Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Liquid-Crystalline Oxygen-Containing Heterocyclic Derivatives. 2 Six-Membered Rings Containing Oxygen as Structural Fragments in Liquid Crystals

Vladimir F. Petrov [a b] & Vladimir I. Yashkichev [c]

[a] LC Works, Sydney, New South Wales, Australia

[b] Gubkin Russian State University of Oil and Gas, Department of Physical Chemistry, Moscow, Russia

[c] The Moscow State Humanitarian University n.a. Sholokhov, Department of Science, Moscow, Russia

Version of record first published: 18 Mar 2010

To cite this article: Vladimir F. Petrov & Vladimir I. Yashkichev (2010): Liquid-Crystalline Oxygen-Containing Heterocyclic Derivatives. 2 Six-Membered Rings Containing Oxygen as Structural Fragments in Liquid Crystals, Molecular Crystals and Liquid Crystals, 518:1, 12-39

To link to this article: http://dx.doi.org/10.1080/15421400903499722

Mol. Cryst. Liq. Cryst., Vol. 518: pp. 12–39, 2010

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903499722

Taylor & Francis
Taylor & Francis Group

Liquid-Crystalline Oxygen-Containing Heterocyclic Derivatives. 2 Six-Membered Rings Containing Oxygen as Structural Fragments in Liquid Crystals

VLADIMIR F. PETROV[1,2]
AND VLADIMIR I. YASHKICHEV[3]

[1]LC Works, Sydney, New South Wales, Australia
[2]Gubkin Russian State University of Oil and Gas, Department of Physical Chemistry, Moscow, Russia
[3]The Moscow State Humanitarian University n.a. Sholokhov, Department of Science, Moscow, Russia

The effect on the physico-chemical properties of introducing the oxygen 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 other derivatives.

Keywords Liquid crystals; oxygen; physico-chemical properties

Introduction

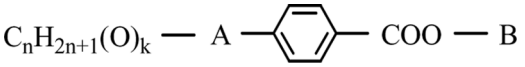
In continuation of our study of the structure–property relationships in oxygen-containing liquid crystals (see, for example, the previous publications [1–5]) we present here a review that examines in some detail the effect of the introduction of the oxygen-containing six-membered rings and based on them systems into the molecular structure of liquid crystals on the appearance of the mesophases and their physico-chemical properties. When possible, the properties of the oxygen-containing derivatives will be compared with those of the corresponding hydrocarbon and heterocyclic derivatives.

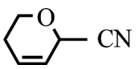
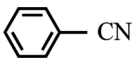
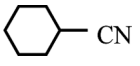
Mesomorphic Properties

The phase transition temperatures of the oxygen-containing derivatives and reference compounds are presented in Tables 1–12 where Cr, P, Sm, SmH, SmC*, SmC, SmB, SmA, N, Ch, BP, and I denote the crystalline, plastic, smectic, smectic

Address correspondence to Vladimir I. Yashkichev, LC Works 159.361 Kent St., Sydney, NSW 2000, Australia. E-mail: lcworks@hotmail.com

Table 1. Mesomorphic properties of some liquid crystals:

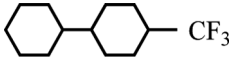
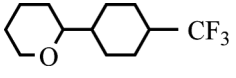
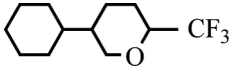
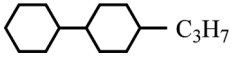
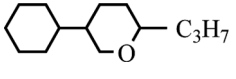
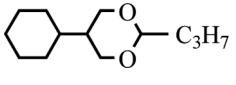
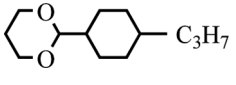
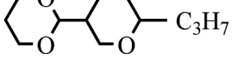


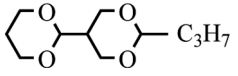
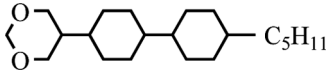
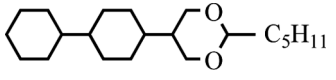
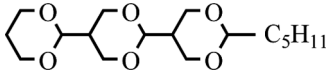
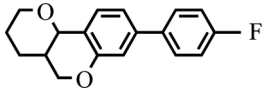
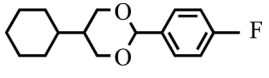
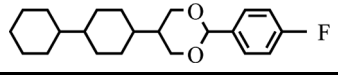
No.	n	k	A	B	Phase transitions (°C)	Ref.
1-1	10	1			Cr 78.5 I	[97]
1-2	10	1			Cr 78.8 SmA (61.4) I	[97]
1-3	10	1			Cr 74.6 SmA 75.8 I	[97]
1-4	10	1			Cr 106.9 I	[97]
1-5	10	1			Cr 59.2 SmB (52) SmA 79.3 I	[97]
1-6	10	1			Cr 90.6 I	[97]
1-7	10	1			Cr 78.1 SmA (57.5) I	[97]
1-8	10	1			P 90 I	[97]
1-9	10	1			Cr 77 I	[97]
1-10	7	0			Cr 82 SmA (69.5) Ch (74.4) I	[98]
1-11	7	0			Cr 104 X 211 I	[99]
1-12	7	0			Cr 99 X 133 I	[100]

H, chiral smectic C*, smectic C, B, A, nematic, cholesteric, blue phase, and isotropic phases, respectively. Values given in parentheses refer to monotropic phase transitions. X is an uncharacterized mesophase.

One of the most useful fragments for the molecular design of liquid crystals is trans-1,4-cyclohexylene [6]. Cyclohexane is known to exist in a chair conformation with the C−C−C−C torsional angle 55° [7]. Two types of positions are available for substituents in cyclohexane. There are the well-known axial and equatorial locations. Axially substituted conformations are generally less stable than equatorial conformations because of non-bonded repulsive interactions across the top of the molecule [8].

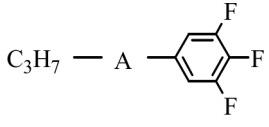
Table 2. Physico-chemical properties of some liquid crystals: C_nH_{2n+1} — A, n = 3

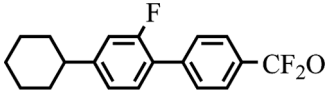
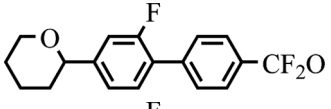
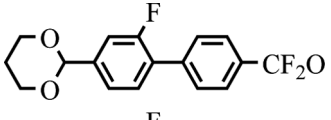
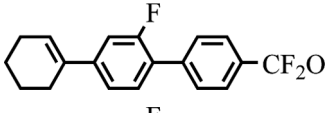
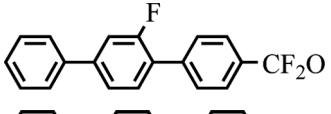
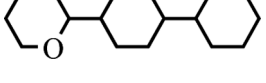
No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	$\gamma_1{}^a$ (mPas)	Ref.
2-1		Cr l9 SmH (8) SmB 41 I	6.8	0.059		[101]
2-2		Cr 7 SmB 15 I	10.5 7.7	0.048	76	[102] [103]
2-3		Cr 59 I	8.8	0.061		[102]
2-4		Cr 65 SmB 83 I	−0.3	0.043	29	[104]
2-5		Cr 28 SmB 62 I	−0.5	0.048	56	[105]
2-6		Cr 22 SmB 73 I	2.5	0.055	79	[104]
2-7		Cr 36 SmB (36) N 36.4 I	1.6	0.045	55	[104]
2-8		Cr 64 SmB (53) I	3.6	0.051	78	[105]

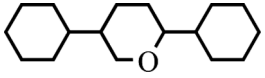
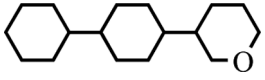
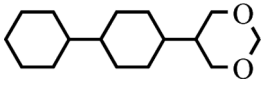
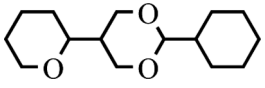
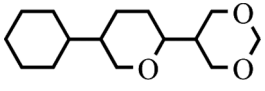
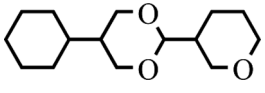
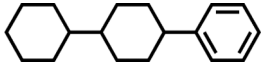
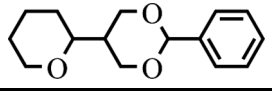
2-9		Cr 82 SmB 125 I	8.3	0.048	98	[104]
2-10		Cr 73 SmB 199 N 215.5 I	2.9	0.083	56[b]	[106]
2-11		Cr 56 SmB 211 I	2.9	0.076	58[b]	[106]
2-12		Cr 169 SmB 234 I				[104]
2-13[c]		Cr 99 SmA 139 I	8.0[d,e]	0.114[d,f]		[107]
2-14[c]		Cr 65 Sm (47.6) N 155 I				[108]
2-15[c]		Cr 133 N 283.6 I	8.5	0.116	72[b]	[106]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b]Kinematic viscosity ν [$mm^2 s^{-1}$] at 20°C.
[c]n = 5.
[d]Extrapolated from 10 wt% solution in ZLI-1565 at [e]$\tau = 0.85$, $\tau = T_{meas}/T_{N\text{-}1}$, K.
[f]$T_{meas} = 25$°C.

Table 3. Physico-chemical properties of some liquid crystals:

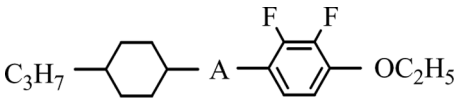


No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	$\gamma_1{}^a$ (mPas)	Ref.
3-1		Cr 76 N 161 I	19.0	0.158		[109]
3-2		Cr 66 SmA 87 N 147 I	22.0	0.155		[109]
3-3		Cr l09 SmA (95) N 153 I	28.0	0.165		[109]
3-4		Cr 78 SmA 109 N 161 I	22.0	0.203		[109]
3-5		Cr 102 SmA 150 N 178 I	22.0	0.240		[109]
3-6		Cr 95 SmB 169 N 246 I	14.0	0.106		[110]

3-7		Cr l02 SmB 118 N 236 I	14.0	0.098		[110]
3-8		Cr 113 N 256 1	11.8	0.102	582	[103]
3-9		Cr 140 N 225.8 I	16.3	0.108	91[b]	[106]
3-10		Cr 133 SmB 161 N 211 I	22.0	0.091		[111]
3-11		Cr ll8 N 206 I	21.0	0.089	1330	[111]
3-12		Cr 106 N 207 I	21.0	0.087	1395	[111]
3-13		Cr 105.8 N 250 I				[112]
3-14		Cr 101 Sm 104 SmA 197 N 223 I	26.0	0.150		[111]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b]Kinematic viscosity ν ($mm^2 s^{-1}$) at 20°C.

Table 4. Physico-chemical properties of liquid crystals:



No.	A	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^b	μ, D	β (°)	Ref.
4-1		Cr 79 SmB (78) N 184.5 I Cr 66.9 SmB 79.9 N 185.1 I	−6.0 −5.4[c]	0.096 −0.114[c]			[113] [114]
4-2		Cr 65.5 N 139.7 I	−7.3[c]	0.107[c]	4.5	89	[114]
4-3		Cr 107.7 SmB (94.6) N 164 I	−3.8[c]	0.112[c]	3.5	63	[114]
4-4		Cr 80 N 173.3 I	−5.9	0.156			[113]
4-5		Cr 96 SmB (93) N 131 I	−5.2	0.111			[115]

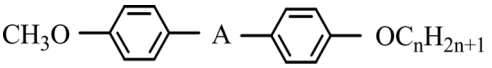
[a]Extrapolated from 10 wt% solution in ZLI-2857 at 20°C.
[b]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[c]Extrapolated from 15 wt% solution in liquid crystal material at 25°C.

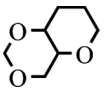
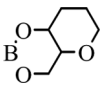
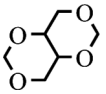
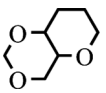
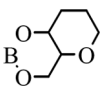
The introduction of the oxygen atom into the cyclohexane ring results in the formation of tetrahydropyran. It has been reported that tetrahydropyran has a chair conformation and its ring is slightly flatter than cyclohexane [9]. Its molecule resembles cyclohexane in geometry excepting the short C−O bond (1.41 Å) compared to the C−C bond (1.54 Å). These two rings have very similar chair-to-twist ring reversal processes [9]. The C−O−C−C, O−C−C−C, and C−C−C−C torsional angles in tetrahydropyran are 59.9, 56.9, and 52.9°, respectively [7].

The introduction of two oxygens into cyclohexane gives the dioxane ring. It has been estimated that the twist conformer of 1,3-dioxane is of higher energy relative to its chair conformer than that in cyclohexane [10]. The oxygen atoms affect the ring size and shape because of different bond lengths, with the C−O bond (1.41 Å) being shorter than the C−C bond (1.54 Å). As a result, the dioxane ring is believed to be hyper (more puckered than cyclohexane) in the O−C−O position of the molecule and hypo (less puckered than cyclohexane) in the C−C−C region of the molecule. The C(2)-C(3)-C(4) bond angle of 107.7° is comparable with that of of tetrahydropyran (108.3°) and lower than that of cyclohexane (111.4°) [7]. In addition to this ring distortion the O(1) and O(3) positions have no hydrogens so that there are no 1,3-syn-axial hydrogen interactions with axial substituents at the C(5) position [10].

In contrast to the results for these monocycles, in the bicycles, such as bicyclo[2.2.2]octane, the rigidity of bridged structure permits more significant conformational effects than in the monocycles [11]. The bridging locks the cyclohexane ring into the boat and/or twist-boat conformation. Bicyclo[2.2.2]octane has two boat cyclohexane rings. The enthalpies of the boat and twist-boat conformers of cyclohexane are 27 and 23 kJ/mol higher that that of the chair conformer. Bicycle[2.2.2]octane has ring strain of 54 kJ/mol and the D_{3h} or D_3 symmetry [11]. There is a slight rotation around threefold axis that lowers the repulsion of the eclipsing hydrogens at C(2) and C(3) positions [11]. Similar geometry can be

Table 5. Mesomorphic properties of some liquid crystals:

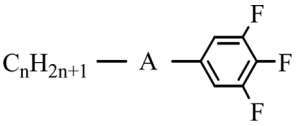


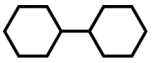
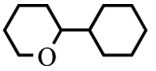
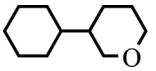
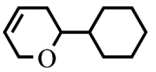
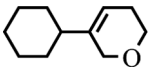
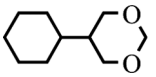
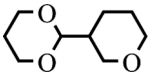
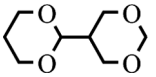
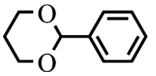
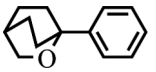
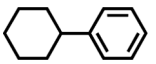
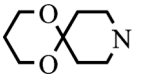
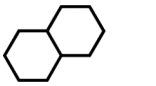
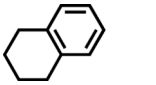
No.	A	n	Phase transilions (°C)	Ref.
5-1		1	Cr 139.8 Ch 170.8 I	[116]
5-2		1	Cr 210.5 N 261 I	[117]
5-3		1	Cr 190 N 270 I	[118]
5-4		1	Cr 247 N 253 I	[119]
5-5		1	Cr 178 N 218 I	[120]
5-6		1	Cr 171 N 260 I	[121]
5-7		1	Cr 195 Ch 206 I	[122]
5-8		1	Cr l58 Ch 211.1 BP	[122]
5-9		1	Cr 222 N (195) I	[123]
5-10		8	Cr 134.7 Ch 151.7 I	[122]
5-11		8	Cr 95 Ch 165.5 BP	[122]
5-12		8	Cr 110.6 Sm ll8.7 N 132.3 I	[124]

proposed for the oxygen-containing 2-oxa- and 2,6,7-trioxabicyclo[2.2.2]octanes [11]. As expected, these structural features can affect the mesomorphic properties of the oxygen-containing liquid crystals.

It is obvious from Table 1 that the phase transition temperatures of three-ring tetrahydropyran derivatives strongly depend on the position of the oxygen atom in the tetrahydropyran ring. So far position 4 gives the liquid crystals exhibiting high clearing (nematic-isotropic or smectic-isotropic phase transition temperatures) and

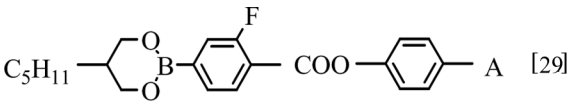
Table 6. Physico-chemical properties of some liquid cryslals:



No.	A	n	Phase transitions (°C)	$\Delta\varepsilon^a$	Δn^a	$\gamma_1{}^a$ (mPas)	Ref.
6-1		3	Cr 66 N 94.1 I	9.7	0.075	160	[102]
6-2		3	Cr 71 I Cr 74 I	14.1 15.0	0.060 0.074	136	[103] [102]
6-3		3	Cr 59 N (50.9) I Cr 57 N (52.2) I	12.2 12.7	0.071 0.078	182	[103] [102]
6-4		3	Cr 74 I	13.3	0.056	203	[103]
6-5		3	Cr 48 I	12.8	0.064	205	[103]
6-6		3	Cr 74 N (51.2) I	17.0	0.068	201	[102]
6-7		3	Cr 87 I	23.7	0.055	241	[103]
6-8		3	Cr 117.3 I				[125]
6-9		3	Cr 86.6 Sm (54.4) I	22.3[b]			[126]
6-10		3	N 83.6 I[a]	15.9	0.147		[127]
6-11		3	Cr 42 N (33) I	12.6	0.142		[128]
6-12		3	Cr 53.8 I	10.3[b]			[129]
6-13		5	Cr 7 I	2.3	0.012	64[c]	[19]
6-14		3	Cr 45 I				[130]
6-15		3	Cr 32 I				[130]

[a]Extrapolated from 10 wt% solution in ZLI-4792 at 20°C.
[b]Extrapolated from 15 wt% solution in liquid crystal material at 25°C.
[c]Kinematic viscosity ν ($mm^2 s^{-1}$) at 20°C.
[d]Extrapolated from 20 wt% solution in liquid crystal material at 25°C.

Table 7. Physico-chemical properties of liquid crystals:



[29]

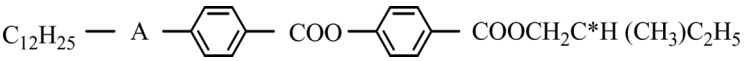
No	A	Phase transitions (°C)	d[a] (Å)	d/L[a]
7-1	CF_3	Cr 74.4 SmA 102.8 I	24.80	1.103
7-2	OCF_3	Cr 48.4 SmA 111 N 113.9 I	25.08	1.062
7-3	CN	Cr 94 N 167 I	23.73[b]	1.039[b]

[a] $T_{meas} = T_{cl} - 20°C$.
[b] $T_{meas} = T_{cl} - 50°C$.

lowest melting (crystal-smectic or crystal-nematic phase transition temperatures) points. Position 3 reduces the clearing temperature and gives the highest melting point and position 2 leads to the disappearance of the mesomorphic properties among those of the corresponding tetrahydropyran derivatives (compounds **1-1** to **1-3**). It is important to note that the corresponding trans-1,3-dioxane derivative **1-4** is not mesomorphic at all. Similar comparison can be made for reference derivatives (compounds **1-5** to **1-9**; Table 1) where the trans-1,4-cyclohexylene derivative shows the lowest melting temperature and rich smectic polymorphism with high smectic thermostability among those of compounds under consideration.

The replacement of the cyclohexane ring by tetrahydropyran in two-ring derivatives lowers their clearing points and the number of the smectic phases (compounds **2-1** to **2-5**; Table 2), whereas moving tetrahydropyran closer to the terminal polar

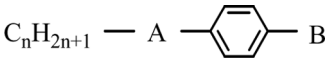
Table 8. Physico-chemical and electro-optical properties of some liquid crystals:



No.	A	Phase transitions (°C)	$\lvert P_s{}^a \rvert$ (nCcm^{-2})	τ (μs)	Θ^a (°)	Ref.
8-1		Cr 69 SmC* 85 SmA 114 I	9.6		13.4	[131]
8-2		Cr 66 SmC* 95 SmA 135 I	1.3[b]	61[b]	13.5[b]	[132]
8-3		Cr 68 SmA 133 I				[132]
8-4		Cr 107 SmA 141				[132]
8-5		Cr 42 SmC* 81 SmA 175 I				[133]

[a] $T_{meas} = T_{SmC^*-SmA} - 15°C$.
[b] $T_{meas} = 85°C$.

Table 9. Mesomorphic properties of some liquid crystals:



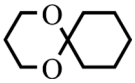
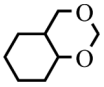
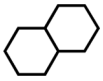
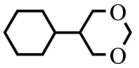
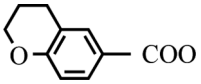
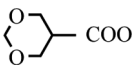
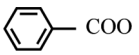
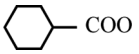
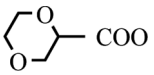
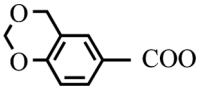
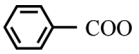
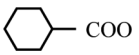
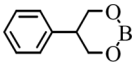
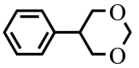
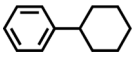
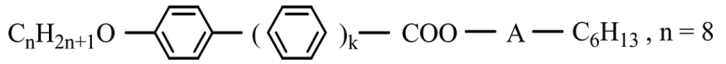
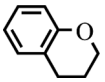
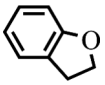
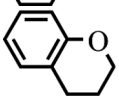
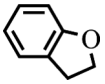
No.	n	A	B	Phase transitions (°C)	Ref.
9-1	4		CN	Cr 61 I	[134]
9-2	4		CN	Cr 42 N (36) I	[135]
9-3	4		CN	Cr 41 N 41 I	[136]
9-4	5		CN	Cr 87 N (85) I	[137]
9-5	4		CN	Cr 61.3 N 116 I	[138]
9-6	4		CN	Cr 74.6 Sm 61.5 N 221.2 I	[108]
9-7	6		CN	Cr 81 N 84 I	[139]
9-8	6		CN	Cr 64 N (47.5) I	[140]
9-9	6		CN	Cr 44.5 N 47 I	[141]
9-10	6		CN	Cr 50 N 73 I	[142]
9-11	6		CN	Cr 91.4 I	[143]
9-12	5		C_3H_7	Cr 97.5 X (74.5) I	[144]
9-13	5		C_3H_7	Cr 22.7 N (19.5) I	[145]
9-14	5		C_3H_7	Cr 44.3 Sm (31.3) N (43.6) I	[145]
9-15	5		CN	Cr 103 N 132.7 I	[146]
9-16	5		CN	Cr 110 N 165 I	[135]
9-17	5		CN	Cr 80 X 160 I	[147]

Table 10. Physico-chemical and electro-optical properties of some liquid crystals:



No.	k	A	Phase transitions (°C)	$\lvert P_s^a \rvert$ ($nCcm^{-2}$)	τ^a_{0-90} (μs)	Ref.
10-1	0		Cr 72 Ch 79 I	~0	670	[148]
10-2	0		Cr 53 Ch 59 I	2.3[b]	205[b]	[148]
10-3	0		Cr 53.3 SmA 59.2 N 62.9 I			[149]
10-4	1		Cr 74 SmC* 154.5 SmA 167.5 Ch 187.5 I	~0[c]	800[c]	[148]
10-5	1		Cr 115 SmC* 140 SmA 183 Ch 185 I	1.4[b] 6.4[d]	195[b]	[148]
10-6[e]	1		Cr 99.8 SmC* (89.1) SmA 134.6 Ch 136.1 I	100[f]		[150]
10-7	1	$OC^*H(CH_3)$	Cr 67 Sm 84 SmC* 107 SmA 152 I	50[g]		[148]

[a]Measured as 15 wt% solution in liquid crystal material at 25°C.
[b]Measured as 10 wt% solution in liquid crystal material at 25°C.
[c]Measured as 25 wt% solution in liquid crystal material at 25°C.
[d]$T_{meas} = 100°C$.
[e]n = 10.
[f]$T_{meas} = 79°C$.
[g]$T_{meas} = 102°C$.

CF_3 group leads to the disappearance of the mesophase (compounds **2-2**, **2-3**). Similar comparison can be made upon the introduction of the dioxane ring with the same positions of its oxygen atoms into the molecular core of weakly polar bicyclohexyl derivatives (compounds **2-4**, **2-6**, **2-7**; Table 2). The replacement of two cyclohexane rings by two dioxane ones significantly enhances the melting and clearing temperatures in comparison with those of the corresponding bicyclohexyl and cyclohexyl-tetrahydropyran derivatives (compounds **2-4**, **2-6**, **2-7**, **2-9**). A similar situation can be seen for three-ring dioxane derivatives (compounds **2-10** to **2-12**: **6-1**, **6-6**; except compound **6-8**. Tables 2 and 6). The simultaneous introduction of tetrahydropyran and dioxane into the molecular core of liquid crystals makes if roughly an average effect on their mesomorphic properties for two- and three-ring derivatives (compounds **2-8**, **6-7**; Tables 2 and 6). For four-ring derivatives such introduction results in the lowest clearing points among compounds under consideration (compounds **3-6** to **3-12**; **3-13**, **3-14**; Table 3). These findings can be expressed by the following orders of increasing of clearing (T_{cl}) and melting temperatures (T_m),

Table 11. Mesomorphic properties of some liquid crystals: C_5H_{11}—⬡—A

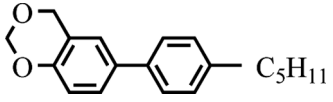
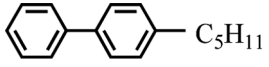
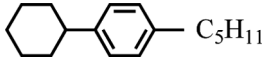
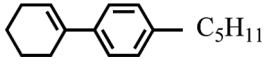
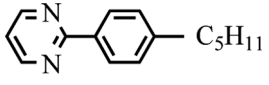
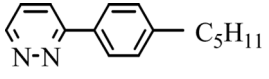
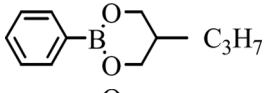
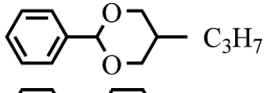
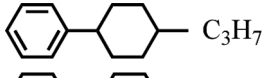
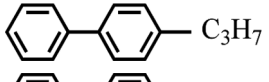
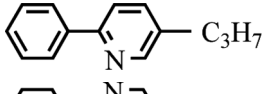
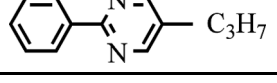
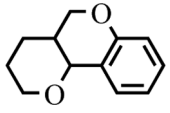
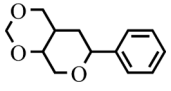
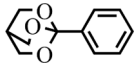
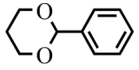
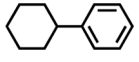
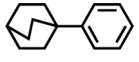
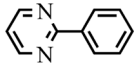
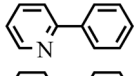
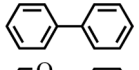
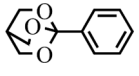
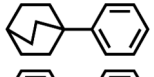
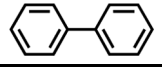
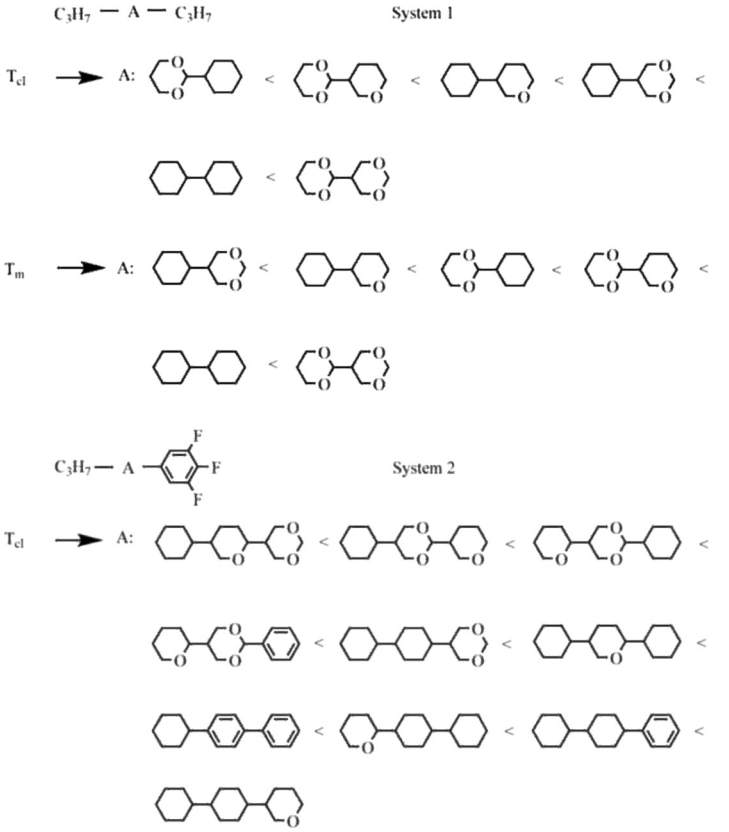
No.	A	Phase transitions (°C)	Ref.
11-1		Cr 144.4 SmA 182.7 I	[151]
11-2		Cr 13 SmB 164 N 166 I	[136]
11-3		Cr < 30 Sm 189.8 I	[152]
11-4		Cr < 30 Sm 181 I	[152]
11-5		Cr 39.5 Sm 189.2 I	[153]
11-6		Cr 83 Sm 92 Sm 164 SmA 208 I	[154]
11-7		Cr 61.5 N 95.8 I	[155]
11-8		Cr_2 45.3 Cr_1 72.4 N 157.3 I	[156]
11-9		Cr 41 Sm 156 N 160 I	[157]
11-10		Cr 29 Sm 160 N 170 I	[157]
11-11		Cr 37 Sm 93.5 N 179 I	[158]
11-12		Cr 101 N 187 I	[159]

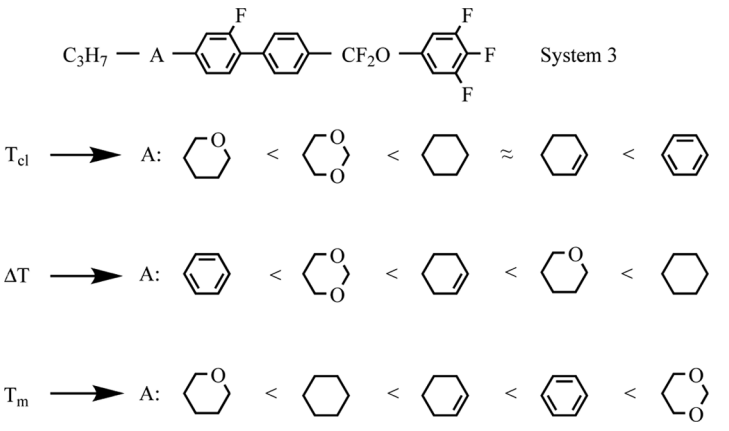
Table 12. Mesomorphic properties of some liquid crystals: C_5H_{11} — A —$(O)_kC_6H_{13}$

No.	A	k	Phase transitions (°C)	Ref.
12-1		1	Cr 63 SmA 73 N 77 I	[107]
12-2		1	Cr 74 I	[160]
12-3		1	Cr 92 I	[161]
12-4		1	Cr 44 SmA (22) N 56 I	[135]
12-5		1	Cr 37 N 44 I	[162]
12-6		1	Cr 66 SmB (54) N 79 I	[163]
12-7		1	Cr 36 N 61 I	[164]
12-8		1	Cr 64.5 N 72 I	[165]
12-9		1	Cr 82 Sm 84 I	[166]
12-10		0	Cr 74 SmB (50) I	[161]
12-11		0	Cr 47 SmB (30) I	[163]
12-12		0	SmE 42 SmB 53.5 I	[167]

nematic ranges (ΔT):



The effect of the introduction of the saturated trans-1,4-cyclohexylene, trans-1,3-dioxan-2,5-diyl, and trans-2,5-tetrahydropyranyl into the molecular core of liquid crystals presented in Table 3 can be expressed by the following orders:

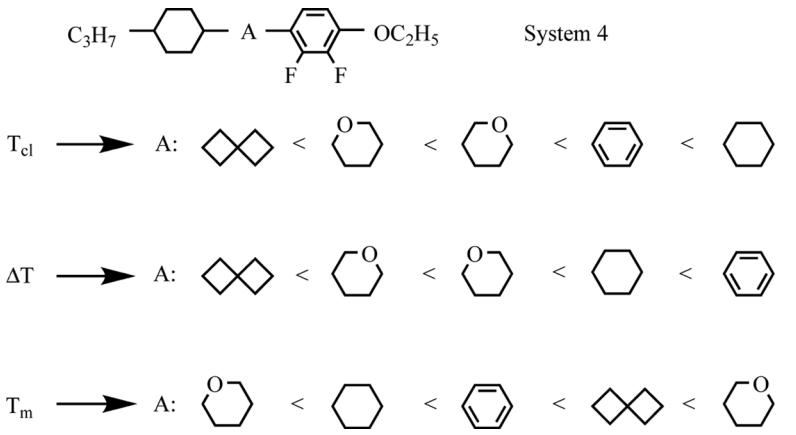


It follows from these orders and Table 3 that the cyclohexane derivatives exhibit the high clearing and low melting points and widest nematic range. The dioxane derivatives show low clearing and highest melting temperatures and moderate

nematic range. The tetrahydropyran derivatives exhibit lowest melting and clearing temperatures, and wide nematic range among compounds **3-1** to **3-5** presented in Table 3. One can say that moving tetrahydropyran in the middle of the molecular core lowers the smectic and nematic thermostabilities (for four-ring derivatives **3-6**, **3-7**; Table 3), and a further move of tetrahydropyran closer to the 3,4,5-trifluorophenyl fragment results in the highest melting and clearing points and disappearance of the smectic B phase among compounds **3-6** to **3-8**. For three-ring derivatives the same move lowers the melting temperatures and creates the nematic phase (compounds **6-2**, **6-3**; Table 6).

The less pronounced mesomorphic behavior of the 3,4-dihydro-6H-pyran derivatives compared with that of the corresponding tetrahydropyran and reference derivatives (compounds **1-10** to **1-12**; **6-2**–**6-5**) can be caused by their half-chair conformation [12–14] with puckering of the oxygen atom by 0.612 Å from the least-squares plane defined by the five carbon atoms [15]. These structural features can be responsible for the appearance of the cholesteric phase in compound **1-10**.

The data presented in Table 4 reveal again the importance of the position of oxygen in the tetrahydropyran ring on the liquid crystal properties. Pointing the oxygen atom of tetrahydropyran toward the 2,3-difluorophenyl fragment gives liquid crystals exhibiting an additional monotropic smectic phase and significantly higher melting and clearing temperatures in comparison with those of the opposite case (compounds **4-2**, **4-3**; Table 4) and the following system:



It is evident from these orders and Table 4 that the cyclohexane derivatives exhibit the highest nematic thermostability, wide nematic range, and low melting temperature. The tetrahydropyran derivatives show moderate clearing points and nematic ranges. The introduction of the tetrahydropyran ring into the molecular core of three-ring di-methoxy derivatives creates only cholesteric phase exhibiting the lowest melting and clearing points in comparison with those of the corresponding reference nematic derivatives (compounds **5-1** to **5-6**; Table 5). It can be seen from Table 6 that 2-oxabicyclo[2.2.2]octane derivative **6-10** shows the highest clearing point compared with those of the corresponding trans-1,3-dioxan-2,5-diyl and trans-1,4-cyclohexylene derivatives **6-9**, **6-11**.

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 [16]. 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 [16]. The stereochemical situation is the same in the heterocylic spirosystem (compound **9-1**; Table 9) as for the spiro[5.5]undecane **6-13**, but the bond angles and bond lengths are different and the barrier for ring inversion is lower [17]. The data presented in Tables 6 and 9 reveal that the 1,5-dioxa-9-azaspiro[5.5]undecane [18] and 1,5-dioxaspiro[5.5]undecane derivatives containing the dioxane ring are not mesomorphic in comparison with those of the corresponding reference derivatives (compounds **6-12** to **6-15**; **9-1** to **9-6**). It can be explained by the significant nonlinearity of the spiranes [19]. Particularly, one can say that the corresponding trans-1,3-dioxane and trans-1,4-cyclohexylene derivatives (compounds **9-2** and **9-3**), liquid crystals containing their fused system (compound **9-4**, approximately), and liquid crystals containing these both two rings (compound **9-6**) show the mesomorphic properties with increasing order of their clearing points.

It has been suggested that the O−C(4)−C(5)−C(6)−O region of the 1,3,2-dioxaborinane ring adopts a rapidly inverting chair conformation where the lone pairs of the oxygen atoms and the vacant p orbital on boron are coplanar and overlap most effectively [20,21]. The inter-conversion of 1,3,2-dioxaborinane goes via transition state with 2,5-twist form and differs from 1,3-dioxane in having a lower potential barrier. It is caused by the decrease in the number of intramolecular independent interactions resulting from the planar configuration of the trigonal boron atom [22]. The study and commercial applications of the mesomorphic 1,3,2-dioxaborinane derivatives have been attracted significant interest [23–31]. Particularly, it has been demonstrated in the literature [29,30] by X-ray diffraction measurements that the introduction of the 1,3,2-dioxaborinane ring into the molecular core of three-ring derivatives creates the dimeric structure ($d/L > 1$, where d is a period of the density wave and L is the molecular length) of their mesophases (compounds **7-1** to **7-3**; Table 7). Some other 1,3,2-dioxaborinane derivatives show low melting and the lowest clearing temperatures in comparison with those of the corresponding reference derivatives (compounds **8-1** to **8-5**; **9-15 to 9-17**; **11-7** to **11-12**; Tables 8, 9, 11). One can say that the presence of two oxygen atoms in the saturated six-membered ring favors the creation of the chiral smectic C^* phase in some liquid crystals (compounds **8-1** to **8-4**; Table 8). Particularly, in the chiral compounds, the 1,3,2-dioxaborinane derivative **8-1** exhibits lower smectic C^* thermostability and range compared with those of the corresponding trans-1,3-dioxane derivative **8-2**. The importance of the molecular structure of liquid crystals can be seen by comparing the thermal efficiency of their rings—trans-1,3-dioxane (D), 1,3,2-dioxaborinane (B), and trans-1,4-cyclohexylene (C):

$$B < C < D \text{ for compounds } \mathbf{9{-}15} \text{ to } \mathbf{9{-}17}$$

$$B < D < C \text{ for compounds } \mathbf{11{-}7} \text{ to } \mathbf{11{-}9}$$

The fusion of the benzene and tetrahydropyran gives the 3,4-dihydro-2H-1-benzopyran (chroman) fragment that adopts a half-chair conformation [32,33]. This structural feature can be responsible for the observed mesomorphic properties of the 3,4-dihydro-2H-1-benzopyran derivatives that show higher clearing points in comparison with those of the corresponding tetrahydropyran, 1,4-phenylene, and reference derivatives (compounds **9-7** to **9-11**; **10-1** to **10-3**; **10-4** to **10-6**). The introduction of nonlinear 3,4-dihydro-2H-1-benzopyran fragment into the molecular core of some weakly polar liquid crystals promotes the formation of the cholesteric phase with wider range in comparison with those of the corresponding 1,4-phenylene and other reference derivatives (compounds **10-1** to **10-3**, **10-4** to **10-6**). A more puckered 1,4-dioxane ring than the cyclohexane one [8] can be responsible for the disappearance of the mesomorphic properties of compounds **9-11** compared with that of the corresponding cyclohexane derivative **9-10**.

Similar fusion of the benzene and 1,3-dioxane gives the 4H-1,3-benzodioxin fragment. It has a twisted structure with a barrier to planarity of $3475\,cm^{-1}$ [34]. The introduction of this fragment into the molecular core of liquid crystals enhances (compounds **9-12** to **9-14**; **11-1**, **11-2**, **11-4**) and lowers (compounds **11-1**, **11-3**, **11-5**, **11-6**) their clearing temperatures compared with those of the corresponding 1,4-phenylene and reference derivatives.

The fusion of the tetrahydropyran and 1,3-dioxane gives the chiral 2,4,7-trioxabicyclo[4.4.0]decane fragment, which can be used as a structural unit in liquid crystals presented in Tables 5 and 12. It is evident from Table 5 that the chiral 2,4,7-trioxa-3-borabicyclo[4.4.0]decane derivatives, which have an additional boron atom in their structure, exhibit the enhanced mesophase thermostability (compounds **5-7**, **5-8**; **5-10, 5-11**), which is opposite to the results found above for the corresponding 1,3,2-dioxaborinane and trans-1,3-dioxane derivatives. Also, it is important to note that the 2,4,7-trioxabicyclo[4.4.0]decane and 2,4,7-trioxa-3-borabicyclo[4.4.0]decane derivatives exhibit higher melting and clearing temperatures than the corresponding tetrahydropyran derivative (compounds **5-1**, **5-7**, **5-8**, Table 5).

It has been shown that 2,4,7,9-tetraoxabicyclo[4.4.0]decane exists in *trans* or *cis* forms [35–37]. Its *cis* system can exist in two possible diastereoisomeric chair–chair forms, O_{inside} and $O_{outside}$, which may inconvert by conformational ring inversion. The *trans* form is both configurationally and conformationally fixed [37]. These structural features can be responsible for the nematic character of the mesophase of the *trans*-2,4,7,9-tetraoxabicyclo[4.4.0]decane derivative and its significantly lower clearing point in comparison with those of the corresponding 2,4,7-trioxabicyclo[4.4.0] decane and 2,4,7-trioxa-3-borabicyclo[4.4.0]decane derivatives (compounds **5-7** to **5-9**; Table 5**)**. Similar lower clearing point and appearance of the nematic phase are also shown by the 1,3,2-dioxaborinane derivative (compounds **5-10** to **5-12**).

The data collated in Table 2 reveal that the nonlinear structure of the *trans*-pyrano[3,2-c][1]benzopyran derivative **2-13** leads to the disappearance of the nematic phase and lowering the clearing point in comparison with those of the corresponding three- and four-ring reference compounds **2-14**, **2-15**. The introduction of the *trans*-pyrano[3,2-c][1]benzopyran into the molecular core of pentyl-hexyloxy derivatives creates the smectic A and nematic phases with high clearing point in comparison with those of the corresponding two-fragment non-mesomorphic 2,4,7-trioxabicyclo[4.4.0]decane, 2,6,7-trioxabicyclo[2.2.2]octane [38] derivatives, trans-1,3-dioxane, and other reference derivatives (compounds **12-1** to **12-9**; Table 12). It is important to note that the replacement of the hexyloxy group by hexyl one in

non-mesomorphic compound **12-3** gives derivative **12-10,** which exhibits the smectic B phase with moderate thermostability. Similar trends have been reported for other tetrahydropyran [39–42], dihydropyran [43–46], 1,3-dioxane [47–53], 3,4-dihydro-2H-1-benzopyran [54–60], 1,3,2-dioxaborinane [61–66], 2,4,7-trioxabicyclo[4.4.0]decane, and 2,4,7-trioxa-3-borabicyclo[4.4.0]decane, [67–73] derivatives and liquid crystals based on oxygen-containing fused and spiro systems [74–76].

The presented results reveal the importance of the molecular structure of oxygen-containing liquid crystals. We can propose that the electronic and geometric structures of the oxygen-containing molecules [9–11,12–17,20–22,32–37] play a very important role in the intra- and intermolecular interactions [77–79] that affect the packing of the molecules, which predominantly influences mesophase stability [77–81]. 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 [81]. Other molecular aspects such as the association [80] or dipole–dipole attraction in polar liquid crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [81].

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 [82]:

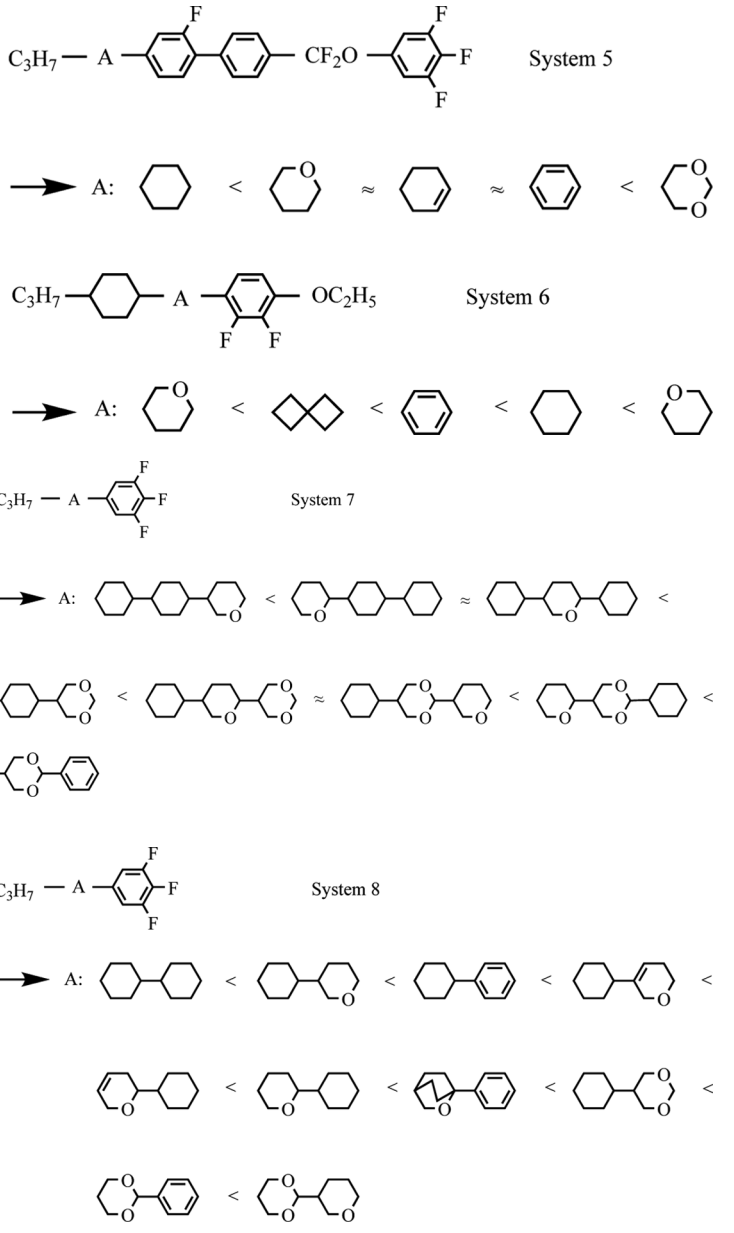
$$\Delta\varepsilon = \mathrm{NhF}/\varepsilon_{\mathrm{o}}[\Delta\alpha - \mathrm{F}\mu^2/\mathrm{kT}(1 - 3\cos^2\beta)]\mathrm{S}, \quad (1)$$

where $\mathrm{h} = 3\varepsilon^*/(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$; $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropy; F is the cavity reaction field; μ is the dipole moment; β is the angle between the molecular long axis and the dipole moment; and N is the number of molecules per unit volume; S is the order parameter.

The total dipole moment and, consequently, the dielectric anisotropy of compounds presented in Tables 2–4 and 6 are strongly affected by values and directions of the dipole moments of the terminal, linking, lateral groups and molecular fragments (see Eq. (1)). When the positions and orientations of the molecular fragments, linking, lateral, and terminal substituents are chosen in such way that their dipole moments contribute mainly to the parallel part of the total dipole moment, the positive dielectric anisotropy of liquid crystals can be achieved (Tables 2, 3, 6). Otherwise, the negative dielectric anisotropy can be obtained for compounds presented in Tables 2 and 4. Note that the replacement of the trans-1,4-cyclohexylene ($\mu = 0$ D) [83] by tetrahydropyran ($\mu = 1.58$ D) [83] and trans-1,3-dioxane ($\mu = 2.06$ D) [83] in liquid crystals correspondingly increases their dielectric anisotropy (in absolute value; compounds **2-1** to **2-9**; **3-1** to **3-3**; **3-6** to **3-12**; **4-1, 4-2**; **6-1** to **6-3**, **6-6**, **6-7**; Tables 2–4, 6). Similar behavior can be observed for the 3,4-dihydro-6H-pyran derivatives (compounds **6-4**, **6-5**) and 2-oxabicyclo[2.2.2]octane derivative **6-10**. Increasing the number of oxygen-containing heterocycles introduced into the molecular core of liquid crystals gives a more pronounced rise of the dielectric anisotropy (compounds **2-4** to **2-9**; **3-6** to **3-12**; **6-1** to **6-3, 6-6, 6-7**). Enhanced value of the dielectric anisotropy (in absolute value) for compound **4-2** compared

with that of compound **4-3** is caused by the increased dipole moment and its almost perpendicular direction to the long molecular axis of former.

One can say that compound **2-13** with its nonlinear *trans*-pyrano[3,2-c][1]benzopyran fragment and four-ring trans-1,3-dioxane derivative **2-15** shows very similar dielectric behavior. The introduction of two oxygen atoms and one nitrogen atom into the spiro[5.5]undecane fragment of derivative **6-13** to obtain compound **6-12** indeed increases the dipole moment of latter and, as a result, its dielectric anisotropy. These findings can be expressed by the following orders of increasing the dielectric anisotropy:

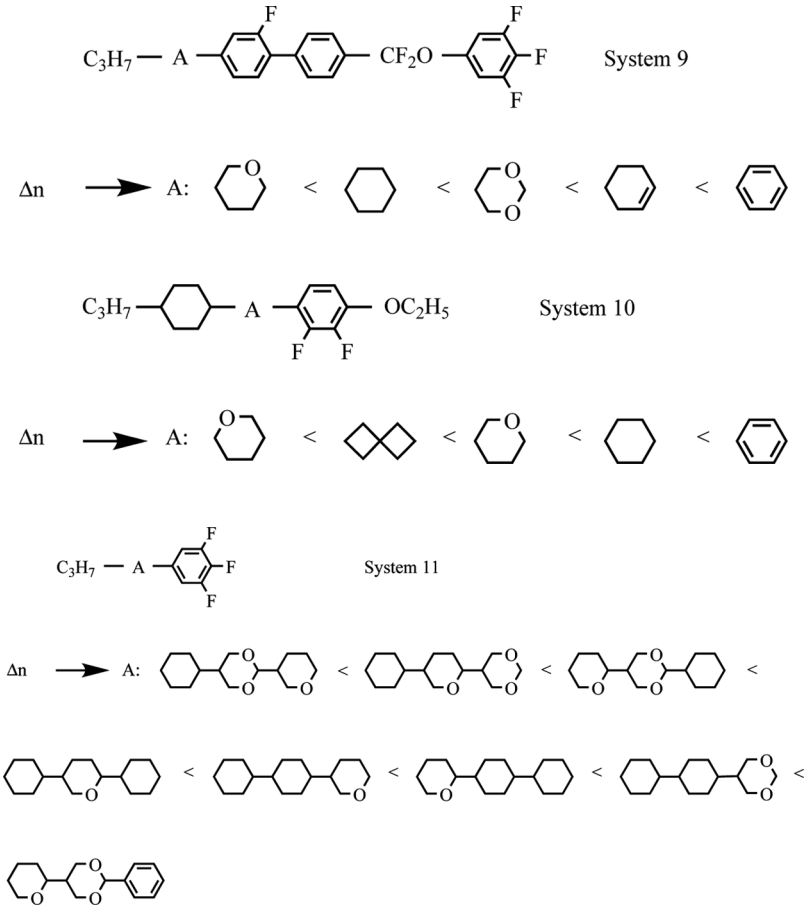


Optical Properties

The phenomenological relation between the refractive index and the electric polarization is defined as [84,85]:

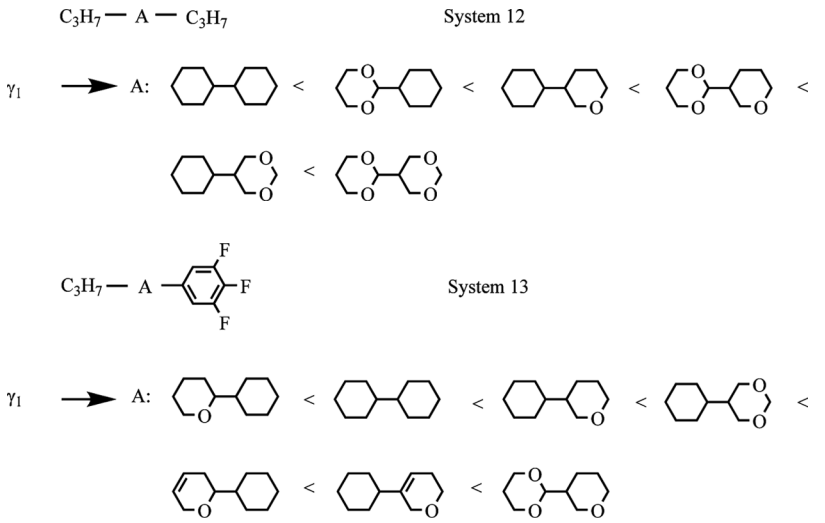
$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^*/3\epsilon_o \tag{2}$$

where the mean polarizability $\alpha^* = (\alpha_{\|} + 2\alpha_{\perp})/3$; 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, 1,4-phenylene derivatives) exhibit an optical anisotropy $\Delta n = n_e - n_o$ that is much larger than that of the corresponding saturated derivatives (compounds **3-1** to **3-5**, **4-1** to **4-5**; Tables 2 and 4). The fluorinated derivatives presented in Tables 2–4 and 6 show similar values of the optical anisotropy that have been observed earlier for other fluorinated derivatives [86]. The influence of the molecular structure of oxygen-containing liquid crystals on the optical anisotropy can be expressed by the following orders:



Viscous Properties

It has been demonstrated that the nematic liquid crystal materials for display applications should have a low viscosity for giving the acceptable response times to liquid crystal displays [87,88]. The rotational viscosity γ_1 of a nematic liquid crystal (NLC) is a dissipative coefficient describing the rate of reorientation of the NLC director [89]. The magnitude of the rotational and flow viscosities depend on molecular structure, intermolecular association, and temperature [90,91]: as temperature increases, viscosity decreases [90–93]. According to the results on flow and rotational viscosity presented in Tables 2, 3, and 6, the introduction of the oxygen-containing molecular fragments into the molecular core liquid crystals usually increases their viscosities in comparison with those of the corresponding trans-1,4-cyclohexylene and reference compounds (compounds **2-4** to **2-9**, **3-8**, **3-11**, **3-12**; **6-1**, **6-3** to **6-7**; Tables 2, 3, 6). Surprisingly low viscosity has been reported for the tetrahydropyran derivative **6-2**. Increasing the number of the oxygen-containing heterocycles in the molecular core of liquid crystals further enhances their viscosity (compounds **2-4** to **2-9**; **6-1** to **6-7**). These findings can be expreesed by the following orders of increasing the viscosity:



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 [94]. 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 [94]. The spontaneous polarization P_s is a quantity that is directly related to the response time τ as a switching device [95]:

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

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, and E is an applied electric field.

According to Scherowsky and Sefkow [96], 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 can be seen from Table 8 that the introduction of the 1,3,2-dioxaborinane ring of liquid crystals enhances their spontaneous polarization compared with that of the corresponding trans-1,3-dioxane derivative, and their tilt angles are approximately equal (compounds **8-1**, **8-2**). According to the data presented in Table 10, the 3,4-dihydro-2H-1-benzopyran derivatives show almost zero value of the spontaneous polarization in comparison with that of the tetrahydropyran and reference compounds (compounds **10-1**, **10-2**; **10-4** to **10-7**). It has been reported that the *cis* isomers of the tetrahydropyran derivatives usually show higher spontaneous polarization than the *trans* ones [41].

Conclusion

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

References

[1] Bezborodov, V. S., Petrov, V. F., & Lapanik, V. I. (1996). *Liq. Cryst.*, *20*, 875.
[2] Karamysheva, L. A., Torgova, S. I., Agafonova, I. F., & Petrov, V. F. (2000). *Liq. Cryst.*, *27*, 393.
[3] Petrov, V. F. (2001). *Liq. Cryst.*, *28*, 217.
[4] Petrov, V. F., & Pavluchenko, A. I. (2003). *Mol. Cryst. Liq. Cryst.*, *393*, 1.
[5] Petrov, V. F. (2006). *Mol. Cryst. Liq. Cryst.*, *457*, 105.
[6] Petrov, V. F., Torgova, S. I., Karamysheva, L. A., & Takenaka, S. (1999). *Liq. Cryst.*, *26*, 1141.
[7] Breed, H. E., Gundersen, G., & Seip, H. M. (1979). *Acta Chem. Scand. A*, *33*, 225.
[8] Riddell, F. G. (1980). *The Conformational Analysis of Heterocyclic Compounds*, Academic Press: London.
[9] Bushweller, C. H., & Gianni, M. H. (1980). Stereodynamics of alcohols, ethers, thio ethers and related compounds. In: *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*, Patai, S. (Ed.), John Wiley & Sons: New York, 215.
[10] Freeman, F., & Le, K. T. (2003). *J. Phys. Chem. A*, *107*, 2908.
[11] Yokoyama, Y., & Hall, H. K., Jr. (1982). Ring-opening polymerization of atom-bridged and bond-bridged bicyclic ethers, acetals and orthoesters. In: *Advances in Polymer Science*, Cantow, H.-J. (Ed.), Springer Verlag: New York, Vol. 42, 107.
[12] Taskinen, E., Alanko, T., & Liebman, J. F. (2006). *Struct. Chem.*, *17*, 323.

[13] Valente, E. J., Santarsiero, B. D., & Schomaker, V. (1979). *J. Org. Chem.*, *44*, 798.
[14] Tecklenburg, M. M. J., & Laane, J. (1989). *J. Am. Chem. Soc.*, *111*, 6920.
[15] Gardiner, M. G., Jones, R. C., Mason, C. M., Smith, J. A., & Wise, L. E. (2007). *Acta Cryst.*, *E63*, o955.
[16] Dodziuk, H. (1986). *J. Chem. Soc., Perkin Trans. II*, 249.
[17] Frach, R., Tschierske, C., Zaschke, H., & Deutscher, H.-J. (1989). *Liq. Cryst.*, *5*, 197.
[18] Kuroyan, R. A. (1991). *Russ. Chem. Rev.*, *60*, 1368.
[19] Schmidt, W., Vogtle, F., & Poetsch, E. (1995). *Liebigs Ann.*, 1319.
[20] Rossi, K., & Pihlaja, K. (1985). *Acta Chem. Scand. B*, *39*, 671.
[21] Davis, F. A., Turchi, I. J., Maryanoff, B. E., & Hutchins, R. O. (1972). *J. Org. Chem.*, *37*, 1583.
[22] Kuznetsov, V. V., & Novikov, A. N. (2003). *Chem. Heterocycl. Comp.*, *39*, 263.
[23] Bezborodov, V. S., Grinkevich, O. A., Grebenkin, M. F., Lapanik, V. I., Minko, A. A., Rzhussky, V. V., Muravsky, A. A., Petrov, V. F., & Ivaschenko, A. V. (1989). US Patent 4853150.
[24] Bezborodov, V. S., & Lapanik, V. I. (1991). *Liq. Cryst.*, *10*, 803.
[25] Reiffenrath, V., Hittich, R., & Plach, H. (1991). German Pat. Appl. DE 4014488 A1.
[26] Matsubara, M., Seto, K., Tabuchi, H., Imazaki, H., & Takahashi, S. (1993). *Bull. Chem. Soc. Jpn.*, *66*, 578.
[27] Matsubara, H., Seto, K., & Takahashi, S. (1994). *Mol. Cryst. Liq. Cryst.*, *241*, 9.
[28] Dabrowski, R., Bezborodov, V. S., Lapanik, V. I., Dziaduszek, J., & Czuprynski, K. (1995). *Liq. Cryst.*, *18*, 213.
[29] Petrov, V. F., Tasaka, T., Okamoto, H., Takenaka, S., & Bezborodov, V. S. (2000). *Mol. Cryst. Liq. Cryst.*, *339*, 167.
[30] Matsubara, H., Tanaka, T., Takai, Y., Sawada, M., Seto, K., Imazaki, H., & Takahashi, S. (1991). *Bull. Chem. Soc. Jpn.*, *64*, 2103.
[31] Kumar, A., Dhar, R., Agrawal, V. K., & Dabrowski, R. (2007). *Phase Trans.*, *80*, 231.
[32] Sipila, K., & Kansikas, J. (2002). *Phosphorus, Sulfur and Silicon*, *177*, 437.
[33] Holmberg, G., & Sjoholm, R. (1971). *Acta Chem. Scand.*, *25*, 1132.
[34] McCann, K., Wagner, M., Choo, J., & Laane, J. (2007). Joint Fall Meeting of the Texas Sections of the APS and AAPT, October 18-20, 2007.
[35] Senderowitz, H., Linden, A., Golender, L., Abramson, S., & Fuchs, B. (1994). *Tetrahedron*, *50*, 9691.
[36] Senderowitz, H., Golender, L., & Fuchs, B. (1994). *Tetrahedron*, *50*, 9707.
[37] Linden, A., Beckhaus, H.-D., Verevkin, S. P., Ruchardt, C., Ganguly, B., & Fuchs, B. (1998). *J. Org. Chem.*, *63*, 8205.
[38] Boros, E. J., Coskan, K. J., King, R. W., & Verkade, J. G. (1966). *J. Am. Chem. Soc.*, *88*, 1140.
[39] Siemensmeyer, K., Tajbakhsh, A. R., Bruce, D. W., Wieczorek, E., Vill, V., & Schimmel, U. (1998). PCT WO 98/03610.
[40] Kobayashi, M., & Shimada, T. (2009). PCT WO 2009/031437.
[41] Buchecker, R., Fuenfschilling, J., & Marck, G. (1997). *Mol. Cryst. Liq. Cryst.*, *302*, 295.
[42] Yano, H., Matsui, S., Takeuchi, H., Miyazawa, K., & Haseba, H. (2000). US Patent 6146718.
[43] Murza, M. M., & Safarov, M. G. (1994). *Chem. Heterocycl. Comp.*, *30*, 771.
[44] Murza, M. M., Safina, D. M., & Kuvatov, Z. Kh. (1993). *Chem. Heterocycl. Comp.*, *29*, 1405.
[45] Sasada, Y., & de Mayer, A. (2004). Japan Pat. Appl. JP 2004315415.
[46] Haseba, Y., Miyazawa, K., Kubo, Y., & Nakagawa, E. (2002). Japan Pat. Appl. JP 2002121190.
[47] Kato, T., Matsui, S., Takeuchi, H., Kubo, Y., & Nakagawa, E. (2002). Eur. Pat. Appl. EP 1170352.
[48] Buchecker, R., Lukac, T., & Reichnard, J. (1999). PCT WO 99/12920.

[49] Miyazawa, K., Takeuchi, H., Yagi, Y., Takeshita, F., & Nakagawa, E. (2000). Eur. Pat. Appl. EP 1026142.
[50] Asep, R., Aoki, Y., Hirose, T., & Nohira, H. (2001). *Liq. Cryst.*, *28*, 785.
[51] Dong, C. C., Styring, P., Goodby, J. W., & Chan, L. K. M. (1999). *J. Mater. Chem.*, *9*, 1669.
[52] Mineta, H., Yui, T., & Matsumoto, T. (1994). US Patent 5275757.
[53] Ohlemacher, A., & Funfschilling, J. (2000). PCT WO 2000/31211.
[54] Shitara, H., Aoki, Y., Hirose, T., & Nohira, H. (2000). *Bull. Chem. Soc. Jpn.*, *73*, 259.
[55] Bonini, B. F., Dolci, N., Gottarelli, G., Masiero, S., Spada, G. P., Mariani, P., & Yang, B. (1996). *Mol. Cryst. Liq. Cryst.*, *290*, 49.
[56] Bernatz, G., Kirsch, P., Best, P., & Goetz, A. (2007). PCT WO 2007/147516 A1.
[57] Sago, K., & Fujita, A. (2007). *Mol. Cryst. Liq. Cryst.*, *479*, 151.
[58] Lauk, U. K., Skrabal, P., & Zollinger, H. (1985). *Helv. Chim. Acta*, *68*, 1406.
[59] Taugerbeck, A., & Klasen-Memmer, M. (2006). German Pat. Appl. DE 102005031554 A1.
[60] Klein, M., Kirsch, P., Poetsch, E., Heckmeier, M., Best, P., Taugerbeck, A., & Klasen-Memmer, M. (2006). PCT WO 2006/040009 A2.
[61] Matsubara, H., Seto, K., Imazaki, H., & Takahashi, S. (1992). *J. Mater. Chem.*, *2*, 83.
[62] Goodby, J. W., Toyne, K. J., Hird, M., Styring, P., Lewis, R. A., Beer, A., Dong, C. C., Glendenning, M. E., Jones, J. C., Lymer, K. P., Slaney, A. J., Minter, V., & Chan, L. K. M. (2000). *Proc. SPIE*, *3955*, 2.
[63] Seto, K., Matsubara, H., Takahashi, S., Tahara, T., Murakami, M., Miyake, S., Masumi, T., Ando, T., & Furukami, A. (1988). *J. Chem. Soc. Chem. Commun.*, 56.
[64] Dong, C. C., Styring, P., Chan, L. K. M., & Goodby, J. W. (1997). *Mol. Cryst. Liq. Cryst.*, *302*, 289.
[65] Meier, J. G., Lagerwall, S. T., Hird, M., & Goodby, J. W. (2000). *Ferroelectrics*, *243*, 87.
[66] Kawada, M., Sagawa, T., & Uesugi, Y. (1995). Japan Pat. Appl. JP 7145174.
[67] Bertini, B., Moineau, C., Sinou, D., & Vill, V. (2001). *J. Carbohydr. Chem.*, *20*, 315.
[68] Bertini, B., Perrin, M., Sinou, D., Thozet, A., & Vill, V. (2003). *J. Carbohydr. Chem.*, *22*, 685.
[69] Bertini, B., Moineau, C., Sinou, D., Gesekus, G., & Vill, V. (2001). *Eur. J. Org. Chem.*, 375.
[70] Vill, V., von Minden, H. M., & Bruce, D. W. (1997). *J. Mater. Chem.*, *7*, 893.
[71] Vill, V., von Minden, H. M., Sinou, D., Moineau, C., & Bolitt, V. (1998). *Proc. SPIE*, *3319*, 109.
[72] Vill, V., Tunger, H.-W., Hensen, K., Stegemeyer, H., & Diekman, K. (1996). *Liq. Cryst.*, *20*, 449.
[73] Stegemeyer, H., Meister, R., Altenbach, H.-J., & Szewczyk, D. (1993). *Liq. Cryst.*, *14*, 1007.
[74] Tschierske, C., Joachimi, D., Vorbrodt, H.-M., Zaschke, H., Wiegeleben, A., Hauser, A., & Demus, D. (1989). *Liq. Cryst.*, *5*, 177.
[75] Tschierske, C., & Zaschke, H. (1989). *Liq. Cryst.*, *5*, 191.
[76] Jansen, A., & Klasen-Memmer, M. (2009). PCT WO 2009/068152.
[77] Osman, M. A. (1983). *Z. Naturforsch.*, *38a*, 693.
[78] de Jeu, W. H. (1983). *Phil. Trans. R. Soc. A*, *309*, 217.
[79] Ostrovskii, B. I. (1999). Packing and molecular conformation, and their relationship with LC phase behaviour. In: *Structure and Bonding*, Mingos, D. M. P. (Ed.), Springer Verlag: New York, Vol. 94, 200.
[80] Schad, Hp., & Osman, M. A. (1981). *J. Chem. Phys.*, *75*, 880.
[81] Osman, M. A., & Revesz, L. (1982). *Mol. Cryst. Liq. Cryst. Lett.*, *82*, 41.
[82] Maier, W., & Meier, G. (1961). *Z. Naturforsch.*, *16a*, 262.
[83] Lide, D. R. (2008). *CRC Handbook of Chemistry and Physics*, CRC Press: New York.

[84] de Jeu, W. H. (1980). *Physical Properties of Liquid Crystalline Materials*, Gordon & Breach: New York.
[85] de Jeu, W. H., Gerristma, C. J., van Zanten, P., & Goosens, W. A. (1972). *Phys. Lett.*, *39A*, 355.
[86] Petrov, V. F., Duan, M., Okamoto, H., Mu, J., Shimizu, Y., & Takenaka, S. (2001). *Liq. Cryst.*, *28*, 387.
[87] Schadt, M. (1992). *Displays*, *13*, 11.
[88] Jakeman, E., & Raynes, E. P. (1972). *Phys. Lett.*, *39A*, 69.
[89] de Gennes, P. G., & Prost, J. (1995). *The Physics of Liquid Crystals*, Clarendon Press: Oxford.
[90] Wu, S.-T., & Wu, C.-S. (1990). *Phys. Rev. A*, *42*, 2219.
[91] Belyaev, V. V. (1989). *Rus. Chem. Rev.*, *58*, 917.
[92] Constant, J., & Raynes, E. P. (1980). *Mol. Cryst. Liq. Cryst.*, *62*, 115.
[93] Diogo, A. C., & Martins, A. F. (1981). *Mol. Cryst. Liq. Cryst.*, *66*, 133.
[94] Martinot-Lagarde, P. (1988). *Ferroelectrics*, *84*, 53.
[95] Escher, C., Geelhaar, T., & Boehm, E. (1986). *Liq. Cryst.*, *3*, 469.
[96] Scherowsky, G., & Sefkow, M. (1991). *Mol. Cryst. Liq. Cryst.*, *202*, 207.
[97] Vill, V., & Thiem, J. (1990). *Z. Naturforsch.*, *45a*, 1345.
[98] Delavier, P., Siemensmeyer, K., Vill, V., Hartwig, A., Gesekus, G., & Tunger, H.-W. (1994). Eur. Pat. Appl. EP 630892 A1.
[99] Krause, J., Eidenschink, R., & Pohl, L. (1980). US Patent 4229315.
[100] Praefcke, K., Schmidt, D., & Eidenschink, R. (1983). US Patent 4419263.
[101] Kirsch, P., Binder, J. T., Lork, E., & Roschenthaler, G.-V. (2006). *J. Fluor. Chem*, *127*, 610.
[102] Kirsch, P., Binder, W., Hahn, A., Jahrling, K., Lenges, M., Lietzau, L., Maillard, D., Meyer, V., Poetsch, E., Ruhl, A., Unger, G., & Frohlich, R. (2008). *Eur. J. Org. Chem.*, 3479.
[103] Poetsch, E., Binder, W., Meyer, V., Heckmeier, M., & Luessem, G. (2005). US Pat. Appl. 2005/0017216 A1.
[104] Kirsch, P., & Poetsch, E. (1998). *Adv. Mater.*, *10*, 602.
[105] Kirsch, P., & Maillard, D. (2006). *Eur. J. Org. Chem.*, 3326.
[106] Poetsch, E., Binder, W., Heckmeier, M., Tarumi, K., & Krause, J. (2002). German Pat. Appl. DE 10217771 A1.
[107] Inoue, S., Yanai, T., Ando, S., Nakazawa, A., Honda, K., Hoshino, Y., & Asai, T. (2005). *J. Mater. Chem.*, *15*, 4746.
[108] Obikawa, T., Ikukawa, S., & Nakayama, J. (1993). US Patent 5238599.
[109] Lietzau, L., Czanta, M., Hirschmann, H., & Wittek, M. (2008). Eur. Pat. Appl. EP 1900792A1.
[110] Lietzau, L., Czanta, M., & Manabe, A. (2008). PCT WO 2008/019746 A1.
[111] Lietzau, L., & Czanta, M. (2006). PCT WO 2006/125511 A1.
[112] Demus, D., Goto, Y., Sawada, S., Nakagawa, E., Saito, H., & Tarao, R. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 1.
[113] Klasen, M., Bremer, M., & Tarumi, K. (2000). *Jpn. J. Appl. Phys.*, *39*, L1180.
[114] Goto, M., Masukawa, T., Kondo, T., & Fujita, A. (2008). *Mol. Cryst. Liq. Cryst.*, *494*, 58.
[115] Reiffenrath, V., Bremer, M., & Klasen-Memmer, M. (2007). PCT WO 2007/033732 A1.
[116] Siemensmeyer, K., Gesekus, G., & Vill, V. (1998). PCT WO 98/14442.
[117] Schubert, H., & Zaschke, H. (1970). *J. Prakt. Chem.*, *312*, 494.
[118] Zaschke, H., Nitsche, K., & Schubert, H. (1977). *J. Prakt. Chem.*, *319*, 475.
[119] Schubert, H., Demus, D., Zaschke, H., Kuschel, F., Pelzl, G., Nothnikz, H.-U., & Schliemann, W. (1982). US Patent 4358589.
[120] Dolling, K., Zaschke, H., & Schubert, H. (1979). *J. Prakt. Chem.*, *321*, 643.

[121] Dimitrova, K., Hauschild, J., Zaschke, H., & Schubert, H. (1980). *J. Prakt. Chem.*, *322*, 933.
[122] Vill, V., Tunger, H.-W., & von Minden, M. (1996). *J. Mater. Chem.*, *6*, 739.
[123] Kohne, B., Praefcke, K., Omar, R. S., & Frolow, F. (1986). *Z. Naturforsch.*, *41b*, 736.
[124] Seto, K., Takahashi, S., & Tahara, T. (1985). *J. Chem. Soc., Chem. Commun.*, 122.
[125] Buchecker, R., Marck, G., & Villiger, A. (1997). US Patent 5667721.
[126] Matsui, S., Kondo, T., Haseba, Y., Tamura, N., Takeuchi, H., & Miyazawa, K. (1998). Japan Pat. Appl. JP 10316969.
[127] Bremer, M., Heckmeier, M., Klasen-Memmer, M., & Lannert, H. (2004). US Patent 6808762 B2.
[128] Tarumi, K., Bartmann, E., Reiffenrath, V., Schoen, S., Pauluth, D., Schuler, B., & Poetsch, E. (1996). German Pat. Appl. DE 19528085 A1.
[129] Tamura, N., Fujita, A., Matsui, S., Takeuchi, H., Tomi, Y., Takeshita, F., & Nakagawa, E. (2001). Eur. Pat. Appl. EP 1072593 A1.
[130] Takatsu, H., Takehara, S., Takeuchi, K., & Iwashita, Y. (2001). *Proc. SPIE*, *4463*, 92.
[131] Murakami, M., Miyake, S., Masumi, T., Ando, T., Fukami, A., Takahashi, S., Seto, S., & Tahara, T. (1988). *Mol. Cryst. Liq. Cryst.*, *162B*, 149.
[132] Haramoto, Y., Kawashima, K., & Kamogawa, H. (1988). *Bull. Chem. Soc. Jpn.*, *61*, 431.
[133] Isogami, M., Hattori, S., Iwasaki, K., Kitamura, T., Mukoh, A., Inukai, T., Furukawa, K., Terashima, K., & Saitoh, S. (1986). US Patent 4576732.
[134] Akutsu, M. (1995). Japan Pat. Appl. JP 7258126.
[135] Vorbrodt, H.-M., Deresch, S., Kresse, H., Wiegeleben, A., Demus, D., & Zaschke, H. (1981). *J. Prakt. Chem.*, *323*, 902.
[136] Eidenschink, R., Krause, J., Pohl, L., & Eichler, J. (1980). *Proc. Int. Conf. on Liq. Cryst.*, Bangalore, India, p. 515.
[137] Tschierske, C., & Zaschke, H. (1988). *J. Prakt. Chem.*, *330*, 1.
[138] Petrzilka, M., & Schleich, K. (1982). *Helv. Chim. Acta*, *65*, 1242.
[139] Bonini, B. F., Carboni, P., Gottarelli, G., Masiero, S., & Spada, G. P. (1994). *J. Org. Chem.*, *59*, 5930.
[140] Zaschke, H., Demus, D., Vorbrodt, H.-M., Hauser, A., & Vogel, J. (1998). German Patent DE 3302218.
[141] Ivashchenko, A. V., Titov, V. V., & Kovshev, E. I. (1976). *Mol. Cryst. Liq. Cryst.*, *33*, 195.
[142] Wiegeleben, A., Deutscher, H.-J., Demus, D., & Altmann, H. (1981). *Z. Chemie*, *21*, 28.
[143] Braun, M., Spieker, B., Hahn, A., & Vill, V. (2002). *Synthesis*, 2129.
[144] Boller, A., Schadt, M., & Villiger, A. (1984). US Patent 4462923.
[145] Osman, M. A. (1982). *Mol. Cryst. Liq. Cryst.*, *82*, 323.
[146] Matsubara, H., Seto, K., Tahara, T., & Takahashi, S. (1989). *Bull. Chem. Soc. Jpn.*, *62*, 3896.
[147] Eidenschink, R., Krause, J., & Pohl, L. (1979). US Patent 4154697.
[148] Takehara, S., Osawa, M., Nakamura, K., Kusumoto, T., Sato, K.-I., Nakayama, A., & Hiyama, T. (1993). *Ferroelectrics*, *148*, 195.
[149] Neubert, M. E., Jirousek, M. R., & Hanion, C. A. (1986). *Mol. Cryst. Liq. Cryst.*, *133*, 223.
[150] Vill, V., Tunger, H.-W., & Borwitzky, A. (1996). *Ferroelectrics*, *180*, 227.
[151] Tuffin, R. P., Goodby, J. W., Hird, M., & Trombotto, S. (2006). PCT WO 2006/048620 A2.
[152] Sugimori, S., Kojima, T., & Tsuji, M. (1983). US Patent 4422951.
[153] Osman, M. A. (1985). *Mol. Cryst. Liq. Cryst.*, *128*, 45.
[154] Liang, J. C., & Cross, J. O. (1986). *Mol. Cryst. Liq. Cryst.*, *133*, 235.
[155] Sun, G., Chen, B., Tang, H., Shi, G., & Xu, S. (2004). *Liq. Cryst.*, *31*, 1151.
[156] Sethofer, N. L. (1982). US Patent 4325830.

[157] Ivaschenko, A. V., Torgova, S. I., Karamysheva, L. A., & Abolin, A. G. (1990). *Liq. Cryst.*, *7*, 475.
[158] 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.
[159] Toyne, K. J., Hird, M., Greenfield, S., & Poetsch, E. (1989). Eur. Pat. Appl. EP 354434.
[160] Vill, V., & Tunger, H.-W. (1995). *J. Chem. Soc., Chem. Commun.*, 1047.
[161] Paschke, R., Zaschke, H., Hauser, A., & Demus, D. (1989). *Liq. Cryst.*, *6*, 397.
[162] Shionozaki, Y. (1985). Japan Pat. Appl. JP 60078931.
[163] Carr, N., Gray, G. W., & Kelly, S. M. (1985). *Mol. Cryst. Liq. Cryst.*, *129*, 301.
[164] Hanna, J., Kogo, K., & Kafuku, K. (2001). US Patent 6224787 B1.
[165] Shionozaki, Y., Mukai, H., Obikawa, T., & Yamada, S. (1989). US Patent 4879060.
[166] Huynh-ba, T., & Osman, M. A. (1989). US Patent 4808333.
[167] Dabrowski, R., & Zytynski, E. (1982). *Mol. Cryst. Liq. Cryst.*, *87*, 109.