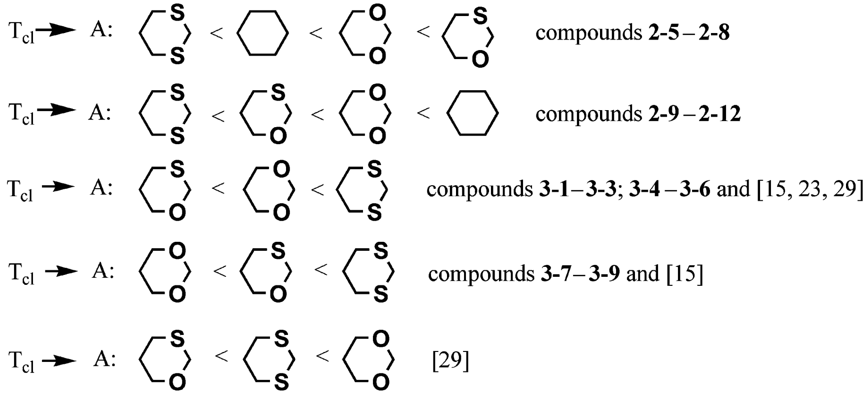
The crystal structures of 3-substituted thietane and thietane dioxides reveal that in the solid state they exist in the puckered structure (with a dihedral angle of 26° for thietane [7] and 43° for thietane dioxide [8]), with S=O bond equatorial in the oxides and the 3-substituted axial for the *trans* isomers. For thietane dioxide, the NMR data agree with either a planar structure or, more likely, a rapid interconversion between two equivalent conformers, as is the case for the unsubstituted thietane [9]. These structural features can be responsible for a low smectic A thermostability of the thietane derivative **1-3** and the absence of the mesophases in the corresponding thietane dioxide derivative **1-4**.

It has been reported that the distortion of tetrahydrothiapyran, which exists in the chair conformation [10], pushes the syn-axial hydrogens closer together than in the cyclohexane [11]. The corresponding tetrahydropyran ring is slightly flatter than cyclohexane [11]. Its molecule resembles cyclohexane in geometry except for the short C–O bond (1.41 Å) compared with the C–C bond (1.54 Å). Although these two rings have very similar chair-to-twist ring-reversal processes [11], because the mesomorphic properties of liquid crystals are influenced by the packing of their molecules [1–3], it can be proposed that the introduction of tetrahydrothiapyran and tetrahydropyran into the molecular structures leads to molecular packing, which is not favorable for the formation of the mesophases in their two-ring derivatives (compounds **1-5** and **1-6**, Table 1). A slightly increased melting point (crystal–smectic, crystal–nematic, or crystal–isotropic phase-transition temperature) of the former compound has been correlated with its larger dipole moment [6]. As can be seen from Table 1, the three-ring tetrahydropyran derivative **1-7** exhibits low nematic thermostability.

The preference for oxygen to be axial in sulphoxides [12] results in the moderate nematic thermostability of compound **1-8**. The mesomorphic properties of the sulphone derivative **1-9** (which shows the highest melting point among compounds **1-7–1-9**) can be affected by the findings that the axial and equatorial S=O bonds are essentially equal in the gas phase for thiacyclohexane-1,1-dioxide [13].

The dihedral angles in the 1,3-dithiane about the various bonds are similar or slightly greater than those in cyclohexane, showing the ring to be marginally more puckered [12]. It prefers the chair geometry and the ΔGo value (the energy difference between the chair and the twist conformers) of 9.4 kcal mol^{-1} is not so different from the values of 9.9 kcal mol^{-1} and 10.3 kcal mol^{-1} recorded for the

1,3-dioxane and cyclohexane, respectively [11]. A study of the equilibrium between *trans* (chair) and *cis* (twist) isomer conformations show and suggest that 1,3-dithiane can adopt the twist conformation much more readily than 1,3-dioxane and cyclohexane [11]. 1,3-oxathiane ring has the expected chair conformation. The coupling constant measurements suggest that the oxygen side of the ring is slightly more puckered than in 1,3-dioxane, and the sulphur side slightly flatter than in 1,3-dithiane. Because of the asymmetry of the ring, two enantiomeric chair conformations exist that may be interconverted by a ring-inversion process [12]. It has been reported that the array of strong delocalizing interactions at C_5 carbon are similar in all these three hetero rings under consideration, and it explains the relative elongation of the equatorial C–H bonds. At all of the other carbons in 1,3-dioxane, 1,3-oxathiane, and 1,3-dithiane, the axial bonds are found to be longer as a result of the dominant anomeric interactions. An important difference between 1,3-dioxane and 1,3-dithiane, however, is that the anomeric interactions in the latter ring are strong, outweighing the strong equatorial delocalizing interactions, whereas the analogous interactions in 1,3-dithiane are rather weak and become dominant only because the competing equatorial interactions are even weaker [14]. It has been demonstrated that the 1,4-dioxane ring has a chair conformation that is slightly more puckered than cyclohexane with average internal ring dihedral angles of 57.9° [12]. The absence of specific interactions in the 1,4-dithiane ring makes it considerably more puckered than cyclohexane [12]. It can be expected that these structural differences of the discussed molecular fragments affect the mesomorphic properties of the corresponding *trans*-1,3-dithian-2,5-diyl, *trans*-1,3-oxathian-2,5-diyl, *trans*-1,3-dioxan-2,5-diyl, *trans*-1,4-dithian-2,5-diyl, *trans*-1,4-dioxan-2,5-diyl, and *trans*-1,4-cyclohexylene derivatives presented in Tables 2–4. As is evident from Table 2, the direction of sulphur atoms of the *trans*-1,3-dithiane ring introduced into the molecular core of two-ring alkyl-alkoxy derivatives plays an important role in the formation of the mesophases. So, pointing sulphur atoms toward the hexyl group results in the formation of the monotropic smectic A and the nematic phases (compound **2-1**), whereas the opposite leads to the disappearance of the smectic phase and the formation of the monotropic nematic phase with slightly reduced thermostability (compound **2-2**). The replacement of the latter ring by the *trans*-1,3-oxathian-2,5-diyl and *trans*-1,3-dioxan-2,5-diyl fragments lowers (compound **2-3**) and increases (compound **2-4**) the clearing temperatures (T_{cl}, nematic–isotropic or smectic–isotropic phase-transition temperatures), respectively. Changing the molecular structure of



SCHEME 1

liquid crystals may affect the efficiency of the introduced molecular fragments A (Tables 2, 3).

The disturbing effect of the terminal SF_5 group on the mesomorphic properties is so strong [22,30] that the introduction of the *trans*-1,3-dithian-2,5-diyl, *trans*-1,3-dioxan-2,5-diyl, and *trans*-1,4-cyclohexylene into the molecular core of two-ring SF_5 derivatives does not create the mesophases (compounds **2-13–2-15**, Table 2).

As is evident from Table 3 and Ref. 26, the *trans*-1,3-dioxan-2,5-diyl derivatives with the chiral terminal groups exhibit more pronounced appearance of the smectic C^* phase than the corresponding *trans*-1,3-dithian-2,5-diyl and *trans*-1,3-oxathian-2,5-diyl derivatives (compounds **3-4–3-6**).

It can be seen from Tables 1–3 that the presence of sulphur atoms in the saturated fragments increases the melting temperatures of liquid crystals with respect to those of the corresponding oxygen and parent derivatives (except compounds **1-1** and **1-2**, Table 1). Similar trends can be observed for the 1,4-dithian-2,5-diyl and corresponding reference derivatives (compounds **3-10–3-12**, Table 3), ionic liquid crystals (which exhibit an increase in the layer spacing when replacing oxygen by a larger sulphur [33], compounds **4-1–4-3**, Table 4) and other sulphur derivatives [23,34–37].

It can be proposed that the electronic and geometrical structures of sulphur-containing rings [7,9–12,14,33,38–47] and the corresponding saturated fragments [7,11,12,14,42–44,48–50] play a very important role in the intra- [14,51] and intermolecular [52–56] interactions affecting molecular packing, which predominantly influences mesophase stability [52–57]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, depending on the electron-density distribution in the molecular groups and fragments under consideration, also influence the packing and hence the stability of the mesophases but play a secondary role compared with the steric factors [57]. Other molecular aspects such as the association [56] or dipole–dipole attraction in polar liquid-crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [57].

STATIC DIELECTRIC PROPERTIES

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are, dielectric constants that are parallel and perpendicular to the nematic director **n,** respectively, and the molecular structure of liquid crystals is described by the theory of Maier and Meier [58]:

$$\Delta\varepsilon = \mathrm{NhF}/\varepsilon_o[\Delta\alpha - \mathrm{F}\mu^2/\mathrm{kT}(1 - 3\cos^2\beta)]\mathrm{S}, \tag{1}$$

where $\mathrm{h} = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = \varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$; $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy; F is the cavity reaction field; μ is the dipole moment; β is the angle between the molecular long axis and the dipole moment; N is the number of molecules per unit volume; and S is the order parameter. It has been shown that meaningful comparisons of the dielectric (as well as optical and elastic) properties of liquid crystals with different nematic–isotropic phase-transition temperatures $\mathrm{T_{N\text{-}I}}$ can only be made at a constant reduced temperature $\tau = \mathrm{T_{meas}/T_{N\text{-}I}}$ [59].

Table 2 presents data on the dielectric properties of liquid-crystal compounds extrapolated from the liquid-crystalline mixtures at 20°C. According to Ref. 59, the extrapolations are not meaningful; however, these estimations are the only way to obtain a rough definition of the dielectric (as well as optical) properties of nonmesomorphic compounds, smectic liquid crystals, and liquid crystals with a narrow nematic range. The order of increasing the dielectric anisotropy of compounds **2-15**, **2-14**, and **2-13** (Table 2) corresponds to the order of increasing the dipole moments of the molecular fragments: cyclohexane, 1,3-dioxane, 1,3-dithiane: 0, 2.15, 2.62 D [60,61].

OPTICAL PROPERTIES

The phenomenological relation between refractive index and the electric polarization is defined as [62,63]:

$$(\mathrm{n}^{*^2} - 1)/(\mathrm{n}^{*^2} + 2) = \mathrm{N}\alpha^*/3\varepsilon_o, \tag{2}$$

where the mean polarizability $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$; the mean refractive index $\mathrm{n}^{*^2} = (\mathrm{n_e^2} + 2\mathrm{n_o^2})/3$; and $\mathrm{n_o}$ is the ordinary and $\mathrm{n_e}$ is the extraordinary refractive indices. From Eq. (2) and the previous paragraph, it follows that sulphur-containing compounds that have a larger induced polarizability [64] exhibit the optical anisotropy $\Delta n = n_e - n_o$, which is larger than that of the corresponding oxygen-containing derivatives and parent systems (compounds **2-13**, **2-14**, and **2-15**, Table 2).

VISCOELASTIC PROPERTIES

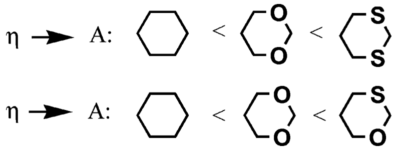
It has been shown that the nematic liquid-crystal materials for display applications should have a low viscosity for giving the acceptable response times to liquid-crystal displays [59,65].

According to Haramoto *et al.* [66,67], the volume viscosity of liquid-crystal materials having the same quantity of the corresponding two-ring *trans*-1,3-dioxan-2,5-diyl, *trans*-1,3-oxathian-2,5-diyl, *trans*-1,3-dithian-2,5-diyl, and *trans*-1,4-cyclohexylene 4-cyanophenyl derivatives increases, depending on the structure A of the fragments, as follows.

These results reveal that the presence of sulphur atoms in the saturated six-membered rings introduced into the molecular core of liquid crystals enhances their viscosity in respect to that of the corresponding oxygen-substituted and parent compounds. The response times τ_{decay}, which are proportional to the volume viscosity [65], show the same behavior for these systems [66,67].

PHYSICOCHEMICAL PARAMETERS OF THE SMECTIC C* PHASE

The spontaneous polarization Ps of the smectic C* liquid crystals is an important parameter because of its linear coupling with an applied electrical field, which is the basis of the application of these materials [68]. The polarization is caused by the cramped rotation of the dipoles of the molecules and varies with the position of these dipoles with respect to the chiral group [68]. The spontaneous polarization Ps is a



SCHEME 2

quantity that is directly related to the response time τ as a switching device [69]:

$$\tau = \gamma_{\varphi} \sin^2 \Theta / \mathrm{P_s E} \tag{4}$$

where γ_{φ} is the rotational viscosity, which refers to the rotation about an axis perpendicular to the director **n** and Ps, Θ is the tilt angle, and E is an applied electric field.

The significant difference in the spontaneous polarization can be observed for the thiirane and oxirane derivatives, with higher values obtained for the latter compounds because of their more pronounced chiral character [49] (compounds **1-1** and **1-2**, Table 1). The *cis* isomers of the thiirane and oxirane derivatives exhibit higher Ps values than the corresponding *trans* isomers. The large steric hindrance to rotation around the molecular long axis in the *cis* isomers could be responsible for the rise of the spontaneous polarization [4].

The strong dipole moment of thietane-1,1-dioxide and the increased rotational hindrance could be a reason for a higher Ps value recorded for the thietane-1,1-dioxide derivative **1-4** compared to that of the corresponding thietane derivative **1-3**, Table 1 and Ref. 5.

CONCLUSION

Systematic studies on the effect of the introduction of the sulphur-containing fragments into the molecular structure on the physico-chemical properties of liquid crystals have been performed, with attempts to correlate the molecular-level parameters with the observed properties. The information presented here may lead to a better understanding of the nature of liquid crystals.

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