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

Chiral liquid crystalline 3,6-disubstituted cyclohex-2-enones, their derivatives and FLC compositions based upon them

V. S. Bezborodov[a]; V. I. Lapanik[a]; G. M. SasnoVski[a]; W. Haase[b]
[a] Institute of Applied Physics Problems, Minsk, Belarus [b] Darmstadt University of Technology, Darmstadt, Germany

To cite this Article Bezborodov, V. S. , Lapanik, V. I. , SasnoVski, G. M. and Haase, W.(2005) 'Chiral liquid crystalline 3,6-disubstituted cyclohex-2-enones, their derivatives and FLC compositions based upon them', Liquid Crystals, 32: 7, 889 — 900

To link to this Article: DOI: 10.1080/02678290500139336

URL: http://dx.doi.org/10.1080/02678290500139336

Liquid Crystals, Vol. 32, No. 7, July 2005, 889–900

Chiral liquid crystalline 3,6-disubstituted cyclohex-2-enones, their derivatives and FLC compositions based upon them

V.S. BEZBORODOV*†, V.I. LAPANIK†, G.M. SASNOVSKI† and W. HAASE‡
†Institute of Applied Physics Problems, 220064, Minsk, Belarus
‡Darmstadt University of Technology, 64287, Darmstadt, Germany

(*Received 1 November 2004; accepted 15 February 2005*)

The synthesis and chemical transformations of 3,6-disubstituted cyclohex-2-enones into new chiral liquid crystalline laterally substituted derivatives of biphenyl, terphenyl or quaterphenyl are presented. The mesomorphic properties of the compounds prepared and physical and electro-optical parameters of FLC compositions based upon them are discussed with an emphasis on structure–property relationships.

1. Introduction

Understanding the structure–property relationships present in liquid crystals (LCs) continues to provide a demanding research challenge. It has been shown that even small structural changes to the molecules forming mesophases may lead to considerable changes in their physico-chemical properties and the electro-optical parameters of the compositions based upon them [1–5]. One of the useful approaches for the design of new liquid crystalline structures having targetted characteristics is the lateral substitution of the molecular core by halogen, alkyl, alkoxy or other groups [6–9].

It has been reported that 3,6-disubstituted cyclohex-2-enones are promising intermediates for the preparation of liquid crystalline compounds. They can be transformed in high yields into various laterally substituted derivatives of cyclohexane, biphenyl or terphenyl [10–13], which are useful components of LC mixtures for display applications. To continue these investigations it was interesting to synthesize new chiral liquid crystalline 3,6-disubstituted cyclohex-2-enones and study the possibility of their conversion into ferroelectric liquid crystals (FLCs) having optimized properties. It should be noted that the different possible reactions for the various substituted cyclohexenones allow these transformations to be achieved selectively and provide the opportunity of preparing FLC compounds with novel combinations of structural fragments in the molecules.

In this paper, we summarize and show how new chiral liquid crystalline laterally substituted derivatives of biphenyl, terphenyl or quaterphenyl can be prepared by the transformation of the corresponding 3,6-disubstituted cyclohex-2-enones. The mesomorphic properties of the compounds prepared and the physical and electro-optical properties of FLC compositions based upon them, are discussed with the emphasis placed on elucidating structure–property relationships.

2. Results and discussion

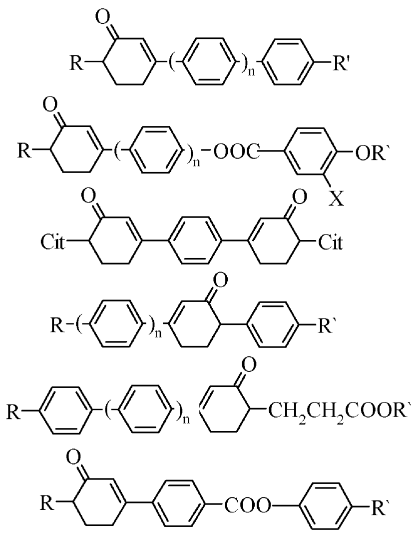
2.1. *Synthesis*

Taking into account the results of our previous investigations [10–15] and that the mesomorphic 3,6-disubstituted cyclohex-2-enones can be easily synthesized in yields of 50–70% by a Michael condensation of the hydrochlorides 4-(2-*N*,*N*-dimethylaminopropanoyl)-1-substituted benzenes (Mannich salts) with 2-alkylacetoacetic esters or 4-substituted phenylacetones in the presence of potassium hydroxide in boiling dioxane or bis(2-methoxyethyl) ether (diglyme) [16, 17], we used this method for the preparation of the unsaturatated cyclic ketones **Ia–g**, **IIa–c**, **IIIa**, **IVa**, **Va**,**b**, **VIa–d** (see tables 1–4) with different combinations of benzene rings and functional groups.

---

*Corresponding author. Email: bezborodov@bsu.by

Liquid Crystals
ISSN 0267-8292 print/ISSN 1366-5855 online © 2005 Taylor & Francis
http://www.tandf.co.uk/journals
DOI: 10.1080/02678290500139336



(Ia-g)

(IIa-c)

(IIIa)

(IVa)

(Va,b)

(VIa-d)

In these structures *R* and *R′* are chiral or non-chiral alkyl (C_nH_{2n+1}), alkoxy (OC_nH_{2n+1}) or oxycarboxylate (OOC_nH_{2n+1}); cit = $(CH_3)_2C = CHCH_2CH_2CH(CH_3)CH_2CH_2$; $n = 0$ or 1; $X = H$ or F;

3,6-Disubstituted cyclohex-2-enones **Ia**–**f**, **IIa**–**c**, **IVa** (see tables 1,2), containing chiral alkoxy, oxycarboxylate or oxybenzoate fragments were synthesized by the dealkylation of the corresponding methoxy derivatives **A** in the presence of aluminum chloride and then by the interaction of the intermediate phenols **B** with chiral alcohols, using the Mitsunobu reaction [18], or by the esterification of them with the corresponding acids in the presence of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) as catalyst (see scheme 1).

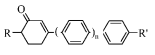
3-(4-Pentylbiphenyl-4′-)-3-citronellyl (**Ic**) and 1,4-bis(6-citronellylcyclohex-2-enon-3-yl)benzene (**IIIa**) have been prepared by the same condensation of ethyl 2-citronellylacetoacetic ester with the corresponding Mannich salts.

The alkaline hydrolysis of the 3-(2-cyanoethyl)-6-(4-substituted phenyl)cyclohex-2-enones **C** and 4-(6-alkylcyclohex-2-enon-3-yl)benzonitriles **D**, using potassium hydroxide in boiling ethylene glycol, leads to the corresponding acids **E**, **F**, which with the chiral alcohols or phenols form the esters **Va**,**b**, **VIa**–**d** (see scheme 2 and tables 3,4).

2.2. *Chemical transformations*

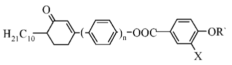
It has been shown that the cyclohex-2-enones can be converted into the corresponding aromatic derivatives using the Grignard reaction or by the interaction with phosphorous pentachloride, *N*-bromosuccinimide or other chemical reagents [19–21]. Taking this into account, we investigated the transformations of 3,6-disubstituted cyclohex-2-enones **Ia**–**g**, **IIa**–**c**, **IIIa**, **IVa**,

Table 1. Transition temperatures of the compounds **Ia**–**g**.



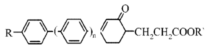
				Transition temperature/°C						
Compound	*R*	*n*	*R′*	Cr		SmC		SmA		I
Ia	$H_{21}C_{10}$	0	$OCH_2CH(CH_3)C_2H_5$	•	56	•	(20)	•	70	•
Ib	$H_{21}C_{10}$	0	$OCH(CH_3)C_6H_{13}$	•		—		—	53	•
Ic	$H_{21}C_{10}$	0	$OOCCH(CH_3)C_2H_5$	•	54	—		•	62	•
Id	$H_{17}C_8$	0	OCit	•	49	—		•	60	•
Ie	$H_{21}C_{10}$	1	$OCH(CH_3)C_4H_9$	•	46	—		•	146	•
If	$H_{21}C_{10}$	1	$OCH(CH_3)C_6H_{13}$	•	64	•	78	•	134	•
Ig	Cit	1	C_5H_{11}	•	<r.t.	•	87	•	155	•

Table 2. Transition temperatures of the esters **IIa**–**c**.



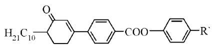
				Transition temperature/°C						
Compound	*R′*	*n*	*X*	Cr		SmC		SmA		I
IIa	$CH_2CH(CH_3)C_2H_5$	1	H	•	56	•	104	•	176	•
IIb	$CH_2CH(CH_3)C_2H_5$	1	F	•	38	•	98	•	171	•
IIc	$CH(CH_3)C_6H_{13}$	2	H	•	67	•	206	•	239	•

Table 3. Transition temperatures of the compounds **Va**,**b**.

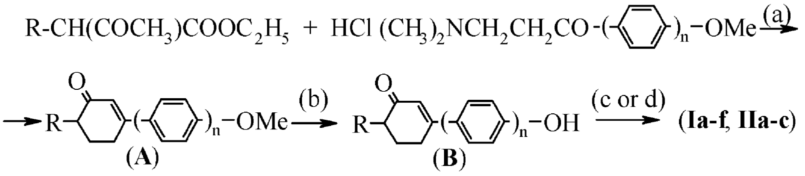


				Transition temperature/°C						
Compound	*R*	*n*	*R′*	Cr		SmC		SmA		I
Va	$H_{21}C_{10}O$	0	$CH(CH_3)C_6H_{13}$	•		—	(43)	•	62	•
Vb	$H_{11}C_5$	1	$CH(CH_3)C_6H_{13}$	•	58	—		•	127	•

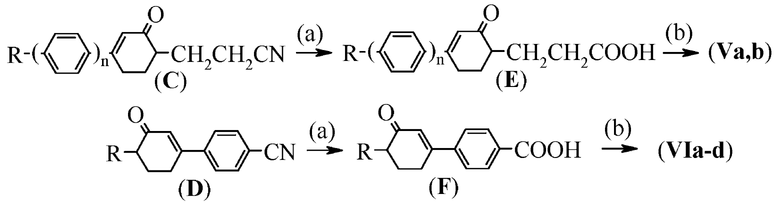
Table 4. Transition temperatures of the esters **VIa**–**d**.



		Transition temperature/°C						
Compound	*R′*	Cr		SmC		SmA		I
VIa	$OCH_2CH(CH_3)OC_2H_5$	•	52	•	98	•	165	•
VIb	$O(CH_2)_3CH(CH_3)C_2H_5$	•	62	•	138	•	190	•
VIc	$OCH(CH_3)COOCH_3$	•	46	•	61	•	83	•
VId	$COOCH(CH_3)C_6H_{13}$	•	57	•	121.5	•	122.5	•

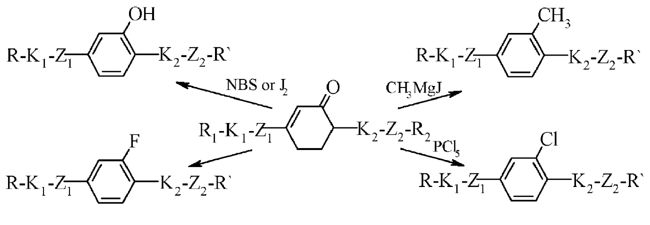


Scheme 1. (a) KOH, dioxane; (b) $AlCl_3$, benzene; (c) $H_5C_2OOCNNCOOC_2H_5$, $P(Ph)_3$, HOR′; (d) HOOCR′ or HOOCPhOR′, DCC, DMAP.



Scheme 2. (a) KOH; (b) HOR′ or HOPhR′, DCC, DMAP.

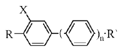
Va,**b**, **VIa**–**d** and found that the new chiral liquid crystalline laterally substituted biphenyls, terphenyls, or quaterphenyls **VIIa**–**i**, **VIIIa**–**f**, **IXa**–**c**, **Xa**–**f**, **XIa**–**j**, **XIIa**–**g** (see tables 5–10) can be prepared under the same reaction conditions (see scheme 3).



In the above structures *R* and *R′* are chiral or non-chiral alkyl (C_nH_{2n+1}) alkoxy (OC_nH_{2n+1}) or oxycarboxylate (OOC_nH_{2n+1}); K_1, K_2=single bond or benzene ring; Z_1, Z_2=single bond, COO or OOC.

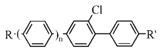
Chloro(methyl)biphenyls, terphenyls or quaterphenyls **VIIa**–**i**, **VIIIa**–**f** (see tables 5,6) were synthesized by treating the 3-(4-methoxyaryl)-6-substituted cyclohex-2-enones **A** with phosphorous pentachloride or using the Grignard reaction with methyl magnesium iodide and then by similar transformations of the intermediated methoxyderivatives **G**, **I**, applied before for the preparation of the cyclohex-2-enones **Ia**–**f**, **IIa**–**c**, **IVa** (see

Table 5. Transition temperatures of the compounds **VIIa–i**.



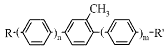
					Transition temperature/°C						
Compound	*R*	*X*	*n*	*R′*	Cr		SmC		SmA		I
VIIa	$H_{17}C_8$	Cl	1	OCit	—		—		—		•
VIIb	Cit	Cl	2	C_5H_{11}	•	<20	•	92	•	110	•
VIIc	$H_{17}C_8$	Cl	2	C_5H_{11}	•	76	—		•	132	•
VIId	$H_{11}C_5$	Cl	2	OC_8H_{17}	•	108	•	139	•	160	•
VIIe	$H_{21}C_{10}$	Cl	2	$OCH(CH_3)C_4H_9$	•	27	•	(27)	•	38	•
VIIf	$H_{21}C_{10}$	Cl	2	$OCH(CH_3)C_6H_{13}$	•	42	•	48	•	64	•
VIIg	$H_{21}C_{10}$	CH_3	2	$OCH(CH_3)C_5H_{11}$	•	22.5	•	28.5	•	50.5	•
VIIh	$H_{21}C_{10}$	CH_3	2	$OCH(CH_3)C_6H_{13}$	•	15	•	28	•	44	•
VIIi	$H_{17}C_8$	Cl	1	$OOCPhOCH(CH_3)C_6H_{13}$	•	24	•	44	•	89	•

Table 6. Transition temperatures of the compounds **VIIIa–f**.



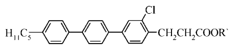
				Transition temperature/°C								
Compound	*R*	*n*	*R′*	Cr		SmC		SmA		N		I
VIIIa	H_9C_4	1	OCit	•		—		—		—	45	•
VIIIb	H_9C_4	1	OC_8H_{17}	•	56	—		—		•	87	•
VIIIc	H_9C_4	1	OC_8H_{17}	•	55	—		—		•	82	•
VIIId	$H_{11}C_5$	2	OC_8H_{17}	•	105	•	122	•	220	•	240	•
VIIIe	$H_{11}C_5$	2	$OOCC_7H_{15}$	•	84	•	95	•	230	•	257	•
VIIIf	$H_{11}C_5$	2	$OCH_2CH(CH_3)C_2H_5$	•	55	•	88	•	189	•	202	•

Table 7. Transition temperatures of the compounds **IXa–c**.



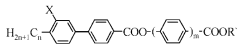
					Transition temperature/°C				
Compound	*R*	*n*	*m*	*R′*	Cr		SmA		I
IXa	$H_{13}C_6(CH_3)HCOOC$	2	1	C_3H_7	•	84	•	163	•
IXb	$H_{21}C_{10}O$	1	2	$COOCH(CH_3)C_6H_{13}$	•	71	•	157	•
IXc	$H_{21}C_{10}O$	1	2	$COOCH(CH_3)COOC_4H_9$	•	23.7	•	162	•

Table 8. Transition temperatures of the compounds **Xa–f**.



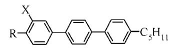
		Transition temperature/°C						
Compound	*R′*	Cr		SmC		SmA		I
Xa	$CH(CH_3)C_4H_9$	•	25	•	59	•	88	•
Xb	$CH(CH_3)C_6H_{13}$	•	32	•	52	•	76	•
Xc	$CH(CH_3)COOC_2H_5$	•	84	—		•	103	•
Xd	$C_6H_4O\ CH(CH_3)C_6H_{13}$	•	73	—		•	123	•
Xf	C_4H_9	•	53	•	66	•	107	•

Table 9. Transition temperatures of the esters **XIa–j**.

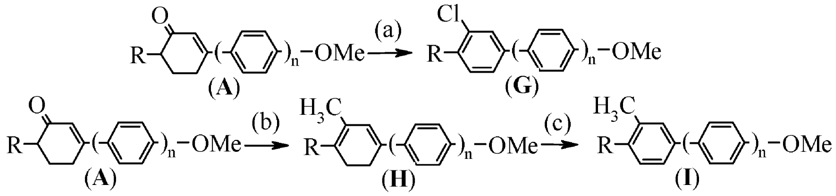


Compound	*n*	*X*	*m*	*R′*	Cr		SmC		SmA		N		I
					Transition temperature/°C								
XIa	5	Cl	1	$CH(CH_3)C_6H_{13}$	•		—		—		—	39	•
XIb	5	Cl	1	$CH_2CH(CH_3)C_2H_5$	•	65	•	(55)	•	94	•	103	•
XIc	10	Cl	1	$CH(CH_3)C_6H_{13}$	•	28	—		•		—	34	•
XId	10	Cl	1	$CH_2CH(CH_3)C_2H_5$	•	36	•	42.5	•		—	92	•
XIf	5	Cl	2	$CH(CH_3)C_6H_{13}$	•	98	•	117	•		—	184	•
XIg	10	Cl	2	$CH(CH_3)C_6H_{13}$	•	72	•	138	•		—	156	•
XIh	10	Cl	2	$CH_2CH(CH_3)C_2H_5$	•	94	•	154	•		—	223	•
XIi	10	CH_3	2	$CH(CH_3)C_6H_{13}$	•	44	•	107	•		—	140	•
XIj	10	CH_3	2	$CH_2CH(CH_3)C_2H_5$	•	68	•	129	•	195	•	200	•

Table 10. Transition temperatures of the compounds **XIIa–g**.



Compound	*R*	*X*	Cr		SmC		SmA		I
			Transition temperature/°C						
XIIa	C_8H_{17}	OH	•	198	—		•	214	•
XIIb	cit	OH	•	167	—		•	171	•
XIIc	C_8H_{17}	OCH_3	•	79	—		•	112	•
XIId	C_8H_{17}	$OOCCH_3$	•	35	—		•	62	•
XIIf	C_8H_{17}	$OCH(CH_3)_2$	•	43	—		•	47	•
XIIg	cit	OCH_3	•	<20	•	32	•	73	•

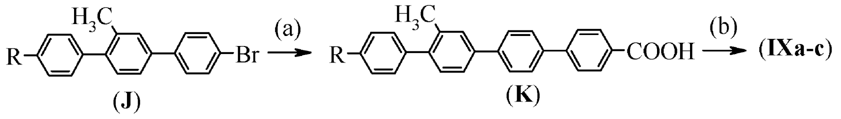


Scheme 3. (a) PCl_5; (b) CH_3MgJ; (c) J_2, iso-PrOH.

scheme 1). Unfortunately, in contrast to the analogous chloroaryls **G**, the aromatization of the intermediated dienes **H** in the conditions of the Grignard reaction proceeds very slowly and does not allow the preparation of the methylterphenyls **I** in one stage in a satisfactory yield. For the isolation of the desired products **I** in a high yield refluxing the reaction mixture in the presence of iodine is required (see scheme 3).

The chiral esters **IXa–c** (table 5) were synthesized by the cross-coupling (Suzuki) reaction [22] of the 4-substituted 2′-methyl(3′-methyl)-4″-bromoterphenyls **J** (prepared from the corresponding 3,6-disubstituted cyclohex-2-enones in the usual way) with 4-carboxyphenylboronic acid and then the esterification of the methylquaterphenylcarboxylic acids **K** with chiral alcohols (see scheme 4).

It should be noted that the esterification and the transformations shown in schemes 2 and 3 were also used for the synthesis of the esters **Xa–f**, **XIa–j** from 3-(2-cyanoethyl)-6-(4-substituted phenyl) cyclohex-2-enones **C** and 4-(6-alkylcyclohex-2-enon-3-yl)benzonitriles **D**.

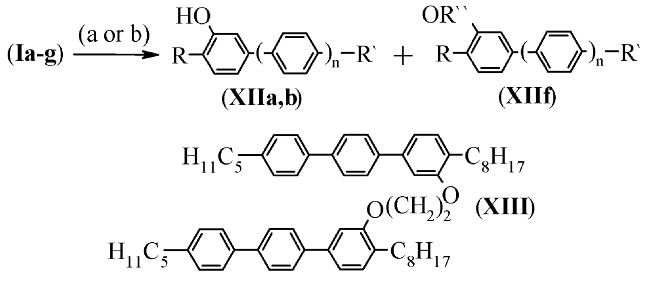


Scheme 4. (a) $(HO)_2BPhCOOH$, $Pd[P(Ph)_3]_4$; (b) HOR′, DCC, DMAP.

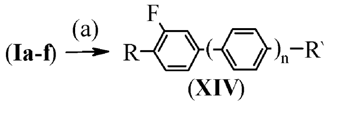
The interaction of the 3,6-disubstituted cyclohex-2-enones **Ia–g** with *N*-bromosuccinimide resulted in the formation of the laterally substituted hydroxy derivatives **XIIa**,**b**, which are intermediates for the synthesis of the corresponding methoxy and acetoxy derivatives **XIIc**,**d**,**g** (see scheme 5 and table 10). As our investigations have shown, the aromatization of the cyclohexenone fragment also proceeds in the presence of iodine in boiling alcohols. However, in that case, the reaction gives a mixture of the hydroxyterphenyls **XIVa**,**b** and the corresponding ethers **XIIf**, **XIII** in 10–15% yield (see scheme 5).

Unlike the laterally substituted chloro derivatives **VIIa–f** the analogous fluoroterphenyls **XIV** cannot be successfully prepared by the fluorination of 3,6-disubstituted cyclohex-2-enones **Ia–f** with diethylaminosulphur trifluoride (DAST) or with a 70% hydrogen fluoride pyridine (HF Py) complex. The reaction proceeds very slowly and results in an unsatisfactory yield of the products **XIV** (see scheme 6). For the synthesis of the chiral laterally substituted fluoroterphenyls or quaterphenyls we have to use other reaction conditions or chemical reagents, or different synthetic routes.

The proton NMR spectra (δ, ppm) of the 3,6-disubstituted cyclohex-2-enones **Ia–g**, **IIa–c**, **IIIa**, **IVa**, **Va**,**b**, **VIa–d** showed that the multiplet at 6.20–6.55 ppm belongs to the proton located at the double bond of the cyclohexenone fragment. The signals at 6.80–7.65 ppm in the proton NMR spectra of the chiral liquid crystalline laterally substituted biphenyls, terphenyls or quaterphenyls **VIIa–h**, **VIIIa–f**, **IXa–c**, **Xa–f**, **XIa–j**, **XIIa–g** correspond to the protons in the aromatic fragments. The signals of the protons located on the first carbon atoms of the alkyl and alkoxy chains and the protons of the methoxy group are observed in the spectra at 2.65, 4.35, 3.80 and 3.90 ppm. The IR spectra of the cyanoderivatives **C**, **D** revealed the intense band at 2220 cm^{-1} which corresponds to the stretching vibrations of the cyano group.



Scheme 5. (a) NBS; (b) J_2, R″ OH.



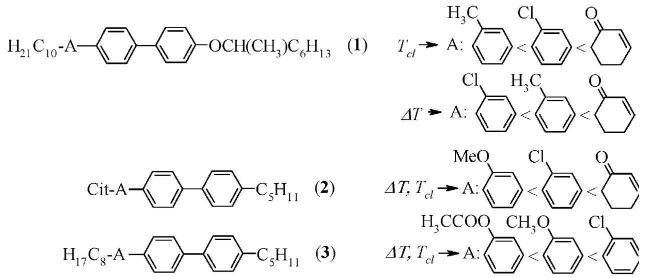
Scheme 6. (a) DAST or HF-Py.

2.3. *Mesomorphic properties*

The phase transition temperatures of the 3,6-disubstituted cyclohex-2-enones **Ia–g**, **IIa–c**, **Va**,**b**, **VIa–d** are listed in tables 1–4. As can be seen from table 1, the 3-(4-substituted phenyl)-6-alkyl cyclohex-2-enones **Ia–d** exhibit the smectic A phase in the temperature range 49–70°C. The introduction of an additional benzene ring results in the appearance of the smectic C phase in a wide temperature range (see compounds **If**,**g** table 1). Similarly, smectic C and A phases are observed for the esters **IIa–c**, **VIa–d** (see tables 2 and 4). It should be noted that the increase in the number of cyclic fragments within these compounds expands significantly the smectic C phase range. The four-ring cyclohexenone **IIc** shows a smectic phase in the overall temperature range 67–206°C. Unlike the esters **IIa–c**, **VIa–d** the ketones **Va**,**b** (see table 3) are characterized by the formation of a monotropic or enantiotropic smectic A phase in the temperature range 58–127°C.

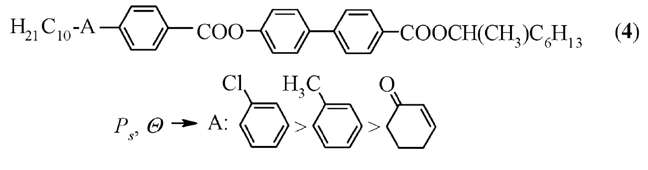
Tables 5–10 show the effect of the introduction of the different lateral substituents in the molecular core of the biphenyl, terphenyl or quaterphenyl derivatives **VIIa–i**, **VIIIa–f**, **IXa–c**, **Xa–f**, **XIa–j**, **XIIa–g** on their mesomorphic properties. The data presented reveal that the lateral substitution has a considerable effect on the phase transition temperatures, which depends upon the chemical structure of the compounds, and the type and the position of lateral substituents. This results in a lowering of the melting and clearing points due to the broadening of the molecules and a weakening of intermolecular interactions. The introduction of a chlorine atom or the methyl, alkoxy or acetoxy groups, coupled with the aromatization of the cylohexenone fragment, is also accompanied by a reduction in the temperature ranges of the smectic C and A phases. Like the 3,6-disubstituted cyclohex-2-enones and other three- or four-ring liquid crystals, these compounds are characterized by similar tendencies in the phase transition temperatures. Increasing the tail lengths and the introduction of an additional ring expand the smectic C and A ranges. It is also interesting to note the disappearance of the smectic C phase for the four-ring esters **IXa–c**, having a lateral methyl group at the benzene ring not connected to the terminal alkyl chain (see table 7). This may be explained by a weakening of the anisotropic intermolecular interactions as a result of the distortion of the coplanarity of the benzene rings caused by steric effects associated with the methyl group.

The efficiency of the cyclic fragment incorporated into the molecular core of the three-ring compounds can be expressed in terms of the orders of increasing clearing temperatures T_{cl} and the mesophase ranges ΔT for the structures **1**, **2** and **3**:



Investigations of the physical properties of compounds **Ia–g**, **IIa–c**, **IIIa**, **IVa**, **Va,b**, **VIa–d**, **VIIa–i**, **VIIIa–f**, **IXa–c**, **Xa–f**, **XIa–j**, **XIIa–g** have shown that their spontaneous polarizations and switching angles vary from 20 to 160 nC cm^{-2} and from 20° to 43°, respectively, and depend upon the chemical structures of the compounds (the type and the position of lateral substituents, and the number of cyclic fragments) (see figures 1 and 2).

The efficiency of the cyclic fragment incorporated into the molecular core of the four-ring compounds may be expressed by the orders of increasing spontaneous polarization $\mathbf{P}_{\mathrm{s}}$ and the switching angle Θ of the structure **4**:



It should be noted that the introduction of an additional benzene ring also leads to an increase of $\mathbf{P}_{\mathrm{s}}$ and Θ. The values of these parameters increase on passing from two-ring to three-ring and then four-ring compounds.

The investigations of the electro-optical properties of the 3,6-disubstituted cyclohex-2-enone derivatives **Ia–g**, **IIa–c**, **IIIa**, **IVa**, **Va,b**, **VIa–d** have revealed their main advantages in comparison with the biphenyl, terphenyl or quaterphenyl derivatives **VIIa–i**, **VIIIa–f**, **IXa–c**, **Xa–f**, **XIa–j**, **XIIa–g**. The spontaneous polarizations of these compounds are not high and vary from 20 to 90 nC cm^{-2} depending upon the chemical structures of the ketones. However, hysterisis-free transmission–voltage curves, and V-shaped or thresholdless switching are observed for them and for their FLC mixtures with one another, over wide temperature ranges and at different frequencies (see figures 3–5).

Detailed investigations have shown that these materials are truly ferroelectric and not antiferroelectic. This behavior may be explained by the geometry of the ester molecules and the specific lateral interactions of the cyclohex-2-enone fragment with the surface.

Additional investigations have shown that V-shaped switching is also observed for the chiral aryl esters of the 4-alkyl-3-chlorobiphenyl-4′-carboxylic acids **XIa–h**. However, unlike the cyclohex-2-enone derivatives, these compounds and mixtures based upon them, and similar to other FLC compounds [23], form V-shaped and hysteresis-free transmission–voltage curves over a wide temperature range, but only at low frequencies of applied electric field.

It is interesting to note that short pitch FLC mixtures with promising parameters for their practical application have been developed based on the chiral aryl esters of 4-alkyl-3-chlorobiphenyl-4′-carboxylic (**XIa–h**) and 4-(6-alkylcyclohex-2-enon-3-yl)benzoic (**VIa–d**) acids (see table 11).

Taking into account that the four ring esters **XIf–j**, and other chiral derivatives of terphenyl **VIIe–i** and quaterphenyl **Xf** are characterized by high birefringence, we also developed high optical anisotropy FLC mixtures based upon them. The data from detailed investigations of the electro-optical properties of the FLC mixtures prepared are presented in table 12 and in figures 6 and 7. Those show that the FLC mixtures have a wide temperature range SmC phase, from <20 to +83°C; a value of spontaneous polarization from 30 to 170 nC cm^{-2}; a tilt angle ranging from 20° to 40°; a helical pitch (>0.2 μm) and a constant value of the optical anisotropy (~0.35). These mixtures have been prepared using different percentages of the biphenyl, terphenyl and quaterphenyl derivatives **VIIa–h**, **VIIIa–f**, **IXa–c**, **Xa–f**, **XIa–j**, **XIIa–g**. It was also found that using methyl laterally substituted esters **XIi,j** and other similar methyl laterally substituted chiral compounds, which

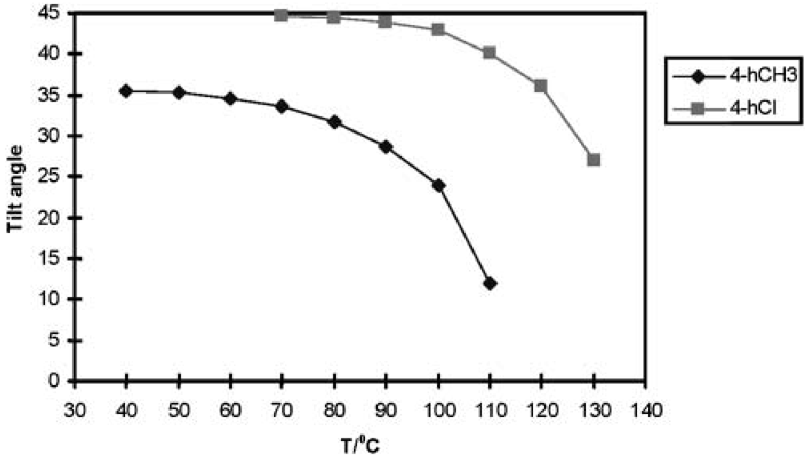


Figure 1. Temperature dependence of the tilt angles of the esters **XI g,i**.

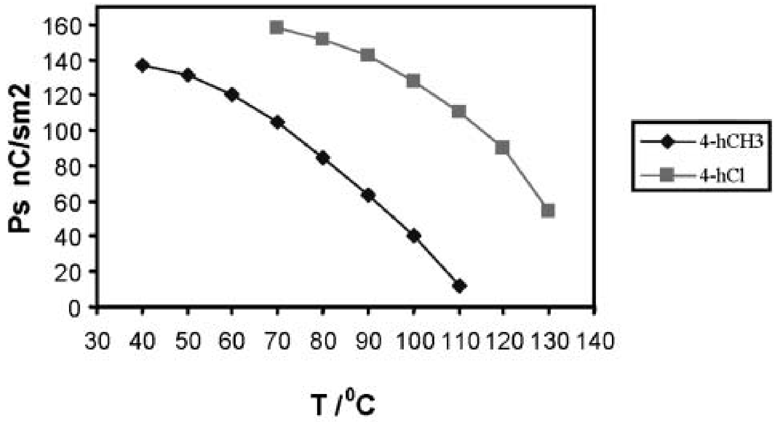


Figure 2. Temperature dependence of the spontaneous polarizations of the esters **XI g,i**.

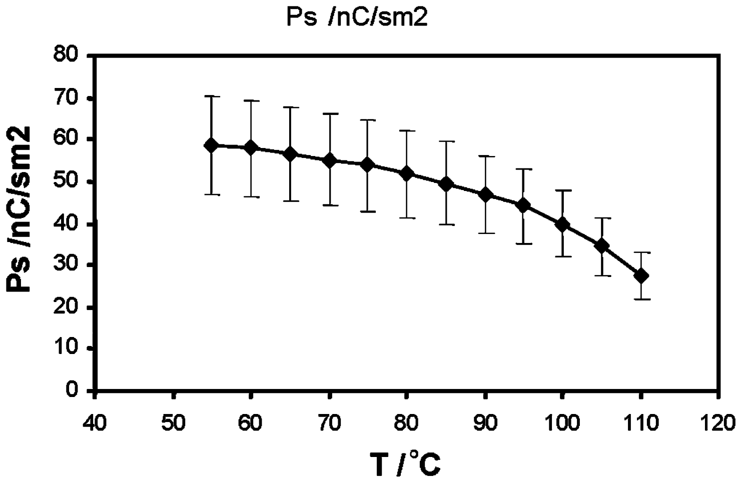


Figure 3. Spontaneous polarization of ester **VId**.

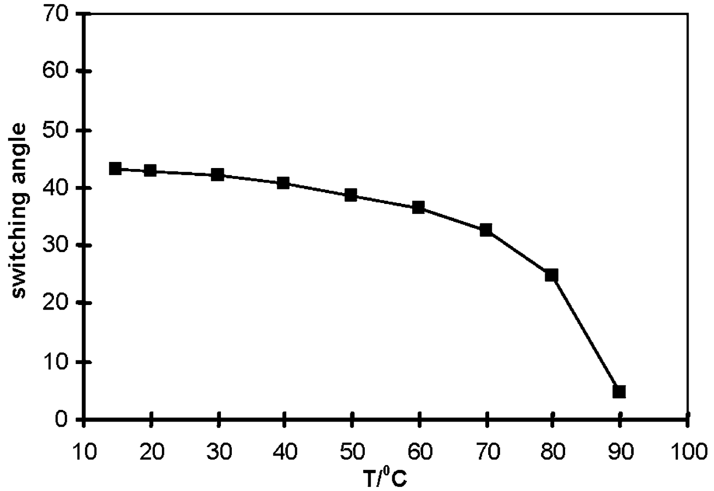


Figure 4. Switching angle of FLC mixture of esters **VIa**,**b**,**d**.

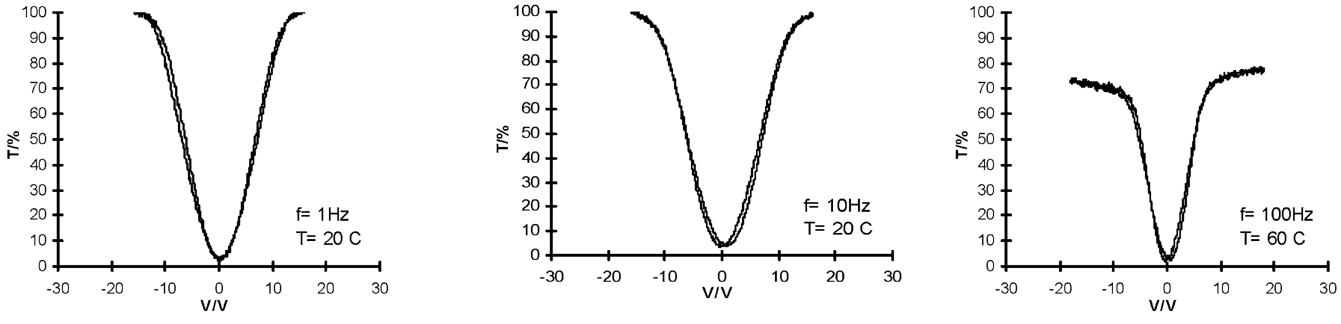


Figure 5. Electro-optical response of FLC mixture of the esters **VIa**,**b**,**d**.

Table 11. Physical parameters of the short pitch FLC mixtures.

Mixture	SmC* temperature range/°C	Operating voltage/ V μm^{-1}	Spontaneous polarization/ nC cm^{-2}	Helical pitch/ μm	Switching angle/°	Δn
LBSP-11	17–120	5.6	79	0.28	73	0.25
LBSP-12	15–120	4.8	80	0.32	70	0.24
LBSP-14	10–70	4.6	120	0.44	76	0.256
LBSP-17	13–102	4	86	0.35	62	0.25
LBSP-23	0–47	2.7	72	0.22	64	0.225
LBSP-43	0–62	3.3	71	0.2	60	0.23
LBSP-58	0–69	4.0	75	0.3	74	0.25
LBSP-59	0–79	2.8	79	0.15	65	0.24

Table 12. Physical parameters of the FLC mixtures with high optical anisotropy. Chemical structures of the components of the FLC mixtures are presented in Table 13.

Mixture	SmC* temperature range/°C	Operating voltage/V μm^{-1}	Spontaneous polarization/ nC cm^{-2}	Tilt angle/°	Δn
LBHS-9	20<−+69	10	173	35.8	0.245
LBHS-12	20<−+85	10	55	31.5	0.335
LBHS-13	20<−+72	10	147	29.2	0.335
LBHS-17	~20−+73	10	75	36.9	0.335
LBHS-19	20<−+83	10	82	30.2	0.34

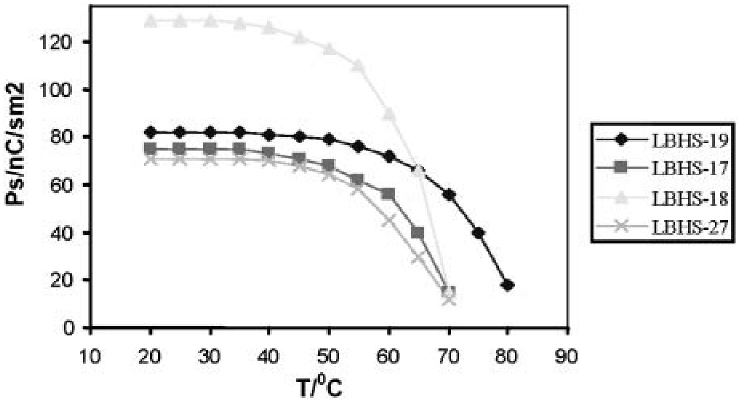


Figure 6. Temperature dependence of the spontaneous polarization of the FLC mixtures.

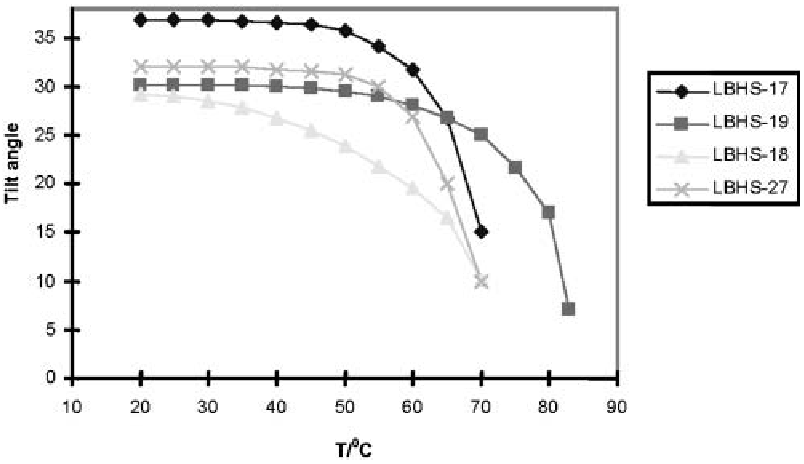


Figure 7. Temperature dependence of the tilt angle of the FLC mixtures.

form a smectic C phase, allows the transition temperature from crystal to smectic C phase to be decreased; and also increases the spontaneous polarization of the FLC mixtures without significant changes in other parameters

These results reveal that the effects on the parameters of the mixtures strongly depend on the chemical structures of their components and that the use of laterally substituted chiral biphenyl, terphenyl or quaterphenyl derivatives (see table 13) is advantageous in the preparation of FLC mixtures having wide temperature range SmC phases, high tilt angles and high optical anisotropy.

The results presented also demonstrate that lateral substitution of the fragments incorporated into the molecular core of the ferroelectric liquid crystals can provide desirable variations in their mesomorphic, dielectric and optical properties, in the values of spontaneous polarization and tilt angle, and these can be used as components in enhanced mixtures for FLC display applications.

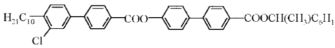
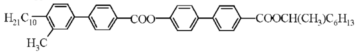
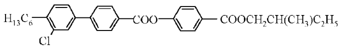
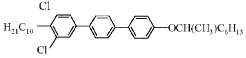
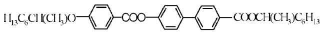
We plan to synthesize other structurally similar LC compounds to assess their ability to generate the SmC phase at low temperature and over wide temperature ranges. We hope that the new results of our investigations may lead to a better understanding of the nature of ferroelectric liquid crystals and facilitate their use in display applications.

3. Experimental

The structures of the compounds prepared were confirmed by ^{1}H NMR and mass spectroscopy. Phase transition temperatures were measured using a Linkam heating stage having a polarizing PZO microscope and also using a Setaram DSC 92.

Electro-optical studies were performed in glass cells supplied with ITO electrodes (with the receptivity

Table 13. The influence of the chemical structures of compounds on the main parameters of FLC-mixtures.

Compound	Δn	tilt angle	$\mathbf{P}_s$	T_{Cr-SmC}	$T_{SmC-SmA}$
	↑	↑	=	=	↑
	↑	=	↑	↓	↑
	=	↑	=	↓	=
	=	↓	↓	↓	=
	=	↑	↑	↓	=

150 Ohm cm^{-2}) and SiO_2 insulating layers 170 nm thick. Aligning layers (nylon 6, 130 nm) were spun and unidirectionally rubbed. The thickness of the cells was about 1.9 µm and measured in each case interferometrically. During the electro-optical measurements the temperature of the cells was controlled with the accuracy 0.3°C and the gradients across the sample did not exceed 1°.

The 3,6-disubstituted cyclohex-2-enones **Ia**–**g**, **IIa**–**c**, **IIIa**, **IVa**, **Va**,**b**, **VIa**–**d**, chloro(methyl)biphenyls, terphenyls or quaterphenyls **VIIa**–**i**, **VIIIa**–**f**, and the esters **Xa**–**f**, **XIa**–**j** were prepared according to previously published methods [10–17, 19–21].

3.1. *Chiral esters of substituted quaterphenylcarboxylic acids (*IXa–c*)*

A mixture of 0.15 mmol tetrakis(triphenylphosphine)-palladium, $Pd(PPh_3)_4$, 3.1 mmol 4-substituted 2′-methyl(3′-methyl)-4″-bromoterphenyl (**J**) (prepared from the corresponding 3,6-disubstituted cyclohex-2-enone by the Grignard reaction with methyl magnesium iodide), 4.1 mmol 4-carboxyphenylboronic acid, 5 ml 2M aqueous sodium carbonate and 35 ml dimethoxyethane was boiled for 35 h. To the mixture, 30% hydrogen peroxide was added slowly at room temperature. The organic layer was shaken with chloroform and the extract dried over anhydrous magnesium sulphate. The solvent was evaporated and the remaining crystals were used in next stage without additional purification.

A mixture of 2.0 mmol 4-substituted 2′-methyl(3′-methyl)quaterphenyl-4‴ carboxylic acid (**K**), 3.5 mmol of the corresponding optically active alcohol, 4.0 mmol dicyclohexylcarbodiimide and a catalytic amount of *N*,*N*-dimethylaminopyridine in 30 ml methylene chloride was stirred over night and the mixture filtered through a silica gel layer. After removing the solvent, the product was isolated by chromatography on silica gel using hexane/ethyl acetate (5/1) as eluant and purified additionally, after removing volatiles, by recrystallization from acetone. The yield was 57–65%. The transition temperatures of the compounds **IXa**–**c** are given in table 7.

3.2. *4-Octyl-3-hydroxy-4″-pentylterphenyl (*XIIa*) and 4-octyl-3-isopropoxy-4″-pentylterphenyl (*XIIf*)*

A mixture of 4.5 mmol 3-(4-pentylbiphenyl-4″)-6-octyl-cyclohex-2-enone and 9.0 mmol iodine was boiled for 45 h in 50 ml isopropyl alcohol, then cooled and water added. The organic layer was extracted into ether. The ethereal extract was washed with aqueous sodium bisulphite, then water and dried over anhydrous magnesium sulphate. The solvent was evaporated and the remaining products isolated by chromatography on silica gel using hexane/ethyl acetate (3/1) as eluant and purified additionally, after removing volatiles, by recrystallization from acetone or isopropyl alcohol. The yield of 4-octyl-3-hydroxy-4″-pentylterphenyl (**XIIa**) was 51% and 4-octyl-3-isopropoxy-4″-pentylterphenyl (**XIIf**) 7%. The transition temperatures of the compounds **XIIa**,**f** are given in table 10.

Acknowledgements

This research work was supported by the Internationales Büro (BMBF/DLR: Project no: BLR02/004).

References

[1] G.W. Gray. *Thermotropic Liquid Crystals, Crytical Reports on Applied Chemistry* Vol. 22, Wiley (1987).

[2] D. Coates. *Liquid Crystals; Applications and Uses* Vol. 1, B. Bahadur (Ed.), pp. 91, World Scientific Publishing (1990).

[3] T. Geelhaar. *Liq. Cryst.*, **24**, 91 (1998).

[4] D. Demus. *Handbook of Liquid Crystals* Vol. 1, edited by, D. Demus, J. Goodby, G.W. Gray, H.-W. Spiess, V. Vill (Eds), pp. 133, Wiley-VCH, Weinheim (1998).

[5] D. Demus, H. Zaschke. *Flussige Kristalle in Tabellen II.* VEB Deutscher Verlag f. Grundstoffindustrie, (1984).

[6] V. Vill. *LiqCryst 3.0, Database of Liquid Crystalline Compounds for Personal Computers.* LCI Publisher GmbH (1997).

[7] V.S. Bezborodov, V.F. Petrov. *Liq. Cryst.*, **23**, 771 (1997).

[8] K. Miyazawa, T. Kato, M. Iton, M. Ushioda. *Liq. Cryst.*, **29**, 1483 (2002).

[9] R. Asep, Y. Aoki, T. Hirose, H. Norita. *Liq. Cryst.*, **28**, 785 (2001).

[10] V.S. Bezborodov, R. Dabrowski. *Mol. Cryst. liq. Cryst.*, **299**, 1 (1997).

[11] V.S. Bezborodov, R. Dabrowski, J. Dziaduszek, V.F. Petrov. *Liq Cryst.*, **23**, 69 (1997).

[12] V.S. Bezborodov, R. Dabrowski, G. Sasnouski, J. Dziaduszek, V.F. Petrov. *Liq Cryst.*, **24**, 647 (1998).

[13] W. Tykarski, V.S. Bezborodov, J. Dziaduszek, R. Dabrowski. *Proc. SPIE*, **3319**, 31 (1998).

[14] V. Bezborodov, R. Dabrowski. *Proc. SPIE*, **2372**, 242 (1994).

[15] V.S. Bezborodov, G. Sasnovski, V. Lapanik, R. Dabrowski, K.H. Uh. *Ferroelectrics*, **212**, 373 (1998).

[16] V.S. Bezborodov, R. Dabrowski, J. Dziaduszek, K. Czuprynski, Z. Raszewski. *Liq. Cryst.*, **20**, 1 (1996).

[17] V.S. Bezborodov, R. Dabrowski, G. Sasnovski, J. Dziaduszek. *Mol. Cryst. Liq. Cryst. Sci. and Technol*, **303**, 297 (1997).

[18] O. Mitsunobu. *Synthesis*, 1 (1981).

[19] V. Bezborodov, V. Lapanik, G. Sasnouski. *Ferroelectrics*, **243**, 49 (2000).

[20] V. Bezborodov, V. Lapanik, G. Sasnouski. *Liq. Cryst.*, **27**, 935 (2000).

[21] V. Bezborodov, V. Lapanik, G. Sasnouski. *Liq. Cryst.*, **28**, 897 (2001).

[22] A. Suzuki. *J . Organomet. Chem.*, **576**, 147 (1999).

[23] S.T. Lagerwall. *Ferroelectric and Antiferroelectric Liquid Crystals*. Wiley-VCH, Weinheim (1999).