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

Liquid crystalline oxygen containing heterocyclic derivatives

V. S. Bezborodov[a]; V. F. Petrov[b]; V. I. Lapanik[a]
[a] R&D Center, Samsung Display Devices Co., Ltd., Korea [b] LCD Team 2, Special Division, Semiconductor Business, Samsung Electronics Co., Ltd., Suwon, Korea

To cite this Article Bezborodov, V. S. , Petrov, V. F. and Lapanik, V. I.(1996) 'Liquid crystalline oxygen containing heterocyclic derivatives', Liquid Crystals, 20: 6, 785 — 796
To link to this Article: DOI: 10.1080/02678299608033173
URL: http://dx.doi.org/10.1080/02678299608033173

LIQUID CRYSTALS, 1996, VOL. 20, NO. 6, 785–796

Liquid crystalline oxygen containing heterocyclic derivatives

by V. S. BEZBORODOV†, V. F. PETROV*‡ and V. I. LAPANIK†
†R & D Center, Samsung Display Devices Co., Ltd., 575, Shin-Dong, Paldal-Do,
445-970 Korea
‡LCD Team 2, Special Division, Semiconductor Business,
Samsung Electronics Co., Ltd., San 24 Nongseo-Lee, Kiheung-eup, Yongin-Gun,
Kyungki-Do, Suwon, P.O. Box 37, 449-900 Korea

(Received 2 January 1996; accepted 15 January 1996)

This paper presents a review of the work on the molecular design of oxygen containing heterocyclic liquid crystals for nematic liquid crystal display applications and examines in some detail the correlations between the molecular structure of liquid crystalline oxygen containing heterocyclic derivatives and their physico-chemical and electro-optical properties.

1. Introduction

There have been many attempts made to introduce an oxygen atom into the molecular rigid core for liquid crystalline derivatives which are suitable for use as components of nematic liquid crystalline materials (see, for example, refs. [1–44]). It has been shown that, among all oxygen containing liquid crystals synthesized, the heterocyclic derivatives incorporating the *trans*-1,3-dioxane or 1,3,2-dioxaborinane groups exhibit the most promising physico-chemical and electro-optical properties and can be used as components of nematic liquid crystalline materials (LCMs) [1–31].

This review is concerned with the effects of change in molecular structure on the physico-chemical and electro-optical properties of liquid crystals formed by the heterocyclic derivatives incorporating the *trans*-1,3-dioxane or 1,3,2-dioxaborinane groups and is aimed at providing a satisfactory selection of the best components of nematic liquid crystalline materials for display applications. For the most part, the review will be concerned with pure, single component liquid crystalline compounds, but the scope may, where necessary, be widened to include the binary mixtures of such liquid crystals and some examples of nematic LCMs including oxygen containing heterocyclic derivatives.

In nematic liquid crystal displays (LCDs) at least ten different liquid crystal material parameters have to be adjusted to achieve optimal display performance. Since a single liquid crystal shows at best one or two distinguished properties [1–44], mixtures consisting of up to twenty or more components have to be developed for a given display application. Liquid crystals which are suitable as the components of nematic liquid crystalline mixtures for display applications should satisfy the special requirements presented in [45].

The principles of the development of nematic liquid crystalline materials for display applications are briefly discussed in [46] and particularly helpful is the review [45]. Some practical examples of nematic LCMs including liquid crystalline heterocyclic derivatives incorporating the *trans*-1,3-dioxane or 1,3,2-dioxaborinane groups are presented in [15, 27–31].

2. Mesomorphic properties

When the structure, and consequently the geometry of a molecule is changed, many molecular parameters are affected and may influence to different degrees the physico-chemical properties of the liquid crystals [45–47].

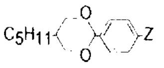
The effects of structural change on the mesomorphic properties of a compound are found to be difficult to rationalize [46, 48], therefore the purpose of this section is to define what relations can be established for liquid crystalline oxygen-containing heterocyclic derivatives, even though these may be empirical.

2.1. *Effect of the terminal group*

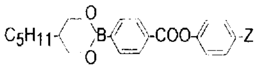
The phase transition temperatures for liquid crystalline heterocyclic derivatives incorporating the *trans*-1,3-dioxane or 1,3,2-dioxaborinane groups are presented in tables 1–5. It can be seen from these tables that for liquid crystals of the following general formulae the clearing points and the nematic ranges grow depending on the terminal substituents Z:

---

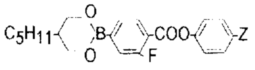
*Author for correspondence.



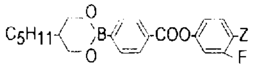
Z: $SCHF_2 < OCHF_2 < OCF_3 < CN < NCS$ (clearing points)



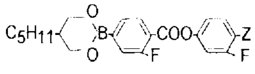
Z: $F < C_5H_{11} < CF_3 < OCF_3 < Cl < NCS < CN$ (clearing points)
Z: $CF_3 \approx OCF_3 < F < NCS < Cl < CN < C_5H_{11}$ (nematic ranges)



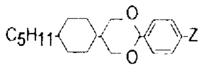
Z: $F < CF_3 < OCF_3 < NCS < CN$ (clearing points)
Z: $CF_3 < OCF_3 < F < NCS < CN$ (nematic ranges)



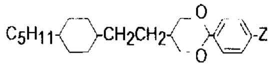
Z: $F < CN < NCS$ (clearing points)
Z: $F < NCS \approx CN$ (nematic ranges)



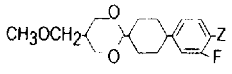
Z: $F < CN < NCS$ (clearing points)
Z: $F < NCS < CN$ (nematic ranges)



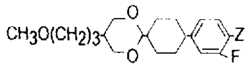
Z: $OCF_3 < F < CN < NCS$ (clearing points)
Z: $OCF_3 < NCS < F < CN$ (nematic ranges)



Z: $F < CN < NCS$ (clearing points)
Z: $F < NCS < CN$ (nematic ranges)

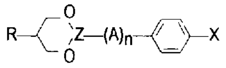


Z: $F < Cl < CN$ (clearing points)
Z: $F < Cl < CN$ (nematic ranges)



Z: $F < Cl < CN$ (clearing points)
Z: $F < Cl < CN$ (nematic ranges)

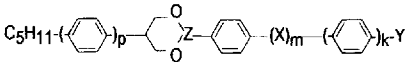
Table 1. Mesomorphic properties of liquid crystals of the general structure.



No.	*R*	*Z*	*X*	*A*	*n*	Mesomorphic behaviour/°C	Reference
1-1	C_5H_{11}	B	CN		0	Cr 48 I	[1]
1-2	C_5H_{11}	CH	CN		0	Cr 56 N (49) I	[2]
1-3	C_5H_{11}	B	C≡C−CN		0	Cr 59 N 75·5 I	[3]
1-4	C_5H_{11}	CH	C≡C−CN		0	Cr 60·3 N 111 I	[4]
1-5	C_5H_{11}	B	C_3H_7		0	Cr 46·2 I	[5]
1-6	C_5H_{11}	B	$COO{-}C_3H_7$		0	Cr 63 S (46) I	[6]
1-7	C_5H_{11}	CH	$C_2H_4{-}CN$		0	Cr 56·4 N (47·9) I	[7]
1-8	C_5H_{11}	CH	NCS		0	Cr 60 S_A 79 I	[8]
1-9	C_5H_{11}	CH	OCF_3		0	Cr 23·6 S_B 34·9 I	[9]
1-10	C_5H_{11}	CH	$OCHF_2$		0	Cr 23 S(4) N (8) I	[9]
1-11	C_5H_{11}	CH	$SCHF_2$		0	Cr 42·5 I	[9]
1-12	C_5H_{11}	CH	CN	C_2H_4	1	Cr 66 N (19) I	[10]
1-13	C_5H_{11}	CH	CN	CH=CH	1	Cr 64 N 102 I	[10]
1-14	C_5H_{11}	CH	OC_4H_9		0	Cr 42 N 52·9 I	[11]
1-15	C_5H_{11}	CH	$OC_2H_4CH{=}CH_2$		0	Cr 31 N 35·2 I	[11]
1-16	$CH_2{=}CHC_3H_6$	CH	OC_4H_9		0	Cr 29 N 30·2 I	[11]
1-17	$C_3H_7CH{-}CH$	CH	OC_4H_9		0	Cr 60 N 62 I	[11]

Parentheses denote a monotropic transition.

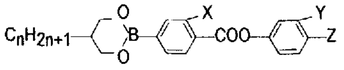
Table 2. Physico-chemical properties of liquid crystals of the general structure.



No.	*Z*	*Y*	*p*	*X*	*m*	*k*	Mesomorphic behaviour/°C	Δε	Reference
2-1	B	CN	1		0	0	Cr 103 N 132·7 I		[12]
2-2	CH	CN	1		0	0	Cr 110 N 165 I		[2]
2-3	CH	NCS	1		0	0	Cr 106 S_B (104·5) S_A 131 N 157 I		[13]
2-4	CH	C_5H_{11}	1		0	0	Cr 84·5 S_B 140 I		[2]
2-5	CH	C_5H_{11}	0		0	1	Cr 77 S_B 107 S_A 119·6 N 159 I		[14]
2-6	B	CN	0	COO	1	1	Cr 127 N 192 I	18·5[a]	[1, 15]
2-7	CH	CN	0	COO	1	1	Cr 138·3 N 231 I		[16]
2-8	B	Cl	0	COO	1	1	Cr 90 N 140 I		[6]
2-9	B	C_5H_{11}	0	COO	1	1	Cr 48 N 132 I		[6]
2-10	CH	C_5H_{11}	0	COO	1	1	Cr 68·7 S_A 98 N 165·6 I		[17]
2-11	CH	C_5H_{11}	0	OOC	1	1	Cr 104·5 N 154·6 I		[18]
2-12	CH	C_5H_{11}	0	COS	1	1	Cr 87·8 N 186·4 I		[19]
2-13	CH	CN	0	COS	1	1	Cr 111·1 N 202·1 I		[19]
2-14	B	F	0	COO	1	1	Cr_2 65·7 Cr_1 70·4 Cr 75·3 S_A 80·6 N 118 I		[20]
2-15	B	OCF_3	0	COO	1	1	Cr 68·9 S_A 138·1 I		[20]
2-16	B	CF_3	0	COO	1	1	Cr_2 71·5 Cr_1 75 Cr 89·5 S_A 135·2 I		[20]
2-17	B	NCS	0	COO	1	1	Cr 131·1 S 145·7 N 188 I		[20]

[a] $T_{meas} = T_{n\text{–}i} - 60$°C.

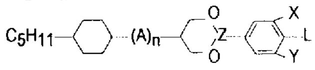
Table 3. Physico-chemical properties of liquid crystals of the general formula.



No.	*n*	*Z*	*X*	*Y*	Mesomorphic behaviour/°C	Δε	Δ*n*	Reference
3-1	3	CN	F	H	Cr 89 N 174 I	38[a]		[21]
3-2	3	CN	Cl	H	Cr 109 N 114 I	29[a]		[21]
3-3	3	CN	F	F	Cr 103 N 143·5 I	83[a]		[21]
3-4	5	CN	H	Cl	Cr 106 N 117 I			[21]
3-5	5	CN	H	F	Cr 82 N 109 I	46·3[b]		[21]
3-6	5	CN	F	H	Cr 94 N 167 I	34·6[b]	0·205[e]	[21, 22]
3-7	5	CN	Cl	H	Cr 93 N 109 I			[21]
3-8	5	CN	Cl	Cl	Cr 86 I			[21]
3-9	5	CN	Cl	F	Cr 59 N 74 I	28·1[c]		[21]
3-10	5	CN	F	Cl	Cr 105 I			[21]
3-11	5	CN	F	F	Cr 63 N 142 I	46[a]	0·171[d]	[21, 22]
3-12	5	F	F	H	Cr 55·5 Cr 61·6 N 80·3 I			[20]
3-13	5	F	H	F	Cr 69·2 S 85 N 99·2 I			[20]
3-14	5	F	F	F	Cr 50·1 S (44·5) N 70·5 I			[20]
3-15	3	CF_3	F	H	Cr_1 86 Cr 106·7 I	32·7[b]	0·125[e]	[20, 22]
3-16	5	CF_3	F	H	Cr 74·4 S_A 102·8 I	31·7[b]	0·115[e]	[20–22]
3-17	3	OCF_3	F	H	Cr 68·8 S_A 77·5 N 108·4 I	28·2[b]	0·115[e]	[20, 22]
3-18	5	OCF_3	F	H	Cr 48·4 S_A 111 N 113·9 I	24·3[b]	0·113[e]	[20–22]
3-19	5	NCS	F	H	Cr 104 N 163·5 I			[20, 21]
3-20	5	NCS	H	F	Cr_1 51 Cr 115·8 S_A 151·1 N 178 I			[20]
3-21	5	NCS	F	F	Cr 49·4 S_A 110·7 N 155·4 I			[20]

[a] $T_{meas} = T_{n\text{–}i} - 60$°C.
[b,e] Extrapolated from the 10 wt % solution in ZLI-1132 at 20°C and 25°C, respectively.
[c] $T_{meas} = T_{n\text{–}i} - 15$°C.
[d] $T_{meas} = 64$°C. Parentheses denote a monotropic transition.

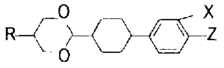
Table 4. Mesomorphic properties of liquid crystals of the general formula.



No.	*Z*	*L*	*X*	*Y*	*A*	*n*	Mesomorphic behaviour/°C	Reference
4-1	B	CN	H	H		0	Cr 92 N 170 I	[6]
4-2	CH	CN	H	H		0	Cr 87 N 222 I	[23]
4-3	CH	CN	H	H	C_2H_4	1	Cr 96·8 N 180·6 I	[23]
4-4	CH	CN	F	H		0	Cr 67·1 N 178·3 I	[23]
4-5	CH	CN	F	H	C_2H_4	1	Cr 85·2 N 145 I	[23]
4-6	CH	CN	F	F		0	Cr 65·4 N 126·2 I	[23]
4-7	CH	CN	F	F	C_2H_4	1	Cr 73 N 104 I	[23]
4-8	CH	NCS	H	H		0	Cr 120·5 E (119) S_A 156 N 227 I	[24]
4-9	CH	NCS	H	H	C_2H_4	1	Cr 70 S_A 120 N 183 I	[24]
4-10	CH	F	H	H		0	Cr 65 S (47·6) N 155·7 I	[23]
4-11	CH	F	H	H	C_2H_4	1	Cr 69·7 S (59·3) N 117·9 I	[23]
4-12	CH	F	F	H		0	Cr 77 N 113·8 I	[23]
4-13	CH	F	F	H	C_2H_4	1	Cr 86·5 N 93·5 I	[23]
4-14	CH	OCF_3	H	H		0	Cr 67 S_B 146 N 150·5 I	[25]

Parentheses denote a monotropic transition.

Table 5. Physico-chemical properties of liquid crystals of the general formula.



No.	*R*	*Z*	*X*	Mesomorphic behaviour/°C	Δε[a]	Reference
5-1	CH_3–CH=CH	F	H	Cr 111 N 160 I	6·8	[26]
5-2	CH_3–CH=CH	F	F	Cr 96 N 125 I	12·4	[26]
5-3	CH_3–CH=CH	Cl	H	Cr 101 N 183 I		[28]
5-4	CH_3–CH=CH	Cl	F	Cr 82 N 144 I	10	[29]
5-5	CH_3OCH_2	CN	H	Cr 115 N 209 I		[31]
5-6	$CH_3O(CH_2)_3$	CN	H	Cr 117 N 200 I		[31]
5-7	$CH_3O(CH_2)_3$	CN	F	Cr 103 N 162 I		[31]
5-8	CH_3OCH_2	Cl	H	Cr 89 N 138 I		[31]
5-9	$CH_3O(CH_2)_3$	Cl	H	Cr 80 S 83 N 142 I		[31]
5-10	$CH_3O(CH_2)_3$	Cl	F	Cr 82 N 106 I		[31]
5-11	CH_3OCH_2	F	H	Cr 95 N 121 I		[31]
5-12	CH_3OCH_2	F	F	Cr 81 N 87 I		[31]
5-13	$CH_3O(CH_2)_3$	F	H	Cr 107 N 123 I		[31]
5-14	$CH_3O(CH_2)_3$	F	F	Cr 71 S 77 N 95 I		[31]

[a] $T = T_{n\text{-}i} - 10°C$.

The presented orders of increasing the clearing temperatures and the nematic ranges reveal that the terminal group efficiency can be different for two-ring and three-ring liquid crystalline compounds and can be affected by introducing lateral substituents and the linking bonds.

The lower efficiency of halogen substituted endgroups can be explained in terms of the predominant influence of monomers of liquid crystals incorporating halogen substituted endgroups on their mesomorphic properties [49]. Similar orders of increasing the clearing temperatures and nematic ranges have been found for other liquid crystalline derivatives [49, 50].

The effect of the introduction of the –COO– bond into the terminal of two-ring 1,3,2-dioxaborinane derivatives is clearly shown in table 1 by comparing the mesomorphic properties of compounds **1-5** and **1-6**, where the latter compound shows the appearance of a monotropic smectic phase.

The data collected in tables 1 and 5 reveal that the introduction of a double bond and its position in the structure of the alkenyl chain strongly affect the mesomorphic behaviour of the *trans*-1,3-dioxane substituted derivatives. The same effects have been found for other liquid crystalline derivatives [26–29] and can be correlated with the rigid core order parameters [51].

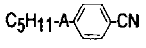
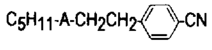
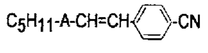
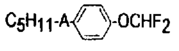
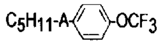
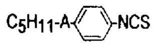
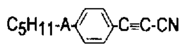
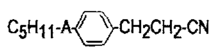
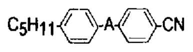
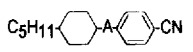
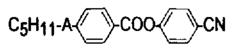
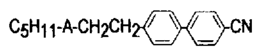
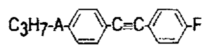
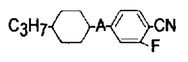
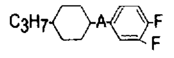
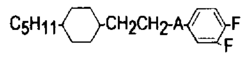
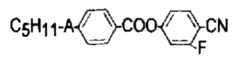
It has been shown that the introduction of chlorovinyl chains into the molecular structure of the *trans*-1,3-dioxane and other derivatives strongly increases their nematic thermostability [52, 53].

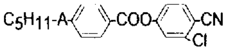
Interestingly, the halogen substituted *trans*-1,3-dioxane derivatives incorporating the terminal ether bond show a slight increase of their clearing points with increasing length of the ether bond (compounds **5-8** and **5-9**, **5-11** and **5-13**), while the corresponding cyano substituted derivatives show the opposite effect (compounds **5-5** and **5-6**, table 5).

2.2. *Effect of the rigid core structure*

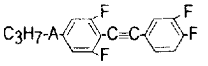
The influence of the rigid core structure on the mesomorphic stability for oxygen containing heterocyclic derivatives and other well-known liquid crystals can be expressed by the following orders of increasing clearing points and the nematic ranges (see tables 1–5 and [54–92]).

For liquid crystals of the following general formulae the clearing points and the nematic ranges, depending on the unit A, grow as follows:

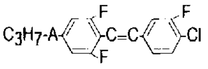
	A: BDox < Ph < Pyr < Dox < Prm < Ch < Bco	(clearing points)
	A: Ph < Prm < Dox < Ch < Bco	(clearing points)
	A: Ph ≈ Dox < Ch A: Dox < Ph < Ch	(clearing points) (nematic ranges)
	A: Ch < Dox < Prm < Pyr	(clearing points)
	A: Ch < Dox < Prm < Pyr	(clearing points)
	A: Ch < Ph < Dox < Prm < Pyr < Bco	(clearing points)
	A: BDox < Dox < Ph < Ch ≈ Prm A: BDox < Dox < Prm < Ph < Ch	(clearing points) (nematic ranges)
	A: Ph < Dox < Ch	(clearing points)
	A: BDox < Dox < Pyr < Ph < Prm A: BDox < Dox < Ph < Prm < Pyr	(clearing points) (nematic ranges)
	A: BDox < Dox ≈ Ph < Pyr < Prm < Ch A: BDox < Pyr < Ph < Prm < Dox < Ch	(clearing points) (nematic ranges)
	A: BDox < Ch < Dox < Prm A: BDox < Dox < Ch ≈ Prm	(clearing points) (nematic ranges)
	A: Ph < Prm < Dox < Ch	(clearing points)
	A: Dox < Ch < Ph A: Ph < Dox < Ch	(clearing points) (nematic ranges)
	A: Dox < Ph < Ch A: Ph < Dox < Ch	(clearing points) (nematic ranges)
	A: Ph < Dox < Pyr < Ch A: Dox < Ph < Pyr < Ch	(clearing points) (nematic ranges)
	A: Dox < Ph < Prm < Ch A: Dox < Ph < Prm < Ch	(clearing points) (nematic ranges)
	A: BDox < Ph < Ch A: BDox < Ch < Ph	(clearing points) (nematic ranges)



A: BDox < Dox < Ph < Ch (clearing points)
A: BDox < Dox < Ph < Ch (nematic ranges)

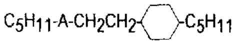


A: Ph < Ch < Pyr < Dox < Prm (clearing points)
A: Ph < Pyr < Prm < Dox < Ch (nematic ranges)

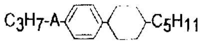


A: Ph < Ch < Pyr < Prm < Dox (clearing points)
A: Prm < Pyr < Ph < Dox < Ch (nematic ranges)

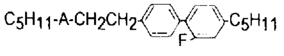
A: Ch < Dox < Prm < Pyr < Ch (clearing points)



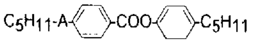
A: Prm < Ph < Dox < Ch (clearing points)



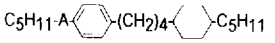
A: Dox < Ph < Pyr < Prm < Bco (clearing points)
A: Ph < Bco < Dox < Pyr ≈ Prm (nematic ranges)



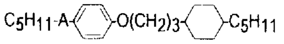
A: Ph < Prm < Dox < Ch (clearing points)



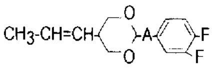
A: BDox < Dox < Ch < Ph < Bco (clearing points)
A: Ph < Ch < Bco < Dox < BDox (nematic ranges)



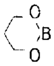
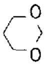
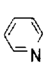
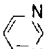
A: Ch < Dox < Prm (clearing points)
A: Ch < Dox < Prm (nematic ranges)



A: Ch ≈ Dox < Prm (clearing points)
A: Ch < Dox < Prm (nematic ranges)



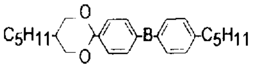
A: Ch < Ph < Pyr (clearing points)
A: Pyr < Ch < Ph (nematic ranges),

where BDox is  , Dox is  , Pyr is  , Prm is  , Ph is  , Ch is  , Bco is  .

The presented orders of increasing the clearing points and nematic ranges for liquid crystals of the given general formulae reveal that the efficiency of the above mentioned molecular fragments depends on their positions in the rigid core and can be affected by introducing either lateral substituents, terminal groups, additional fragments, or linking bonds.

As can be seen from tables 1 and 4, and [1–31], the effect of the introduction of different linking groups into the molecular structure of liquid crystals is most marked in the case of three-ring compounds: thus, the introduction of $-CH_2CH_2-$, $-C{\equiv}C-$ and $-CH{=}CH-$ linking groups into the rigid core or into the terminal position of liquid crystalline oxygen containing heterocyclic derivatives has distinctly opposite effects on the mesomorphic behaviour of these compounds. The $-CH_2CH_2-$ linking group increases molecular flexibility, which in turn leads to effectively broadening the molecule and reducing the effect of intermolecular attractive forces. It also decreases the melting and clearing points of the liquid crystalline oxygen-containing heterocyclic derivatives (compounds **1-2** and **1-12**, **1-2** and **1-7**, **4-2** and **4-3**, **4-4** and **4-5**, **4-6** and **4-7**, **4-8** and **4-9**, **4-10** and **4-11**, **4-12** and **4-13**). On the other hand, the $-C{\equiv}C-$ and $-CH{=}CH-$ linking groups increase the conjugation length of the π-electrons and, therefore, enchance molecular polarizability, which increases the nematic thermostability (compounds **1-1** and **1-3**, **1-2** and **1-4**, **1-2** and **1-13**). The same effects have been found for other liquid crystalline derivatives [4, 93].

The effects of the introduction of the –COO–, –OOC–, and –COS– linking bonds into the rigid core of *trans*-1,3-dioxane derivatives are shown in table 2 (compounds **2-10**–**2-12**). Thus for liquid crystals of the following general formula the clearing points and nematic ranges depend on the linking bond *B* as follows:



B: OOC < COO < COS (clearing points)
B: OOC < COO < COS (nematic ranges)

The data collected in tables 2–5 reveal that the lateral F and Cl substitutions have a considerable effect on the mesomorphic properties of the oxygen containing heterocyclic derivatives resulting in reduction of the smectic and nematic thermostabilities due to the lateral substituents broadening the molecule and reducing the intermolecular forces (compounds **2-6** and **3-4**–**3-11**; **2-14** and **3-12**–**3-14**; **2-15** and **3-17**, **3-18**; **2-16** and **3-15**, **3-16**; **2-17** and **3-19**–**3-21**; **4-2** and **4-4**, **4-6**; **4-3** and **4-5**, **4-7**; **4-10** and **4-12**; **4-11** and **4-13**; **5-1** and **5-2**; **5-3** and **5-4**; **5-6** and **5-7**; **5-9** and **5-10**; **5-11** and **5-12**; **5-13** and **5-14**). The same effects have been found for other liquid crystalline derivatives [46].

3. Static dielectric properties

The relationship between the dielectric anisotropy $\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$, where $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ are dielectric constants, that are parallel and perpendicular, respectively, to the nematic director **n**. This is described by the theory of Maier and Meier [94]:

$$\Delta\varepsilon = NhF/\varepsilon_0[\Delta\alpha - F\mu^2/kT(1 - 3\cos^2\beta)]S, \qquad (1)$$

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 (N–I) transition temperatures $T_{\text{n-i}}$ can only be made at a constant reduced temperature $\tau = T/T_{\text{n-i}}$ [95].

Tables 2, 3, 5 and 6 present some data on the dielectric properties of liquid crystalline compounds measured at a constant reduced temperature and extrapolated from the host liquid crystal mixture at 20°C. According to [95], the extrapolations are not meaningful; however, these estimations are only one way to obtain a rough definition of the dielectric (as well as the optical and elastic) properties of the non-mesomorphic components of liquid crystalline materials, smectic liquid crystals, and liquid crystals with a narrow nematic range.

Among all compounds considered in this work, 1,3,2-dioxaborinane derivatives exhibit the highest values of $\Delta\varepsilon$ due to the coincidence of the dipole moments of the boron atom and the terminal groups, leading to the increase of the overall molecular dipole moment along the director (see, for example, table 6; equation (1)). The introduction of the halogen atoms into the lateral positions of the oxygen containing heterocyclic liquid crystals has a considerable effect on their dielectric anisotropy (compounds **2-6** and **3-5**, **3-6**, **3-11**; **5-1** and **5-2**; tables 2, 3 and 5). This can be rationalized in terms of the contribution of the individual halogen dipole moments to the overall molecular dipole moment. It has been found that for definite chemical structures of liquid crystals, the dielectric anisotropy $\Delta\varepsilon$ decreases approximately in the same sequence as values of the dipole moments for terminal groups [69]: CN, NCS, $OCHF_2$, OCF_3, F diminish: 4·05, 3·59, 2·46, 2·36, 1·47 D, respectively.

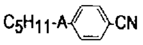
It has been shown that mesogenic molecules possessing strongly polar end groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [96–98], but the antiparallel association predominates and reduces the effective dipole moment [99]:

$$\mu_{\text{eff}}^2 = g\mu^2, \qquad (2)$$

$$\mu_{\text{eff}}^2 = \frac{9kT(\varepsilon_{\text{i}} - \varepsilon_{\text{i}}^{\infty})(2\varepsilon_{\text{i}} + \varepsilon_{\text{i}}^{\infty})}{4\pi N\varepsilon_{\text{i}}(\varepsilon_{\text{i}}^{\infty} + 2)^2}, \qquad (3)\ [99]$$

where $\varepsilon_{\text{i}}^{\infty} = 1{\cdot}05n_{\text{i}}^2$ and g is the correlation factor.

The results presented in table 6 reveal that the relationship between the correlation factor g and the molecular structures of the liquid crystalline derivatives which can be expressed by the following order of increasing g:



A: Pyr < Ph < Prm < Dox < Ch

4. Optical properties

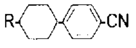
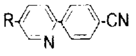
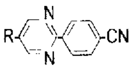
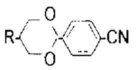
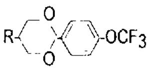
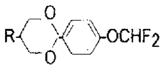
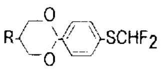
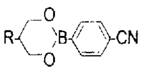
The phenomenological relation between the refractive index and the electric polarization is defined as [100, 101]:

$$(n^{*2} - 1)/(n^{*2} + 2) = N\alpha^*/3\varepsilon_0, \qquad (4)$$

where the mean polarizability $\alpha^* = (\alpha_{\parallel} + 2\alpha_{\perp})/3$, the mean refractive index $n^{*2} = (n_{\text{e}}^2 + 2n_{\text{o}}^2)/3$, n_{o} is the ordinary and n_{e} is the extraordinary refractive indices. From equation (4) and the previous section, it follows that aromatic compounds which have the large induced polarizability of their highly conjugated π-electron system exhibit optical anisotropy $\Delta n = n_{\text{e}} - n_{\text{o}}$ that is much larger than that of non-aromatic compounds (mixtures **1**, **2**, **4** and **3**, **5**, **6** table 7).

It has been found that the liquid crystals incorporating halogen substituted endgroups (halogenated LCs) exhibit the lower values of the optical anisotropy compared to that of the corresponding cyano derivatives (compounds **3-6** and **3-16**, **3-18**; **1-2** and **1-9**–**1-11**, tables 3 and 6; see also [49, 50]). This can be explained in terms of reducing the effective conjugation length of the π-electron system resulting in a shorter resonance wavelength of UV absorption spectrum for the halogenated liquid crystals than for the corresponding cyano derivatives [102].

Table 6. Physico-chemical properties of some liquid crystals.

No.	Formula, $R = C_5H_{11}$	μ/D	$\varepsilon_\perp$	$\Delta\varepsilon$	g^b	k_p at 40°C	Δn	$\nu/mm^2 s^{-1}$	Reference
6-1		4·63	5·59[a]	10·28[a]	0·590	0·6333	0·099[a]	21·5[c]	[22, 108–110]
6-2		4·8	6·63[a]	13·33[a]	0·530[d]	0·6523	0·178[a]	26·3[c]	[55, 108–111]
6-3		6·0	10·9[e]	17·8[e]	0·518	0·6538	0·214[f]	50[f]	[50]
6-4		6·0	8·0[f]	34·0[f]	0·580		0·224[f]	55[f]	[47, 111]
1-2		6·0	8·0[f]	17·4[f]	0·585[d]		0·141[f]	47[f]	[22, 47, 111]
1-9				10[f]		0·6854	0·040[f]		[9, 22]
1-10				14·6[f]		0·7168	0·044[f]	9[f]	[9, 22]
1-11				16·1[f]			0·050[f]		[9]
1-1				37·7[f]			0·114[f]		[22]

[a] $T_{meas} = T_{n-i} - 10°C$.
[b] $T_{meas} = T_{n-i}$.
[c] $T_{meas} = 22°C$.
[d] Extrapolated to $T_{meas} = T_{n-i}$ [111].
[e] $\tau = T_{meas}/T_{n-i}$, $K = 0·95$.
[f] Extrapolated from 10 wt % solution in ZLI-1132 at 20°C.

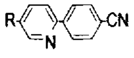
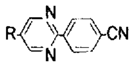
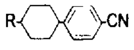
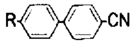
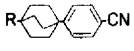
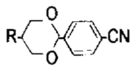
5. Viscoelastic properties

It has been shown that the nematic liquid crystalline materials for display applications should have a low viscosity for giving acceptable response times to LCDs [95, 103]. According to the theoretical predictions and the results on the kinematic viscosity ν, volume viscosity η and rotational viscosity γ_1 presented in tables 7 and 8, viscosity is minimized in molecular structures of liquid crystals of minimal polarity and polarizability, with short terminal groups and lacking lateral substituents, see also [45, 46, 49, 50].

It has been demonstrated that halogenated LCs exhibit lower values of viscosity compared to that of the corresponding cyano derivatives (compounds **1-2** and **1-10**, table 6; see also [49, 50]). This can be explained in terms of the predominant influence of the monomers of halogenated LCs on their viscous properties [49].

The elastic constant ratio K_3/K_1 of liquid crystalline materials is the crucial parameter for super twisted nematic liquid crystal displays (STN-LCDs) defining their electro-optical performance [104]. Table 7 presents some data on K_3/K_1 for binary mixtures of two-ring *trans*-1,3-dioxane cyano derivatives and other well-known cyano derivatives. It has been found that elastic constant ratio K_3/K_1 of two-ring liquid crystalline cyano derivatives is a linear function of the squared dimeric density wave period d_2^2 obtained from an X-ray diffraction study of their nematic phases [105]. This fact, the

Table 7. Physico-chemical and electro-optical properties[a] of binary mixtures ($C_5:C_7 = 40\%$ mol: 60% mol) of the liquid crystals [50].

No.	Formula	$T_{n-i}/°C$	$\gamma_1{}^b/P$	E^b/eV	$K_3/K_1{}^c$	$\varepsilon_\perp{}^c$	$\Delta\varepsilon^c$	$\Delta\varepsilon/\varepsilon_\perp{}^c$	Δn^c	U_{90}	U_{10}	τ^1_{on}	τ^2	τ_{off}
										/V			/ms	
1		44·1	1·84	0·54	1·25	10·7	16	1·5	0·175	1·08	1·54	75	20	105
2		51·0	1·90	0·565	1·06	8·7	19·6	2·86	0·174	1·07	1·48	70	20	90
3		56·4	1·00	0·410	1·68	5·4	9·2	1·71	0·100	1·67	2·32	133	33	46
4		39·0	1·10	0·546	1·37	6·0	11·7	1·95	0·184	1·30	1·78	85	21	69
5		106	3·60	0·458	1·93	5·4	8·6	1·59	0·114	2·10	3·20	190^d	70^d	140^d
6		49·8	$1·34^e$	5590^f	$1·43^e$	$8·9^e$	$13·3^e$	$1·5^e$	$0·089^{e,g}$	[112, 113]				

[a] d—cell gap = 10 μm, $U = 3$ V, $T_{meas} = 25°C$.
[b] $T_{meas} = 25°C$.
[c] $\tau = T_{meas}/T_{n-i}$, $K = 0·95$.
[d] $U = 4$ V.
[e] $T_{meas} = T_{n-i} - 10°C$.
[f] $\tau = 0·92$, $[E] = K$.
[g] $\lambda = 520$ nm.

results of the X-ray diffraction study [106] and dielectric investigations [99], and the data on the correlation factor g presented in table 6 reveal that for fifth and older homologues of two-ring cyano derivatives the balance in the monomer–dimer system $2M \Leftrightarrow D$ is biased towards dimers defining the liquid crystal properties [45, 105].

6. Molecular packing

It has been shown that liquid crystal molecular packing plays a very important role in the creation of their mesophases [107] and defines their optical properties [100]. Table 6 presents the values of the molecular packing coefficient k_p for the fifth homologues of the two-ring *trans*-1,3-dioxane and other well-known derivatives. The molecular packing coefficient is expressed as [108]

$$k_p = N_A V\rho/M, \tag{5}$$

where N_A is Avogadro's number, ρ is the density, M is the molecular weight, 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 atomic radii and chemical bond lengths. The observed difference in k_p for the compounds presented in table 6 can be associated with the difference in the energy of intermolecular interactions (and therefore with the difference in the activation energy of the rotational viscosity observed for these compounds in table 7 [108]).

7. Comparative characteristics of liquid crystals

Selection of the best components for liquid crystal materials and prediction of new chemical structures needs comprehensive comparative investigations of physico-chemical and electro-optical characteristics of liquid crystalline compounds. It has been shown that the dielectric, diamagnetic, viscous, and elastic constants as well as the nematic–isotropic transitions of solutions of homologues approximately obey the additive rule [109]. This fact is employed for the comparison of physico-chemical and electro-optical properties of liquid crystalline *trans*-1,3-dioxane derivatives and other liquid crystals having narrow nematic ranges by using binary

Table 8. Physico-chemical and electro-optical parameters of the liquid crystal mixtures.

Mixture	$T_{n\text{-}i}$/°C	$\Delta\varepsilon$	$\Delta\varepsilon/\varepsilon_\perp$	Δn	η/mPas	U_{10}	U_{90}	τ_{off}	τ^1_{on}	τ^2_{on}
		at $T = 20$°C				/V		/ms		
A 1	65·8	12·0	1·56	0·163		1·45	1·95	60	90	25
A 2	64·7	9·3	1·37	0·109		1·65	2·15	70	100	30
A 3	40·8	13·2	1·60	0·102		1·20	1·65	80	110	25
B 1	68·4	13·6	1·70	0·179		1·40	1·85	60	120	30
B 2	67·7	13·2	1·73	0·164		1·45	2·00	60	100	25
B 3	62·3	17·8	1·91	0·157		1·23	1·65	70	130	35
C	42·0	8·1	1·98	0·1680	12·9	1·69^a	2·38^a			
90 wt % **C** + 10 wt % **3-21**	49·0	9·0	2·19	0·1782	15·2	1·36^a	1·98^a			
90 wt % **C** + 10 wt % **3-11**	47·0	9·4	2·04	0·1685	16·1	1·15^a	1·70^a			

The mixtures **A 1**, **A 2**, **A 3** were composed of 26 wt % of the 4-ethoxyphenyl ester of *trans*-4-butylcyclohexanecarboxylic acid, 16 wt % of the 4-ethoxyphenyl ester of *trans*-4-hexylcyclohexanecarboxylic acid, 10 wt % of the 5-propyl-2-[4-(4-pentylcyclohexyl)-phenyl]pyridine, 19 wt % of the third and 29 wt % of the fifth homologues belonging to 5-alkyl-2-(4-cyanophenyl)pyridines, *trans*-2-(4-cyanophenyl)-5-alkyl-1,3-dioxanes, 2-(4-cyanophenyl)-5-alkyl-1,3,2-dioxaborinanes, respectively [22]. Measuring conditions of electro-optical parameters: $d = 10\,\mu$m, $T = 25$°C, $U_{meas} = 2\,U_{10}$ [22, 114].

The mixtures **B 1**, **B 2**, **B 3** were composed of 26 wt % of the 4-ethoxyphenyl ester of *trans*-4-butylcyclohexanecarboxylic acid, 16 wt % of the 4-ethoxyphenyl ester of *trans*-4-hexylcyclohexanecarboxylic acid, 19 wt % of the 5-propyl-2-(4-cyanophenyl)pyridine, 29 wt % of the 5-pentyl-2-(4-cyanophenyl)pyridine, and 10 wt % of 5-(4-pentylcyclohexyl)-2-(4-cyanophenyl)pyridine, 4-cyano-4′-(4-pentylcyclohexyl)biphenyl, compound **3-3**, respectively [22]. Measuring conditions of electro-optical parameters: $d = 10\,\mu$m, $T = 25$°C, $U_{meas} = 2\,U_{10}$ [22].

Mixture **C**: 4-(*trans*-4-propylcylohexyl)benzenoisothiocyanate—42 wt %, 4-(*trans*-4-hexylcyclohexyl)benzenoisothiocyanate—40 wt % and 4-(*trans*-octylcyclohexyl)benzenoisothiocyanate—18 wt % [20].

[a] $T = 20$°C.

mixtures (containing a pentyl and a heptyl homologue) which give a broad nematic range. Table 7 shows that, by choosing a particular structure of liquid crystalline cyano derivatives, the physico-chemical properties can be varied over a wide range and a desired set of electro-optical parameters can be obtained.

In order to include into the comparison liquid crystalline 1,3,2-dioxaborinane derivatives, some liquid crystalline mixtures containing these compounds and other well-known liquid crystals were prepared. Table 8 presents some results on physico-chemical and electro-optical properties of prepared liquid crystal mixtures.

From the table, it follows that using liquid crystalline 1,3,2-dioxaborinane derivatives as the components of liquid crystalline materials gives the lowest values of the threshold voltage U_{10} and saturation voltage U_{90} of the twist-effect compared to that of other liquid crystalline derivatives. These results can be used for the development of liquid crystalline materials for low power consumption LCDs [15].

8. Conclusions

From the design of specific molecular structures and from investigations into the physico-chemical and electro-optical properties we have demonstrated a wide range of material parameters in liquid crystalline oxygen containing heterocyclic derivatives, which are of real use for nematic liquid crystal display applications.

References

[1] Bezborodov, V. S., 1989, *Zh. org. Khim.*, **25**, 2168.

[2] Vorbrodt, H.-M., Deresch, S., Kresse, H., Wiegeleben, A, Demus, D., and Zaschke, H., 1981, *J. prakt. Chem.*, **323**, 902.

[3] Seto, K., Takahashi, S., and Tahara, T., 1985, *Mol. Cryst. liq. Cryst. Lett.*, **2**, 197.

[4] Petrzilka, M., 1984, *Mol. Cryst. liq. Cryst.*, **111**, 329.

[5] Wachtler, A., Krause, J., Eidenschink, R., Eichler, J., and Scheuble, B., 1986, German Pat. Appl. 3608714.

[6] Takahashi, S., Seto, K., and Matsubara, H., 1990, *Senryo To Yakuhin*, **35**, 88.

[7] Petrzilka, M., 1983, German Pat. Appl. 3246440.

[8] Dabrowski, R., Dziaduszek, J., and Szczucinski, T., 1985, *Mol. Cryst. liq. Cryst.*, **124**, 241.

[9] Pavluchenko, A. I., Smirnova, N. I., Petrov, V. F., Fialkov, Y. A., Shelyazhenko, S. V., and Yagupolsky, L. M., 1991, *Mol. Cryst. liq. Cryst.*, **209**, 225.

[10] Andrews, B. M., Gray, G. W., and Bradshaw, M. J., 1985, *Mol. Cryst. liq. Cryst.*, **123**, 257.

[11] Schadt, M., Buchecker, R., Leenhouts, F., Boller, A., Villiger, A., and Petrzilka, M., 1986, *Mol. Cryst. liq. Cryst.*, **139**, 1.

[12] Matsubara, H., Seto, K., Tahara, T., and Takahashi, S., 1989, *Bull. chem. Soc. Jpn.*, **62**, 3896.

[13] Dabrowski, R., Dziaduszek, J., Witkewicz, Z.,

ADAMSKA, G., and STOLARZ, Z., 1988, Pol. Patent 143675.

[14] SZULC, J., CZUPRYNSKI, K., DABROWSKI, R., and PRZEDMOJSKI, J., 1993, *Liq. Cryst.*, **14,** 1377.

[15] BEZBORODOV, V. S., GRINKEVICH, O. A., GREBENKIN, M. F., LAPANIK, V. I., MINKO, A. A., RZHUSSKY, V. V., MURAVSKY, A. A., PETROV, V. F., and IVASCHENKO, A. V., 1989, U.S. Patent 4 853 150.

[16] HSU, Y. Y., 1982, U.S. Patent 4 313 878.

[17] HSU, Y. Y., 1983, *Proc. SPIE*, **386,** 72.

[18] HSU, Y. Y., 1980, U.S. Patent 4 200 580.

[19] HSU, Y. Y., 1984, U.S. Patent 4 424 372.

[20] DABROWSKI, R., BEZBORODOV, V. S., LAPANIK, V. J., DZIADUSZEK, J., and CZUPRYNSKI, K., 1995, *Liq. Cryst.*, **18,** 213.

[21] BEZBORODOV, V. S., and LAPANIK, V. I., 1991, *Liq. Cryst.*, **10,** 803.

[22] PETROV, V. F., 1990, PhD Thesis, Organic Intermediates & Dyes Institute, Moscow.

[23] OBIKAWA, T., IKUKAWA, S., and NAKAYAMA, J., 1990, European Patent Application EP 400 861.

[24] DABROWSKI, R., DZIADUSZEK, J., SZCZUCINSKI, T., STOLARZOWA, Z., and CZUPRYNSKI, K., 1989, *Liq. Cryst.*, **5,** 209.

[25] KURMEIER, H. A., SCHEUBLE, B., POETSCH, E., and FINKENZELLER, U., 1987, German Patent Application DE 3732284.

[26] SCHADT, M., BUCHECKER, R., and VILLIGER, A., 1990, *Liq. Cryst.*, **7,** 519.

[27] BOLLER, A., BUCHECKER, R., SCHADT, M., and VILLIGER, A., 1988, European Patent Application EP 315 014.

[28] SCHADT, M., and VILLIGER, A., 1990, European Patent Application EP 433 836.

[29] SCHADT, M., 1993, *Liq. Cryst.*, **14,** 73.

[30] DABROWSKI, R., BEZBORODOV, V., LAPANIK, V., DZIADUSZEK, J., ZMIJA, J., RASZEWSKI, Z., and PARKA, J., 1992, *Proc. SPIE*, **1845,** 266.

[31] TANAKA, Y., TAKATSU, H., TAKEUCHI, K., SCHADT, M., and BUCHECKER, R., 1992, U.S. Patent 5 171 472.

[32] DIMITROVA, K., HAUSCHILD, J., ZASCHKE, H., and SCHUBERT, H., 1980, *J. prakt. Chem.*, **322,** 933.

[33] EIDENSCHINK, R., and WEBER, G., 1983, German Patent Application DE 3322982.

[34] HARAMOTO, Y., SANO, M., and KAMOGAWA, H., 1986, *Bull. chem. Soc. Jpn.*, **59,** 1337.

[35] PASCHKE, R., ZASCHKE, H., HAUSER, A., and DEMUS, D., 1989, *Liq. Cryst.*, **6,** 397.

[36] KOHNE, B., PRAEFCKE, K., OMAR, R. S., and FROLOW, Z., 1986, *Z. Naturforsch. (b)*, **41,** 736.

[37] BARTULIN, J., MARTINEZ, R., MULLER, H. J., FAN, Z. X., and HAASE, W., 1992, *Mol. Cryst. liq. Cryst.*, **220,** 67.

[38] KARAMYSHEVA, L. A., KOVSHEV, E. I., PAVLUCHENKO, A. I., ROITMAN, K. V., TITOV, V. V., TORGOVA, S. I., and GREBYONKIN, M. F., 1981, *Mol. Cryst. liq. Cryst.*, **67,** 241.

[39] PAVLUCHENKO, A. I., SMIRNOVA, N. I., TITOV, V. V., KOVSHEV, E. I., and DJUMAEV, K. M., 1976, *Mol. Cryst. liq. Cryst.*, **37,** 35.

[40] TSCHIERSKE, C., and ZASCHKE, H., 1988, *J. prakt. Chem.*, **330,** 1.

[41] KARAMYSHEVA, L. A., GEIVANDOVA, T. A., ROITMAN, K. V., LJUKMANOV, N. F., and KOVSHEV, E. I., 1983, *Mol. Cryst. liq. Cryst.*, **99,** 169.

[42] SAKASHITA, K., KAGEYAMA, Y., and IKEMOTO, I., 1992, European Patent Application EP 467 721.

[43] VILL, V., BACHMANN, F., THIEM, J., PELYVAS, I. F., and PUDLO, P., 1992, *Mol. Cryst. liq. Cryst.*, **213,** 57.

[44] KARAMYSHEVA, L. A., TORGOVA, S. I., AGAFONOVA, I. F., and SHTIKOV, N. M., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 217.

[45] PETROV, V. F., 1995, *Proc. SPIE*, **2408,** 84.

[46] COATES, D., 1990, *Liquid Crystals: Applications and Uses*, Vol. 1, edited by B. Bahadur (Singapore: World Scientific Publishing Co., Pte., Ltd.), p. 91.

[47] POHL, L., and FINKENZELLER, U., *ibid.*, p. 139.

[48] DE JEU, W. H., 1992, *Phase Transitions in Liquid Crystals*, edited by S. Martelluci and A. N. Chester (New York: Plenum Press), Chap. 1 and 2.

[49] PETROV, V. F., 1995, *Liq. Cryst.*, **19,** 729.

[50] PAVLUCHENKO, A. I., PETROV, V. F., and SMIRNOVA, N. I., 1995, *Liq. Cryst.*, **19,** 811.

[51] RICHTER, W., FUNG, B. M., and SCHADT, M., 1990, *Liq. Cryst.*, **8,** 63.

[52] SEILS, F., and SCHADT, M., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 127.

[53] SEILS, F., and SCHADT, M., 1992, 21 Freiburger Arbeitstagung Flussigkristalle (Freiburg: University of Freiberg), Vortrag 6.

[54] BUCHECKER, R., MARCK, G., and SCHADT, M., 1995, *Mol. Cryst. liq. Cryst.*, **260,** 93.

[55] GRAY, G. W., 1986, *Wissenschaftl. Beitrage-Univ., Halle*, **52,** 22.

[56] GOTO, Y., NIGORIKAWA, K., and ISOYAMA, T., 1987, European Patent Application EP 240 320.

[57] BARTMANN, E., DORSCH, D., FINKENZELLER, U., KURMEIER, H.-A., and POETSCH, E., 1990, Freiburger Arbeitstagung Flussigkristalle, P8.

[58] GOTO, Y., OGAWA, T., SAWADA, S., and SUGIMORI, S., 1991, *Mol. Cryst. liq. Cryst.*, **209,** 1.

[59] SETHOFER, N. L., 1982, U.S. Patent 4 325 830.

[60] PAVLUCHENKO, A. I., PURVANYATSKAS, G., 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., and TITOV, V. V., 1989, European Patent Application EP 310 676.

[61] TOYNE, K. J., HIRD, M., GREENFIELD, S., and POETSCH, E., 1989, European Patent Application EP 354 434.

[62] TORGOVA, S. I., ABOLIN, A. G., KARAMYSHEVA, L. A., and IVASHENKO, A. V., 1988, *Zh. org. Khim.*, **24,** 192.

[63] CARR, N, GRAY, G. W., and KELLY, S. M., 1985, *Mol. Cryst. liq. Cryst.*, **129,** 301.

[64] SUGIMORI, S., KOJIMA, T., GOTO, Y., ISOYAMA, T., and NIGORIKAWA, K., 1984, European Patent Application EP 119 756.

[65] REIFFENRATH, V., and POETSCH., E., 1989, German Patent Application DE 39393116.

[66] GRAY, G. W., HARRISON, K. J., and NASH, J. A., 1975, *Pramana*, Suppl. 1, 381.

[67] BOLLER, A., CEREGHETTI, M., and SCHERRER, H., 1977, *Z. Naturforsch. (b)*, **33,** 433.

[68] EIDENSCHINK, R., 1983, *Mol. Cryst. liq. Cryst.*, **94,** 119.

[69] PAVLUCHENKO, A. I., SMIRNOVA, N. I., PETROV, V. F., GREBYONKIN, M. F., and TITOV, V. V., 1991, *Mol. Cryst. liq. Cryst.*, **209,** 155.

[70] Kojima, T., Tsuji, M., and Sugimori, S., 1982, German Patent Application DE 3223637.

[71] Villiger, A., Boller, A., and Schadt, M., 1979, *Z. Naturforsch. (b)*, **34**, 1535.

[72] Takatsu, H., Sasaki, M., Tanaka, Y., and Sato, H., 1985, U.S. Patent 4 726 910.

[73] Klug, R., Pauluth, D., Reiffenrath, V., and Bartmann, E., 1992, German Patent Application DE 4105743.

[74] Dabrowski, R., Dziaduszek, J., Szczucinski, T., and Raszewski, Z., 1984, *Mol. Cryst. liq. Cryst.*, **107**, 411.

[75] Kresse, H., Ponike, E., Demus, D., Zaschke, H., Scherf, K.-D., Schafer, W., and Herzberg, E., 1988, DDR-WP 275 701 (East German Patent).

[76] Goto, Y., and Ushioda, M., 1992, U.S. Patent 5 167 858.

[77] Gray, G. W., Toyne, K. J., Lacey, D., Poetsch, E., and Weber, G., 1988, European Patent Application EP 256 636.

[78] Schadt, M., and Villiger, A., 1990, European Patent Application EP 433 835.

[79] Kuhnert-Brandstatter, M., and Seidel, D., 1982, *Microchim. Acta*, **1**, 243.

[80] Carr, N., Gray, G. W., and Kelly, S. M., 1985, *Mol. Cryst. liq. Cryst. Lett.*, **1**, 53.

[81] Kelly, S. M., and Schadt., M., 1984, *Helv. Chim. Acta*, **67**, 1580.

[82] Sasaki, M., Takatsu, H., and Sato, H., 1983, German Patent Application DE 3339216.

[83] Adomenas, P., Adomeniene, O., and Gureviciene, J.-J., 1985, 6th Liquid Crystal Conference of Socialist Countries, Halle, DDR (Martin-Luther-Universität) Abstracts, A8.

[84] Bezborodov, V. S., Lapanik, V. I., Adomenas, P. V., and Sirutkaitis, R., 1992, *Liq. Cryst.*, **11**, 373.

[85] Hsu, Y. Y., 1984, U.S. Patent 4 424 371.

[86] Kelly, S. M., and Leenhouts, F., 1990, European Patent Application EP 410 233.

[87] Kelly, S. M., 1991, *Mol. Cryst. liq. Cryst.*, **204**, 27.

[88] Kelly, S. M., 1989, European Patent Application EP 344 557.

[89] van der Veen, J., 1976, *J. Phys. (Paris)*, Suppl. C3, **37**, 13.

[90] Dabrowski, R., Dziaduszek, J., Drzewinski, W., Czuprynski, K., and Stolarz, Z., 1990, *Mol. Cryst. liq. Cryst.*, **191**, 171.

[91] Dabrowski, R., and Zytynski, E., 1982, *Mol. Cryst. liq. Cryst.*, **87**, 109.

[92] Cox, R. J., and Cleak, N. J., 1976, *Mol. Cryst. liq. Cryst.*, **37**, 263.

[93] Petrzilka, M., 1984, *Mol. Cryst. liq. Cryst.*, **111**, 347.

[94] Maier, W., and Meier, G., 1961, *Z. Naturforsch. (a)*, **16**, 262.

[95] Schadt., M., 1992, *Displays*, **13**, 11.

[96] de Jeu, W. H., 1983, *Phil. Trans. R. Soc. A*, **309**, 217.

[97] Toriyama, K., and Dunmur, D. A., 1985, *Mol. Phys.*, **56**, 479.

[98] Dunmur, D. A., and Palffy-Muhoray, P., 1992, *Mol. Phys.*, **76**, 1015.

[99] Schad., Hp., and Osman, M. A., 1981, *J. chem. Phys.*, **75**, 880.

[100] de Jeu, W. H., 1980, *Physical Properties of Liquid Crystalline Materials* (New York: Gordon & Breach).

[101] de Jeu, W. H., Gerristma, C. J., van Zanten, P., and Goosens, W. A., 1972, *Phys. Lett. A*, **39**, 355.

[102] Khoo, I.-C., and Wu, S.-T., 1993, *Optics and Nonlinear Optics of Liquid Crystals* (Singapore: World Scientific Publishing Co., Pte., Ltd.), Chap. 1·7.

[103] Jakeman, E., and Raynes, E. P., 1972, *Phys. Lett. A*, **39**, 69.

[104] Guy, S. C., 1993, *Displays*, 32.

[105] Grebyonkin, M. F., Petrov, V. F., and Ostrovsky, B. I., 1990, *Liq. Cryst.*, **7**, 367.

[106] Petrov, V. F., Ivanov, S. A., Grebyonkin, M. F., and Pavluchenko, A. I., 1990, *Russ. J. phys. Chem.*, **64**, 421.

[107] Osman, M. A., 1983, *Z. Naturforsch.*, **38A**, 693.

[108] Belyaev, V. V., Grebyonkin, M. F., and Petrov, V. F., 1990, *Russ. J. phys. Chem.*, **64**, 509.

[109] Osman, M. A., and Schad, Hp., 1983, *J. chem. Phys.*, **78**, 906.

[110] Schadt, M., Petrzilka, M., Gerber, P. R., and Villiger, A., 1985, *Mol. Cryst. liq. Cryst.*, **122**, 241.

[111] McDonnell, D. G., Raynes, E. P., and Smith, R. A., 1989, *Liq. Cryst.*, **6**, 515.

[112] Schadt, M., and Gerber, P. R., 1982, *Z. Naturforsch.*, **37A**, 165.

[113] Gerber, P. R., and Schadt, M., 1982, *Z. Naturforsch.*, **37A**, 179.

[114] Grebyonkin, M. F., Petrov, V. F., Belyaev, V. V., Pavluchenko, A. I., Smirnova, N. I., Kovshev, E. I., Titov, V. V., and Ivaschenko, A. V., 1985, *Mol. Cryst. liq. Cryst.*, **129**, 245.