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Sulfur as a Structural Element in Calamitic Liquid Crystals. 2 Terminal, Linking, Axial and Lateral Substitutions. 3 Sulfur-Containing Rings

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Sulfur as a Structural Element in Calamitic Liquid Crystals. 2 Terminal, Linking, Axial and Lateral Substitutions. 3 Sulfur-Containing Rings

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The effect on the physico-chemical properties of introducing the sulfur atom into the molecular structure of liquid crystals is discussed and rationalized in terms of existent theories; a comparison is made with the corresponding hydrocarbon and oxygen derivatives.

Keywords Liquid crystals; physico-chemical properties; sulfur

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Introduction

In continuation of our study of the structure–property relationships in sulfur-containing liquid crystals (see, for example, the previous publications [1–6]) we present here a review that examines in some detail the effect of the introduction of the sulfur atom into the molecular structure of calamitic liquid crystals on the appearance of the mesophases and their physico-chemical properties. When possible, the properties of the sulfur derivatives will be compared with those of the corresponding hydrocarbon and oxygen derivatives. Because sulfur significantly differs from oxygen in the electronic and geometrical parameters [2], we would expect to observe the difference in the mesomorphic and physico-chemical properties of the corresponding sulfur, oxygen, as well as hydrocarbon derivatives.

Mesomorphic Properties

The phase transition temperatures of the sulfur derivatives and reference compounds are presented in Tables 1–17 where Cr, Sm, Sm*, SmE, SmC^*_A, SmA*, SmC*, SmC, SmB, SmA, N, Ch, and I denote the crystalline, smectic, chiral smectic, smectic E, chiral smectic C^*_A, A*, C*, smectic C, B, A, nematic, cholesteric, and isotropic phases,

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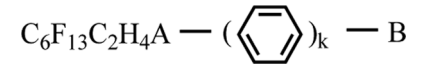
Table 1. Mesomorphic properties of liquid crystals:



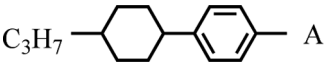
No.	A	k	B	Phase transitions (°C)	Ref.
1-1	SCO	1	NO_2	Cr 87.6 Sm 89.9 I	[7]
1-2	OCO	1	NO_2	Cr 55 Sm (51) l	[8]
1-3	O	1	NO_2	Cr 22 SmA 41 I	[9]
1-4	SCO	2	H	Cr 51.6 SmA 152 I	[10]
1-5	OCO	2	H	Cr 70.5 SmA 72 I	[10]
1-6	O	2	H	Cr 81.4 SmE 96.1 SmA 105.5 I	[10]

respectively. Values given in parentheses refer to monotropic phase transitions. X is an uncharacterized mesophase.

Terminal Substitution

It is evident from Table 1 that the introduction of the thioester connector between the terminal fluorinated group and molecular core of one-ring and two-ring derivatives results in the formation of the smectic phases with the highest clearing temperatures

Table 2. Physico-chemical properties of some liquid crystals:



No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	ν^a ($mm^2 s^{-1}$)	Ref.
2-1	$CH_2SC_4F_9$	Cr 29.6 SmB 39 I				[11]
2-2	$CH_2SC_6F_{13}$	Cr 53.5 SmB 71.8 I				[11]
2-3	SF_5	Cr 11 I	12.0	0.087	133	[12]
2-4	OSF_5	?	5.9	0.089		[13]
2-5	SO_2F	Cr 72 I	**2**2.4[b]	0.063[b]	48[b]	[14]
2-6	$SCHF_2$	Cr 12.5 I	10.6[b]	0.044[b]	18.5[b]	[1]
2-7	$OCHF_2$	Cr −14.9 I	8.3[b]	0.044[b]	5[b]	[1]
2-8	CF_3	Cr 22 I	8.6[b]	0.036[b]		[12]
2-9	CHF_2	Cr l4 I	3.7			[15]
2-10	CH_2F	Cr 7 I				[16]
2-11	F	Cr 31 I	4.3[b]	0.100[b]		[12]
2-12	OC_3H_6F	Cr 38.5 I				[17]
2-13	C_2F_5	Cr 18 I	3.9[b]			[18]
2-14	NCS	Cr 39 N 41 I	12.0[c]	0.170[c]	8[d]	[19]
2-15	CONCS	Cr 33.5 N 38.2 I				[20]

[a]Extrapolated from 10 wt% solution in ZLl-4792 at 20°C.
[b]Extrapolated from 10 wt% solution in ZLI-1132 at 20°C.
[c,d]Extrapolated from 15wt% solution in liquid crystal material at 25°C and 20°C, respectively.

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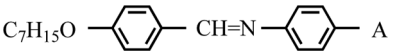
Table 3. Mesomorphic properties ofliquid crystals:



No.	A	Phase transitions (°C)	Ref.
3-1	$C_2F_4SF_5$	I 70 N 62 SmA 53 Sm 52 X	[21]
3-2	F	Cr 57 SmB (56.4) SmA 61.61	[22]
3-3	Cl	Cr 59.4 SmB 89.4 SmA 97.51	[22]
3-4	Br	Cr 64.5 SmB 100.7 SmA 103.8 1	[22]
3-5	I	Cr 80.1 SmB 110.71	[22]

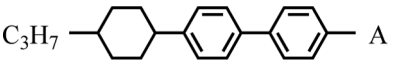
(nematic-isotropic or smectic-isotropic phase transition temperatures) among compounds under consideration. It can be illustrated by the orders of increasing the clearing temperature T_{cl} in dependence on the structure of the connector A:

$$A : O < OCO < SCO \text{ (compounds } \mathbf{1\text{-}1} \text{ to } \mathbf{1\text{-}3}\text{);}$$

$$A : OCO < O < SCO \text{ (compounds } \mathbf{1\text{-}4} \text{ to } \mathbf{1\text{-}6}\text{)}$$

These different orders reveal the importance of the molecular structure of liquid crystals. Similar trends can be observed for two-ring phenylcyclohexanes having CH_2S connectors (compounds **2-1**, **2-2**, Table 2). Though other sulfur and/or

Table 4. Physico-chemical properties of liquid crystals:



No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	v^b ($mm^2 s^{-1}$)	Ref.
4-1	SF_4CF_3	Cr 197 N 209.7 I	10.6	0.150		[23]
4-2	SF_5	Cr l09 N (87.8)	14.3	0.154		[23]
4-3	SO_2F	Cr 156 I	27.1[b]	0.179[b]	200	[14]
4-4	SCF_3	Cr 59 N 109 I				[24]
4-5	CF_3	Cr l34 I	13.0	0.165		[23]
4-6	F	Cr 98.3 N 153.4 I	4.7[c]	0.096[c]	24.4[d]	[25]
4-7	$OCHF_2$	Cr 82 Sm 121.1 N 169.4 I	10.2[b]	0.170[b]		[1]
4-8	OCF_2Cl	Cr 96 Sm 112.5 N 123 I	9.2[b]	0.154[b]		[26]
4-9	OCF_3	Cr 90 SmB 129 N 151.4 I	8.9[b]	0.166[b]	14.0[b]	[27]
4-10	OCH_2CF_3	Cr 100 SmB 170 SmA 194 I				[28]
4-11	C_2F_4Cl	Cr 79 I	9.0			[29]
4-12	$OCF_2CF{=}CF_2$	Cr 43.5 Sm 169.6 N 180.4 I	5.0[e]	0.160[e]		[30]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b]Extrapolated from 10 wt% solution in ZLI-1132 at 20°C.
[c,d]Extrapolated from 20 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[e]Extrapolated from 10 wt% solution in liquid crystal material at 25°C.

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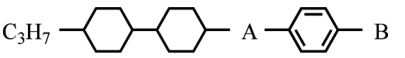
Table 5. Physico-chemical properties of liquid crystals:



No.	A	B	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	Ref.
5-1	CF_2O	SF_5	Cr 67 N 116.5 I	11.8	0.080	[31]
5-2	CF_2O	NCS	Cr 43 N 223.8 1	10.9	0.178	[32]
5-3	COO	SF_5	Cr 90 N 152.8 I	12.3	0.087	[12]
5-4	COO	F	Cr 70.5 N 183.1 I			[33]
5-5	COO	Cl	Cr 82.8 N 214.9 I			[33]
5-6	COO	OCF_3	Cr 52 SmB 126 N 187.4 I	6.2	0.078	[34]
5-7	COS	F	Cr 75.2 Sm 138.4 N 200.1 I			[35,36]
5-8	COO	F	Cr 70.5 N 183.1 I			[33]
5-9	OCO	F	Cr 89.3 N 182.2 I			[37]
5-10	CH_2	F	Cr 63 I			[38]
5-11	C_2H_4	F	Cr 48 Sm 84 N 137 I	6.0^b	0.100^b	[39]
5-12	C_4H_8	F	Cr 56 SmB 87 N 116 I			[40]
5-13	C_3H_6O	F	Cr 78 N 124 I			[40]
5-14	$CH{=}CHCH_2O$	F	Cr 75 N 127 I			[40]
5-15	$CH{=}CHC_2H_4$	F	Cr 33 SmB 74 N 135 I			[40]
5-16	$CH(CH_3)CH_2$	F	Cr 106 N 118 I			[41]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b]Extrapolated from 10 wt% solution in ZLI-1132 at 20°C.

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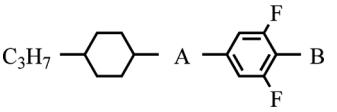
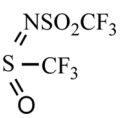
fluorine-containing phenylcyclohexanes are not mesomorphic (compounds **2-3** to **2-13**, Table 2), the isothiocyanato derivatives **2-14** and **2-15** exhibit the nematic phases, which are formed mainly by their dimers [4]. The data presented in Tables 2–6 show that low thermal efficiency of the SF_5 derivatives (see, for example, compounds **2-3**, **4-2**, **5-1**, **5-3**, **6-1**, [52]) can be increased by the introduction of the perfluoroalkyl connector between the terminal SF_5 group and molecular core of liquid crystals, which now show the nematic phase with moderate clearing point compared to those of the corresponding smectic halogen derivatives (compounds **3-1** to **3-5**). It is interesting to note that the introduction of the SF_4 connector between the terminal CF_3 group and molecular core of three-ring derivatives produces only a nematic phase with the highest clearing and melting points among compounds **4-1** to **4-12** presented in Table 4. It can be seen from Tables 2, 4, and 6 that the terminal substitution of liquid crystals by SO_2F, $SCHF_2$, SCF_3, SCH_2CF_3 groups, depending on the liquid crystal's core structure, does not produce any mesophase (compounds **2-5**, **2-6**, **4-3**, **6-2**, **6-3**) or produce it with low thermal efficiency (compound **4-4**) in comparison with those of the corresponding reference compounds. It can be expressed by the following orders of increasing the clearing temperature in dependence on the terminal substituent A (Table 4):

$$\begin{aligned} A : SF_5 < SCF_3 < OCF_2Cl < OCF_3 < F < OCHF_2 \\ < OCF_2CF{=}CF_2 < OCH_2CF_3 < SF_4CF_3 \end{aligned}$$

Table 6. Physico-chemical properties of liquid crystals:



No.	A	B	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	Ref.
6-1		SF_5	Cr 103 I	21.4	0.132	[31]
6-2		$SCHF_2$	Cr 79 I	12.3	0.141	[42]
6-3		SCH_2CF_3	Cr 81 I	7.8	0.134	[42]
6-4		F	Cr 42 N (33) I	12.8	0.142	[43]
6-5		CF_3	Cr 86 I	21.5	0.149	[31]
6-6		OCH_2CF_3	Cr 83 N 104.6 I		0.152	[44]
6-7		OCH_2CF_2H	Cr 81 N 121.6 I	10.4	0.153	[45]
6-8		CF_2CHF_2	Cr 77 I	15.6	0.130	[46]
6-9		$COCF_3$	Cr 57 N (49.5) I		0.164	[47]
6-10		OCF_2CFHCF_3	Cr 60.7 N 127.6 I			[48]
6-11		$OCH_2CF_2CF_2H$	Cr 88 N 91.1 I		0.138	[49]
6-12		NCS	Cr 62.9 N 202.4 I	17.6[b]	0.231[b]	[50]
6-13		$COCF_3$	Cr 43 N 103.5 I	17.5	0.091	[47]
6-14		CF_2CH_3	Cr 66 N 78.9 I	8.6	0.077	[46]
6-15		OCH_2CF_2H	Cr 54 N 155.2 I	7.8	0.089	[49]
6-16			Cr 101 I	18.1	0.119	[51]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b]Extrapolated from 15 wt% solution in liquid crystal material at 20°C.

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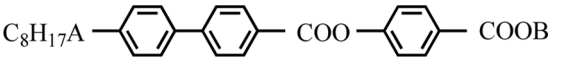
Table 7. Physico-chemical properties of liquid crystals:



No.	A	B	Phase transitions (°C)	$\|P_s\|^a$ (nCcm^{-2})	Θ^a (°)	Ref.
7-1	O	$C^*H(CH_3)CH_2OCH_2CH_2SCH_3$	I 134.4 SmA* 103.9 SmC* 90.1 SmC^*_A67.6 Sm* 39.3 Cr	19	18	[53]
7-2	O	$C^*H(CH_3)CH_2OCH_2CH_2CH_3$	I 159.4 SmA* 126.2 SmC* 87.9 Sm* 39.5 Cr	13	17	[54]
7-3	S	$CH_2C^*H(CH_3)C_2H_5$	Cr 61.5 SmC* 107.5 SmA 146.7 I			[55]
7-4	O	$CH_2C^*H(CH_3)C_2H_2$	Cr 80 SmC* 121 SmA 165 Ch 171 I			[56]
7-5	—	$CH_2C^*H(CH_3)C_2H_5$	Cr 57 SmC* 89 SmA 134 Ch 140 I			[56]

$^a T_{meas} = T_{SmC^*} - {}_{SmA^*} - 20°C$.

As in the case of two-ring derivative, the three-ring isothiocyanato derivatives **5-2**, **6-12** exhibit only nematic phases with low melting (crystal-smectic or crystal-nematic phase transition temperatures) and high clearing points among compounds under consideration. Compound **6-16** is not mesomorphic. It was not expected that the introduction of such a large and branched substituent could produce the mesomorphic properties in compound **6-16**.

It is evident from Tables 7 and 8 that the introduction of the sulfur atom into the chiral chain of chiral liquid crystals, depending on the position and structures of the chains and molecular core, can increase the number of the mesophases (compounds **7-1** and **7-2**) and decrease the smectic C* thermostability and clearing point (compounds **7-1** and **7-2**; **8-4** and **8-5**) compared to those of the corresponding reference compounds. The effect of the introduction of the sulfur atom into the achiral chain of chiral liquid crystals can be illustrated by the following orders of

Table 8. Mesomorphic properties of liquid crystals:

No.	A	B	n	Phase transitions (°C)	Ref.
8-1	$C_8H_{17}S$	O	6	Cr 51 SmA (45) I	[57]
8-2	$C_8H_{17}O$	O	6	Cr 69.9 SmC* 79.6 SmA 96.2 I	[58]
8-3	C_8H_{17}	O	6	Cr 62 SmA (59) I	[59]
8-4	$C_{11}H_{23}O$	S	2	Cr 58.6 SmC* (51.2) SmA 58.5 I	[60]
8-5	$C_{11}H_{23}O$	O	2	Cr 58 SmC* 72.7 SmA 76.7 I	[61]

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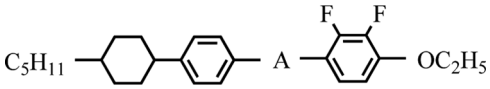
Table 9. Physico-chemical properties of liquid crystals:



No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	η^b (mm^2s^{-1})	Ref.
9-1	SCH_2	Cr 67.7 I	−3.9	0.147		[70]
9-2	CF_2O	Cr 61.4 N 131.4	−4.2			[71]
9-3	OCF_2	Cr 49.9 N 104.91	−4.3	0.108	49	[72]
9-4	CF=CF	Cr 70 N 213.5 I	-5.3^c	0.228^d		[73]
9-5	C≡C	Cr 73 N 21 7 I				[74]
9-6	C_2H_4	Cr 49 SmB (31) N 107.3 I				[75]
9-7	—	Cr 68 SmA 87 N 172 1	-4.1^c	0.180^e	46^e	[76]

[a,b]Extrapolated from 15 wt% solution in liquid crystal material at 25°C and 20°C, respectively.
[c]Extrapolated from 10 wt% solution in ZLI-2857 at 20°C.
[d]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[e]Extrapolated from 10 wt% solution in ZLI-1132 at 20°C.

increasing clearing points in dependence of the structure of the achiral chains: T_{cl}:

R < RS < RO (compounds **7-3** to **7-5**); RS < R < RO (compounds **8-1** to **8-3**);

smectic C* thermostabilities T_s:

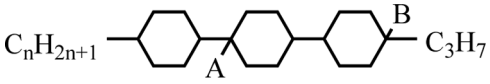
R < RS < RO (compounds **7-3** to **7-5**);

smectic C* ranges ΔTs:

R < RO < RS (compounds **7-3** to **7-5**),

where R, RS, RO are the corresponding alkyl, alkylthio, and alkoxy groups. These orders reveal the importance of the molecular structure of liquid crystals. Another

Table 10. Physico-chemical properties of liquid crystals:



No.	n	A	B	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^b	Ref.
10-1	3	NCS	H	Cr 65 N 103 I	−5.0	0.008	[85]
10-2	3	H	NCS	Cr 110 N 123.1 I	−4.7	0.008	[85]
10-3	5	CONCS	H	Cr 52 N 60.5 I	−3.0	0.004	[85]
10-4	2	H	H	Sm 223.7 I			[86]

[a]Extrapolated from 10 wt% solution in ZLI-2857 at 20°C.
[b]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.

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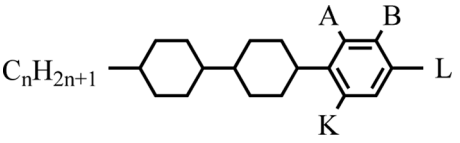
Table 11. Physico-chemical properties of liquid crystals:



No.	n	A	B	K	L	Phase transitions (°C)	Δe^a	Δn^a	Ref.
11-1	3	F	NCS	H	C_3H_7	Cr 35 I	−1.9		[88]
11-2	3	F	F	CH_3	C_3H_7	Cr 82.8 N (44.4) I	-2.6^b	0.127^b	[89]
11-3	3	H	H	H	C_3H_7	Cr <25 Sm l77.5 I			[90]
11-4	5	F	NCS	H	F	Cr 58.9 N (52.4) I	3.5	0.082	[50]
11-5	5	F	F	H	F	Cr 41.7 N 122.5 I	1.8	0.079	[50]
11-6	5	H	H	H	F	Cr 69.4 Sm 75.5 N 157.5 I	7.0^c	0.090^c	[39,91]

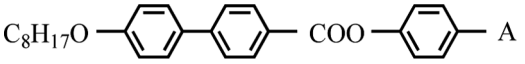
[a]Extrapolated from 15 wt% solution in liquid crystal material at 25°C.
[b]Extrapolated from 15 wt% solution in liquid crystal material Chisso at 25°C.
[c]Extrapolated from 10 wt% solution in ZLI-1132 at 20°C.

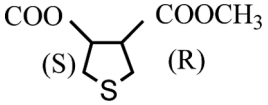
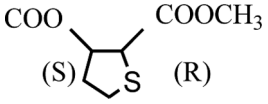
point is that the terminal alkoxy groups favor the formation of the chiral smectic C* phase, which can have a wider range in the corresponding alkylthio derivatives. In the case of compounds presented in Table 8, the introduction of the sulfur atom into the achiral chain of liquid crystals results in the disappearance of the smectic C* phase compared with that of the corresponding alkoxy derivative (compounds **8-1**, **8-2**). Similar trends have been reported for other terminally sulfur substituted liquid crystals [62–69].

Linking Substitution

It is evident from Table 5 that the introduction of the thioester linkage into the molecular core of liquid crystals produces the mesophases that exhibit the highest smectic and nematic thermostabilities in comparison with those of the corresponding

Table 12. Physico-chemical properties of liquid crystals:



No.	A	Phase transitions (°C)	$\lvert P_s\rvert^a$ (nCcm^{-2})	Ref.
12-1		Cr 76.5 SmC* 81.6 I	28	[94]
12-2		Cr 84.7 Sm_2 85.1 Sm_1 97.1 Ch 100.6 I		[94]

[a]Measured as 20 wt% solution in liquid crystal material at 20°C.

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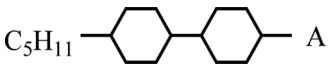
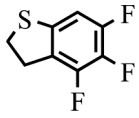
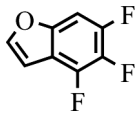
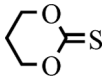
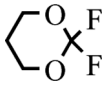
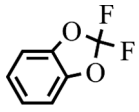
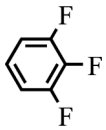
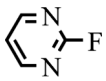
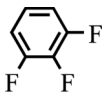
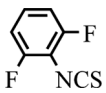
Table 13. Physico-chemical properties of liquid crystals:



No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	$\gamma_1{}^a$ (mPas)	Ref.
13-1		Cr 80 N 153 I	10.1	0.117	1168	[99]
13-2		Cr 75 N 172.5 I	12.6	0.123	698	[99]
13-3		Cr 104 SmB	9.6	0.115		[100]
13-4		Cr 55 SmB 123 I				[100]
13-5		Cr 77 N 93.6 I				[101]
13-6		Cr 88 N 102.4 I	8.4	0.072	233	[102]
13-7		Cr 72 N 179 I	12.9	0.075		[43]
13-8		Cr 41.7 N 122.5 I	1.8[b]	0.079[b]		[50]
13-9		Cr 58.9 N (52.4) I	3.5[b]	0.082[b]		[50]

[a]Extrapolated from 10 wt% solution in ZL1-4792 at 20°C.
[b]Extrapolated from 15 wt% solution in liquid crystal material at 20°C.

reference derivatives (compounds **5-7** to **5-16**). It can be illustrated by the following orders of increasing the clearing points in dependence on the linkage A:

$$\begin{aligned} A : CH_2 &< C_4H_8 < CH(CH_3)CH_2 < C_3H_6O < CH{=}CHCH_2O \\ &< CH{=}CHC_2H_4 < C_2H_4 < OCO < COO < COS \end{aligned}$$

Among liquid crystal derivatives presented in Table 9, compound **9-1** containing SCH_2 linkage is not mesomorphic due to its significant nonlinearity [77]. The

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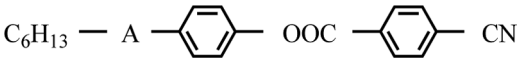
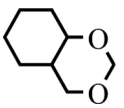
Table 14. Mesomorphic properties of liquid crystals:



No.	A	Phase transitions (°C)	Ref.
14-1		Cr 85 N 146 I	[104]
14-2		Cr l56 N 245 I	[105]
14-3		Cr l08 SmA lll N 224 I	[106]
14-4		Cr l35 Sm l70 N 232 I	[107]
14-5		Cr l52 N 258 decomp.	[108]

clearing temperatures of these compounds increase in dependence on the linkage A in the following order:

$$A : SCH_2 < OCF_2 < C_2H_4 < CF_2O < SB < CF{=}CF < C{\equiv}C$$

where SB is the single bond.

Similar trends have been shown for other liquid crystals containing sulfur-substituted linkages [78–84].

Axial Substitution

The data presented in Table 10 reveal that the axial NCS or CONCS substitution of the trans-1,4-cyclohexylene derivatives (compounds **10-1** to **10-3**) significantly reduces the clearing points in comparison with those of parent derivative (compound **10–4**, rough comparison because it is different homolog). In this case, we can say that the axial NCS or CONCS substitutions work as the lateral ones, which usually reduce the intermolecular interactions and consequently, the clearing points [87]. The position of the axial substituent NCS in the molecular core of liquid crystals plays an important role in their mesomorphic properties: the axial substituent A in the middle of the core gives more significant reduction of the melting and clearing points in comparison with those of the axial substituent B at the terminal position of the core (compounds **10-1**, **10-2**).

Lateral Substitution

One can say that the lateral isothiocyanato substitution of liquid crystals results in the largest drop in the clearing temperatures or disappearance of the mesomorphic

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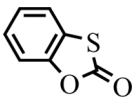
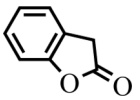
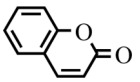
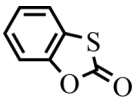
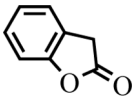
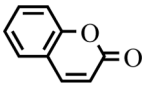
Table 15. Physico-chemical properties of liquid crystals:

$C_5H_{11}O$ — ( )$_k$ — COO — A

No.	k	A	Phase transitions (°C)	d[a] (Å)	d/L[a]	Ref.
15-1	1		Cr 84 I			[109]
15-2	1		Cr 81 N (35) I			[110]
15-3	1		Cr 88 N (78) I			[111]
15-4	2		Cr 141 SmA 171 N 191 I	25	1.04	[109]
15-5	2		Cr 143 SmA (127) N 222 I	23.9	0.99	[110]
15-6	2		Cr 155 N 249 I			[111]

$T_{meas} = T_{SmA–N} - 10°C$.

properties in comparison with those of the corresponding derivatives having other lateral substituents and parent compounds (compounds **11-1** to **11-3**, **11-4** to **11-6**; **13-8**, **13-9**; Tables 11 and 13). It can be explained by the largest size of the NCS group among lateral substituents under consideration [4]. Such a large substituent would reduce the intermolecular interactions and destroy the liquid crystal packing in the most significant way [87].

Sulfur-Containing Rings

Tetrahydrothiophene. It has been reported that tetrahydrothiophene belongs to the C_s point group and it has the dipole moment $\mu = 1.73$ D [92]. The spectroscopic studies have shown that its molecule is characterized by a C_2 symmetry equilibrium twisted configuration and a barrier to hindered pseudorotation of 775 cm^{-1} at the C_s bent configuration and a barrier to planarity of 4250 cm^{-1} [93]. As we can see from Table 12, four-ring tetrahydrothiophene derivatives exhibit the chiral mesophases with moderate thermostabilities (compounds **12-1**, **12-2**). Moving the sulfur atom in the ring closer to the terminal $COOCH_3$ group (compound **12-2**) gives rich smectic polymorphism and creates the cholesteric phase in comparison with those of the corresponding compound **12-1**. The mesomorphic properties of these compounds show usual dependence on the position of the sulfur atom in the

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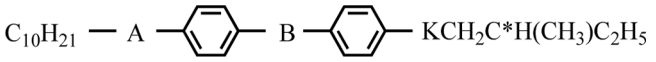
Table 16. Mesomorphic properties of liquid crystals:



No.	A	B	K	Phase transitions (°C)	Ref.
16-1		COO	O	Cr l04 SmB 136 SmA 153 I	[113]
16-2		COO	O	Cr 66 SmB lll SmA 134 I	[114]
16-3		COO	O	Cr 66 SmB 100 SmA 136 I	[113]
16-4		COO	COO	Cr 113 SmA 150 I	[113]
16-5		COO	COO	Cr 89 SmA 134 I	[114]
16-6		COO	COO	Cr 59 SmC* 93 SmA 137 I	[115]
16-7		OCO	O	Cr 92 Sm (58) Ch l38 I	[116]
16-8		OCO	O	Cr 88 Sm (47) Ch l22 I	[116]
16-9		OCO	O	Cr 69 Sm (51) SmC* (58) Ch 123 I	[116]

ring, which has been observed earlier for other heterocyclic liquid crystal derivatives [6, 95–98]. The thermal data presented in Table 13 reveal that the fused systems based on tetrahydrothiophene can be used as the building fragments in liquid crystals (compound **13-1**) that show the high clearing temperature and wide nematic range in comparison with those of the corresponding reference compounds **13-2** to **13-9**. The great number of the lateral and terminal fluorine atoms introduced into the fragment A give mainly the nematic phases for the presented liquid crystals (Table 13) having this fragment [87].

1,3-Oxathiolane. It has been demonstrated that the 1,3-oxathiolane derivatives mainly exist in the enveloped conformations [103]. These facts and the smallest size of 1,3-oxathiolane among rings under consideration can be responsible for the significantly lower melting and clearing points of the 2,4-disubstituted 1,3-oxathiolane derivative **14-1** compared with those of the corresponding reference compounds **14-2** to **14-5**, which have sulfur- and/or oxygen-containing saturated rings and fragments.

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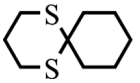
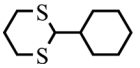
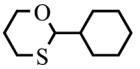
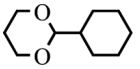
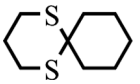
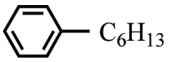
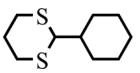
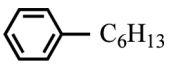
Table 17. Mesomorphic properties of liquid crystals:

No.	A	B	Phase transitions (°C)	Ref.
17-1		CN	Cr 81 N (29) I	[118]
17-2		CN	Cr 130 N 228 I	[119]
17-3		CN	Cr 103 Sm (70) N 205 I	[120]
17-4		CN	Cr 98 N 191 I	[121]
17-5		CN	Cr 50 N 73 I	[122]
17-6		CN	Cr 64 N (47.5) I	[123]
17-7[a]		CN	Cr 63 Sm 72 I	[124]
17-8[a]		CN	Cr 47 N 79 I	[122]
17-9			Cr 55 Sm 106 N 122 I	[118]
17-10			Cr 91 Sm 226 SmB 238 N 286 I	[119]

[a]C_5 homolog.

Benzo[1,3]oxathiol-2-one. It can be seen from Table 15 that the ketonization of the fused system based on 1,3-oxathiolane results in the formation of benzo[1,3] oxathiol-2-one, which can be used as the structural fragment in liquid crystals. One can say that the introduction of benzo[1,3]oxathiol-2-one into the molecular core of liquid crystals, depending on their structures, leads to the disappearance of the mesophases or formation of the mesophases with the lowest clearing temperature in comparison with those of the corresponding reference ketones (compounds **15-1** to **15-3**; **15-4** to **15-6**). It has been demonstrated that X-ray diffraction studies of the benzo[1,3]oxathiol-2-one and benzofuran-2-one derivatives **15-4** and **15-5** reveal their monolayer smectic A formation despite their polar character [109,110].

Sulfur-containing six-membered rings. It has been shown that sulfur-containing six-membered rings [112] can be used as the structural fragments in liquid crystals [3].

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Here we discuss the influence of the sulfur atom in the saturated six-membered ring on the appearance of the chiral mesophases in liquid crystals. It can be seen from Table 16 that, depending on the structure of the chiral chain, the replacement of the sulfur atom by the oxygen one in 1,3-oxathiane promotes the creation of the chiral smectic C^* phase (compounds **16-5** and **16-6**; **16-8** and **16-9**). Similar trends can be observed from the comparison of the mesomorphic properties of the 1,3-dioxane and 1,3-dithiane derivatives (compounds **16-1** and **16-3**, **16-4** and **16-6**, **16-7** and **16-9**). The 1,3-dithiane derivatives exhibit the highest melting and clearing points among compounds under consideration (compounds **16-1** to **16-9**; Table 16). The data presented in Table 16 reveal the importance of the molecular structure of liquid crystals on their mesomorphic properties: the different mesophases (Sm, SmB, SmC^*, SmA, Ch) can be formed for compounds having the same ring A (1,3-dithiane or 1,3-oxathiane or 1,3-dioxane) by changing the linkage B or/and the terminal chiral group.

It has been shown that the spirane skeleton is chiral if under experimental conditions the rings can be considered nonplanar. The consequence of the chirality of the spiro atom is the differentiation of substitution at positions 1 and 5 and the lower stability of equatorial substitution at position 1 that of axial substitution [117]. The spiro junction of the rings can cause distortions of the tetrahedral arrangement around the spiro atom. For example, the equatorial hydrogen atoms on C(1) and C(2) are closer to the axial hydrogen atoms on the other rings than those on C(5) and C(7). This should lead to differentiation of bond lengths and angles around the C(6) center of chirality [117]. The stereochemical situation is the same in the heterocylic spirosystems (compounds **17-1**, **17-9**; Table 17) as for the spiro[5.5] undecane **17-7**, but the bond angles and bond lengths are different and the barrier for ring inversion is lower [118]. The thermal data presented in Table 17 reveal that the introduction of the spiro system based on 1,3-dithiane into the molecular core of liquid crystals significantly lowers their clearing points in comparison with those of the corresponding reference compounds having one-ring and two-ring fragments (compounds **17-1** and **17-2** to **17-6**; **17-9** and **17-10**). Similar results have been observed for the spiro[5,5]undecane derivatives (compounds **17-7**, **17-8**, [125]) and can be explained by the significant nonlinearity of the spiranes [125]. Similar trends have been reported for other liquid crystals that have sulfur-containing rings [98,126–128].

It can be proposed that the electronic and geometric structures of the sulfur-containing molecules [2–4,92,93,103,112,118] play a very important role in the intra- and intermolecular interactions [129–131] that affect the packing of the molecules, which predominantly influences mesophase stability [129–133]. Anisotropic dispersion interactions, and consequently the anisotropy of polarizability, depending on the electron density distribution in the molecular fragments under consideration, also influence the packing and hence the stability of the mesophases but play a secondary role compared to the steric factors [133]. Other molecular aspects such as the association [132] or dipole–dipole attraction in polar liquid-crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [133].

Static Dielectric Properties

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are, respectively, dielectric constants, that are parallel and perpendicular to the nematic

director **n** and molecular structure of liquid crystals is described by the theory of Maier and Meier [134]:

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

where $h = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_\parallel + 2\varepsilon_\perp)/3$; $\Delta\alpha = (\alpha_\parallel - \alpha_\perp)$ 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, and N is the number of molecules per unit volume; S is the order parameter.

It is evident from Tables 2, 4–6, 11, 13 and the literature [4,52,135] that for the define molecular structure of liquid crystals, their dielectric anisotropy decreases approximately in the same sequence as the values of dipole moments for the terminal groups: SO_2CF_3, SO_2CHF_2, $SOCHF_2$, $SOCF_3$, SF_5, SF_4CF_3, NCS, CF_3, SCF_3, $SCHF_2$, $OCHF_2$, OCF_3, Cl, Br, F, I diminish: 4.32, 4.08, 3.93, 3.88, 3.44, 2.93, 2.85, 2.54, 2.50, 2.48, 2.46, 2.36, 1.59, 1.57, 1.47, 1.40.

The total dipole moment and, consequently, the dielectric anisotropy of compounds presented in Tables 2, 4–6, 9–11, and 13 are strongly affected by values and directions of the dipole moments of the terminal, linking, lateral group, and molecular fragments (see Eq.(1)). When the positions and orientations of the axial, linking, and lateral substituents are chosen in such way that their dipole moments contribute mainly to the perpendicular part of the total dipole moment, the negative dielectric anisotropy of liquid crystals can be achieved (Tables 9–11).

Optical Properties

The phenomenological relation between the refractive index and the electric polarization is defined as [136, 137]:

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

where the mean polarizability $\alpha^* = (\alpha_\parallel + 2\alpha_\perp)/3$; the mean refractive index $n^{*2} = (n_e^2 + 2n_o^2)/3$; n_o is the ordinary and n_e is the extraordinary refractive indices. From Eq. (2) and the previous section, it follows that compounds that have a large induced polarizability of their highly conjugated π-electron system (for example, isothiocyanato derivatives) exhibit an optical anisotropy $\Delta n = n_e - n_o$ that is much larger than that of the corresponding halogen(s)-substituted derivatives (compounds **2-3** to **2-8**, **2-11**, **2-14**; **5-1**, **5-2**; **6-12** to **6-16**; Tables 2, 5, 6, [52]). A decrease in optical anisotropy for compounds with the halogenated terminal, linking, and lateral groups (Tables 2, 4–6, 9–11, 13) can be explained in terms of a reduction in the effective conjugation of the π-electron system resulting in a shorter resonance wavelength of the UV absorption spectrum for the halogen(s)-substituted liquid crystals than for the corresponding parent compounds or having hydrogenated groups [52, 138–141]. The axial and lateral NCS substitutions do not contribute so much to the optical anisotropy of liquid crystals (Tables 10 and 11) and work as usual lateral substitutions [87].

Viscous Properties

It has been shown that the nematic liquid crystal materials for display applications should have a low viscosity for providing acceptable response times to liquid crystal

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displays [142, 143]. The rotational viscosity γ_1 of a nematic liquid crystal (NLC) is a dissipative coefficient describing the rate of reorientation of the NLC director [144]. The magnitude of the rotational and flow viscosities depend on molecular structure, intermolecular association, and temperature [145–146]: as temperature increases, viscosity decreases [145–148]. According to the results on flow and rotational viscosity presented in Tables 2, 4, 9, and 13, the introduction of the sulfur atom(s) into the terminal groups and molecular fragments of liquid crystals usually increases their viscosities in comparison with those of the corresponding parent and reference compounds (compounds **2-3**, **2-5** to **2-7**, **2-14**; **4-3**, **4-6**, **4-9**; **13-1**, **13-2**, **13-6**).

Physical Properties of the Smectic C* Phase

The spontaneous polarization P_s of the smectic C* liquid crystals is an important parameter due to its linear coupling with an applied electrical field, which is the basis of the application of these materials [149]. 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 [149]. The spontaneous polarization P_s is a quantity that is directly related to the response time τ as a switching device [150]:

$$\tau = \gamma_\phi \sin^2\Theta / P_s E \tag{3}$$

where γ_ϕ is the rotational viscosity, which refers to the rotation about an axis perpendicular to the director **n** and P_s; Θ is the tilt angle; E is an applied electric field.

According to Scherowsky and Sefkow [151], liquid crystals should have the following structural features in order to obtain high spontaneous polarization:

1. a high dipole moment perpendicular to the longitudinal molecular axis;
2. short distances between the chiral center and the lateral dipole and the mesogenic part, respectively;
3. a restriction of free rotation in the chiral region.

It is evident from Table 7 that the introduction of the sulfur atom into the chiral chain of liquid crystals enhances their spontaneous polarization and tilt angle compared with those of the corresponding parent derivative (compounds **7-1**, **7-2**). The introduction of the tetrahydrothiophene ring into the molecular core of liquid crystals gives the moderate value of the spontaneous polarization (compound **12-1**; Table 12).

Conclusion

Systematic studies on introducing the sulfur atom(s) into the molecular structure of calamitic liquid crystals on the creation of the mesophases and their physicochemical properties 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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