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Sulphur as a Structural Element in Calamitic Liquid Crystals: Terminal, Linking and Lateral Substitutions

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The effect on the physicochemical properties of calamitic liquid crystals of introducing sulphur atoms into their terminal, linking, and lateral groups is discussed and rationalized in terms of existing theories; a comparison is made with the corresponding oxygen-containing and other reference liquid crystals.

Keywords: liquid crystals; physicochemical properties; sulphur

INTRODUCTION

In continuation of our study of the structure–property relationships in liquid crystals (see, for example, the previous publications [1–3]), we present here a review that examines in some detail the effect of the introduction of sulphur atoms into the terminal, linking, and lateral groups of calamitic liquid crystals on the appearance of the mesophases and their physicochemical properties. When possible, the physicochemical properties of sulphur-containing liquid crystals are compared with those of the corresponding oxygen-containing liquid crystals and other reference liquid crystals.

Because the electronegativity of sulphur (2.5) is smaller than that of oxygen (3.5) [4], and it is significantly larger than oxygen and carbon (covalent radii are 1.04 Å, 0.66 Å, and 0.77 Å, respectively [5]), it can be expected that the introduction of sulphur atoms into the molecular structure of liquid crystals can produce significant variations in their molecular geometry that reflect the changes in covalent radii, relative electronegativity, and effective hybridization. Consequently, there can be changes in the bonding and the physicochemical properties of these systems.

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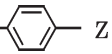
Mesomorphic Properties

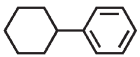
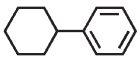
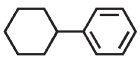
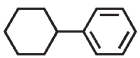
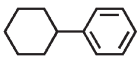
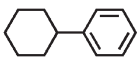
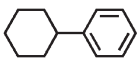
The phase-transition temperatures of some sulphur-containing liquid crystals and the corresponding reference compounds are presented in Tables 1–8, where Cr, SmE, SmB, SmC, SmA, N, SmK*, SmJ*, SmI*, SmC^*_A, SmC^*_γ, SmC*, SmC^*_α, TGB_A, Ch, BP, and I are the crystalline, smectic E, smectic B, smectic C, smectic A, nematic, smectic K*, smectic J*, smectic I*, smectic C^*_A, smectic C^*_γ, smectic C*, smectic Cα*, smectic A twist-grain boundary, cholesteric, blue, and isotropic phases, respectively; X is an uncharacterized mesophase. Values given in parentheses refer to monotropic phase transitions.

Terminal Substitution

As is evident from Table 1, fluorinated thioethers exhibit significantly lower clearing temperatures (nematic–isotropic or smectic–isotropic phase-transition temperatures) in comparison with those of the corresponding fluorinated ethers and the parent difluoromethyl and trifluoromethyl derivatives (compounds **1-3**–**1-10**). Two-ring difluoromethyl thioethers are usually nonmesomorphic (compounds **1-1** and **1-3**). In the case of the trifluoromethylthio and trifluoromethoxy derivatives (compounds **1-8** and **1-9**), a lower nematic thermostability of the former compound can be explained by more pronounced orthogonal conformation of the corresponding trifluoromethylthiobenzene [11]. Similarly, lower clearing points have been recorded for fluorinated sulphoxides in comparison with those of the corresponding fluoroalkyl and fluoroalkyl ketones (compounds **1-7**, **1-11**, and **1-12**). The introduction of the difluoromethylsulphone and pentafluorosulphuranyl groups results in the disappearance of the mesophases with respect to those of the corresponding reference and previously mentioned compounds (compounds **1-5**–**1-7**, and **1-11**–**1-15**). These findings and some results presented in Refs. 8 and 12–14 reveal that terminal substitution by the sulphonyl-based groups do not create the mesophases. Such phase behaviour of these compounds can be correlated with their structures, which seem to be unfavorable for the formation of the mesophases. Particularly, methyl phenylsulphone, in the gas phase, was shown to have the bent form [15].

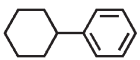
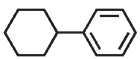
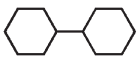
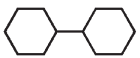
The data collated in Table 2 shows that the terminal isothiocyanato substitution produces liquid crystals showing higher clearing temperatures than the corresponding isocyanato (compounds **2-1** and **2-2**) and thiocyanato derivatives (compounds **2-4**, **2-5**, **2-7**, **2-8**, **2-11**, and **2-12**). Interestingly, the isothiocyanato derivatives exhibit higher (compounds **2-1** and **2-3**) and lower (compounds **2-4** and **2-6**)

TABLE 1 Physicochemical Properties of Liquid Crystals: C_nH_{2n+1} — A —  — Z

No.	n	A	Z	Phase transitions, °C	$\Delta\varepsilon^a$	$\Delta n^{a,b}$	ν^a, mm^2s^{-1}	Ref.
1-1	3		$SCHF_2$	Cr 12.5 I	10.6	0.044	18.5	[6]
1-2	3		$OCHF_2$	Cr - 14.9 I	8.3	0.044	5	[6]
1-3	5		$SCHF_2$	Cr 42.5 I	16.1	0.050		[6]
1-4	5		$OCHF_2$	Cr 23 Sm (4) N (8) I	14.6	0.044		[6]
1-5	5		$SCHF_2$	Cr 56.2 Sm 94.7 N 114 I	11.4 3.8[c]	0.174		[6]
1-6	5		$OCHF_2$	Cr 69.5 Sm 119.6 N 167.5 I	9.7 3.5[d]	0.154		[6]
1-7	5		CHF_2	Cr 122 N 161.8 I	4.4			[7]
1-8	5		SCF_3	Cr 60 SmB 78 N 105.2 I	9.4	0.149	39	[8]
1-9	5		OCF_3	Cr 43 SmB 128 N 147.4 I	8.9	0.140	16	[9]
1-10	5		CF_3	Cr 123 N 124.2 I	12.9	0.159	32	[9]
1-11	5		$SOCHF_2$	Cr 102 N 108.5 I	16.3	0.151	350	[8]

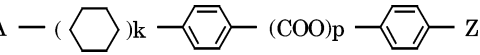
(*Continued*)

TABLE 1 Continued

No.	n	A	Z	Phase transitions, °C	$\Delta\varepsilon^a$	$\Delta n^{a,b}$	ν^a, mm^2s^{-1}	Ref.
1-12	5		$COCHF_2$	Cr 80 N 158 I	10.2		83	[8]
1-13	5		SO_2CHF_2	Cr 119 I	13.1	0.155	500	[8]
1-14	3		SF_5	Cr 121 I	11.6[e]	0.094[e]		[10]
1-15	3		SCF_3	Cr 51 N 109.5 I	8.6	0.100		[8]

[a,e]Extrapolated from 10 wt% solution in ZLI-1132 and ZLI-4792, respectively at 20°C.
[b]$\lambda = 589\,nm$.
[c]$\tau = T_{meas}/T_{N-I} = 0.95; T_{meas}, T_{N-I}, K$.
[d]$\tau = 0.88$.

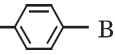
TABLE 2 Physicochemical Properties of Liquid Crystals:

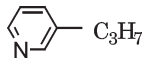
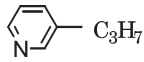
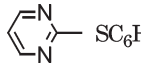
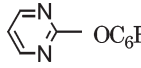
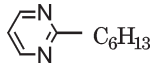
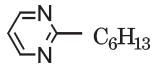
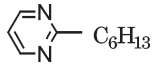
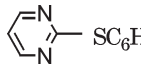
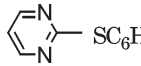
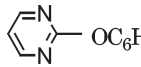
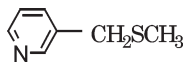
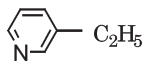
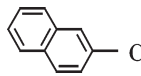
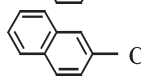
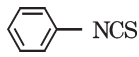
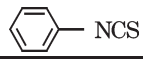


No.	A	k	P	Z	Phase transitions, °C	Δε	Ref.
2-1	C_5H_{11}	0	0	NCS	Cr 53 SmE 74.5 I		[16]
2-2	C_5H_{11}	0	0	NCO	Cr 132 I		[16]
2-3	C_5H_{11}	0	0	NC	Cr 35 N (30) I		[17]
2-4	C_5H_{11}	0	1	NCS	Cr 88 N (45) I		[18]
2-5	C_5H_{11}	0	1	SCN	Cr 68 I		[19]
2-6	C_5H_{11}	0	1	NC	Cr 52.5 N (50.5) I		[20]
2-7	$C_9H_{19}O$	0	1	NCS	Cr 70.4 SmA 93.9 I		[21]
2-8	$C_9H_{19}O$	0	1	SCN	Cr 41 SmA (14) I		[19]
2-9	$C_9H_{19}O$	0	1	CN	Cr 62 SmA (59) N 84 I		[22]
2-10	$C_{10}H_{21}O$	0	1	OCN	Cr 56.7 SmA 62.1 N 63 I		[23]
2-11	C_5H_{11}	1	1	NCS	Cr 118.5 SmA 129 N 235 I	3.4[a]	[24]
2-12	C_5H_{11}	1	1	SCN	Cr 104 N 124.5 I	4.5[b]	[24]
2-13	C_5H_{11}	1	1	CN	$Cr_1$82 Cr_2 111 N 225.5 I	7.9[a]	[24]
2-14	$C_5H_{11}O$	0	0	$COSC_6H_{13}$	Cr 91 SmB 121 SmA 149.5 I		[25]
2-15	$C_5H_{11}O$	0	0	$COOC_6H_{13}$	Cr 66 SmE (60) SmB 67 SmA 85 I		[26]

[a] $T_{meas} = T_{N–I} - 30°C$.
[b] $T_{meas} = T_{N–I} - 10°C$.

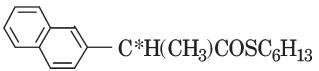
clearing points with respect to those of the corresponding isocyano derivatives. It reveals the importance of the molecular core's structure. The melting temperatures (crystal–smectic or crystal–nematic phase-transition temperatures) are higher for the NCS derivatives in comparison with those of the corresponding SCN derivatives (compounds **2-4**, **2-5**, **2-7**, **2-8**, **2-11**, and **2-12**). The thiocyanato derivatives show lower clearing temperatures than the corresponding cyano derivatives (compounds **2-5**, **2-8**, **2-9**, **2-12**, **2-13**, and **6-3**, Tables 2, 6). The replacement of the thiocyanato by the isocyanato group leads to the disappearance of the nematic phase and reduction of the clearing point (an approximate comparison, compounds **2-8** and **2-10**). The decreased mesomorphic thermostability of the thiocyanato group in comparison with that of the NCS (isothio cyanato) and CN (cyano) groups has been explained in terms of increased bent angle ($\sim 80^\circ$) of the cyano moiety in this group [27,28]. It has been reported that the planar phenyl isothiocyanate with its bent C_1–N=C=S chain [5,29] and phenyl isocyanate, which has more stable planar isomer [30–32] with its N=C=O group (assumed to be linear [32]), which is tilted at an angle of $\sim 140^\circ$ to the C_2 phenyl axis [32], exhibit almost the same corresponding bond lengths C_1–N and N=C and slightly different valence angles $<C_1$–N=C, with a higher value recorded for the former compound [5,29,31]. The study of vinyl isocyanate and vinyl cyano ether has

TABLE 3 Physicochemical Properties of Liquid Crystals: A  B

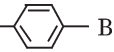
No.	A	B	Phase transitions, °C	Δn[a]	Ref.
3-1	$C_5H_{11}S$		Cr 40.5 I		[59]
3-2	C_5H_{11}		Cr 20 Sm (5) I		[60]
3-3	C_6H_{13}		Cr 31 SmA 33 I		[61]
3-4	C_6H_{13}		Cr 45 SmA 71 I		[61]
3-5	C_6H_{13}		Cr 30 SmB 42.5 SmA 53 I		[62]
3-6	$C_6H_{13}S$		Cr 50 SmA 57.5 I		[63]
3-7	$C_6H_{13}O$		Cr 44 SmB 59 SmA 89 I		[61]
3-8	$C_6H_{13}O$		Cr 30 SmA 74.5 I		[61]
3-9	$C_6H_{13}S$		Cr 40 SmA 48.5 I		[64]
3-10	$C_6H_{13}O$		Cr 71 SmA 104.5 I		[62]
3-11			Cr 64 Sm 86 N 148.5 I		[59]
3-12			Cr 65.8 Sm 78 N 168 I		[65]
3-13	C_4H_9S		Cr 93.2 N 114.8 I	0.360	[66]
3-14	C_4H_9O		Cr 125 N 159 I	0.330	[67]
3-15	C_4H_9S		Cr 78.4 SmB 78.6 I	0.400	[68]
3-16	C_4H_9O		Cr 116.5 SmB 118.5 I	0.353	[69]

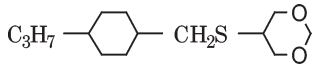
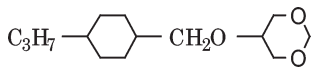
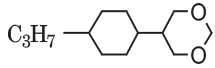
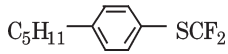
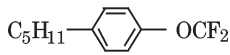
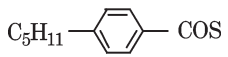
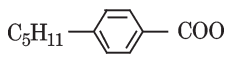
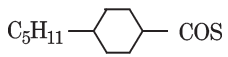
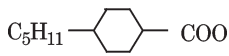
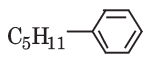
[a]Extrapolated from the liquid-crystal mixture at $\tau = 0.7815$, $\lambda = 589$ nm.

TABLE 4 Physicochemical Properties of Liquid Crystals: $C_nH_{2n+1}Y$ — (⬡)k — A — (⬡)p — Z

No.	n	Y	k	A	p	Z	Phase transitions, °C	d, Å	d/L	|Ps|, nCcm^{-2}	Θ,°	Ref.
4-1	14	S	1	C≡CCOO	2	$COOC^*H(CH_3)C_6H_{13}$	Cr 52.9 SmC^* 68.7 SmA 78.1 I			85[a]	25[a]	[70]
4-2	14	O	1	C≡CCOO	2	$COOC^*H(CH_3)C_6H_{13}$	Cr 80.3 SmC_A^* (39.5) SmC_γ^* (48.2) SmC^* 91.3 SmC_z^* 91.3 TGB_A 95.6 I			90[a]	30[a]	[70]
4-3	12	O	2	COO	0		I 129.1 SmA 128.6 SmC^* 86.9 Cr			5[b]		[71]
4-4	12	O	2	COO	0		I 132 SmA 115.3 SmC^* 112.3 SmC_A^* 70.6 Cr			35[b]		[72]
4-5[c]	8	O	2	COO	1	$S^*(O)CH_2C^*H(CH_3)C_2H_5$	Cr 161 SmC^* (146) SmA 176 I			3.9[d]	23[d]	[73]
4-6	8	O	2	COO	1	$CH_2C^*H(CH_3)C_2H_5$	Cr 74 Sm K^* (61) SmJ^* (72) SmI^* 79 SmC^* 132 SmA 171 Ch 174 I					[74]
4-7	16	O	1	COO	1	C≡C—⬡—$S^*(O)OC^*H(CH_3)C_6H_{13}$	Cr 64.4 SmA 96.7 SmA 92.4 I Cr 64.4 SmA 96.7 I	46.5[e]	1.01[e]		22.5[f]	[75]
4-8	16	O	1	COO	1	C≡C—⬡—$C(O)OC^*H(CH_3)C_6H_{13}$	Cr 76 Sm (69) SmC^* 104 SmA^* 114 I	46.5[e] 43.8[g]	1.01[e] 0.82[g]		21.3	[76]

[a] $T_{meas} = T_{SmC^*\text{-}SmA} - 30°C$.
[b] $T_{meas} = T_{SmC^*\text{-}SmA} - 2°C$.
[c] $\tau = 108^d$ μs.
[d] Measured as 5 wt % solution in the liquid-crystal mixture.
[e] $T_{meas} = T_{SmA\text{–}I} - 10°C$.
[f] $T_{meas} = 60°C$.
[g] SmA^* phase.

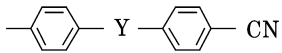
TABLE 5 Physicochemical Properties of Liquid Crystals: A  B

No.	A	B	Phase transitions, °C	Δn^a	ν^a, mm^2s^{-1}	Ref.
5-1		CN	Cr 74 N 94 I			[142]
5-2		CN	Cr 119 N 149 I			[142]
5-3		CN	Cr 89.5 N 222.7 I			[143]
5-4		CF_3	Cr 51 I	0.044	28	[144]
5-5		CF_3	Cr 46 I	0.046	10	[144]
5-6		CH_3	Cr 50 N (48) I			[145]
5-7		CH_3	Cr 44 N (16) I			[145]
5-8		CH_3	Cr 54 N (38.5) I			[145]
5-9		CH_3	Cr 47.5 N (45) I			[145]
5-10		CH_3	Cr 40 I			[146]

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

revealed more pronounced stability of the *cis*-isomers in respect to that of the corresponding *trans*-isomers in these compounds, which have the NCO and OCN groups bent about 10° and 5°, respectively, from linearity [33]. The increased barrier height of the internal rotation owing to the methyl group of methyl thiocyanate in comparison with that of the corresponding methyl cyanate has been attributed to a stronger steric repulsion of the methyl group with the cyano moiety in CH_3SCN because its angle $<C_1-S-C$ is much narrower than the angle $<C_1-O-C$ of CH_3OCN [34]. It has been demonstrated that the NC bond length and polarizability are larger than those of the CN bond [35,36]. However, the C_1-N distance in phenylisocyanide is shorter than C_1-C_7 distance in benzonitrile [35,37].

It can be proposed that these geometrical and electronic structures of the isothiocyanato, thiocyanato, isocyanato, cyanato, isocyano, and cyano groups [5,29–48] affect through intra- [49–51] and intermolecular [52–56] interactions the molecular packing and consequently the

TABLE 6 Physicochemical Properties of Liquid Crystals: A  CN

No.	A	Y	Phase transitions, °C	d_1 Å	d_2, Å	d_2/L	$\varepsilon_\perp$	$\Delta\varepsilon$	$\Delta\varepsilon/\varepsilon_\perp$	Δn	k_p	Ref.
6-1	C_5H_{11}	COS	Cr 76 N 98 I		21.3	1.08	9[a]	15[a]	1.67[a]	0.173[b,c]	0.6410[d] 0.6606[e,f]	[148–150]
6-2	C_5H_{11}	SOC	Cr 67.5 N 102 I	18.6	29.3	1.49	4.8[a]	5.4[a]	1.13[a]	0.171[b,c]	0.6422[d] 0.6553[e,f]	[148,150,151]
6-3	C_5H_{11}	COO	Cr 64.4 N (55.4) I				10.2[a]	20[a]	1.96[a]	0.157[b,g]	0.6526[e]	[152–154]
6-4	C_5H_{11}	OOC	Cr 93 N 35 I									[155]
6-5	C_5H_{11}	—	Cr 22.5 N 35 I	14.3[b]	24.8[b]	1.38[b]	6.6[h]	13.3[h]	2.02[h]	0.178[h]	0.6523[e]	[78,156–158]
6-6	C_4H_9S	COS	Cr 92.6 N 94.6 I							0.299[e,i]		[159]
6-7	C_4H_9S	CSO	Cr 92.9 I							0.294[e,i]		[159]
6-8	C_4H_9S	CSS	Cr 111.1 N (70.9) I							0.399[e,i]		[159]
6-9	C_4H_9S	COO	Cr 82.2 N (56.3) I							0.258[e,i]		[159]
6-10	C_4H_9S	—	Cr 64.8 N (35.5) I							0.303[e,i]		[77]

[a] $\tau = 0.98$.
[b] $T_{meas} = T_{N-I} - 10°C$.
[c] $\lambda = 589\,nm$.
[d] $T_{meas} = 79°C$.
[e] $T_{meas} = 40°C$.
[f] The value of the density is extrapolated to that at 40°C.
[g] $\lambda = 546\,nm$.
[h] $\tau = 0.96$.
[i] Extrapolated from the liquid-crystal mixture at $\tau = 0.7815$.

formation of the mesophases in the corresponding derivatives containing these groups (see Table 2).

Compounds **2-14** and **2-15** (Table 2) show that the introduction of the thioester between the biphenyl core and the terminal hexyl group produces liquid crystals exhibiting a higher smectic A thermostability and the absence of the smectic E phase in comparison with those of the corresponding ester derivative. Actually, these COS and COO groups are working as the linkages that usually enhance the clearing points of the parent systems (see the next paragraph and Refs. 57 and 58).

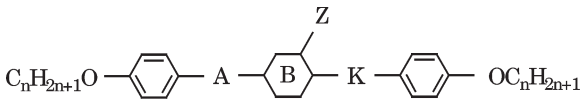
As is evident from Tables 3 and 4, alkylthio-substituted liquid crystals show lower clearing points than the corresponding alkyl and alkoxy derivatives (compounds **3-1**–**3-16**, **4-1**, and **4-2**). There are some opposite cases presented by compounds **3-5** and **3-6** and Refs. 77 and 78. Alkylthio substitution in both terminal positions lowers the clearing temperatures with respect to those of the corresponding di-alkoxy and di-alkyl derivatives (compounds **3-5**, **3-9**, and **3-10**). However, di-alkylthio derivatives exhibit enhanced (compounds **3-3** and **3-9**) and decreased (compounds **3-6** and **3-9**) clearing temperatures compared with those of the corresponding alkyl-alkylthio and alkylthio-alkyl derivatives, respectively. Lower clearing points (observed in many cases) of alkylthio derivatives with respect to those of the corresponding alkyl derivatives have been explained in terms of a lower rotation barrier around C−S bond relative to the C−C bond, which facilitates the formation of the sterically demanding *trans*-gauche conformers, which in turn increase the disorder of the system [79]. However, according to Castellano et al. [80], a low polarity of alkylthio groups is responsible for the decreased clearing temperatures of alkylthio derivatives with respect to those of the corresponding alkoxy derivatives. We also have to take into account that a nonplanar structure of methylthiobenzene with a dihedral angle of 45.3° compared with a planar structure of methoxybenzene [81] could affect the molecular packing of the SCH_3 derivatives showing lower clearing points or even the absence of the mesophases in comparison with those of the corresponding OCH_3 derivatives [80,82,83]. It has been demonstrated that the alkylthio substitution of the homologous series of three-ring cyano derivatives promotes earlier appearance of the reentrant nematic phase Nre and the smectic A phase with respect to those of the corresponding alkoxy and alkyl derivatives [84,85]. The reentrant nematic phase is observed for only one member of the alkylthio-substituted series compared with two later appearances of this phase in the corresponding alkoxy derivatives. However, the nematic phase shows an earlier disappearance in the homologous series of alkylthio-substituted derivatives [84].

TABLE 7 Physicochemical Properties of Liquid Crystals: $C_nH_{2n+1}O$ — ()k — A —  — Z

No.	n	k	A	Z	Phase transitions, °C	|Ps|, nCcm^{-2}	τ, μs	Ref.
7-1	12	1	COS	$OCH_2C^*H(CH_3)C_2H_5$	Cr 63 SmC* 77 SmA 78 I			[160]
7-2	12	1	COO	$OCH_2C^*H(CH_3)C_2H_5$	Cr 49 SmC* 52 SmA 65 I			[161]
7-3	12	1	—	$OCH_2C^*H(CH_3)C_2H_5$	Cr 75.3 Sm (73.9) SmH* 77.4 SmC* 78.9 SmA 79.8 I			[162]
7-4	16	1	COS	$OCH_2C^*H(CH_3)C_2H_5$	Cr 67.9 Sm (51.3) SmC* 76.1 SmA 79.5 I			[160]
7-5	16	1	—	$OCH_2C^*H(CH_3)C_2H_5$	Cr 78.9 I			[162]
7-6	10	1	COS	$OOCC^*H(Cl)CH(CH_3)_2$	Cr 72 SmC* 75 SmA 84 I	$\sim 100^a$	$\sim 4^b$	[163]
7-7	10	1	COO	$OOCC^*H(Cl)CH(CH_3)_2$	Cr 66 SmC* (45) SmA 68 Ch 70 BP 72 I	$\sim 100^a$	$\sim 2.2^b$	[163,164]
7-8	10	1	—	$OOCC^*H(Cl)CH(CH_3)_2$	Cr 82 SmC* (69) SmA 81 I			[165]
7-9	10	2	SOC	$OC^*H(CH_3)C_6H_{13}$	Cr 68.6 SmC* 106.4 Ch 129.6 I	$\sim 45^c$		[166]
7-10	10	2	OOC	$OC^*H(CH_3)C_6H_{13}$	Cr 72.4 SmC* 104.8 Ch 130.5 I	$\sim 42^a$		[167]

[a] $T_{meas} = T_{SmC^*\text{-}SmA} - 10°C$.
[b] $T_{meas} = 47°C$.
[c] $T_{meas} = 90°C$.

TABLE 8 Mesomorphic Properties of Liquid Crystals:



No.	n	A	B	Z	K	Phase transitions, °C	Ref.
8-1	1	SOC		H	COS	Cr 210 N 311 I	[172]
8-2	1	OOC		H	COO	Cr 209 N 285 I	[172]
8-3	1	—		H	—	Cr_2 238 Cr_1 259 Sm 265.5 × 267.5 I	[173]
8-4	1	SOC		H	COS	Cr 202 N 241 I	[172]
8-5	1	OOC		H	COO	Cr 142 N 245 I	[172]
8-6	1	COS		H	SOC	Cr 178 N 312 I	[172]
8-7	1	COO		H	OOC	Cr 213 N 297 I	[172]
8-8	8	COO		$SC_{12}H_{25}$	OOC	Cr 55 N 55 I	[209]
8-9	8	COO		$C_{12}H_{25}$	OOC	Cr 56 N 69.5 I	[210]
8-10	8	COO		$COSC_6H_{13}$	OOC	Cr 63 N 79 I	[211]
8-11	8	COO		$COOC_6H_{13}$	OOC	Cr 59 N 96.5 I	[211]
8-12	8	COO		C_6H_{13}	OOC	Cr 62 N 81.5 I	[210]
8-13	8	COO		$COSCH_2$ 	OOC	Cr 78 N 80 I	[212]
8-14	8	COO		$COOCH_2$ 	OOC	Cr 98 N 98 I	[212]
8-15	8	COO		H	OOC	Cr 123 Sm 129 N 195 I	[210]

As is evident from Table 4, alkylthio substitution of the chiral nonracemic compound can reduce a number of the mesophases and lower the smectic C* thermostability in comparison with those of the corresponding alkoxy derivatives (compounds **4-1** and **4-2** and Ref. 70).

A comparison of the phase-transition temperatures of compounds **4-3** and **4-4** (Table 4) reveals that the introduction of the thioester into the terminal chiral group significantly lowers the SmC* thermostability

and slightly reduces the clearing point with respect to those of the corresponding ester derivative.

It has been shown that the stereogenic sulphur atom in sulphoxides is usually configurationally stable at room temperature; thus, sulphoxides may be chiral based on this property alone [86]. This feature of the sulphoxides was used in the design of ferroelectric-liquid-crystal (FLC) sulphoxide derivative **4-5** that exhibits a slightly higher clearing temperature and a lower number of the mesophases with respect to those of the corresponding reference compound **4-6** that do not have the sulphoxide group. In compound **4-5**, the restriction of free rotation of the alkyl chain, resulting from the methyl side close to the chiral sulphur center, fixes the dipole at the S=O moiety and reduces the probability of unfavorable conformers [73]. An example of using an optically active alkylsulphinate group in the design of FLCs was realized in compound **4-7**, which consists of two diastereomers having opposite configurations at the chiral sulphur center and showing lower clearing temperatures and smectic C^* thermostability (only one enantiomer) in comparison with those of the corresponding reference compound **4-8**.

The reported evidence for the planar equilibrium conformation of thiophenol with the barrier to internal rotation significantly lower than that of the corresponding phenol [87], and less effective participation of the sulphur in hydrogen bonding in comparison with that of the oxygen (because of the difference in their electronegativities, see introduction) [4], could be responsible for a lower nematic thermostability of the SH derivatives with respect to that of the corresponding OH derivatives [88].

As is evident from Tables 1–4, the terminal sulphur-substitution of liquid crystals increases (compounds **1-1**–**1-4**, **1-8**, **1-9**, **1-11**, **1-12**, **2-1**, **2-3**, **2-4**, **2-6**, **2-14**, **2-15**, **3-1**–**3-3**, **3-5**–**3-9**, and **4-3**–**4-6**) and lowers (compounds **1-5**–**1-8**, **1-10**, **2-1**, **2-2**, **2-8**, **2-9**, **3-3**, **3-4**, **3-6**–**3-16**, **4-1**, **4-2**, **4-7**, and **4-8**) their melting temperatures (crystal–smectic or crystal–nematic phase-transition temperatures) in comparison with those of the corresponding oxygen-substituted and other reference compounds.

Similar trends have been observed for other liquid crystals having sulphur-substituted terminal groups [2,6,12–14,27,28,57,58,68,69,71,79,89–132].

Linking Substitution

It has been demonstrated that the introduction of the following sulphur-containing linking groups into the molecular core of 2–4 ring liquid-crystal derivatives increases their polarizability and does not

create the mesophases: S, S−S, CH_2SO_2, SO_3 [132–139]. To our knowledge, only six ring derivatives containing the sulphone linkage exhibit monotropic mesophases [140]. These results have been explained in terms of the significant molecular nonlinearity, which is not favorable for the formation of the mesophases [5,50,81,132,135].

It can be seen from Table 5 that the introduction of the CH_2S and CH_2O linkages into the molecular core of compound **5-3** to produce compounds **5-1** and **5-2** lowers their nematic thermostabilities, with more significant effects recorded for compound **5-1**. Its clearing point has been correlated with its more pronounced molecular flexibility [141, 142]. However, the introduction of two SCH_2 linkages into the molecular core of three-ring derivatives gives a notable flexibility between their rigid moieties and results in the disappearance of the mesophases [147]. The introduction of the SCF_2 and OCF_2 linkages into the molecular core of two-ring derivatives does not create the mesophases (compounds **5-4** and **5-5**). These compounds differ in the melting temperatures, with a higher value recorded for the former.

The data presented in Tables 5–7 reveal that the introduction of the thioester COS group into the molecular core of liquid crystals increases (compounds **5-6**, **5-7**, **6-1**–**6-4**, **6-6**, **6-9**, **7-1**, **7-2**, **7-6**, and **7-7**) and lowers (compounds **5-8**, **5-9**, **7-9**, **7-10**, and [Refs. 84 and 168–170]) the clearing temperatures in comparison with those of the corresponding ester derivatives. The enhanced clearing points of some COS derivatives have been explained in terms of their higher intermolecular interactions (caused by their higher transverse dipole moments) compared with those of the corresponding COO derivatives [84]. In the meantime, the parent compounds without the linkages exhibit lower (compounds **5-6**, **5-10**, **6-1**, **6-2**, **6-5**, **6-6**, **6-10**, **7-4**–**7-8**) and higher (compounds **7-1** and **7-3**) clearing temperatures with respect to those of the corresponding thioester derivatives. The introduction of the CSO linkage results in the disappearance of the mesophase (compound **6-7**). However, the CSS linking substitution forms liquid crystals exhibiting the monotropic nematic phase (compound **6-8**). It is useful to express the thermal efficiency of the linkages by the following orders of increasing the clearing temperatures (T_{cl}), compounds **6-6**–**6-10**: T_{cl}: CSO < SB < COO < CSS < COS, where SB is the single bond.

Interestingly, this order is not supported by the corresponding order of increasing the anisotropy of polarizability $\Delta\alpha$, which is the main reason of the increasing nematic thermostability, according to the Mayer–Saupe theory [93,129,171]:

$$\Delta\alpha\text{: SB} < \text{COO} < \text{COS} < \text{CSO} < \text{CSS [77,159]}$$

Changing the molecular structure of liquid crystals may affect the order of increasing the clearing temperatures [66]:

$$T_{cl}\text{: SB} < \text{COO} < \text{COS} < \text{CSS}$$

It has been shown that the COS linking substitution results in later appearance of the reentrant nematic phase in the homologous series of three-ring cyano derivatives and earlier disappearance of the nematic phase with respect to those of the corresponding COO derivatives [84].

In the chiral systems presented in Table 7, the COS linking substitution increases the smectic C* thermostability in comparison with that of the corresponding ester and parent derivatives (compounds **7-1**, **7-2**, **7-4**–**7-8**) and lowers this parameter with respect to that of the corresponding parent compound (compounds **7-1** and **7-3**). More enhanced smectic C* thermostability of the COS derivatives compared with that of the corresponding esters has been explained in terms of their tighter intermolecular packing and stronger lateral forces between molecules caused by longer C−S bonds, which leads to less steric hindrance and thereby more planarity and resonance [163].

The introduction of two thioester linkages into the molecular core of liquid crystals increases (compounds **8-1**–**8-3**, **8-6**, and **8-7**, Table 8) and lowers (compounds **8-4** and **8-5**) the clearing temperatures compared with those of the corresponding ester and parent derivatives. It again reveals the importance of the molecular structure of liquid crystals. In the meantime, the direction of two ester linkages gives more pronounced influence on the nematic thermostability of the ester derivatives **8-2** and **8-7** in comparison with those of the corresponding thioester derivatives **8-1** and **8-6**.

It follows from Tables 5–8 that the introduction of sulphur atoms into the linking groups of liquid crystals increases (compounds **5-4**–**5-10**, **6-1**, **6-2**, **6-3**, **6-5**–**6-10**, **7-1**, **7-2**, **7-6**, **7-7**, **8-1**, **8-2**, **8-4**, and **8-5**) and lowers (compounds **5-1**–**5-3**, **6-2**, and **6-4**, **7-1**, **7-3**–**7-6**, **7-8**–**7-10**, **8-1**, **8-3**, **8-6**, and **8-7**) the melting temperatures in comparison with those of the corresponding oxygen-substituted derivatives and parent systems without linking groups. Although the COS and corresponding CSO derivatives show very similar melting points (compounds **6-6** and **6-7**, Table 6), the introduction of the COS linkage into the molecular core of 4-n-pentyl-4′-cyanobiphenyl gives a higher melting temperature compared with that of the corresponding SOC derivative (compounds **6-1** and **6-2**, Table 6). The combination of two thioester groups (SOC, COS) introduced into the molecular core of the three-ring weakly polar derivatives favors a higher melting point with respect to that of the corresponding derivative having the COS,

SOC combination (compounds **8-1** and **8-6**, Table 8). Interestingly, the corresponding ester derivatives exhibit the opposite behavior (compounds **8-2** and **8-7**). Similar trends have been reported for other liquid crystals containing sulphur-substituted linkages [23,66,106,107,126,166,168,174–207].

Lateral Substitution

It has been reported that in many cases increasing the size of lateral substituents can lower the clearing temperatures of liquid crystals [208]. A similar situation can be observed for some laterally substituted materials where the substituents contain sulphur, oxygen (which is smaller than sulphur [5]) atoms, and parent systems (compounds **8-8**, and **8-9**, and **8-10**–**8-15**) presented in Table 8. The melting temperatures of laterally sulphur-substituted liquid crystals show lower (compounds **8-8**–**8-10**, and **8-13**–**8-15**) and higher (compounds **8-10**–**8-12**) clearing points in comparison with those of the corresponding oxygen-substituted derivatives and other reference compounds. Similar trends have been demonstrated for other liquid crystals containing sulphur-substituted lateral groups [213,214].

It is believed that the electronic and geometrical structures of sulphur-substituted groups [4,10,11,29–31,34,38–43,48–50,87,215–223] and the corresponding oxygen-substituted and other reference groups [4,5,35,36,44–48,51,87,217,218,224–229] play a very important role in the intra- [49–51] and intermolecular [52–56] interactions affecting molecular packing, which predominantly influences mesophase stability [52–56,230]. 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 to the steric factors [230]. 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 [230].

X-ray diffraction (XRD) of the liquid crystals is one of the useful methods for studying the effects of the association of liquid-crystalline molecules on the structure of their phases and consequently on the properties of liquid crystals formed by these molecules [156,231–234]. It has been shown that, depending on the molecular structure, the monomeric density wave with the period d_1 (period d_1 is related to the fluctuation-layer structure formed by separate molecules) [119,122,127,235–237] or dimeric density wave with the period d_2

[117,122,238] can be observed for the NCS and SCN (thiocyanato) (only dimeric density wave) derivatives.

The XRD pattern of 4-n-pentyl-4′-cyanobiphenyl (compound **6-5**, Table 6) shows two incommensurate density waves: monomeric with period d_1 and dimeric with period d_2 [156]. The introduction of the SOC and COS thioester linkages between two phenyl rings in compound **6-5** results in increasing the ratio d_2/L (lowering molecular overlapping in the creation of the dimers, where L is the molecular length, compound **6-2**, Table 6) and the disappearance of the monomeric density wave and lowering the ratio d_2/L (compound **6-1**). XRD of weakly polar sulphur-containing liquid crystals reveals the formation of the monolayer smectic phases with the ratio $d/L \leq 1$ (compounds **4-7**, **4-8**, Table 4). Similar trends have been observed for other sulphur-containing liquid crystals [21,92,99,132,140,185,239–244]. The crystal phases of some sulphur-containing liquid crystals have been studied in Refs. [148 and 245–250].

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**. Molecular structure of liquid crystals is described by the theory of Maier and Meier [251]:

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

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, 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 $T_{\mathrm{N-I}}$ can only be made at a constant reduced temperature $\tau = T_{\mathrm{meas}}/T_{\mathrm{N-I}}$ [252].

Tables 1, 2, and 6 present data on the dielectric properties of liquid-crystalline compounds measured at a constant reduced temperature and extrapolated from the liquid-crystalline mixtures at 20°C. According to Ref. 252, 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. From these tables, it follows that for the definite 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_2CHF_2, CN, $SOCHF_2$, SCN, SF_5, NCS, CF_3, SCF_3, $SCHF_2$, $OCHF_2$, OCF_3 diminish (4.08, 4.05, 3.93, 3.62, 3.44, 2.85, 2.54, 2.50, 2.48, 2.46, 2.36) [6,215,253–255]. Taking into consideration the angles, β of the dipole moments could provide a more accurate analysis of the dielectric properties of the discussed compounds [215,253–255].

As is evident from Table 6, the introduction of the COS and SOC linkages into the molecular core of compound **6-5** increases and lowers the dielectric anisotropy (compounds **6-1** and **6-2**, respectively), because the total dipole moment is being increased and decreased, respectively (see Eq. 1). A lower value of the $\Delta\varepsilon$ of the thioester derivative **6-1** in respect to that of the corresponding ester derivative **6-3** is caused by a lower value of the dipole moment of the thioester group ($\mu = 1.43$ D) compared with the value of $\mu = 1.89$ D of the corresponding ester group [49]. The introduction of the SOC linkage into the molecular core of liquid crystals gives the lowest value of the ratio $\Delta\varepsilon/\varepsilon_\perp$ (among compounds **6-1**–**6-3**, **6-5**, Table 6), which is a very important parameter for the development of liquid-crystalline materials for super-twisted nematic display applications [252]. Similar trends have been reported for other sulphur-containing liquid crystals [6,8,23,93,115,122]. The dielectric relaxation processes have been studied in Refs. [112,113,120,195,198,240, and 256–266].

OPTICAL PROPERTIES

The phenomenological relation between refractive index and the electric polarization is defined as [267,268]:

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

where the mean polarizability $\alpha^* = (\alpha_\parallel + 2\alpha_\perp)/3$; the mean refractive index $n^{*2} = (n_e^2 + 2n_o^2)/3$; n_o is the ordinary and n_e is the extraordinary refractive index. From Eq. (2) and the previous paragraph, it follows that sulphur-containing compounds that have a larger induced polarizability [49,66,159,269] exhibit the optical anisotropy $\Delta n = n_e - n_o$, which is larger than that of the corresponding oxygen-containing derivatives (compounds **1-3**–**1-6**, **1-8**, **1-9**, **3-13**–**3-16**, **6-1**, **6-3**, and **6-6**–**6-9**, Tables 1, 3, and 6). Sometimes, the extrapolation gives very similar values of the Δn for the corresponding sulphur- and oxygen-containing liquid crystals (compounds **1-1**, **1-2**, **1-11**, **1-13**–**1-15**, **5-4**, and **5-5**), which are due to the approximate character of such calculations.

As is evident from Table 6, changing the direction of the thioester linkage or replacing the COS group by the CSO linkage does not much change the optical anisotropy of the corresponding liquid crystals (compounds **6-1**, **6-2**, **6-6**, and **6-7**). The introduction of the thioester COS, SOC, CSO, and ester linkages reduces the effective conjugation of the π-electron systems and results in decreasing the Δn in comparison with that of the corresponding parent system (compounds **6-1**–**6-3**, **6-5**–**6-7**, **6-9**, and **6-10**). The introduction of the CSS (dithio-ester) linkage into the molecular core of compound **6-10** to obtain compound **6-8** results in the largest anisotropy of polarizability among those of compounds **6-6**–**6-10** [77,159], which in turn provides the highest optical anisotropy for compound **6-8**. Similar trends have been demonstrated for other sulphur-containing liquid crystals [6,8,23,66,68,69,77,93, 115,121,122].

VISCOELASTIC PROPERTIES

It has been shown that the nematic liquid-crystalline materials for display applications should have a low viscosity for giving the acceptable response times for liquid-crystal displays [252,270]. According to the results on the kinematic viscosity ν presented in Tables 1 and 5, terminally and linking sulphur-substituted derivatives exhibit larger values than the corresponding oxygen-substituted and unsubstituted derivatives (compounds **1-1**, **1-2**, **1-8**–**1-13**, **5-4**, and **5-5**). These results can be correlated with a larger size of sulphur-containing terminal and linking groups caused by a larger size of the sulphur atom [5]. Similar trends have been reported for other sulphur-containing liquid crystals [6,8,102,122].

In the bulk of nematic liquid crystals, elastic properties are determined by three elastic constants (Oseen–Frank constants), corresponding to the restoring forces opposing splay (K_{11}), twist (K_{22}), and bend (K_{33}) [271–273]. It has been demonstrated that the elastic constants depend on molecular structure, intermolecular association, and temperature of nematics [271,274,275]. The ratio K_{33}/K_{11} was found to be less than unit for a weakly polar two-ring thioester derivative [276], which is similar in value to those of other weakly polar derivatives [3].

MOLECULAR PACKING

It has been shown that liquid-crystalline molecular packing plays an important role in the creation of mesophases [53,55] and defines their optical properties [267]. The molecular packing coefficient is expressed in Ref. 157 as

$$k_{\mathrm{p}} = N_{\mathrm{A}} V \rho / M \tag{3}$$

where N_{A} is the Avogadro number, ρ is the density, M is the molecular weight, and V is the intrinsic (van der Waals) volume of the molecule, calculated from the van der Waals volume increments of the individual atoms or by using the average radii and chemical bond lengths [277].

As is evident from Table 6, the replacement of the COS linkage by the SOC linking group slightly increases and lowers the molecular packing coefficient at 79 and 40°C, respectively (it reveals the different temperature dependences of the molecular packing for compounds **6-1** and **6-2**). However, the ester and biphenyl derivatives exhibit less dense molecular packing in comparison with that of the corresponding thioester derivatives (compounds **6-1**–**6-3** and **6-5**).

PHYSICOCHEMICAL PARAMETERS OF THE SMECTIC C* PHASE

The spontaneous polarization $\mathrm{P_s}$ 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 [278]. 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 [278]. The spontaneous polarization Ps is a quantity that is directly related to the response time τ as a switching device [279]:

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

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.

As is evident from Table 4, the terminal alkylthio substitution lowers the absolute value of the spontaneous polarization in comparison with that of the corresponding alkoxy substitution (compounds **4-1** and **4-2**). It has been correlated with the decreased transverse dipole moment of the sulphur atom in comparison with that of the oxygen [70]. The increased size of the sulphur molecule [5] could hinder the tilted packing of the molecules resulting in a lower tilt angle (compounds **4-1** and **4-2**) [70]. These compounds exhibit similar values of the rotational viscosity [70].

It is evident from Table 4 that compound **4-3**, which has the thioester in its terminal group, exhibits a significantly lower Ps with respect to that of the corresponding ester derivative **4-4**.

The introduction of the sulphoxide group into the terminal group leads to the appearance of small spontaneous polarization and moderate tilt angle and response time (compound **4-5**, Table 4) [73].

It should be noted that the alkylsulphinate derivative **4-7** exhibits a similar value for the tilt angle with respect to that of the corresponding alkylester derivative **4-8** (Table 4).

The data presented in Table 7 reveal that the corresponding two-ring thioester and ester derivatives show very similar values of Ps (compounds **7-6**, **7-7**, **7-9**, and **7-10**). It could be caused by less pronounced influence of the transversive dipole moments of the COS and COO groups on the spontaneous polarization in comparison with that of the C−Cl bond [163] and C−CH_3 bond. The response times of compounds **7-6** and **7-7** are slightly different, with a higher value recorded for the former compound. Equal tilt angles for some corresponding thioester and ester derivatives have been reported [200]. Similar trends have been shown for other sulphur-containing liquid crystals [89–91,98,99,132,166,192,200,240,256].

CONCLUSION

Systematic studies on the effect of terminal-, linking-, and lateral-group sulphur substitutions on the physicochemical properties of calamitic 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.

REFERENCES

[1] Pavluchenko, A. I., Petrov, V. F., & Smirnova, N. I. (1995). *Liq. Cryst.*, *19*, 811.
[2] Petrov, V. F. (2001). *Liq. Cryst.*, *28*, 217.
[3] Petrov, V. F. (2002). *Liq. Cryst.*, *29*, 805.
[4] Paul, I. C. (1974). In: *The Chemistry of the Thiol Group*, Patai, S. (Ed.), Wiley: New York, 111.
[5] Hargittai, I. (1985). *The structure of volatile sulphur compounds*, D. Reidel Publishing: Boston.
[6] Pavluchenko, A. I., Smirnova, N. I., Petrov, V. F., Fialkov, Y. A., Shelyazhenko, S. V., & Yagupolsky, L. M. (1991). *Mol. Cryst. Liq. Cryst.*, *209*, 225.
[7] Bartmann, E., Dorsch, D., Poetsch, E., Hittich, R., & Rieger, B. (1991). Eur. Pat. Appl. EP 449 015.
[8] Bartmann, E., Dorsch, D., & Finkenzeller, U. (1991). *Mol. Cryst. Liq. Cryst.*, *204*, 77.
[9] Bartmann, E., Dorsch, D., Finkenzeller, U., Kurmeier, H. A., & Poetsch, E. (1990). *19th Freiburger Arbeitstagung Flussigkristalle*, Freiburg University: Freiburg, Germany, 8.

[10] Kirsch, P., Bremer, M., Heckmeier, M., & Tarumi, K. (1999). *Angew. Chem. Int. Ed*., *38*, 1989.
[11] Kapustin, E. G., Bzhezovsky, V. M., & Yagupolski, L. M. (2001). *J. Fluor. Chem*., *113*, 227.
[12] Zaschke, H. (1977). *Z. Chem*., *17*, 63.
[13] Liu, C.-T. (1981). *Mol. Cryst. Liq. Cryst*., *74*, 25.
[14] Takeda, H., Sakurai, Y., Takenaka, S., Miyake, H., Doi, T., Kusabayashi, S., & Takagi, T. (1990). *J. Chem. Soc. Faraday Trans*., *86*, 3429.
[15] Hargittai, I. (1988). In: *The Chemistry of Sulphones and Sulphoxides*, Patai, S. Rappoport, Z., & Stirling, C. (Eds.), Wiley: New York, 33.
[16] Dabrowski, R. & Zytynski, E. (1982). *Mol. Cryst. Liq. Cryst*., *87*, 109.
[17] Bailey, A. L. & Bates, G. S. (1991). *Mol. Cryst. Liq. Cryst*., *198*, 417.
[18] Dabrowski, R., Dziaduszek, J., & Szczucinski, T. (1984). *Mol. Cryst. Liq. Cryst. Lett*., *102*, 155.
[19] Bezborodov, V. S. & Grinkevich, O. A. (1982). *J. Org. Chem. USSR*, *18*, 1155.
[20] Boller, A. & Scherrer, H. (1975). US Patent 3 *925*, 444.
[21] Heppke, G., Pfeiffer, S., Ranft, A., & Shashidhar, R. (1991). *Mol. Cryst. Liq. Cryst*., *206*, 31.
[22] Nguyen, H. T. (1983). Mol. Cryst. Liq. Cryst., *91*, 285.
[23] Kawada, M. (1995). Japan Pat. Appl. JP 71 45374.
[24] Dabrowski, R., Dziaduszek, J., Szczucinski, T., & Raszewski, Z. (1984). *Mol. Cryst. Liq. Cryst*., *107*, 411.
[25] Goodby, J. W. (1984). In: *Liquid Crystals and Ordered Fluids*, Griffin, A. C. & Johnson, J. F. (Eds.), Plenum Press: New York, Vol. 4, 175.
[26] Goodby, J. W. & Pindak, R. (1981). *Mol. Cryst. Liq. Cryst*., *75*, 233.
[27] Okamoto, H., Hayashi, M., & Takenaka, S. (1996). *Liq. Cryst*., *20*, 647.
[28] Okamoto, H., Hayashi, M., & Takenaka, S. (1996). *Bull. Chem. Soc. Jpn*., *69*, 1437.
[29] Onda, M., Kambayashi, S., Sakaizumi, Y., & Yamaguchi, T. (1976). *J. Mol. Struct*., *34*, 299.
[30] Remko, M., Klimo, V., Cizmarik, J., & Fiserova, M. (1987). *Z. Phys. Chem*., *268*, 874.
[31] Bouchy, A. & Roussy, G. (1973). *Compt. Rend. Acad. Sci. Paris*, *C277*, 143.
[32] Balfour, W. J., Dingle, T. W., & Ram, R. S. (1982). *J. Mol. Spectr*., *96*, 306.
[33] Olsen, J. F. (1979). *J. Mol. Struct*., *57*, 251.
[34] Sakaizumi, T., Namikawa, M., & Ohashi, O. (1995). *J. Mol. Struct*., *345*, 189.
[35] Bak, B., van Eijck, B. P., & Kierkegaard, C. (1973). *J. Mol. Struct*., *18*, 429.
[36] Runge, W. (1983). In: *The Chemistry of Triple-Bonded Functional Groups*, Patai, S. & Rappoport, Z. (Eds.), Wiley: New York, 1.
[37] Casado, J., Nygaard, L., & Sorensen, G. O. (1971). *J. Mol. Struct*., *8*, 211.
[38] Del Bene, J. & Jaffe, H. H. (1968). *J. Phys. Chem*., *48*, 1807.
[39] Beard, C. I. & Dailey, B. P. (1949). *J. Am. Chem. Soc*., *71*, 929.
[40] Danford, M. D. & Livingston, R. L. (1955). *J. Am. Chem. Soc*., *77*, 2944.
[41] Pauling, L. (1960). *The nature of the chemical bond*, Cornell University Press: New York, 269f.
[42] Rabalais, J. W., McDonald, J. M., Scherr, V., & Glynn, S. P. (1971). *Chem. Rev*., *71*, 73.
[43] Giffard, M., Cousseau, J., & Martin, G. J. (1985). *J. Chem. Soc. Perkin Trans. 2*, *157*.
[44] Ugi, I. (1971). *Isonitrile chemistry*, Academic Press: New York.
[45] Patai, S. & Rappoport, Z. (1983). *The chemistry of triple-bonded functional groups*, Wiley: New York.

[46] Dimitrova, Y. (1996). *J. Mol. Struct*., *362*, 23.
[47] Dimitrova, Y. (1997). *J. Mol. Struct. (Theochem.)*, *391*, 241.
[48] Yanari, I., Staral, J. S., & Roberts, J. D. (1979). *Org. Magn. Reson*., *12*, 340.
[49] Scheithauer, S. & Mayer, R. (1979). *Thio- and dithiocarboxylic acids and their derivatives*, Georg Thieme: Stuttgart.
[50] Oae, S. (1977). *Organic chemistry of sulphur*, Plenum Press: New York.
[51] Bzhezovsky, V. M. & Kapustin, E. G. (2002). *Rus. J. Org. Chem*., *38*, 591.
[52] Hori, K., Kuribayashi, M., & Iimuro, M. (2000). *Phys. Chem. Chem. Phys*., *2*, 2863.
[53] Osman, M. A. (1983). *Z. Naturforsch*., *38A*, 693.
[54] de Jeu, W. H. (1983). *Phil. Trans. R. Soc. A*, *309*, 217.
[55] Ostrovskii, B. I. (1999). In: *Structure and Bonding*, Mingos, D. M. P. (Ed.), Springer Verlag: New York, Vol. 94, 200.
[56] Schad, H. & Osman, M. A. (1981). *J. Chem. Phys*., *75*, 880.
[57] De Givenchy, E. T., Guittard, F., Bracon, F., & Cambon, A. (1999). *Liq. Cryst*., *26*, 1371.
[58] De Givenchy, E. T., Guittard, F., Bracon, F., & Cambon, A. (1999). *Liq. Cryst*., *26*, 1163.
[59] Petrov, V. F. & Pavluchenko, A. I. (2002). *Mol. Cryst. Liq. Cryst*., *383*, 63.
[60] Petrov, V. F., Pavluchenko, A. I., & Smirnova, N. I. (1995). *Mol. Cryst. Liq. Cryst*., *265*, 47.
[61] Zaschke, H. (1980). In: *Advances in Liquid Crystal Research and Applications*, Bata, L. (Ed.), Pergamon Press: Oxford; Akademiai Kiado: Budapest, 1059.
[62] Hanna, J., Kogo, K., & Kafuku, K. (1998). Eur. Pat. Appl. EP 864 631.
[63] Vill, V. (1992). Landolt-Bornstein, Group IV: Macroscopic Properties of Matter. In: *Liquid Crystals*, Thiem, J. (Ed.), Springer Verlag: New York, Vol. 7a, 127.
[64] Zaschke, H., Arndt, S., Wayner, V., & Schubert, H. (1977). *Z. Chem*., *17*, 293.
[65] Pavluchenko, A. I., Purvanyatskas, G. V., Smirnova, N. I., Grebenkin, M. F., Petrov, V. F., Barnik, M. I., Ivaschenko, A. V., Korotkova, N. I., Kovshev, E. I., Rabinovich, A. Z., Bumagin, N. A., Andrjukhova, N. P., Beletskaya, I. P., Maltsev, S. D., & Titov, V. V. (1988). PCT WO 88/07992.
[66] Seed, A. J., Toyne, K. J., Goodby, J. W., & Hird, M. (2000). *J. Mater. Chem*., *10*, 2069.
[67] Hird, M., Toyne, K. J., Gray, G. W., Day, S. E., & McDonnell, D. G. (1993). *Liq. Cryst*., *15*, 123.
[68] Cross, G. J., Seed, A. J., Toyne, K. J., Goodby, J. W., Hird, M., & Artal, M. C. (2000). *J. Mater. Chem*., *10*, 1555.
[69] Hird, M., Seed, A. J., Toyne, K. J., Goodby, J. W., Gray, G. W., & McDonnell, D. G. (1993). *J. Mater. Chem*., *3*, 851.
[70] Robinson, W. K., Miller, R. J., Gleeson, H. F., Hird, M., Seed, A. J., & Styring, P. (1996). *Ferroelectrics*, *180*, 291.
[71] Wu, S.-L. & Hsieh, W.-J. (1996). *Ferroelectrics*, *180*, 259.
[72] Wu, S.-L., Chen, D.-G., Chen, S.-J., Wang, C.-Y., Shy, J.-T., & Hsiue, G.-H. (1995). *Mol. Cryst. Liq. Cryst*., *264*, 39.
[73] Nishide, K., Nakayama, A., Kusumoto, T., Hiyama, T., Takehara, S., Shoji, T., Osawa, M., Kuriyama, T., Nakamura, K., & Fujisawa, T. (1990). *Chem. Lett*., 623.
[74] Goodby, J. W. & Leslie, T. M. (1984). *Mol. Cryst. Liq. Cryst*., *110*, 175.
[75] Soldera, A., Nicoud, J.-F., Galerne, Y., Skoulios, A., & Guillon, D. (1992). *Liq. Cryst*., *12*, 347.
[76] Nguyen, H. T., Twieg, R. J., Nabor, M. F., Isaert, N., & Destrade, C. (1991). *Ferroelectrics*, *121*, 187.
[77] Seed, A. J., Toyne, K. J., & Goodby, J. W. (1995). *J. Mater. Chem*., *5*, 653.

[78] Gray, G. W., Harrison, K. J., & Nash, J. A. (1973). *Electron. Lett*., *9*, 130.
[79] Dalcanale, E., Arena, C., Catellani, M., & Chiusoli, G. P. (1992). *Liq. Cryst*., *12*, 905.
[80] Castellano, J. A., Goldmacher, J. E., Barton, L. A., & Kane, J. S. (1968). *J. Org. Chem*., *33*, 3501.
[81] Naumov, V. A. (1988). In: *Stereochemical Applications of Gas-Phase Electron Diffraction*, Part B, Hargittai, I. & Hargittai, M. (Eds.), VCH: New York, 93.
[82] Goulding, M., Greenfield, S., Parri, O., & Coates, D. (1995). *Mol. Cryst. Liq. Cryst*., *265*, 27.
[83] van Meter, J. P. & Klandermann, B. H. (1973). *Mol. Cryst. Liq. Cryst*., *22*, 271.
[84] Nguyen, H. T., Destrade, C., Twieg, R. J., & Betterton, K. (1990). *Liq. Cryst*., *8*, 419.
[85] Sigaud, G., Nguyen, H. T., Hardouin, F., & Gasparoux, H. (1981). *Mol. Cryst. Liq. Cryst*., *69*, 81.
[86] Andersen, K. K. (1988). In: *The Chemistry of Sulphones and Sulphoxides*, Patai, S., Rappoport, Z., & Stirling, C. (Eds.), Wiley: New York, 55.
[87] Larsen, N. W. & Nicolaisen, F. M. (1974). *J. Mol. Struct*., *22*, 29.
[88] Marcos, M., Melendez, E., Ros, M. B., & Serrano, J. L. (1989). *Mol. Cryst. Liq. Cryst*., *167*, 239.
[89] Sebastiao, P., Merry, S., Sieffert, M., Nicoud, J. F., Galerne, Y., & Guillon, D. (1998). *Ferroelectrics*, *212*, 133.
[90] Cherkaoui, M. Z., Nicoud, J.-F., Galerne, Y., & Guillon, D. (1995). *J. Phys. II. France*, *5*, 1263.
[91] Cherkaoui, M. Z., Nicoud, J.-F., Galerne, Y., & Guillon, D. (1997). *J. Chem. Phys*., *106*, 7816.
[92] Cherkaoui, M. Z., Nicoud, J.-F., Galerne, Y., & Guillon, D. (1999). *Liq. Cryst*., *26*, 1315.
[93] Petrov, V. F., Duan, M., Okamoto, H., Mu, J., Shimizu, Y., & Takenaka, S. (2001). *Liq. Cryst*., *28*, 387 and references therein.
[94] Abe, K., Yang, X., Yano, S., Kato, T., & Takeuchi, H. (2000). *Liq. Cryst*., *27*, 839.
[95] Muller, I., Hemmerling, W., & Wingen, R. (1988). *Ferroelectrics*, *85*, 393.
[96] Maier, W. & Englert, G. (1958). *Z. Electrochemie*, *62*, 1020.
[97] McDonnell, D. G., Day, S. E., Coates, D., Jenner, J. A., Hird, M., & Toyne, K. J. (1994). US Patent 5 352 381.
[98] Naijoh, S., Inoue, C., Kurotaki, A., & Nagai, K. (1991). US Patent 5 055 225.
[99] Soldera, A., Nicoud, J. F., Skoulious, A., Galerne, Y., & Guillon, D. (1994). *Chem. Mater*., *6*, 625.
[100] Shinjo, K., Takiguchi, T., Kitayama, H., Katagiri, K., Yamashita, M., Togano, T., Terada, M., & Sato, J. (1990). Eur. Pat. Appl. EP 352 480.
[101] van Meter, J. P. & Klandermann, B. H. (1973). *Mol. Cryst. Liq. Cryst*., *22*, 285.
[102] Sharma, N. K., Muller, I., Wingen, R., Dubal, H. R., Escher, C., & Olendorf, D. (1987). *Mol. Cryst. Liq. Cryst*., *151*, 225.
[103] Hemmerling, W., Dubal, H.-R., Escher, C., Illian, G., Inoguchi, Y., Muller, I., Murakami, M., Ohlendorf, D., & Wingen, R. (1990). German Pat. Appl. DE 3 827 600.
[104] Muller, I., Dubal, H.-R., Escher, C., Hemmerling, W., Ohlendorf, D., & Wingen, R. (1988). German Patent DE-OS 3 709 618.
[105] Demus, D. & Sackmann, H. (1963). *Z. Phys. Chem*., *222*, 127.
[106] Zaschke, H. & Hyna, C. (1979). *J. Prakt. Chem*., *321*, 629.
[107] Harufuji, T., Saito, S., Okabe, E., & Saito, H. (1999). Japan Patent Appl. JP 11043485.

[108] Bremer, M., Pauluth, D., Krause, J., & Tarumi, K. (1998). German Pat. Appl. DE 196 24 590.
[109] Reiffenrath, V. & Bremer, M. (1999). German Pat. Appl. DE 198 04 894.
[110] Wand, M. D., Vohra, R. T., Thurmes, W. N., & More, K. M. (1996). *Ferroelectrics*, *180*, 333.
[111] Kirsch, P., Unger, G., Lenges, M., Krause, J., & Heckmeier, M. (2003). UK Pat. Appl. GB 2 379 442.
[112] Urban, S., Dabrowski, R., Dziaduszek, J., Janik, J., & Moscicki, J. K. (1999). *Liq. Cryst*., *26*, 1817.
[113] Urban, S., Czuprynski, K., Dabrowski, R., Gestblom, B., Janik, J., Kresse, H., & Schmalfuss, H. (2001). *Liq. Cryst*., *28*, 691.
[114] Spadlo, A., Dabrowski, R., Filipowicz, M., Stolarz, Z., Przedmojski, J., Gauza, S., Fan, C. Y. H., & Wu, S.-T. (2003). *Liq. Cryst*., *30*, 191.
[115] Kirsch, P., Bremer, M., Kirsch, A., Manabe, A., Poetsch, E., Reiffenrath, V., & Tarumi, K. (2000). *Mol. Cryst. Liq. Cryst*., *346*, 193.
[116] Poetsch, E., Manabe, A., Reiffenrath, V., Reuter, M., Krause, J., & Pauluth, D. (2001). Eur. Pat. Appl. EP 1 126 006.
[117] Duan, M., Tasaka, T., Okamoto, H., Petrov, V. F., & Takenaka, S. (2000). *Liq. Cryst*., *27*, 1195.
[118] Okamoto, H., Petrov, V. F., & Takenaka, S. (1999). *Liq. Cryst*., *26*, 691.
[119] Dabrowski, R., Przedmojski, J., Baran, J. W., & Pura, B. (1986). *Cryst. Res. Technol*., *21*, 567.
[120] Urban, S., Gestblom, B., & Dabrowski, R. (1998). *Liq. Cryst*., *24*, 681.
[121] Gauza, S., Wang, H., Wen, C.-H., Wu, S.-T., Seed, A. J., & Dabrowski, R. (2003). *Jap. J. Appl. Phys*., *42*, 3463.
[122] Petrov, V. F. & Shimizu, Y. (2001). *Mol. Cryst. Liq. Cryst*., *363*, 107 and references therein.
[123] Wu, S. L., Huang, F. K., Uang, B. J., Tsai, W. J., & Liang, J. J. (1995). *Liq. Cryst*., *18*, 715.
[124] Wu, S. L., You, J. H., & Uang, B. J. (2001). *Liq. Cryst*., *28*, 69.
[125] Shelyazhenko, S. V., Dronkina, M. I., Fialkov, Y. A., & Yagupolskii, L. M. (1988). *J. Org. Chem. USSR*, *24*, 555.
[126] Zaschke, H., Isenberg, A., & Schubert, H. (1979). *J. Prakt. Chem*., *321*, 619.
[127] Pavluchenko, A. I., Smirnova, N. I., Petrov, V. F., Grebyonkin, M. F., & Titov, V. V. (1991). *Mol. Cryst. Liq. Cryst*., *209*, 155.
[128] Formasieri, G., Guittard, F., & Geribaldi, S. (2003). *Liq. Cryst*., *30*, 251.
[129] Petrov, V. F., Torgova, S. I., Karamysheva, L. A., & Takenaka, S. (1999). *Liq. Cryst*., *26*, 1141.
[130] Zverkova, T. I., Kovshev, E. I., Moklyachuk, L. I., Fialkov, Yu, A., & Yagupolskii, L. M. (1980). In: *Advances in Liquid Crystal Research and Applications*, Bata, L. (Ed.), Pergamon Press: Oxford; Akademiai Kiado: Budapest, 991.
[131] Wu, S.-L., Wang, K.-J., & Yu, M.-C. (2002). *Ferroelectrics*, *276*, 93.
[132] Cherkaoui, M. Z., Nicoud, J.-F., & Guillon, D. (1994). *Chem. Mater*., *6*, 2026.
[133] Klug, R., Pauluth, D., Reiffenrath, V., & Bartmann, E. (1992). German Patent DE-OS 4 105 743.
[134] Kossmehl, G. & Budwill, D. (1987). *Z. Naturforsch*., *42b*, 478.
[135] Koden, M., Hayashi, S., Nishimura, K., Kusabayashi, S., & Takenaka, S. (1984). *Mol. Cryst. Liq. Cryst*., *106*, 31.
[136] Gussoni, M., Rui, M., & Zerbi, G. (1998). *J. Mol. Struct*., *447*, 163.
[137] Ogata, Y., Takagi, K., & Yamada, S. (1997). *J. Chem. Soc., Perkin Trans. 2*, 1629.
[138] Jones, B. & Chapman, F. (1952). *J. Chem. Soc*., 1829.

[139] Saito, S., Terashima, K., Inukai, T., & Furukawa, K. (1985). Eur. Pat. Appl. EP 153 826.
[140] Matsunaga, Y. & Yuri, T. (1993). *Mol. Cryst. Liq. Cryst.*, *237*, 145.
[141] Rozsondai, B., Moore, J. H., Gregory, D. C., & Hargittai, I. (1977). *Acta Chim. Acad. Sci. Hung.*, *94*, 321.
[142] Kleinpeter, E., Kohler, H., Lunow, A., Tschierske, C., & Zaschke, H. (1988). *Tetrahedron*, *44*, 1609.
[143] Obikawa, T., Ikukawa, S., & Nakayama, J. (1993). US Patent 5 238 599.
[144] Bartmann, E. (1996). *Adv. Mater.*, *8*, 570.
[145] Deutscher, H.-J., Laaser, B., Dolling, W., & Schubert, H. (1978). *J. Prakt. Chem.*, *320*, 191.
[146] Baeyens-Volant, D. & David, C. (1985). *Mol. Cryst. Liq. Cryst.*, *116*, 217.
[147] Kim, O. K., Lee, H. S., Yoon, T. H., & Shashidhar, R. (1991). *Liq. Cryst.*, *10*, 725.
[148] Haase, W., Paulus, H., & Ibrahim, I. H. (1984). *Mol. Cryst. Liq. Cryst.*, *107*, 377.
[149] Raines, R. D., Heffner, W. R., Cladis, P. E., & Marcus, M. (1982). *Mol. Cryst. Liq. Cryst. Lett.*, *72*, 263.
[150] Ibrahim, I. H. & Haase, W. (1979). *J. Phys.*, *40*, 191.
[151] El-Gamal, M. A., Kandil, S. H., Abd El-Hamid, E., & Ibrahim, I. H. (1988). *Chemtronics*, *3*, 107.
[152] Boller, A., Cereghetti, M., Schadt, M., & Scherrer, H. (1977). *Mol. Cryst. Liq. Cryst.*, *42*, 215.
[153] Titov, V. V., Kovshev, E. I., Pavluchenko, A. I., Lazareva, V. T., & Grebenkin, M. F. (1975). *J. Phys. Colloq.*, *36*, C1-387.
[154] Kovshik, A. P., Denite, Y. I., Ryumtsev, E. I., & Tsvetkov, V. N. (1975). *Sov. Phys. Crystallogr.*, *20*, 861.
[155] Totani, K., Matsumoto, G., Iwasaki, K., & Jinnai, T. (1978). German Patent DE-OS 2 524 004.
[156] Grebyonkin, M. F., Petrov, V. F., & Ostrovsky, B. I. (1990). *Liq. Cryst.*, *7*, 367.
[157] Belyaev, V. V., Grebyonkin, M. F., & Petrov, V. F. (1990). *Rus. J. Phys. Chem.*, *64*, 509.
[158] Schadt, M., Petrzilka, M., Gerber, P. R., & Villiger, A. (1985). *Mol. Cryst. Liq. Cryst.*, *122*, 241.
[159] Seed, A. J., Toyne, K. J., Goodby, G. W., & McDonnell, J. G. (1995). *J. Mater. Chem.*, *5*, 1.
[160] Yoshinaga, K., Katogiri, K., Kobayashi, T., & Shinjo, K. (1987). German Patent DE-OS 3 629 446.
[161] Keller, P. (1984). *Ferroelectrics*, *58*, 3.
[162] Inoue, H., Sato, S., Terashima, K., Inukai, T., & Furukawa, K. (1985). Eur. Pat. Appl. EP 131 373.
[163] Twieg, R. J., Betterton, K., Nguyen, H. T., Tang, W., & Hinsberg, W. (1989). *Ferroelectrics*, *91*, 243.
[164] Mohr, K., Kohler, S., Worm, K., Pelzl, G., Diele, S., Zaschke, H., Demus, D., Andersson, G., Dahl, I., Lagerwall, S. T., Skarp, K., & Stebler, B. (1987). *Mol. Cryst. Liq. Cryst.*, *146*, 151.
[165] Sakurai, T., Mikami, N., Higuchi, R., Honma, M., & Yoshino, K. (1988). *Ferroelectrics*, *85*, 469.
[166] Cluzeau, P., Ismaili, M., Anakkar, A., Foulon, M., Babeau, A., & Nguyen, H. T. (2001). *Mol. Cryst. Liq. Cryst.*, *362*, 185.
[167] Terashima, K., Ichihashi, M., Kikuchi, M., Furukawa, K., & Inukai, T. (1986). *Mol. Cryst. Liq. Cryst.*, *141*, 237.

[168] Neubert, M. E., Zemnicka-Merchant, B., Jirousek, M. R., Laskos, S. J., Leonhardt, D., & Sharma, R. B. (1988). *Mol. Cryst. Liq. Cryst.*, *154*, 209.
[169] Hsu, Y. Y. (1984). US Patent 4 424 372.
[170] Hsu, Y. Y. (1982). US Patent 4 313 878.
[171] Maier, W. & Saupe, A. (1959). *Z. Naturforsch.*, *14a*, 882.
[172] Dewar, M. J. S. & Riddle, R. M. (1975). *J. Am. Chem. Soc.*, *97*, 6658.
[173] Vill, V. (1992). Landolt-Bornstein, Group IV: Macroscopic Properties of Matter. In: *Liquid Crystals*, Thiem, J. (Ed.), Springer Verlag: New York, Vol. 7c, 38.
[174] Todoroff, T. G., Marande, R., Boyd, D., & Uhrich, D. L. (1983). *Mol. Cryst. Liq. Cryst.*, *95*, 367.
[175] Okamoto, H., Wu, J., Morita, Y., & Takenaka, S. (2002). *Bull. Chem. Soc. Jpn.*, *75*, 175.
[176] Schantz, C. A. & Johnson, D. L. (1978). *Phys. Rev. A*, *17*, 1504.
[177] Kanbe, S., Ota, T., Takei, K., & Shionozaki, Y. (1980). UK Pat. Appl. GB 2 043 633.
[178] Andou, T., Matsui, S., Miyazawa, K., Takeuchi, H., Koizumi, Y., Sekiguchi, Y., Nakagawa, E., & Takeshita, F. (2000). Eur. Pat. Appl. EP 1 043 299.
[179] Kim, Y. B. & Seno, M. (1976). *Mol. Cryst. Liq. Cryst.*, *36*, 293.
[180] Neubert, M. E., Cline, R. E., Zawalski, M. J., Wildmann, P. J., & Ekachai, A. (1981). *Mol. Cryst. Liq. Cryst.*, *76*, 43.
[181] Neubert, M. E., Leung, K., Laskos, S. J., Ezenyilimba, M. C., Jirousek, M. R., Leonhardt, D., Williams, B. A., & Ziemnicka-Merchant, B. (1989). *Mol. Cryst. Liq. Cryst.*, *166*, 181.
[182] Goodby, J. W. (1984). In: *Liquid Crystals and Ordered Fluids*, Griffin, A. C. & Johnson, J. F. (Eds.), Plenum Press: New York, Vol. 4, 75.
[183] Kohne, B., Praefcke, K., & Heppke, G. (1979). *Israel J. Chem.*, *18*, 197.
[184] Kohne, B., Praefcke, K., Heppke, G., & Richter, E. J. (1979). *Israel J. Chem.*, *18*, 199.
[185] Berti, C., Marianucci, E., Pilati, F., & Toselli, M. (1992). *Liq. Cryst.*, *12*, 821.
[186] Nguyen, H. T., Salleneuve, C., Babeau, A., Roubineau, A., & Destrade, C. (1987). *Mol. Cryst. Liq. Cryst. Lett.*, *4*, 93.
[187] Gorria, P., Barois, P., Nguyen, H. T., Sigaud, G., Navailles, L., Garland, C. W., & Haga, H. (1999). *Mol. Cryst. Liq. Cryst.*, *330*, 175.
[188] Sato, H., Takatsu, H., & Tazume, M. (1979). German Pat. Appl. DE 2 847 639.
[189] Krause, J. & Pohl, L. (1977). German Pat. Appl. DE 2 603 293.
[190] Nohira, H., Kamei, M., Nakamura, S., Katagiri, K., Terada, M., Yamashita, M., Yamada, Y., Shinjo, K., Iwaki, T., Hioki, C., Yoshida, A., & Uchimi, T. (1987). Eur. Pat. Appl. EP 267 585.
[191] Era, S., Yokokura, H., Iwasaki, K., Nakata, T., Kitamura, T., & Mukoh, A. (1985). Eur. Pat. Appl. EP 162 437.
[192] Kitamura, T., Kondo, K., Sudo, Y., Matsumura, K., Kawada, M., & Sugihara, Y. (1990). Eur. Pat. Appl. EP 388 960.
[193] Janulis, E. P., Novack, J. C., Papapolymerou, G. A., Tristani-Kendra, M., & Huttman, W. A. (1988). *Ferroelectrics*, *85*, 375.
[194] Reynolds, R. M., Maze, C., & Oppenheim, E. (1976). *Mol. Cryst. Liq. Cryst.*, *36*, 41.
[195] Simeao Carvalho, P., Chaves, M. R., Destrade, C., Nguyen, H. T., & Glogarova, M. (1996). *Liq. Cryst.*, *21*, 31.
[196] Glogarova, M., Sverenyak, H., Nguyen, H. T., & Destrade, C. (1993). *Ferroelectrics*, *147*, 43.
[197] Nassif, L., Jakli, A., & Seed, A. J. (2001). *Mol. Cryst. Liq. Cryst.*, *365*, 171.
[198] Simeao Carvalho, P., Glogarova, M., Chaves, M. R., Nguyen, H. T., Destrade, C., Rouillon, J. C., Sarmento, S., & Ribeiro, M. J. (1996). *Liq. Cryst.*, *21*, 511.

[199] Laux, V., Isaert, N., Joly, G., & Nguyen, H. T. (1999). *Liq. Cryst*., *26*, 361.
[200] Twieg, R. J., Betterton, K., Hinsberg, W., Wong, P., Tang, W., & Nguyen, H. T. (1991). *Ferroelectrics*, *114*, 295.
[201] Laux, V., Isaert, N., Nguyen, H. T., Cluzeau, P., & Destrade, C. (1996). *Ferroelectrics*, *179*, 25.
[202] Neubert, M. E., Keast, S. S., Dixon-Polverine, Y., Herlinger, F., Jirousek, M. R., Leung, K., Murray, K., & Rambler, J. (1994). *Mol. Cryst. Liq. Cryst*., *250*, 109.
[203] Simeao Carvalho, P., Glogarova, M., Chaves, M. R., Destrade, C., & Nguyen, H. T. (1996). *Liq. Cryst*., *21*, 115.
[204] Nabor, M. F., Nguyen, H. T., Destrade, C., Marcerou, J. P., & Twieg, R. J. (1991). *Liq. Cryst*., *10*, 785.
[205] Neubert, M. E., Colby, C., Ezenyilimba, M. C., Jirousek, M. R., Leonhardt, D., & Leung, K. (1988). *Mol. Cryst. Liq. Cryst*., *154*, 127.
[206] Neubert, M. E., Sharma, R. B., Citano, C., Jirousek, M. R., & Paulin, J. L. (1991). *Mol. Cryst. Liq. Cryst*., *196*, 145.
[207] Nguyen, H. T., Rouillon, J. C., Cluzeau, P., Sigaud, G., Destrade, C., & Isaert, N. (1994). *Liq. Cryst*., *17*, 571.
[208] Bezborodov, V. S. & Petrov, V. F. (1997). *Liq. Cryst*., *23*, 771.
[209] Weissflog, W. & Demus, D. (1985). *Mol. Cryst. Liq. Cryst*., *129*, 235.
[210] Weissflog, W. & Demus, D. (1984). *Cryst. Res. Technol*., *19*, 55.
[211] Vill, V. (1995). Landolt-Bornstein, Group IV: Macroscopic Properties of Matter. In: *Liquid Crystals*, Thiem, J. (Ed.), Springer Verlag: New York, Vol. 7e, 253, 254.
[212] Weissflog, W. & Demus, D. (1988). *Liq. Cryst*., *3*, 275.
[213] Bialecka-Florjanczyk, E. & Orzeszko, A. (2000). *J. Mater. Chem*., *10*, 1527.
[214] Melon-Ksyta, D., Orzeszko, A., Borys, W., & Czuprynski, K. (2002). *J. Mater. Chem*., *12*, 1311.
[215] Yagupolskii, L. M., Ilchenko, A. Y., & Kondratenko, N. V. (1974). *Rus. Chem. Rev*., *43*, 32.
[216] Schaffer, T., Penner, G. H., Sebastian, R., Peeling, J., & Beaulieu, C. (1991). *Can J. Chem*., *69*, 1047.
[217] Matsushita, T., Osamura, Y., Misawa, N., Nishimoto, K., & Tsuno, Y. (1979). *Bull. Chem. Soc. Jpn*., *52*, 2521.
[218] Bohm, S. & Exner, O. (2002). *J. Mol. Struct. (Theochem.)*, *578*, 103.
[219] Hargittai, I. (1978). *Sulphone molecular structures*, Springer Verlag: New York.
[220] Shorter, J. (1988). In: *The Chemistry of Sulphones and Sulphoxides*, Patai, S., Rappoport, Z., & Stirling, C. (Eds.), Wiley: New York, 483.
[221] Bzhezovskii, V. M., Kapustin, E. G., & Il'chenko, N. N. (2000). *Rus. J. Gen. Chem*., *70*, 745.
[222] Bzhezovskii, V. M., Kapustin, E. G., Il'chenko, N. N., Kulik, N. I., & Gorb, L. C. (2000). *Rus. J. Gen. Chem*., *70*, 1766.
[223] Remizov, A. B., Bilalov, F. S., & Pominov, I. S. (1987). *Spectrochimica Acta*, *43A*, 475.
[224] White, J. M., Bateman, S. A., Kelly, D. P., & Martin, R. F. (1996). *Acta Cryst. C*, *52*, 2785.
[225] Guadagnini, P. H., Oliveira, A. E., Bruns, R. E., & de Barros Neto, B. (1997). *J. Am. Chem. Soc*., *119*, 4224.
[226] Hojer, G., Meza-Hojer, S., & Gaytan, F. (1977). *Acta Chem. Scand. B*, *31*, 445.
[227] Spellmeyer, D. C., Grootenhuis, P. D. J., Miller, M. D., Kuyper, L. F., & Kollman, P. A. (1990). *J. Phys. Chem*., *94*, 4483.
[228] Schaffer, T. & Sebastian, R. (1989). *Can. J. Chem*., *67*, 1148.

[229] Facelli, J. C., Orendt, A. M., Jiang, Y. J., Pugmire, R. J., & Grant, D. M. (1996). *J. Phys. Chem.*, *100*, 8268.
[230] Osman, M. A. & Revesz, L. (1982). *Mol. Cryst. Liq. Cryst., Lett.*, *82*, 41.
[231] Bradshaw, M. J., Raynes, E. P., Fedak, I., & Leadbetter, A. J. (1984). *J. Phys.*, *45*, 157.
[232] Brownsey, G. J. & Leadbetter, A. J. (1980). *Phys. Rev. Lett.*, *44*, 1608.
[233] Petrov, V. F., Ivanov, S. A., Grebenkin, M. F., & Pavluchenko, A. I. (1990). *Rus. J. Phys. Chem.*, *64*, 421.
[234] Ostrovskii, B. I., Pavluchenko, A. I., Petrov, V. F., & Saidachmetov, M. A. (1989). *Liq. Cryst.*, *5*, 513.
[235] Lobko, T. A. & Ostrovskii, B. I. (1992). *Mol. Mats*, *1*, 99.
[236] Czuprynski, K., Dabrowski, R., Baran, J., Zywocinski, A., & Przedmojski, J. (1986). *J. Phys.*, *47*, 1577.
[237] van der Veen, J. (1976). *J. Phys. Colloque*, *37*, C3-13.
[238] Sarkar, P., Mandal, P., Paul, S., Paul, P., Dabrowski, R., & Czuprynski, K. (1999). *Mol. Cryst. Liq. Cryst.*, *330*, 159.
[239] Ekachai, A., de Vries, A., Neubert, M. E., & Spielberg, N. (1981). *J. Chem. Phys.*, *74*, 4048.
[240] Pfeiffer, M., Soto, G., Wrobel, S., Haase, W., Twieg, R., & Betterton, K. (1991). *Ferroelectrics*, *121*, 55.
[241] Mach, P., Pindak, R., Levelut, A.-M., Barois, P., Nguyen, H. T., Huang, C. C., & Furenlid, L. (1998). *Phys. Rev. Lett.*, *81*, 1015.
[242] Mach, P., Pindak, R., Levelut, A.-M., Barois, P., Nguyen, H. T., Baltes, H., Hird, M., Toyne, K., Seed, A., Goodby, J. W., Huang, C. C., & Furenlid, L. (1999). *Phys. Rev. E*, *60*, 6793.
[243] Ocko, B. M., Birgeneau, R. J., Litster, J. D., & Neubert, M. E. (1984). *Phys. Rev. Lett.*, *52*, 123.
[244] Chan, K. K., Deutsch, M., Ocko, B. M., Pershan, P. S., & Sorensen, L. B. (1985). *Phys. Rev. Lett.*, *54*, 127.
[245] Walz, L., Haase, W., & Ibrahim, I. H. (1991). *Mol. Cryst. Liq. Cryst.*, *200*, 43.
[246] Lokanath, N. K., Revannasiddaiah, M. A., Sridhar, M. A., & Prasad, J. S. (2001). *Mol. Cryst. Liq. Cryst.*, *364*, 703.
[247] Karczmarzyk, Z., Ossowska-Chrusciel, M. D., & Chrusciel, J. (2001). *Mol. Cryst. Liq. Cryst.*, *357*, 117.
[248] Chrusciel, J., Pniewska, P., & Ossowska-Chrusciel, M. D. (1995). *Mol. Cryst. Liq. Cryst.*, *258*, 325.
[249] Ossowska-Chrusciel, M. D., Karczmarzyk, Z., & Chrusciel, J. (2002). *Mol. Cryst. Liq. Cryst.*, *382*, 37.
[250] Sridhar, M. A., Lokanath, N. K., Krishnegowda, D., Revanasiddaiah, D., & Prasad, J. S. (1997). *Mol. Cryst. Liq. Cryst.*, *299*, 509.
[251] Maier, W. & Meier, G. Z. (1961). *Naturforsch. A*, *16*, 262.
[252] Schadt, M. (1992). *Displays*, *13*, 11.
[253] Minkin, V. I., Osipov, O. A., & Zhdanov, Y. A. (1970). *Dipole moments in organic chemistry*, Plenum Press: New York.
[254] Lutskii, A. E., Obukhova, E. M., Prezhdo, V. V., Yagupolskii, L. M., Gandelsman, L. Z., & Sedova, L. N. (1970). *Theor. Exp. Chem.*, *6*, 685.
[255] McClellan, A. L. (1963). *Tables of experimental dipole moments*, W. H. Freeman: San Francisco.
[256] Wrobel, S., Hiller, S., Pfeiffer, M., Marzec, M., Haase, W., Twieg, R., & Betterton, K. (1995). *Liq. Cryst.*, *18*, 21.

[257] Chrusciel, J., Wrobel, S., Kresse, H., Urban, S., & Otowski, W. (1985). *Mol. Cryst. Liq. Cryst*., *127*, 57.
[258] Chrusciel, J., Kresse, H., & Urban, S. (1992). *Liq. Cryst*., *12*, 711.
[259] Chrusciel, J., Wrobel, S., Janik, J. A., Janik, J. M., & Kresse, H. (1981). *Acta Phys. Pol. A*, *59*, 431.
[260] Chrusciel, J., Wrobel, S., Kresse, H., Urban, S., & Otowski, W. (1990). *Mol. Cryst. Liq. Cryst*., *192*, 107.
[261] Chrusciel, J., Bamezai, R. K., Kresse, H., Urban, S., & Wrobel, S. (1990). *Mol. Cryst. Liq. Cryst*., *192*, 101.
[262] Chrusciel, J., Bormuth, F.-J., Haase, W., & Wrobel, S. (1990). *Mol. Cryst. Liq. Cryst*., *192*, 95.
[263] Chrusciel, J., Gestblom, B., Makrenek, M., Haase, W., Pfeiffer, M., & Wrobel, S. (1993). *Liq. Cryst*., *14*, 565.
[264] Wrobel, S. (1985). *Mol. Cryst. Liq. Cryst*., *127*, 67.
[265] Kundu, S. K., Chaudhuri, B. K., Seed, A., & Jakli, A. (2003). *Phys. Rev. E*, *67*, 041704.
[266] Pfeiffer, M., Hiller, S., Wrobel, S., & Haase, W. (1993). *Ferroelectrics*, *147*, 419.
[267] de Jeu, W. H. (1980). *Physical properties of liquid crystalline materials*, Gordon & Breach: New York.
[268] de Jeu, W. H., Gerristma, C. J., van Zanten, P., & Goosens, W. A. (1972). *Phys. Lett*., *39A*, 355.
[269] Batsanov, S. S. (2002). *Rus. J. Gen. Chem*., *72*, 1153.
[270] Jakeman, E. & Raynes, E. P. (1972). *Phys. Lett*., *39A*, 69.
[271] de Jeu, W. H. & Claassen, W. A. P. (1977). *J. Chem. Phys*., *67*, 3705.
[272] Oseen, C. W. (1933). *Trans. Faraday Soc*., *29*, 883.
[273] Frank, F. C. (1958). *Discuss. Fraday Soc*., *25*, 19.
[274] van Dijk, J. W., Beens, W. W., & de Jeu, W. H. (1983). *J. Chem. Phys*., *79*, 3888.
[275] Gruler, H. (1973). *Z. Naturforsch*., *23a*, 474.
[276] Majoros, S. J., Brisbin, D. J., Johnson, D. L., & Neubert, M. E. (1979). *Phys. Rev. A*, *20*, 1619.
[277] Bondi, A. (1968). *Physical properties of molecular crystals, liquids and gases*, Wiley: New York.
[278] Martinot-Lagarde, P. (1988). *Ferroelectrics*, *84*, 53.
[279] Escher, C., Geelhaar, T., & Boehm, E. (1986). *Liq. Cryst*., *3*, 469.