Molecular Crystals and Liquid Crystals

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

Ketonization in Calamitic Liquid Crystals

Vladimir F. Petrov [a]

[a] LC Works, Camberwell, Vic., Australia

Version of record first published: 31 Aug 2006

To cite this article: Vladimir F. Petrov (2005): Ketonization in Calamitic Liquid Crystals, Molecular Crystals and Liquid Crystals, 432:1, 29-45

To link to this article: http://dx.doi.org/10.1080/154214090892762

Mol. Cryst. Liq. Cryst., Vol. 432, pp. 29–45, 2005

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/154214090892762

Taylor & Francis
Taylor & Francis Group

Ketonization in Calamitic Liquid Crystals

Vladimir F. Petrov
LC Works, Camberwell, Vic., Australia

The effect of introducing the keto groups into their molecular structure on the physicochemical properties of calamitic liquid crystals is discussed and rationalized in terms of existent theories.

Keywords: keto groups; liquid crystals; physicochemical properties

INTRODUCTION

Ketones are one of the most important and widespread functional groups found in nature [1]. This article considers the characteristic substituent effects that underline the physicochemical properties of calamitic liquid crystals (LCs) containing terminal, linking, and lateral keto-substituted groups. Many of these effects can be correlated with the geometric and electronic structure of the keto groups and their positions in the molecule. In ketones the bonds between the carbon and the oxygen atoms of the keto group are of σ and π types and have the lengths of 1.20 Å [2]. The oxygen has two lone-pair electrons; one lone-pair orbital is mainly of type 2s, and the other lone-pair orbital is of type 2p and its axis is perpendicular to the direction of the π orbitals [2]. The carbonyl groups are well known by their tendency to form the hydrogen bonds [1,3–6]. One can observe the mesomeric effect caused by the conjugation of the carbonyl group with another double bond or with a lone pair of electrons in ketones [2]. Keto-enol tautomerism is also well known in these compounds, which shows the dominance of the enol forms [1,4–11]. As expected, these features of the keto groups introduced into the molecular structure of calamitic liquid crystals can affect their physicochemical properties.

Address correspondence to Vladimir F. Petrov, LC Works, 6/68 Brinsley Road, Camberwell, Vic. 3124, Australia. E-mail: lcworks@hotmail.com

MESOMORPHIC PROPERTIES

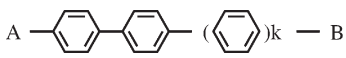
The phase-transition temperatures of some ketones and reference compounds are presented in Tables I–VI where Cr, Sm, SmE, SmC, SmC*, SmCα*, SmCγ*, SmC$_A^*$, SmB, SmA, N, and I denote the crystalline, smectic, smectic E, C, C*, Cα*, Cγ*, C$_A^*$, B, A, nematic, and isotropic phases, respectively. X is an unknown mesophase.

Terminal Keto Substitution

It has been demonstrated that the preferred conformation of the acetyl group of acetophenone is in the plane of the phenyl ring [12]. Such a planar structure has been confirmed by X-ray crystal studies [13]. Acetophenone has a barrier to rotation about the phenyl–carbonyl bond equal to 5.4 kcal/mol, which is higher than that of the corresponding methyl benzoate (4.92 kcal/mol [14]). Methyl benzoate in the liquid state contains, in addition to the main conformer with a planar structure and trans form of the ester group, a small amount of the conformer of a different geometric structure [15]. In the corresponding toluene, the orthogonal form is more stable (13.94 kcal/mol) than the planar one [16].

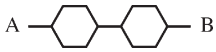
According to Chow and Li [17], electrostatic force is most important factor for ketones in which the high polarity of keto group can apply a strong field effect onto nearby atoms. For the corresponding nonpolar alkyl derivatives, orbital interactions can be transmitted either

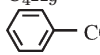
TABLE I Mesomorphic Properties of Liquid Crystals:



No.	A	B	K	Phase transitions, °C	Reference
1-1	C_5H_{11}	COC_5H_{11}	0	Cr 106 SmA 109.5 I	18
1-2	C_5H_{11}	C_5H_{11}	0	Cr 26 Sm 47.6 Sm 52.2 I	19
1-3	C_5H_{11}	OC_6H_{13}	0	Cr 82 Sm 84 I	20
1-4	$C_5H_{11}CO$	COC_5H_{11}	0	Cr 165 I	21
1-5	$C_5H_{11}CO$	OC_6H_{13}	0	Cr 120.5 SmA 145.3 I	22
1-6	$C_5H_{11}CO$	$OOCC_5H_{11}$	0	Cr 87.5 SmE 91 SmB 111.5 SmA 140 I	23
1-7	C_5H_{11}	$OOCC_5H_{11}$	0	Cr 47.5 Sm 87.4 I	20
1-8	C_7H_{15}	$COCH_3$	1	Cr 233.5 Sm 258 I	24
1-9	$C_7H_{15}CO$	$COCH_3$	1	Cr 230 SmC 238.5 N 250.5 I	25
1-10	$C_5H_{11}CO$	COC_5H_{11}	1	Cr 236 Sm 267 I	26
1-11	C_5H_{11}	C_5H_{11}	1	Cr 192 Sm 213 I	26
1-12	$C_5H_{11}OOC$	$COOC_5H_{11}$	1	Cr 141 SmA 203 I	26

TABLE II Physicochemical Properties of Some Liquid Crystals:



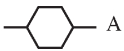
No.	A	B	Phase transitions,°C	$\Delta\varepsilon$	Δn	ν, mm^2s^{-1}	Reference
2-1	C_5H_{11}	COC_3H_7	Cr 52 Sm 97.3 I				3
2-2	C_5H_{11}	C_3H_7	Cr 23 SmB 96 I				27
2-3	C_5H_{11}	OC_4H_9	Cr 30 SmB 92 I				28
2-4	C_5H_{11}	$COOC_3H_7$	Cr 34.9 Sm 78.6 I				29
2-5	C_5H_{11}	$COCH_2COC_2H_5$	Cr 52 X 94 I		0.065[a]	23[a]	30
2-6	C_3H_7	COC_4H_9	Cr 55 Sm 96.2 I				3
2-7	C_3H_7	$CH_2COC_3H_7$	Cr 56 SmB 92 I				27
2-8	C_3H_7	$C_2H_4COC_2H_5$	Cr 65 SmB 84 I				27
2-9	C_3H_7	C_4H_9	Cr -6 SmB 94 I				31
2-10	C_3H_7		Cr 108 N 197.5 I	17[b]	0.140[b]	33[c]	32
2-11	C_3H_7		Cr 54.1 Sm 96.6 N 155.2 I	4[d]	0.097[d]	16[d]	33,34

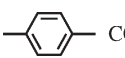
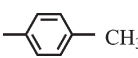
[a,d]Extrapolated from 10 wt% solution at 20 °C in ZLI-3086 and ZLI-4792, respectively.
[b]Extrapolated from 15 wt% solution in the liquid-crystal material at 25 °C
[c]Extrapolated from 15 wt% solution in the liquid-crystal material at 20 °C, η, volume viscosity, mPas.

through space or through bond more effectively than electrostatic force.

It is believed that the structural and electronic features of these groups may influence the mesomorphic properties of the liquid crystals containing them.

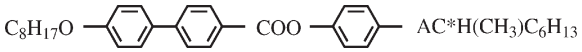
As is evident from Tables I–IV, the terminal ketonization of liquid crystals increases (compounds **1-1–1-3**, **1-5**, **1-6 1-7**, **2-1–2-4**, **2-6**, **2-9–2-11**, **3-1–3-10**, **4-1–4-3**) and decreases (compounds **2-7–2-9**) the clearing points (nematic–isotropic or smectic–isotropic phase-transition temperatures) in comparison that those of the corresponding fluoro, trifluoromethyl, alkyl derivatives, esters and alkoxy derivatives that have the same number of carbon atoms in their alkoxy chains (excluding compound **4-3** in which the C=O bond is replaced by the oxygen). The increased clearing temperatures of ketones have been explained in terms of their increased polarizability, which is caused by the conjugation between the keto and phenyl groups, and the formation of the hydrogen bonds between the keto group and the hydrogen atom in the ortho position [3]. These bonds keep the keto group in plane and enhance molecular rigidity [3]. Some of these results do not support the theory of Maier and Saupe that increasing the

TABLE III Physico-chemical Properties of Some Liquid Crystals: C_5H_{11}  A — ()k — B

No.	A	k	B	Phase transitions, °C	$\varepsilon_\perp$	$\Delta\varepsilon$	$\lvert\Delta\varepsilon/\varepsilon_\perp\rvert$	Δn	ν, mm^2s^{-1}	K_{11}, pN	K_{33}/K_{11}	Reference
3-1	—	1	COC_2H_5	Cr 56.6 N 69 I	6.90[a]	1.40[a]	0.20[a]	0.086[a]		8.30[a]	1.01[a]	35
3-2	—	1	OCH_3	Cr 41 N (31) I		–0.50[b]		0.090[b]				36
3-3	—	1	C_2H_5	Cr 5.5 I								37
3-4	COO	1	COC_2H_5	Cr 84.9 SmA (74.5) N 105.8 I	6.70[c]	0.90[c]	0.12[c]			7.20[c]	1.06[c]	35
3-5	COO	1	C_2H_5	Cr 42 N (29) I								38
3-6	COO	1	OC_3H_7	Cr 41 N 71.3 I	3.92[d]	–0.82[d]	0.21[d]			6.23[d]	0.93[d]	39
3-7	—	2	$COCF_3$	Cr 70 N 141.2 I		17.70[e]		0.196[e]	60[e]			40
3-8	—	2	CF_3	Cr 123 N 124.2 I		12.90[e]		0.159[e]	32[e]			41
3-9	—	1	COO  $COCH_3$	Cr 127.5 N 208 I	10.00[f]	9.50[f]	0.95[f]	0.098[f]	89[f]	9.08[f]	1.02[f]	42
3-10	—	1	COO  CH_3	Cr_1 99 Cr_2 106 N 175 I	3.13[f]	0.52[f]	0.17[f]					42

[a] $\tau = T_{meas}/T_{N\text{-}I} = 0.95$, T_{meas}, $T_{N\text{-}I}$, K.
[b, e] Extrapolated from 10 wt% solution at 20°C in ZLI-3086 and ZLI-1132, respectively.
[c] $\tau = 0.96$.
[d] $T_{meas} = T_{N\text{-}I} - 10$°C.
[f] $T_{meas} = T_{N\text{-}I} - 30$°C.

TABLE IV Physicochemical Properties of Liquid Crystal:

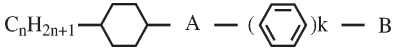


No.	A	Phase transitions, °C	$\mu_{A\perp}$,D	|Ps|, nCcm^{-2}	Θ, deg.	Reference
4-1	CO	I 150 SmA 132 SmC* (60) Sm 63.2 Cr	1.99	112[a]	21	43
4-2	COO	Cr 68 Sm (65.5) SmCγ^* 118.5 SmC* 122 SmA 149.8 I I 148 SmA 122 SmCα^* 120.9 SmC* 119.2 SmCγ^* 118.4 SmC$_A^*$	1.23	70[a]	21	43–45
4-3	O	Cr 65.7 Sm 83 SmC* 108 SmA 149 I	0.68	38[a]	17	43, 44

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

anisotropy of polarizability should enhances the nematic thermostability [46]. In this case, ketones, which have higher and lower values of polarizability than the corresponding alkyl derivatives and esters [47,48], should always exhibit higher and lower clearing points, respectively.

TABLE V Mesomorphic Properties of Some Liquid Crystals:



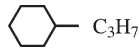
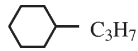
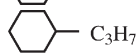
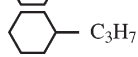
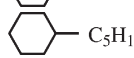
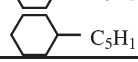
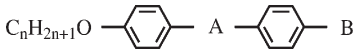
No.	n	A	k	B	Phase transitions, °C	Reference
5-1	4	CO	2	CN	Cr 111 I	96
5-2	4	—	2	CN	Cr 120 N 202 I	97
5-3	4	CH_2	2	CN	Cr 84 I	96
5-4	4	COO	2	CN	Cr 79.8 N 241.9 I	98
5-5	4	CH_2O	2	CN	Cr 93 N 193 I	98
5-6	5	CH_2CO	2	CN	Cr 139 Sm (138) N 153 I	99
5-7	5	—	2	CN	Cr 96 N 222 I	100
5-8	5	CH_2CH_2	2	CN	Cr 79 SmA 86 N 184 I	101
5-9	5	$COCH_2$	1		Cr 60 Sm 104.8 I	3
5-10	5	CH_2CO	1		Cr 95 Sm 127 I	3
5-11	5	—	1		Cr 41 SmA 156 N 160 I	102
5-12	5	COO	1		Cr 41 Sm 75 Sm 127 N 191.8 I	103
5-13	5	COCO	0		Cr 71 Sm 83 I	104
5-14	5	COO	0		Cr 52 SmB 72 I	105

TABLE VI Mesomorphic Properties of Some Liquid Crystals:



No.	n	A	B	Phase transitions, °C	Reference
6-1	12	—	$COCH_2COC_{12}H_{25}$	Cr 124.4 SmA 125.8 I	106
6-2	12	$COCH_2CO$	$C_{12}H_{25}$	Cr 62.5 Sm 76.5 I	107
6-3	12	$COCH_2CO$	$OC_{12}H_{25}$	Cr 73.1 Sm 94 I	108
6-4	12	$COCH_2$	$OC_{12}H_{25}$	Cr 105 I	109
6-5	12	COOCO	$OC_{12}H_{25}$	Cr 51.5 Sm 59 I	110
6-6	9	COCO	OC_9H_{19}	Cr_1 60 Cr_2 68 I	111
6-7	9	$COCH_2CO$	OC_9H_{19}	Cr 71.7 Sm 91.2 I	108
6-8	9	COO	OC_9H_{19}	Cr 78.6 Sm 81.7 N 88.7 I	112
6-9	9	OOCCOO	OC_9H_{19}	Cr 82 SmC 80 N 81 I	112
6-10	9	COOOOC	OC_9H_{19}	Cr 69.5 N 105 I	112
6-11	9	COCH=CH	OC_9H_{19}	Cr 81 I	113
6-12	9	COCH=CHCO	OC_9H_{19}	Cr 98 SmC (94) I	114
6-13	9	OOCCH=CHCOO	OC_9H_{19}	Cr 100 SmC 108 N 115 I	112
6-14	9	—	OC_9H_{19}	Cr 115 I	21

The melting temperatures (crystal–nematic, or crystal–smectic, or crystal–isotropic phase transition temperatures) of ketones can be higher (compounds **1-1**–**1-3**, **1-5**–**1-7**, **2-1**–**2-4**, **2-6**–**2-11**, **3-1**, and **3-3**–**3-6**, **3-9**, and **3-10**) and lower (compounds **3-7**, **3-8**, **4-1**–**4-3**) with respect to those of the corresponding reference compounds.

It has been shown that calculated potential map of 3-pentanone (which is a function of the torsional angles φ_1 and φ_2) contains significantly larger areas of low energy in comparison with that of 2-pentanone [49]. Moreover, the steric hindrance to internal rotations in the aliphatic ketones is higher when the dipole of the C=O bond is in the middle of the chain than toward the end [50]. In the corresponding pentane-2,4-dione, there are three diketo conformers and six enol ones, and its skeletal system of oxygen and carbon atoms has been assumed to be planar [4]. One can expect that these features of aliphatic ketones affect the mesomorphic properties of compounds that have them as the terminal groups. For example, moving the keto bond in the terminal group from the molecular core decreases the clearing temperature and increases the melting point (compounds **2-6** –**2-8**, Table II). It follows from Table I that the introduction of two carbonyl groups in both terminal positions lowers (compounds **1-1**, **1-2**, **1-4**, **1-8**, and **1-9**) and increases (compounds **1-10**–**1-12**) the clearing temperatures in comparison with those of the corresponding alkyl-ketones, dialkyls, and diesters.

Similarly, the melting temperatures of ketones can be lower (compounds **1-8** and **1-9**) and higher (compounds **1-1**, **1-2**, **1-4**, **1-10**–**1-12**) with respect to those of the corresponding reference compounds.

As is evident from Table II, the terminal introduction of the β-diketone group can enhance the melting temperature (compounds **2-2** and **2-5**) and keep the same value (compounds **2-1** and **2-5**) compared with those of the corresponding ketene and alkyl derivatives, whereas the clearing point of the β-diketone derivative **2-5** is lower than those of the ketone **2-1** and alkyl derivative **2-2**. Similar trends have been reported for other ketones [25,51–89].

Linking Keto Substitution

It has been found that the benzophenone (BZ) molecule has C_2 symmetry in the crystal state [90]. The dihedral angle between the phenyl rings of BZ is 52.4° [91]. The angle between the planes defined by a phenyl ring and the keto group is about 33° [90,92,93]. The barrier to internal rotatation of this molecule is 7 kcal/mol for the planar conformation and 14 kcal/mol for the book conformation [91]. At the minimum-energy conformation, the internal bond angle is calculated to be 121° [91]. The minimum-energy path for conformational interconversion in BZ is determined by a balance between maintaining of π-conjugation among the keto group and the phenyl ring and avoiding the mutual repulsion of the phenyl rings [93]. According to Shibakami and Sekiya [94], the corresponding crystal phenyl benzoate has a dihedral angle between two phenyl rings equal to 128.3°. The O(1)–C(7)–C(6)–C(1) dihedral angle, which characterizes the torsion between the C(1)–C(6) ring and the COO group in the phenyl benzoate, is 170.1°. The C(7)–O(1)–C(8)–C(9) angle, which characterizes the torsion between the C(8)–C(13) ring and the COO group, is equal to 67.5°, whereas the parent biphenyl has the minimum-energy conformation with a torsional angle between the rings of 50.8° and a barrier to rotation of 3.2 kcal/mol for the planar conformation [91].

As expected, 4,4′-disubstitution of the bent BZ molecule did not create the mesophases [95]. Similar absence of the mesophases can be observed for the bent compounds that have the keto and methylene linkages (compounds **5-1**–**5-5**, Table V), whereas the ethanone derivatives exhibit significantly lower clearing temperatures or no mesophases with respect to those of the corresponding reference compounds (compounds **5-6**–**5-12**, **6-4**, and **6-5**). Particularly lower clearing point of the ethanone derivative in comparison with that of the corresponding ester has been explained in terms of increased flexibility of the former derivative, whereas more pronounced

conjugation of the oxygen lone-pair electrons with the double bond in the latter drivative enhances its rigidity [95]. The increased conjugation of the carbonyl group of ethanone with the phenyl fragment can be responsible for the enhanced clearing temperature of compound **5-10** compared with that of the corresponding derivative **5-9** that has the keto group connected to the "inactive" saturated cyclohexane ring. It is evident from Table V that the introduction of the α-diketone linkage into the molecular core of the saturated dicyclohexanes forms the smectic phase and shows higher thermostability and melting point than those of the corresponding ester (compounds **5-13** and **5-14**).

According to Gabe et al. [115], the dihedral angle between the five-atom planes of the rings of benzil is equal to 103.6° and the torsional angle between the C=O bonds is 108.4°. In the corresponding dibenzoyl methane the carbonyl groups show approximately planar configuration as for benzyl [116]. It follows from Table VI that 4,4′-dinonyloxy substitution of benzyl does not create the mesophases (compounds **6-6**–**6-14**). Similar absence of the mesophases has been observed for the propenone derivative **6-11** and parent biphenyl derivative **6-14**. It can be proposed that increasing the conjugation among the C=O bonds of the α-diketone and propenone linkages and the phenyl rings of the aromatic systems results in more pronounced nonlinearity and in consequent disappearance of the mesophases in comparison with those of the corresponding nonaromatic systems, whereas linking β-diketone (which has a lower repulsive interaction between the two carbonyl oxygen atoms than α-diketone [116,117]) substitution of the diphenyl systems can lead to higher clearing temperatures with respect to those of the corresponding ethanone, ester, and other reference and parent compounds (compounds **6-3**–**6-11**, **6-14**; excepting compound **6-12** and diphenylester of fumaric acid **6-13**, Table VI).

The data collated in Table VI reveal that the terminal β-diketone substitution results in significantly higher clearing and melting temperatures than the linking β-diketone substitution (compounds **6-1** and **6-2**). It can be explained in terms of enhanced conjugation of the carbonyl groups with the phenyl rings, which results in more pronounced molecular nonlinearity in the latter case [118]. Similar trends have been discussed for other derivatives that have linking keto groups [78,118–142].

Lateral Keto Substitution

It has been reported about using the keto group as a bridge between the molecular cores and introduced lateral substitutents [143–145]

in some derivatives with mesomorphic properties basically follows similar trends observed for other laterally substituted liquid crystals [146].

X-ray diffraction of liquid crystals is one of useful methods for the study of the structure of their mesophases [147,148]. As in the case of weakly polar alkyl and alkoxy derivatives [149], monolayer formation ($d/L \leq 1$, where d is the layer spacing, L is the molecular length) and a dimeric density wave ($d/L > 1$) have been observed for ketones [51,52,56,60,80,88,120].

It can be proposed that the electronic and geometric structures of the keto based groups [4,12–14,17,91,115,116,150–155] play a very important role in the intra- and intermolecular interactions [6,151,156–158] that affect the packing of the molecules, which predominantly influences mesophase stability [156–160]. 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 [160]. Other molecular aspects such as the association [159] or dipole–dipole attraction in polar liquid-crystalline derivatives, which can influence the packing of the molecules, also affect the stability of the mesophases [160].

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 [161]:

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

where $\mathrm{h} = 3\varepsilon^*(2\varepsilon^* + 1)$, $\varepsilon^* = (\varepsilon_{\parallel} + 2\varepsilon_{\perp})/3$, $\Delta\alpha = (\alpha_{\parallel} - \alpha_{\perp})$ is the polarizability anisotropies; 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.

As is evident from Tables II and III, the terminal keto substitution increases the positive dielectric anisotropy $\Delta\varepsilon$ (and changes its negative sign in some cases) and its perpendicular part $\varepsilon_{\perp}$ of liquid crystals in comparison with those of the corresponding alkyl, alkoxy, and other reference derivatives (compounds **2-10**, **2-11**, **3-1**, **3-2** [approximately], **3-4**, **3-6**–**3-10**). These results are due to the enhanced dipole moments

(for example, the dipole moments in absolute values and β angles of acetophenone, methoxybenzene, and toluene diminish in the following order: 2.96 D and 132°; 1.28 D and 72°; 0.37 D and 0° [162]) and polarizability of terminal ketones [47,48,162], whereas the introduction of the keto groups in both terminal positions of two-ring dialkyl phenylcyclohexanes results in the appearance of the moderate negative dielectric anisotropy caused by the cancellation of the parallel parts of the carbonyl dipole moments [3].

It has been shown that decreasing the ratio $\Delta\varepsilon/\varepsilon_\perp$ (in absolute value) is favorable for supertwisted nematic display applications [163]. As can be seen from Table III, liquid crystals with the terminal keto groups show lower and larger values of this ratio in respect to those of the corresponding alkoxy and alkyl derivatives, respectively (compounds **3-4**, **3-6**, **3-9**, and **3-10**; see also **3-1**).

It has been demonstrated that mesogenic molecules possessing strongly polar terminal groups form associated pairs. Both head-to-head and head-to-tail pairing occurs [157], but antiparallel association predominates and reduces the effective dipole moment [159]. Despite the increased dipole moments of ketones **3-1** and **3-4**, compared with those of the corresponding alkoxy derivatives (compound **3-2**, approximately), they show nonassociating behavior [35,36].

OPTICAL PROPERTIES

The phenomenological relation between the refractive index and the electric polarization is defined as [164,165]:

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

where the mean polarizability $\alpha=(\alpha_\parallel+2\alpha_\perp)/3$; the mean refractive index $n^{*^2}=\left(n_e^2+2n_o^2\right)/3$, and n_o is the ordinary and n_e is the extraordinary refractive indices. From Equation (2) and the previous paragraph, it follows that the ketones that have a larger induced polarizability [47,48,162] exhibit the optical anisotropy $\Delta n = n_e - n_o$, which is larger than that of the corresponding reference compounds without the keto groups (compounds **2-10**, **2-11**, **3-7**, and **3-8**; see also **2-5**, **3-1**, **3-9**; Tables II and III). These results can be explained in terms of a reduction in the effective conjugation of the π-electron system, resulting in a shorter resonance wavelength of the UV absorption spectrum for the corresponding liquid crystals without the terminally introduced keto groups than for ketones [18], and the alkoxy derivatives show similar behavior (compounds **3-1** and **3-2**, approximately).

VISCOELASTIC PROPERTIES

It has been shown that the nematic liquid-crystalline materials for display applications should have a low viscosity for giving the acceptable response times to liquid crystal displays (LCDs) [163,166]. According to the results on the kinematic viscosity ν presented in Tables II and III, the terminal ketonization increases the viscosity of liquid crystals (compounds **2-10**, **2-11**, **3-7**, and **3-8**; see also **2-5**) in respect to that of the reference compounds without the keto groups. These results can be explained in terms of larger sizes of keto-substituted terminal groups.

In the bulk of nematic LCs elastic properties are determined by three elastic constants (Oseen–Frank constants) corresponding to the restoring forces opposing splay (K_{11}), twist (K_{22}), and bend (K_{33}) [167,168]. It has been shown that the elastic constants depend on molecular structure, intermolecular association, and temperature of nematic LCs [169–171]. The elastic constant ratio K_{33}/K_{11} of liquid crystals is an important parameter for supertwisted nematic liquid-crystal displays (STN-LCDs) and define their electrooptical performance [172]. The data collated in Table III show similar elastic behavior of weakly polar terminal ketones and the corresponding alkoxy derivatives (compounds **3-4** and **3-6**; see also **3-1**), and their low elastic ratios should be favorable for the STN-LCD applications [172].

PHYSICAL PROPERTIES OF THE SMECTIC C* PHASE

The spontaneous polarization Ps of the smectic C^* liquid crystals is an important parameter because of its linear coupling with an applied electrical field, which is the basis of the application of these materials [173]. 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 [173]. The spontaneous polarization Ps is a quantity that is directly related to the response time τ as a switching device [174]:

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

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

As can be seen from Table IV, the terminal ketonization of the chiral liquid crystals results in the largest value of the spontaneous polarization in comparison with that of the corresponding ester and oxygen derivatives (compounds **4-1**–**4-3**) These results can be

correlated with the dipole moments $\mu_{A\perp}$ of the group adjacent to the asymmetric carbon atom in the direction perpendicular to the molecular long axis. The tilt angle is similar for the ketone and ester derivatives **4-1** and **4-2**, and it is slightly lower for the oxygen derivative **4-3**.

CONCLUSION

Systematic studies on the introduction of the keto group into the molecular structure of calamitic liquid crystals and their effects on the creation of the mesophases and their physicochemical properties have been performed, with attempts to correlate the molecular level parameters with the observed properties. The information here presented may lead to a better understanding of the nature of liquid crystals.

REFERENCES

[1] Patai, S. (1966). *The Chemistry of the Carbonyl Group*. Wiley: New York.
[2] Berthier, G. & Serre, J. (1966). In: *The Chemistry of the Carbonyl Group.*, Patai, S. (Ed.). Wiley: New York, p. 1.
[3] Osman, M. A. & Hyunh-Ba, T. (1984). *Mol. Cryst. Liq. Cryst.*, *116*, 141.
[4] Emsley, J., Freeman, N. J., Parker, R. J., & Overill, R. (1986). *J. Chem. Soc., Perkin Trans 2*, 1479.
[5] Emsley, J., Ma, L. Y. Y., Bates, P. A., & Hurthouse, M. (1988). *J. Mol. Struct.*, *178*, 297.
[6] Zheglova, D., Denkov, N., & Kol'tsov, A. I. (1984). *J. Mol. Struct.*, *115*, 371.
[7] Burdett, J. L. & Rogers, M. T. (1964). *J. Am. Chem. Soc.*, *86*, 2105.
[8] Apeloig, Y., Arad, D., & Rappoport, Z. (1990). *J. Am. Chem. Soc.*, *112*, 9131.
[9] Delchev, V. B., Mikosh, H., & Nikolov, G. S. (2001). *Monatsch. Chem.*, *132*, 339.
[10] Nadler, E. B. & Rappoport, Z. (1987). *J. Am. Chem. Soc.*, *109*, 2112.
[11] Emsley, J. & Freeman, N. J. (1987). *J. Mol. Struct.*, *161*, 181.
[12] Abraham, R. J., Chadwick, D. J., & Sancassan, F. (1982). *Tetrahedron*, *38*, 3245.
[13] Tanimoto, Y., Kobayashi, H., Nagakura, S., & Sato, Y. (1973). *Acta Crystallogr.*, *B29*, 1822.
[14] Pawar, D. M., Wilson, K. K., & Noe, E. A. (2000). *J. Org. Chem.*, *65*, 1552.
[15] Sedlacek, P., Stokr, J., & Schneider, B. (1981). *Collect. Czech. Chem. Commun.*, *46*, 1646.
[16] Rudolph, H. D., Dreizler, H., Jaeschke, A., & Wending, P. (1967). *Z. Naturforsch.*, *22a*, 940.
[17] Chow, T. & Li, L.-P. (1999). *Tetrahedron*, *55*, 6067.
[18] Dabrowski, R. & Zytynski, E. (1982). *Mol. Cryst. Liq. Cryst.*, *87*, 109.
[19] Osman, M. A. (1983). *Z. Naturforsch.*, *38a*, 693.
[20] Huynh-Ba, T. & Osman, M. (1989). *Eur. Pat. Appl.*, *EP84*, 194.
[21] Vill, V. (1992). Liquid Crystals. In: *Landolt-Bornstein, Group IV: Macroscopic Properties of Matter*, Vol. 7a, Thiem, J. (Ed.). Springer Verlag: New York, pp. 76, 86.
[22] Demus, D., Richter, L., Rurup, C.-E., Sackmann, H., & Schubert, H. (1975). *J. Phys. Colloq.*, *36*, C1-349.

[23] Dubois, J.-C. (1978). *Ann. Phys.*, *3*, 131.
[24] Sadashiva, B. K. & Subba Rao, G. S. R. (1977). *Mol. Cryst. Liq. Cryst.*, *38*, 345.
[25] Malthete, J., Billard, J., Canceill, J., Gabard, J., & Jacques, J. (1976). *J. Phys. Colloq.*, *37*, C3-1.
[26] Schubert, H., Lorenz, H.-J., Hoffmann, R., & Franke, F. (1966). *Z. Chem.*, *6*, 337.
[27] Kelly, S. M. (1994). *Liq. Cryst.*, *17*, 211.
[28] Eidenschink, R., Gray, G. W., Toyne, K. J., & Wachtler, A. E. F. (1988). *Mol. Cryst. Liq. Cryst. Lett.*, *5*, 171.
[29] Inoue, H., Fukui, M., Goto, Y., & Tokita, S. (1985). US Patent 4, 507, 222.
[30] Eidenschink, R. & Scheuble, B. (1987). German Pat. DE-OS 3 617 431.
[31] Miyazawa, K. & Goto, Y. (1995). *Mol. Cryst. Liq. Cryst.*, *260*, 277.
[32] Harufuji, T., Tamura, N., Inagaki, J., & Kubo, Y. (2002). Japan. Pat. Appl. JP 20022338518.
[33] Saito, H., Nakagawa, E., Matsushita, T., Takeshita, F., Kubo, Y., Matsui, S., Miyazawa, K., & Goto, Y. (1996). *IEICE Trans. Electron.*, *E79-C*, 1027.
[34] Plach, H., Bartmann, E., Poetsch, E., Naemura, S., & Rieger, B. (1992). *SID 92 Digest*, p. 13.
[35] Schad, Hp. & Kelly, S. M. (1985). *Z. Naturforsch.*, *40a*, 932.
[36] Finkenzeller, U., Kurmeier, A., & Poetsch, E. (1989). *Proc. 18th Freiburger Arbeitstagung Flussigkristalle*. Freiburg University: Germany, p. 1.
[37] Petrzilka, M. (1984). *Mol. Cryst. Liq. Cryst.*, *111*, 345.
[38] Deutscher, H.-J., Laaser, B., Dolling, W., & Schubert, H. (1978). *J. Prakt. Chem.*, *320*, 191.
[39] Schadt, M., Buchecker, R., Leenhouts, A., Boller, A., Villiger, A., & Petrzilka, M. (1986). *Mol. Cryst. Liq. Cryst.*, *139*, 1.
[40] Bartmann, E., Dorsch, D., & Finkenzeller, U. (1991). *Mol. Cryst. Liq. Cryst.*, *204*, 77.
[41] Bartmann, E., Dorsch, D., Finkenzeller, U., Kurmeier, H. A., & Poetsch, E. (1990). *Proc. 19th Freiburger Arbeitstagung Flussigkristalle*. Freiburg University: Germany, p. 8.
[42] Dabrowski, R., Dziaduszek, J., Sczucinski, T., & Raszewski, Z. (1984). *Mol. Cryst. Liq. Cryst.*, *107*, 411.
[43] Yoshizawa, A., Nishiyama, I., Fukusama, M., Hirai, T., & Yamane, M. (1989). *Jap. J. Appl. Phys.*, *28*, L1269.
[44] Furukawa, K., Terashima, K., Ichihashi, M., Saitoh, S., Miyazawa, K., & Inukai, T. (1988). *Ferroelectrics*, *85*, 451.
[45] Takanishi, Y., Sato, D., Ishikawa, K., & Takezoe, H. (2000). *Ferroelectrics*, *245*, 111.
[46] Maier, W., & Saupe, A. (1959). *Z. Naturforsch.*, *14a*, 882.
[47] Miller, K. J. (1990). *J. Am. Chem. Soc.*, *112*, 8533.
[48] Matsuzawa, N. & Dixon, D. A. (1992). *J. Phys. Chem.*, *96*, 6232.
[49] Suter, U. W. (1979). *J. Am. Chem. Soc.*, *101*, 6481.
[50] Vij, J. K. & Hufnagel, F. (1991). *J. Phys. Chem.*, *95*, 6142.
[51] Ohta, K., Takenaka, O., Hasebe, H., Morizumi, Y., Fujimoto, T., & Yamamoto, I. (1991). *Mol. Cryst. Liq. Cryst.*, *195*, 103.
[52] Diele, S., Tosch, S., Mahnke, S., & Demus, D. (1991). *Cryst. Res. Tech.*, *26*, 809.
[53] Ishibashi, S. & Kobayashi, S. (1991). *Liq. Cryst.*, *10*, 715.
[54] Schubert, H. & Dehne, H. (1972). *Z. Chem.*, *12*, 241.
[55] Thompson, N. J., Gray, G. W., Goodby, J. W., & Toyne, K. J. (1991). *Mol. Cryst. Liq. Cryst.*, *200*, 109.
[56] Furman, I., Butcher, R. J., Catchings, R. M., & Weiss, R. G. (1992). *J. Am. Chem. Soc.*, *114*, 6023.

[57] Furman, I. & Weiss, R. G. (1992). *J. Am. Chem. Soc.*, *114*, 1381.
[58] Dabrowski, R. & Czuprynski, K. (1987). *Mol. Cryst. Liq. Cryst.*, *146*, 341.
[59] Takeda, H., Sakurai, Y., Takenaka, S., Miyake, H., Doi, T., & Kusabayashi, S. (1990). *J. Chem. Soc., Faraday Trans.*, *86*, 3429.
[60] Albertini, G., Caciuffo, R., Fanelli, E., Mariani, P., Poeti, G., Rustichelli, F., & Torquati, G. (1984). *Mol. Cryst. Liq. Cryst.*, *114*, 65.
[61] Trivedi, K. N. & Thakkar, D. M. (1984). *Mol. Cryst. Liq. Cryst.*, *106*, 95.
[62] Kumegawa, N. & Araya, K. (1993). *Proc. 19th Japan. Liq. Cryst. Conf.* Japan Liquid Crystal Society: Japan, p. 218.
[63] Malthete, J., Canceill, J., Gabard, J., & Jacques, J. (1981). *Tetrahedron*, *37*, 2815.
[64] Wiegeleben, A., Deresch, J., Demus, D., & Konstantinoff, I. I. (1979). *Z. Phys. Chem.*, *260*, 357.
[65] Dave, J. S. & Kurian, G. (1975). *J. Phys. Colloq.*, *36*, C1-403.
[66] Neubert, M. E., Herlinger, F. C., Jirousek, M. R., & de Vries, A. (1986). *Mol. Cryst. Liq. Cryst.*, *139*, 299.
[67] Kawamura, I. & Imai, Y. (1989). Eur. Pat. Appl. EP 304 359.
[68] Arora, S. L., Taylor, T. R., & Fergason, J. L. (1970). *J. Org. Chem.*, *35*, 1705.
[69] Arora, S. L., Taylor, T. R., & Fergason, J. L. (1970). *Liq. Cryst. Ord. Fluid.*, *1*, 321.
[70] Fishel, D. L. & Patel, P. R. (1972). *Mol. Cryst. Liq. Cryst.*, *17*, 139.
[71] Criswell, T. R., Klandermann, B. H., & Batesky, D. C. (1973). *Mol. Cryst. Liq. Cryst.*, *22*, 211.
[72] Yoshizawa, A., Yokoyama, A., & Nishiyama, I. (1992). *Liq. Cryst.*, *11*, 235.
[73] Kobayashi, S. & Ishibashi, S. (1992). *Mol. Cryst. Liq. Cryst.*, *220*, 1.
[74] Cereghetti, M., Marbet, R., & Schleich, K. (1982). *Helv. Chim. Acta*, *65*, 1318.
[75] Petrzilka, M. & Schleich, K. (1982). *Helv. Chim. Acta*, *65*, 1242.
[76] Kobayashi, S., Ishibashi, S., & Tsuru, S. (1991). *Mol. Cryst. Liq. Cryst.*, *202*, 103.
[77] Kiryanov, A. A., Sampson, P., & Seed, A. (2000). *J. Mater. Chem.*, *11*, 3068.
[78] Schubert, H., Hoffman, S., Hauschild, J., & Marx, I. (1977). *Z. Chem.*, *17*, 414.
[79] Byron, D., Matharu, A., Wilson, R., & Wright, G. (1995). *Mol. Cryst. Liq. Cryst.*, *265*, 61.
[80] Dabrowski, R., Przedmojski, J., Baran, J. W., & Pura, B. (1986). *Cryst. Res. Technol.*, *21*, 567.
[81] Nishiyama, I., Yoshizawa, A., Fukumasa, M., & Hirai, T. (1989). *Jap. J. Appl. Phys.*, *28*, L2248.
[82] Eidenschink, R., Krause, J., & Pohl, L. (1979). US Patent 4,154,697.
[83] Varech, D., Lacombe, L., & Jacques, J. (1984). *Nouv. J. Chim.*, *8*, 445.
[84] Bezborodov, V. S., Sasnouski, G., & Lapanik, V. I. (2000). *Liq. Cryst.*, *27*, 935.
[85] Hamplova, V., Bubnov, A., Kaspar, M., Novotna, V., Pociecha, D., & Glogarova, M. (2003). *Liq. Cryst.*, *30*, 627.
[86] Kosata, B., Kozmik, V., Svoboda, J., Novotna, V., Vanek, P., & Glogarova, M. (2003). *Liq. Cryst.*, *30*, 603.
[87] Hamplova, V., Bubnov, A., Kaspar, M., Novotna, V., & Glogarova, M. (2003). *Liq. Cryst.*, *30*, 493.
[88] Matsushima, J., Takanishi, Y., Ishikawa, K., Takezoe, H., Fukuda, A., Park, C. S., Jang, W. G., Kim, K. H., Maclennan, J. E., Glaser, M. A., & Clark, N. A. (2002). *Liq. Cryst.*, *29*, 27.
[89] Gallardo, H., Zucco, C., & Da Silva, L. (2002). *Mol. Cryst. Liq. Cryst.*, *373*, 181.
[90] Fleisher, E. B., Sung, N., & Hawkinson, S. (1968). *J. Phys. Chem.*, *72*, 4311.
[91] Kendrick, J. (1990). *J. Chem. Soc., Faraday Trans.*, *86*, 3995.
[92] Schaefner, T. & Penner, G. H. (1986). *J. Chem. Phys.*, *85*, 6249.
[93] Gough, K. M. & Wildman, T. A. (1990). *J. Am. Chem. Soc.*, *112*, 9141.

[94] Shibakami, M. & Sekiya, A. (1995). *Acta Crystallogr.*, *C51*, 326.
[95] Destrade, C., Ngyuen, H. T., & Gasparoux, H. (1980). *Mol. Cryst. Liq. Cryst.*, *59*, 273.
[96] Karamysheva, L. A., Geyvandova, T. A., Agafonova, I. F., Roitman, K. V., Torgova, S. I., Geyvandov, R. K., & Petrov, V. F. (1990). *Mol. Cryst. Liq. Cryst.*, *191*, 247.
[97] Hanna, J., Kogo, K., & Kafuku, K. (2001). US Patent 6,224,787.
[98] Gray, G. W. & McDonnell, D. G. (1979). *Mol. Cryst. Liq. Cryst.*, *53*, 147.
[99] Solladie, G. & Zimmermann, R. (1985). *J. Org. Chem.*, *50*, 4062.
[100] Eidenschink, R. (1983). *Mol. Cryst. Liq. Cryst.*, *94*, 119.
[101] Fearon, J. E., Gray, G. W., Ifill, A. D., & Toyne, K. J. (1985). *Mol. Cryst. Liq. Cryst.*, *124*, 89.
[102] Ivaschenko, A. V., Torgova, S. I., Karamysheva, L. A., & Abolin, A. G. (1990). *Liq. Cryst.*, *7*, 475.
[103] Osman, M. A. (1982). *Mol. Cryst. Liq. Cryst.*, *82*, 323.
[104] Praefcke, K., Schmidt, D., & Heppke, G. (1979). *Israel. J. Chem.*, *18*, 195.
[105] Deutscher, H. J., Korber, M., & Schubert, H. (1980). *Advances in Liquid Crystal Research and Applications*, Bata, L. (Ed.). Pergamon Press: Oxford, Akademiai Kiado: Budapest, p. 1075.
[106] Ohta, K., Takenaka, O., Hasebe, H., Morizumi, Y., Fujimoto, T., & Yamamoto, I. (1991). *Mol. Cryst. Liq. Cryst.*, *195*, 123.
[107] Prasad, V. & Sadashiva, B. K. (1991). *Mol. Cryst. Liq. Cryst.*, *195*, 161.
[108] Ohta, K., Muroki, H., Hatada, K.-I., Takagi, A., Ema, H., Yamamoto, I., & Matsuzaki, K. (1986). *Mol. Cryst. Liq. Cryst.*, *140*, 163.
[109] Veber, M., Fugnitto, R., Strzelecka, H. (1983). *Mol. Cryst. Liq. Cryst.*, *96*, 221.
[110] Vill, V., & Thiem, J. (1990). *Z. Naturforsch.*, *45a*, 1205.
[111] Ohta, K., Takagi, A., Muroki, H., Yamammoto, I., & Matsuzaki, K. (1987). *Mol. Cryst. Liq. Cryst.*, *147*, 15.
[112] Vill, V. (1994). Liquid Crystals. In: *Landolt-Bornstein, Group IV: Macroscopic Properties of Matter*, Vol. 7b, Thiem, J. (Ed.). Springer Verlag: New York, pp. 138, 340, 344, 345.
[113] Veber, M., Jallabert, C., & Strzelecka, H. (1987). *Synth. Commun.*, *17*, 693.
[114] Schubert, H., Koch, R., & Weinbrecher, Chr. (1966). *Z. Chem.*, *6*, 467.
[115] Gabe, E. J., Le Page, Y., Lee, F. L., & Barclay, L. R. C. (1981). *Acta Crystallogr.*, *B37*, 197.
[116] Morantz, D. J. & Wright, A. J. C. (1971). *J. Chem. Phys.*, *54*, 692.
[117] Aleman, C., Navarro, E., & Puiggali, J. (1996). *J. Phys. Chem.*, *100*, 16131.
[118] Barbera, J., Cativiela, C., Serrano, J. L. Zurbano, M. M. (1992). *Liq. Cryst.*, *11*, 887.
[119] Koden, M., Takenaka, S., & Kusabayashi, S. (1982). *Mol. Cryst. Liq. Cryst.*, *88*, 137.
[120] Sadashiva, B. K., Rani Rao, P., & Srikanta, B. S. (1989). *Mol. Cryst. Liq. Cryst.*, *168*, 103.
[121] Coates, D. & Gray, G. W. (1976). *J. Chem. Soc., Perkin Trans. 2*, 863.
[122] Gray, G. W., Lacey, D., Scrowston, R. M., Shenouda, I. G., & Toyne, K. J. (1988). *Mol. Cryst. Liq. Cryst.*, *164*, 101.
[123] Godquin-Giroud, A.-M. & Billard, J. (1983). *Mol. Cryst. Liq. Cryst.*, *97*, 287.
[124] Carr, N. & Gray, G. W. (1989). *Liq. Cryst.*, *6*, 467.
[125] Thomson, N. J., Goodby, J. W., & Toyne, K. J. (1992). *Mol. Cryst. Liq. Cryst.*, *213*, 187.
[126] Schubert, H., Sagitdinov, I. A., & Svetkin, J. V. (1975). *Z. Chem.*, *15*, 222.
[127] Dabrowski, R., Dziaduszek, J., Szczucinski, T., Stolarzowa, Z., & Czuprynski, K. (1989). *Liq. Cryst.*, *5*, 209.

[128] Sugimori, S., Isoyama, T., Nigorikawa, K., Ogawa, T., Naoyuki, K., & Yoshito, Y. (1987). US Patent 4,684,478.
[129] Chan, L. K. M., Gemmell, P. A., Gray, G. W., Lacey, D., & Toyne, K. J. (1989). *Mol. Cryst. Liq. Cryst.*, *168*, 229.
[130] Gunjima, T. & Ryutaro, T. (1983). Eur. Pat. Appl. EP 102 047.
[131] Hyunh-Ba, T. & Osman, M. A. (1983). German Patent DE-OS 3 332 690.
[132] Ohta, K., Ishii, A., Yamamoto, I., Muroki, K., & Matsuzaki, K. (1985). *Mol. Cryst. Liq. Cryst.*, *116*, 299.
[133] Brown, D. H. & Styring, P. (2003). *Liq. Cryst.*, *30*, 23.
[134] Miyazawa, K., Takeuchi, H., Yagi, Y., Takeshita, F., & Nakagawa, E. (2000). Eur. Pat. Appl. EP 1 026 142.
[135] Phan, T. H. & Basturk, N. (1982). *Mol. Cryst. Liq. Cryst. Lett.*, *82*, 89.
[136] Vora, R. A. & Prajapati, A. K. (1999). *Mol. Cryst. Liq. Cryst.*, *332*, 329.
[137] Vora, R. A. & Gupta, R. (1981). *Mol. Cryst. Liq. Cryst.*, *67*, 215.
[138] Benicewicz, B. C., Huang, S. J., & Johnson, J. F. (1982). *Mol. Cryst. Liq. Cryst.*, *89*, 217.
[139] Benicewicz, B. C., Huang, S. J., & Johnson, J. F. (1981). *Mol. Cryst. Liq. Cryst.*, *72*, 9.
[140] Pyzuk, W., Krowczynski, A., & Gorecka, E. (1991). *Liq. Cryst.*, *10*, 593.
[141] Pociecha, D., Krowczynski, A., Szydlowska, J., Gorecka, E., Glogarova, M., & Przedmojski, J. (1997). *J. Mater. Chem.*, *7*, 1709.
[142] Pociecha, D., Krowczynski, A., Maciejczuk, U., & Szydlowska, J. (2001). *Liq. Cryst.*, *28*, 1093.
[143] Weissflog, W. & Demus, D. (1988). *Liq. Cryst.*, *3*, 275.
[144] Weissflog, W. & Demus, D. (1984). *Cryst. Res. Tech.*, *19*, 55.
[145] Reiffenrath, V. & Bremer, M. (1999). German Pat. Appl. DE 198 04 894.
[146] Bezborodov, V. S. & Petrov, V. F. (1997). *Liq. Cryst.*, *23*, 771.
[147] Brownsey, G. J. & Leadbetter, A. J. (1980). *Phys. Rev. Lett.*, *44*, 1608.
[148] Grebyonkin, M. F., Petrov, V. F., & Ostrovskii, B. I. (1990). *Liq. Cryst.*, *7*, 367.
[149] Petrov, V. F. (2002). *Liq. Cryst.*, *29*, 805.
[150] Bohm, S. & Exner, O. (2002). *J. Mol. Struct. (Theochem.)*, *578*, 103.
[151] Wiberg, K. B. & Martin, E. (1985). *J. Am. Chem. Soc.*, *107*, 5035.
[152] McAllister, M. A. & Tidwell, T. T. (1994). *Can. J. Chem.*, *72*, 882.
[153] Cerfontain, H., Kruk, C., Rexwinkel, R., & Stunnenberg, F. (1987). *Can. J. Chem.*, *65*, 2234.
[154] Rathna, A. & Chandrasekhar, J. (1991). *J. Chem. Soc., Perkin Trans. 2*, 1661.
[155] van der Velden, G. P. M., de Boer, E., & Veeman, W. S. (1980). *J. Phys. Chem.*, *84*, 2634.
[156] Osman, M. A. (1983). *Z. Naturforsch.*, *38a*, 693.
[157] de Jeu, W. H. (1983). *Phil. Trans. R. Soc. A*, *309*, 217.
[158] Ostrovskii, B. I. (1999). In: *Structure and Bonding*, Mingos, D. M. P. (Ed.). Springer Verlag: New York, Vol. 94, p. 200.
[159] Schad, Hp. & Osman, M. A. (1981). *J. Chem. Phys.*, *75*, 880.
[160] Osman, M. A. & Revesz, L. (1982). *Mol. Cryst. Liq. Cryst., Lett.*, *82*, 41.
[161] Maier, W. & Meier, G. (1961). *Z. Naturforsch.*, *16a*, 262.
[162] Minkin, V. I., Osipov, O. A., & Zhdanov, Yu. A. (1970). *Dipole Moments In Organic Chemistry*. Plenum Press: New York.
[163] Schadt, M. (1992). *Displays*, *13*, 11.
[164] de Jeu, W. H. (1980). *Physical Properties of Liquid Crystalline Materials*. Gordon and Breach: New York.
[165] de Jeu, W. H., Gerristma, C. J, van Zanten, P., & Goosens, W. A. (1972). *Phys. Lett.*, *39A*, 355.

[166] Jakeman, E. & Raynes, E. P. (1972). *Phys. Lett.*, *39A*, 69.
[167] Oseen, C. W. (1933). *Trans. Faraday Soc.*, *29*, 883.
[168] Frank, F. C. (1958). *Discuss. Faraday Soc.*, *25*, 19.
[169] Van Dijk, J. W., Beens, W. W., & de Jeu, W. H. (1983). *J. Chem. Phys.*, *79*, 3888.
[170] De Jeu, W. H. & Classen, W. A. P. (1977). *J. Chem. Phys*., 67, 3705.
[171] Gruler, H. (1973). *Z. Naturforsch.*, *23a*, 474.
[172] Guy, S. C. (1993). *Displays*, *14*, 32.
[173] Martinot-Lagarde, P. (1988). *Ferroelectrics*, *84*, 53.
[174] Escher, C., Geelhaar, T., & Boehm, E. (1986). *Liq. Cryst.*, *3*, 469.