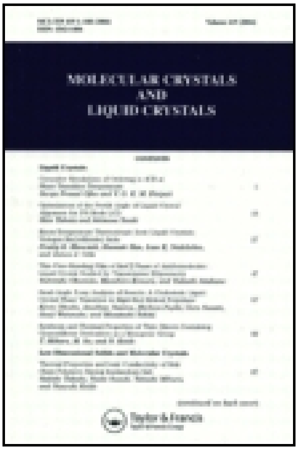

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Synthesis and Properties of New Liquid Crystalline Materials

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Synthesis and Properties of New Liquid Crystalline Materials

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(*Received August 11, 1980*)

1 INTRODUCTION

In the last years several reviews on liquid crystalline substances were published.[1–9] These reviews concern different topics, however, mainly aspects of practical use of liquid crystals. Now we try to give a survey on the activities of the Halle Liquid Crystal Group in the last years with respect to synthesis and physicochemical investigation of new materials for liquid crystal displays.

2 SUBSTITUTED PHENYL 4-*n*-ALKYLCYCLOHEXANOATES

In the substance class of the 4-*n*-alkylcyclohexanoates[9,10] especially the 4-cyanophenyl and 4-*n*-alkyloxyphenyl esters are of interest. The synthesis may be done according to well described procedures.[11] Figure 1 displays the properties of an example typical for the cyanophenyl esters. Due to the high stability with respect to chemical and thermal influences and UV irradiation, the relatively high dielectric anisotropy and low viscosity, these cyanophenyl esters are well suited for use in electrooptical displays. There are mixtures of several of these substances with clearing points above 70°C and threshold voltages about 1.5 V. They may be remarkably supercooled and show short transient times. Figure 2 displays the properties of a mixture which we use

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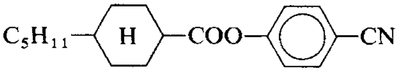
† Invited lecture, presented at Eighth International Liquid Crystal Conference, Kyoto (Japan), June 30–July 4, 1980.



Cr 47.2 N 79.2 is

Melting enthalpy: $\Delta H = 26.7$ kJ/mole

Dielectric anisotropy: $\Delta\varepsilon = +7$ (50°C)

Viscosity: $\eta_1 = 12$ cSt (50°C)

Optical anisotropy: $\Delta n = 0.10$ (50°C)

Threshold voltage in twist cells:

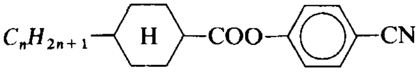
$U_{thr} = 1.4$ V/500 Hz, 50°C

FIGURE 1

as a basic mixture. Such basic mixtures may be modified by addition of one or more compounds of the same or other substance classes. E.g., by addition of two 4-*n*-alkyloxyphenyl 4-*n*-alkylcyclohexanoates[13] we obtained mixtures with melting temperatures about 0°C and threshold voltages of 1.7 V, clearing temperatures about 70°C.

The substituted phenyl alkylcyclohexanoates are well miscible with standard substances as alkylcyanobiphenyls, cyanophenyl alkylbenzoates and pyrimidine derivatives.[12,13]

Basic Mixture Mi 14



$n = 3$ 34.5 mole %

$n = 4$ 31 mole %

$n = 5$ 34.5 mole %

Melting: 10–14°C (metastable)
12–16°C (stable)

Clearing: 72°C

In twist cells:

$U_0 = 1.4$ V/500 Hz (25°C)

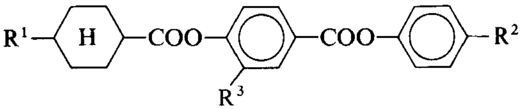
t_{on} (50%) = 560 ms ($U = 3.4$ V, 20°C)

t_{off} (50%) = 180 ms ($d = 20$ μm, 20°C)

FIGURE 2

3 4-SUBST.-PHENYL-4-[4-*n*-ALKYLCYCLOHEXYLCARBONYLOXY]-3-SUBST. BENZOATES

The transition temperatures of some esters of this type[14,15] are displayed in Figure 3. Compared with the analogous benzoates,[16] the melting points are lower, the clearing temperatures remarkably higher. Their chemical and thermal stability is comparable with the benzoates. The cyano substituted compounds possess high positive dielectric anisotropy and are well miscible with standard substances.

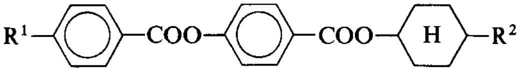


R^1	R^2	R^3	m.p.	cl.p.
C_2H_5	C_4H_9	H	66	180
C_2H_5	$C_8H_{17}O$	H	58	175
C_2H_5	CN	H	90	235
C_4H_9	CN	CH_3	103	184
C_6H_{13}	$C_7H_{15}O$	C_2H_5	44	117

FIGURE 3

4 4-SUBST.CYCLOHEXYL 4-[4-SUBST.-BENZOYLOXY]-BENZOATES

The transition temperatures of some examples are listed in Figure 4. Obviously the exchange of the substituted phenyl group[16] by the cyclohexyl ring in esters of this type[14,15] does not promote the liquid crystalline properties as in the case of the above mentioned cyclohexanoates. However, these three ring compounds may be useful as additives in mixtures.



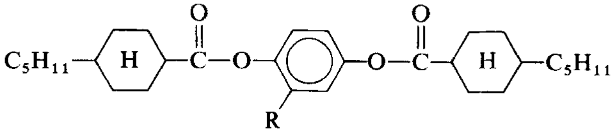
R^1	R^2	m.p.	cl.p.
C_6H_{13}	CH_3	60	105
C_6H_{13}	C_5H_{11}	73	146
C_2H_5O	C_4H_9O	95	150

FIGURE 4

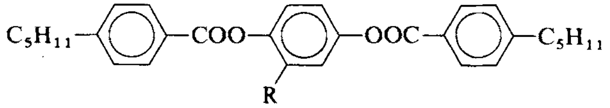
5 3-SUBST.-HYDROQUINONE BIS-[4-*n*-ALKYLCYCLOHEXANOATES]

These derivatives of alkylcyclohexyl carboxylic acids[14,15] possess lower melting and higher clearing temperatures than the corresponding benzoates,[17–20] see Figure 5.

These esters exhibit negative dielectric anisotropy. Due to their advantageous transition temperatures they can be used in displays on the basis of the dynamic scattering effect.



R	Cr		S		N		is
H	·	123	—		·	216	·
CH_3	·	77	—	—	·	186	·
C_2H_5	·	43	—	—	·	133	·
Cl	·	70	—	—	·	190	·
CN	·	66	·	96	·	176	·



R	Cr		N		is
H	·	125	·	188	·
CH_3	·	78	·	146	·
C_2H_5	·	63	·	100	·
Cl	·	79	·	145	·
CN	·	86	·	129	·

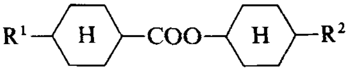
FIGURE 5

6 4-SUBST.-CYCLOHEXYL 4-*n*-ALKYLCYCLOHEXANOATES

The above mentioned cyclohexane derivatives prove the ability of the cyclohexane ring to exchange each one of the benzene rings in substituted phenyl benzoates without loss of the liquid crystalline properties. Therefore, the exchange of both the benzene rings by cyclohexane also seemed to allow the synthesis of liquid crystalline substances. Independently Osman and Revesz[21] as well as our group[22–25] realized the synthesis of 4-subst.-cyclohexyl 4-*n*-alkylcyclohexanoates.

As the selected examples in Figure 6 prove, the dialkyl series tends strongly to smectic behaviour. Only the lowest members are nematic. The introduction of the cyano group, which in the biphenyl derivatives was so helpful in obtaining nematic substances, enhanced the melting temperature without producing a stable nematic phase.

trans, trans-4-subst.-cyclohexyl 4-*n*-alkylcyclohexanoates



R^1	R^2	Cr		S		N		is	Ref.
CH_3	C_3H_7	·	19.9	—		(·	−18.2)	·	21
C_3H_7	C_3H_7	·	22.8	—		·	36.6	·	21
C_3H_7	C_5H_{11}	·	24	·	51.5	·	54	·	22–25
C_7H_{15}	C_5H_{11}	·	27	·	78.5	—		·	22–25
C_5H_{11}	CN	·	59.8	—		(·	16†)	·	21

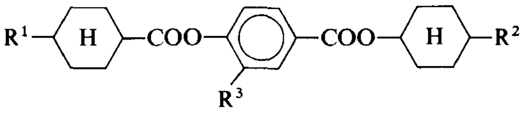
† Extrapolated from mixtures.

FIGURE 6

The dialkyl derivatives are expected to have extremely low optical anisotropics which may be useful for guest-host and Schadt-Helfrich-displays.[21] Otherwise, as the low off-times of their mixtures in electrooptical cells indicate, they possess low viscosities.

7 4-SUBST.-CYCLOHEXYL 4-[4-ALKYLCYCLOHEXANOYLOXY]-BENZOATES

As the bis-cyclohexanoates of the substituted hydroquinones prove, three ring compounds with two cyclohexane moieties can have pronounced nematic properties. Therefore the introduction of an additional benzene ring into the substituted cyclohexyl alkylcyclohexanoates was done.[24,25] Figure 7 shows some examples. They have relatively low melting temperatures, high clearing points and small positive dielectric anisotropy. Up to higher chain lengths the homologs show only nematic behaviour.



R^1	R^2	R^3	m.p.	cl.p.
C_2H_5	C_4H_9	H	62	162
C_2H_5	C_5H_{11}	H	59	163
C_2H_5	C_5H_{11}	CH_3	53	163
C_4H_9	C_4H_9	CH_3	75	175

FIGURE 7

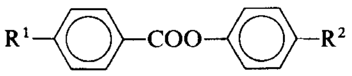
8 NEW SUBSTITUTED PHENYL BENZOATES WITH POSITIVE DIELECTRIC ANISOTROPY

Well known substituted phenyl benzoates with high positive dielectric anisotropy are the 4-hydroxybenzonitrile[26,27] and the 4-hydroxy-cinnamonitrile[27] esters of 4-substituted benzoic acids, see e.g. Nos. 1 and 2 in Figure 8. All derivatives of cinnamic acids are sensitive against UV-irradiation, they tend to cis-trans-isomerization.

Therefore, we synthesized and investigated the saturated analogon to the 4-hydroxy-cinnamonitrile esters, namely the 4-(β-cyanethyl)-phenyl 4-subst.-benzoates,[28] in which that photoisomerization is impossible. No. 3 in Figure 8 is an example, some properties of which are listed in Figure 9. The clearing temperatures of this substance class are generally lower than that of the hydroxybenzonitrile and hydroxy-cinnamonitrile ester, therefore many cyanethylphenyl esters show only monotropic liquid crystalline properties.

If in the hydroxy-cinnamonitrile the α-H-atom is exchanged by the CN-group, the 1-hydroxy-4-dicyanoethenyl-benzene results. We prepared different esters[29] of this product, e.g. No. 4 in Figure 8, and Figure 10. It is obvious

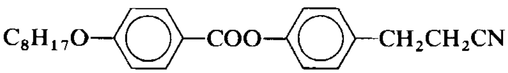
Substituted phenyl benzoates



No.	R^1	R^2	m.p.	cl.p.	$\Delta\varepsilon$	Ref.
1	$C_8H_{17}O$	CN	75.6	88.0	+13.7 (76°C)	26, 27
2	C_4H_9	CH=CH—CN	106.0	154.0	+10.7 (125°C)	27
3	$C_8H_{17}O$	CH_2—CH_2—CN	56	58	+ 5.5 (54°C)	28
4	$C_6H_{13}COO$	CH=C$(CN)_2$	84	102	+ 9.5 (80°C)	29

FIGURE 8

4-(β-cyanethyl)-phenyl 4-*n*-octyloxybenzoate



Cr 56 N 58 is

$\Delta\varepsilon = +5.5$ 54°C)

$\eta_1 = 79$ cSt (54°C)

Relaxation frequency of $\varepsilon_{\parallel}$: 0.9 MHz (53°C)

For frequencies > 1 Mz: $\Delta\varepsilon < 0$

Suited for "two frequency addressing displays"

FIGURE 9

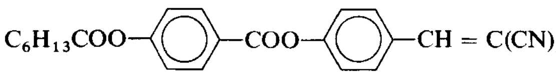
from the chemical formula, that photochemical processes cannot change the conformation of the dicyan-ethenyl side chain. The extremely strong electron acceptor properties of this substance class may cause coloured EDA-complexes in mixtures.[30] Otherwise, this substance class shows a pronounced smectogenic behaviour.

9 SUBSTITUTED 2-PHENYL-(1,3)-DIOXANES

In the substance classes of heterocyclic liquid crystalline compounds with which the Halle Liquid Crystal Group is concerned already for many years,[5,7,31] now a new example can be presented. Derived from 1,3-dioxane, a lot of differently substituted compounds were synthesized[32] according to the way displayed in Figure 10 a.

1,3-Dioxane derivatives are obtained by reaction of propane 1,3-dioles and substituted aldehydes in the presence of catalytic amounts of acids (e.g. *p*-toluene-sulfonic acid) with aceotropic removal of water. By repeated re-crystallization from methanol and *n*-hexane pure trans-isomers were obtained.

4-Dicyanoethenyl-phenyl 4-*n*-Heptanoyloxybenzoate



Cr 84 N 102 is

$\Delta\varepsilon = +9.5\ (80°C)$

$\eta_1 = 63$ cSt (80°C)

Substance has strong electron acceptor properties: in mixtures often EDA-complexes

(a) Synthesis of 1,3-dioxane derivatives

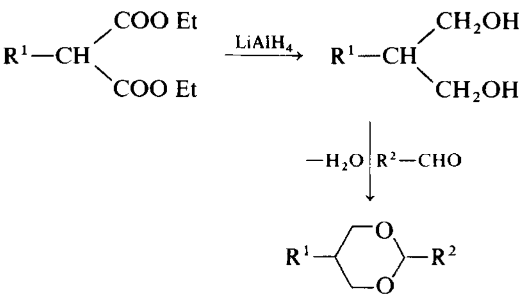


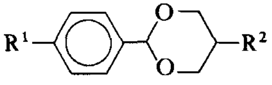
FIGURE 10

The substituted propane-1,3-dioles were synthesized by reduction of the diethyl malonates with $LiAlH_4$.

The substituted 2-phenyl-1,3-dioxanes[32,33] may be compared with the analogous substituted phenyl-cyclohexanes. Figure 11 shows the nematogenic character of dioxane derivatives with different substituents. Contrary to the phenylcyclohexanes[34,35] with low hypothetic clearing temperatures, the di-alkyl-substituted phenyldioxanes are enantiotropic liquid crystalline but they show strong smectic tendency.

Of special interest are the cyano substituted derivatives, e.g. Figures 12, 13. The clearing points of the two ring compounds are lower than the corresponding melting points. Due to their very low melting enthalpies, they show remarkable melting point depressions in mixtures. Mixtures of two or

5-Subst.-2-subst.phenyl-1,3-dioxanes



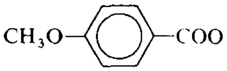
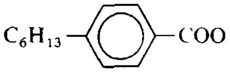
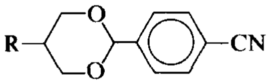
R^1	R^2	m.p.	cl.p.
C_4H_9O	C_5H_{11}	40	53
$C_5H_{11}O$	C_5H_{11}	38	50.5
	C_7H_{15}	85	193
	C_7H_{15}	80.5	148.5

FIGURE 11

5-Subst.-2-[4-cyanophenyl]-1,3-dioxanes



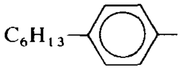
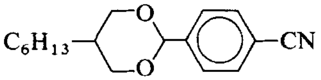
n	m.p.	cl.p.	
5	56	52	η_1 = 16. 8 (41°C) Δn = 0.08 (40°C) ΔH_{melt} = 21 kJ/mole
6	47	40.5	ΔH_{melt} = 22 kJ/mole
7	54	53	$\Delta \varepsilon$ = +11 (42°C) Δn = 0.09 (42°C)
	84	151	Δn = 0.14 (94°C) ΔH_{melt} = 34.8 kJ/mole

FIGURE 12

5-*n*-Hexyl-2[4-cyanophenyl]-1,3-dioxane



Twist cell, 35°C

$U_{\text{thr}} = 0.65$ V/50 Hz
$t_{\text{on}}(50\%) = 376$ ms ($U = 1.3$ V)
$t_{\text{off}}(50\%) = 190$ ms ($d = 21$ μm)

FIGURE 13

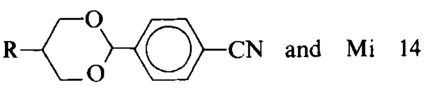
more 5-alkyl-2-[4-cyanophenyl]-1,3-dioxanes are therefore enantiotropic nematic, however, at lower temperatures also enantiotropic smectic phases exist. Added to standard mixtures as e.g. Mi 14 the two and three ring cyano substituted dioxanes yield mixtures with acceptable transition temperatures and low threshold voltages, see Figure 14.

Compared with the 4-*n*-alkyl-4′-cyano-phenyl-cyclohexanes (PCH),[35] the corresponding dioxanes possess somewhat lower optical anisotropics, but higher dielectric anisotropics. The latter phenomenon may be explained by the occurrence of additional dipole moments due to the oxygen atoms in the dioxane ring.

10 3,6-DISUBSTITUTED 1,2,4,5-TETRAZINES

In 1968 the guest-host-effect was proposed as a new principle for colour switching displays.[36] Till now, displays on the basis of this effect were not

Mixtures of



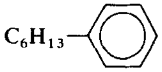
R	mole %	m.p.	cl.p.	U_0(V)
C_6H_{13}	10	−5.5 to +9	66	1.3
Mi 14	90			
C_6H_{13}	1.8			
	8.2	1 to 10	74	1.2
Mi 14	90			

FIGURE 14

realized in a large technical scale. This may be due mainly to the low light stability and the poor solubility of the available dyestuffs. In order to find new useful dyestuffs we tried to combine the colour absorption with liquid crystalline properties. Therefore our efforts started from the tetrazine ring which is absorbing in the visible spectrum and does allow to produce derivatives with liquid crystalline properties.[31]

Figure 15 displays the way of synthesis of different 3,6-disubstituted 1,2,4,5-tetrazines[37,39–41] by reaction of substituted benzimidoester hydrochloride 1 with aliphatic resp. aromatic amidinehydrochlorides 2 in the presence of hydrazine hydrate and following oxidation with sodium nitrite. The bye-products 4 and 5 are separated by recrystallization. Figures 16 and 17 show the transition temperatures of tetrazine derivatives with three resp. two rings.

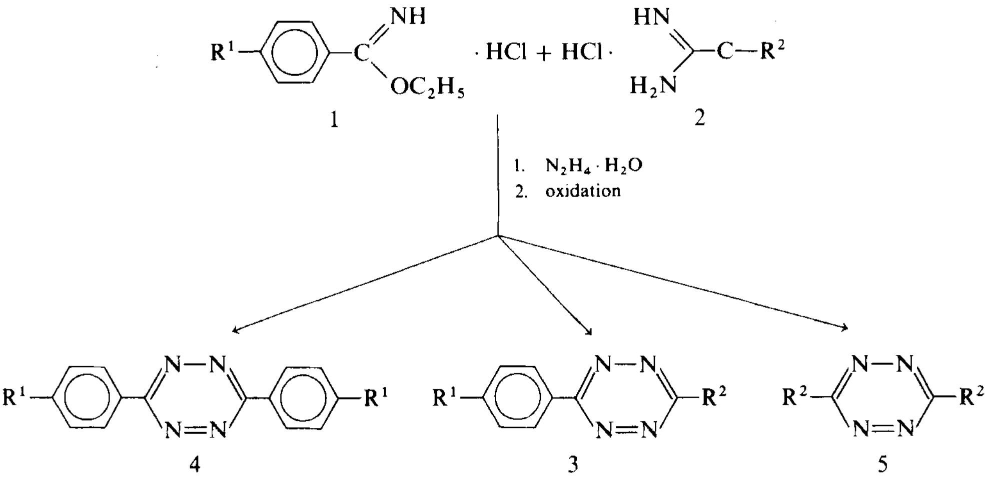
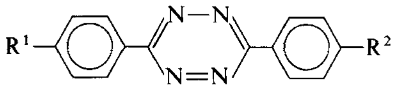


FIGURE 15

3,6-Bis-[4-subst.-phenyl]-1,2,4,5-tetrazines

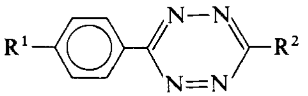


R¹	R²	Cr		N		is
$C_6H_{13}O$	C_9H_{19}	·	119	[a]	175	·
$C_7H_{15}O$	H	·	107	·	129	·
$C_9H_{17}O$	H	·	128	·	131	·

[a] Transition S/N 153.5°C.

FIGURE 16

3-*n*-Alkyl-6-[4-*n*-Alkyloxyphenyl]-1,2,4,5-tetrazines



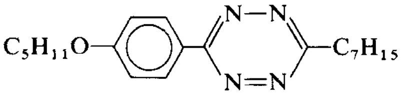
R^1	R^2	Cr		S_C		S_A		N		is
C_4H_9O	C_5H_{11}	·	55	·	—	—	—	·	59	·
C_4H_9O	C_6H_{13}	·	49	(·	43)	—	—	·	57	·
C_4H_9O	C_7H_{15}	·	47	(·	43.5)	—	—	·	62	·
$C_5H_{11}O$	C_4H_9	·	48	—	—	·	49	—	—	·
$C_5H_{11}O$	C_5H_{11}	·	60	—	—	—	—	(·	59.5)	·
$C_5H_{11}O$	C_6H_{13}	·	65	—	—	—	—	(·	58.5)	·
$C_5H_{11}O$	C_7H_{15}	·	49	·	52.5	—	—	·	63	·
$C_6H_{13}O$	C_5H_{11}	·	55	—	—	·	68	—	—	·
$C_6H_{13}O$	C_7H_{15}	·	58	·	67	·	74	·	76	·

FIGURE 17

All these compounds possess pronounced liquid crystalline properties, nematic and partly smectic phases. Compared with the analogous terphenyl resp. biphenyl derivatives, the tetrazines have a stronger tendency to exhibit nematic behaviour.

In Figure 18 the different properties of a substituted phenyltetrazine are

3-*n*-Heptyl-6-[4-*n*-pentyloxyphenyl]-1,2,4,5-tetrazine



cr 49.5 S_C 52.5 N 63 is

$\Delta H_{melt} = 26$ kJ/mole

Optical properties:

$\Delta n = 0.15$ (57°C, $\lambda = 646$ nm)

Optical spectrum:

1. Band in the visible region (555 nm); $\varepsilon = 550$ l · mole^{-1} cm^{-1}; $n \rightarrow \pi^*$ band, transition moment perpendicular to the ring plane, negative dichroism.
2. Band in the UV region (298 nm): $\varepsilon = 32{,}000$ l · mole^{-1} cm^{-1}.

Electrooptical properties:

Freedericksz transition in the pure substance, $d = 10$ μm

		U_{thr}(V)	t_{on}(ms) at $U = 3U_{thr}$	t_{off}(ms)
smectic C	(50°C)	14	29	46
nematic	(56°C)	7	18	110

FIGURE 18

listed. The tetrazines possess medium optical anisotropy. The most remarkable property is the absorption band at 555 nm, which causes the strong red colour of the tetrazine derivatives. The transition moment of this band is directed perpendicular to the molecular long axis, therefore these compounds exhibit negative dichroism.

Due to their positive dielectric anisotropy the Freedericksz transition may be observed already in the pure compounds, in the nematic as well as in the S_C phases.[37,38] The decay times of the Freedericksz transition in the S_C phase are remarkably lower than those of the nematic phases which offers interesting possibilities for practical applications in displays.

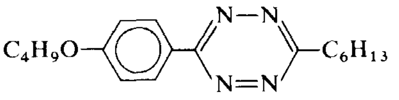
Of course, the main value of the tetrazine derivatives is not its use in the pure state, but the application as dyes for guest-host-effect displays. In this case the tetrazines may be added in amounts of 5 to 30% to standard mixtures, e.g. Mi 14 as compiled in Figure 19. The tetrazine derivatives are unexpectedly stable with respect to UV irradiation. Therefore they offer a good chance for the technical realization of guest-host-effect displays which are nearly colourless in the ground state and show red signs by electrical excitation. Addition of a second dye with positive dichroism allows the construction of displays which are switching from one colour to another.

11 SOME REMARKS ABOUT MOLECULAR STRUCTURE AND PROPERTIES

In the last years, in the field of liquid crystal synthesis the most remarkable advances were achieved by introduction of heterocyclic rings and the cyclohexane moiety. Besides expected effects, the introduction of these groups into the molecules yielded certain changes of the properties which could not be predicted so directly.

Mixture of

Basic Mixture Mi 14 80 mole %



20 mole %

m.p. 5–11°C
cl.p. 59°C

Can be supercooled to −15°C without appearance of smectic phases.

Planar oriented sample, one polarizer

Dichroic rato 4.5 (25°C)

U_{thr}: 1.4 Volt

FIGURE 19

In Figure 20 the optical (Δn^2) and the dielectric anisotropies ($\Delta\varepsilon$) of the 4-*n*-pentyl-benzoic acid resp. cyclohexane carboxylic acid are compared.[42] The differences between Δn^2 and $\Delta\varepsilon$ can be explained by a certain amount of monomeric molecules, the dipole moments of which are directed more or less perpendicular to the long axis. The double molecules, however, do not possess permanent electric dipole moments, therefore Δn^2 is a measure for the anisotropy of the polarizability. As expected, Δn^2 is much lower in the cyclohexane derivative. In all measured examples, the densities of the cyclohexane derivatives are lower than those of the benzene derivatives.[43] Therefore the relatively high clearing point of the pentyl cyclohexane carboxylic acid is surprising considering only the molecular attractive forces in the sense of the Maier-Saupe-theory.

In many other cases, e.g. in Figure 21, the clearing points of the cyclohexane derivatives are higher than those of the benzene derivatives. The comparison of the UV absorption spectra indicates that the high $\Delta\varepsilon$ of the cyanophenyl hexylbenzoate must be due partly to mesomeric effects which are not possible in the case of the cyclohexane derivative. Careful studies[42] in substituted phenyl benzoates, azobenzenes and pyrimidines prove the general role of such mesomeric effects for the dielectric properties.

Otherwise, the high clearing points of cyclohexane derivatives only can be explained by steric effects. Figure 22 shows the molecular structure of a substituted 2-phenyl-1,3-dioxane according to a complete structure analysis in the solid state.[44] As can be seen the molecule is nearer to an optimal elongated shape than a corresponding biphenyl derivative.

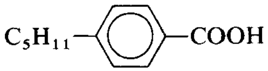
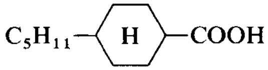
	$\Delta\varepsilon$	$\Delta n^2 = n_e^2 - n_0^2$	cl.p. (°C)
	0.35	0.42	127
	0.05	0.14	105

FIGURE 20

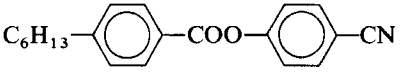
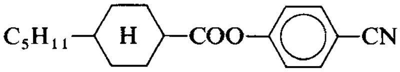
	$\Delta\varepsilon$ (τ = 0.026)	cl.p. (°C)	λ max (nm)
	+17	48	245
	+6.3	79	235

FIGURE 21

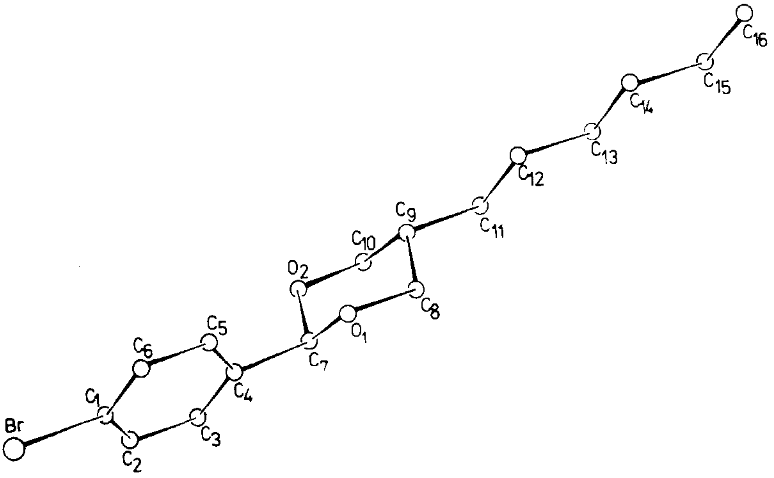


FIGURE 22

The occurrence of smectic phases instead of nematics very often is an undesirable effect for application of liquid crystals. In many cases the complex relations do not allow a clear prediction of smectic behaviour. As the comparison of the highly polar (e.g. cyano substituted) with less polar substituted compounds (e.g. biphenyl derivatives) shows, the high polarity favours nematic behaviour. Following an argument of de Jeu, this may be due to the better possibilities of distribution of the polar groups (which are repulsing one to another) in the nematic compared with the smectic state. Otherwise, as new results in binary systems indicate,[45,46] highly polar liquid crystal molecules can cause the formation of electron donor acceptor (EDA) complexes. Such complexes exist as defined pairs in fixed positions which obviously enhance the thermal stability of smectic phases considerably, so that in many cases smectic intermediate phases appear in binary systems of molecules which in the pure state are only nematic. The nematic clearing temperatures, however, seem to be not remarkably influenced.

Combinations of molecules which are highly polar substituted tend to the formation of EDA-complexes and intermediate smectic phases, if the groups are highly electron drawing resp. pushing. If the influence of the polar groups is not so pronounced also smectic intermediate phases may appear but without detectable EDA-complexes. The appearance of the smectic phases then may be interpreted in terms of dipole–dipole interactions. Obviously the differentiation into pure EDA resp. pure dipole–dipole interaction sometimes is not possible, but the influence of both effects can overlap.

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