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New chiral dopants for ferroelectric liquid crystals

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New chiral dopants for application in ferroelectric liquid crystal mixtures are presented. They derive from chirally modified biphenylcyclohexylcarbonitriles, lactates and optically active 2-cyano-2-methylalkanoates. Synthetic routes to the new compounds are shown and the physical properties of the new compounds in a non-chiral smectic C host are reported.

1. Introduction

Reducing the symmetry of tilted smectic phases by adding a chiral polar dopant to a host with an appropriate smectic phase results in ferroelectric liquid crystal mixtures [1]. Apart from the customary aromatic esters [2], it has been found that laterally fluorinated aromatic compounds [3] and derivatives of pyrimidines, pyridines and 1,3,4-thiadiazoles provide basic materials for hosts with a broad smectic C phase range, low viscosity and good alignment properties [4]. Including some compounds incorporating a 1,4-disubstituted cyclohexane ring [5], which may be substituted preferably by an additional axial nitrile group [6], there is a considerable number of non-chiral liquid crystal compounds suitable for the preparation of S_C host mixtures. For this reason we have focussed our interest on the development of new chiral dopants. These chiral dopants must satisfy certain basic requirements which are as follows.

(*a*) They must be chemically stable, especially with regard to racemization and ultraviolet light.

(*b*) They must be accessible with reproducible enantiomeric purity from common chiral precursors.

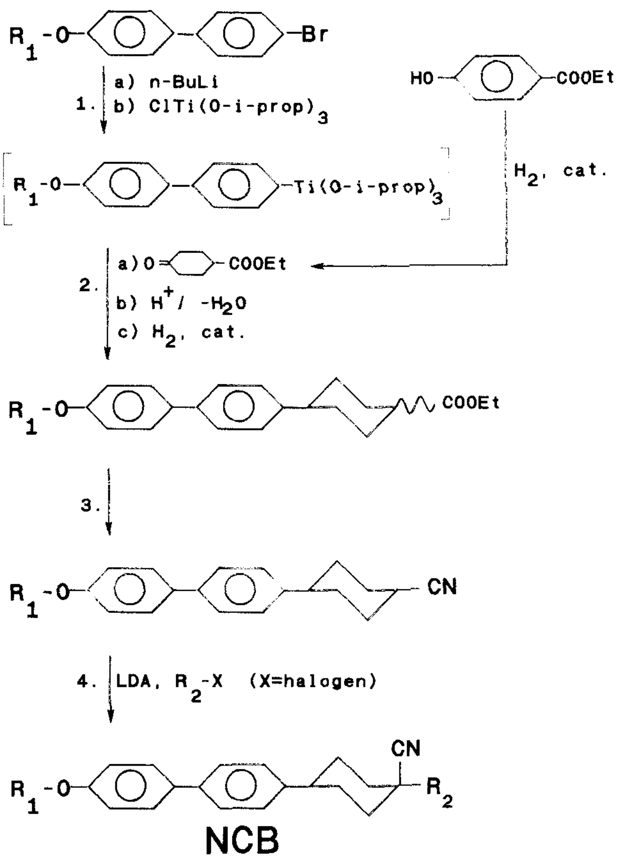
(*c*) With an appropriate induced spontaneous polarization, P_S, the dopants should lead to fast switching times. This necessitates a low ratio of rotational viscosity to P_S for the mixture.

(*d*) The length of the helical pitch caused by the chiral dopant must be sufficiently long to allow good alignment properties in the cholesteric phase and to allow unwinding by surface forces in the S_C^* phase. Otherwise it would be necessary to compensate the pitch by another dopant.

(*e*) The dopants should not depress the S_C–S_A transition of the host significantly, but the existence of an intrinsic mesophase or S_C^* phase is not a prerequisite.

2. Chiral biphenylcyclohexylcarbonitriles

In order to develop new dopants for ferroelectric liquid crystal mixtures it is advisable to start from well known existing structures exhibiting an S_C phase. For this purpose the biphenylcyclohexylcarbonitriles (NCBs) seem to be suitable candidates. They show a broad S_C phase range between 50 and 120°C [6]. An exceptional advantage of NCBs is the strong permanent acentral transverse dipole of the cyano group. This should give rise to a high spontaneous polarization by coupling it rigidly



Scheme 1. Synthetic route to biphenylcyclohexylcarbonitriles.

with a chiral group in the side chain. NCBs are easily available by the following synthetic route (see scheme 1):

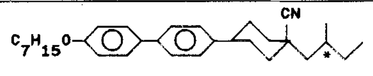
(1) metallation of 4-alkoxy-4′-bromobiphenyl with butyllithium and transmetallation with chloro-triisopropoxy-titanium,
(2) chemoselective reaction of the titanium organic compound with ethyl-4-oxo-cyclohexanecarboxylate, subsequent elimination of water and hydrogenation,
(3) functional group interconversion of an ester group to a carbonitrile group,
(4) introduction of a second side chain.

The last step is readily performed by alkylation, because in *trans*-4-(4′-alkoxy-4-biphenyl)-cyanocyclohexane the proton adjacent to the nitrile group is activated and can be removed by strong bases. The nitrile-stabilized carbanion reacts efficiently with electrophiles, e.g. alkylating agents, yielding preferably axially cyano substituted products [7].

Using alkyl halides derived from optically active dihydrocitronellol and 2-methylbutanol, which are available from the chiral pool, we have synthesized some optically active NCBs with branched chains at the cyano terminated side of the core (see table 1).

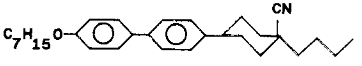
In comparison with the straight chain homologues, the S_C–S_A or S_C–N transition temperature is, at most, slightly depressed by the branching, whereas the depression

Table 1. Comparison of the transition temperatures of branched and straight chain NCBs and the spontaneous polarization of chiral NCBs.

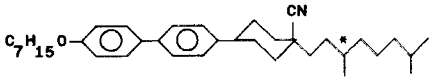


C 66°C S_C^* 107°C S_A 112°C Ch 131°C I

$P_S(T_{S_C^* \rightarrow S_A} - 20\,K) = 16\,nC\,cm^{-2}$

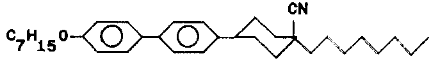


C 93°C S_G (54°C) S_C 107°C N 156°C I



C 89°C S_C^* 109°C S_A 118°C I

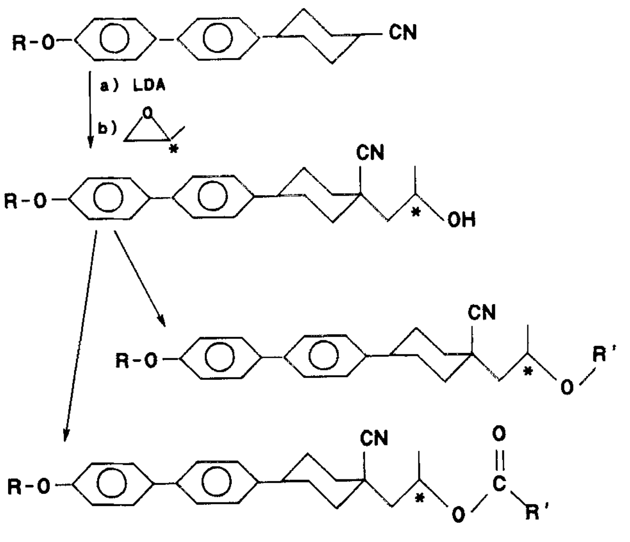
$P_S(T_{S_C^* \rightarrow S_A} - 20\,K) = 34\,nC\,cm^{-2}$



C 85°C S_F (43°C) S_C 112°C S_A 148°C N 151°C I

of the clearing point is more significant. The spontaneous polarization of the pure compounds is shown in table 1 at a temperature 20 K below the upper phase transition of the S_C^* phase. Surprisingly, the 3,7-dimethyloctyl-NCB **2** exhibits a considerably higher spontaneous polarization than the 2-methylbutyl-NCB **1**, though the chiral centre of the latter is located one atom closer to the core.

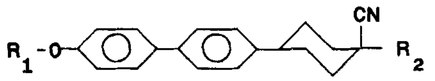
NCBs with polar groups at the chiral centre in the side chain can be obtained by the reaction of the above nitrile-stabilized carbanion with optically active propylene-oxide (see scheme 2). The oxirane is opened regioselectively at the less substituted carbon atom, resulting in the formation of an optically active alcohol as precursor for ethers and esters.

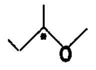
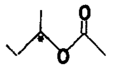
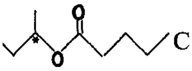


Scheme 2. Synthetic route to the chiral NCB derivatives **3–5**.

As can be seen from table 2, an enhancement of the spontaneous polarization is achieved by the introduction of functional groups with increasing polarity directly

Table 2. Influence of polar groups on phase transition temperatures and the magnitude of the spontaneous polarization of chiral NCBs measured at $T_{S_C^* \to S_A/Ch} - 20\,K$.



	R_1	R_2	Phase transitions	P_S/nC cm^{-2}
1	C_7H_{15}		C 66°C S_C^* 107°C S_A 112°C Ch 31°C I	16
3	C_8H_{17}		C 71°C S_C^*(70°C) Ch 107°C I	64
4	C_8H_{17}		C 68°C S_C^* 74°C Ch 88°C I	156
5	C_8H_{17}		C 32°C S_C^* 67°C Ch 68°C I	251

linked to the chiral centre in the side chain. Optimizing the chain length finally leads to NCB ester **5** which has a spontaneous polarization of 313 nC cm^{-2} at room temperature, a switching time of 50 μs at 35°C with an electrical field of 15 V μm^{-1}. Compounds with very high spontaneous polarization are of special interest for the development of mixtures for the electroclinic effect. A mixture with a S_A^* phase range from 18 up to 70°C made from 60 per cent of the chiral ester **5** exhibits an induced tilt angle of 9° at a temperature of 25°C by applying an electric field of 30 V μm^{-1}.

3. Chiral NCBs and lactate-ethers as dopants

In order to compare the efficiency of the various chiral dopants, we have established a standard screening procedure. A non-chiral S_C host (ZLI-3234 B, transition temperatures: S_C 76°C S_A 80°C N 96°C I) being composed of phenylpyrimidines and NCBs is doped with 10 per cent of the chiral compound under investigation. The transition temperatures of the resulting mixture are compared with those of the host; spontaneous polarization, tilt angle and switching time are measured as a function of temperature. The experimental data in table 3 were obtained at 20°C. The switching time, τ, is determined from the transmission characteristics through crossed polarizers on application of a square wave voltage across a cell of 3–4 μm thickness with a polyimid orientation layer. We define τ as the time from the field reversal until the transmission detected by a photodiode reaches 90 per cent. These 0–90 per cent values are two to three times longer than the common 10–90 per cent values. For comparison they are normalized to a field strength E of 15 V μm^{-1} assuming that τ is proportional to E^{-1}.

Without significantly affecting the upper S_C phase transition temperature of the host switching times of 520 and 140 μs are obtained with the ether and ester derivatives **3** and **5**, respectively, thus reflecting the different spontaneous polarizations of these dopants (see table 3). An ethyl lactate group bonded by an ether linkage to the biphenyl side of the NCB core (**6**) results in nearly the same spontaneous polarization as the ester derivative **5**, but in a shorter switching time and a depressed S_C phase. The simple biphenyl-lactate-ether **7** exhibits an S_C–S_A phase transition at 60°C and a switching time of 105 μs at moderate spontaneous polarization [8]. From table 4 we

Table 3. Physical properties of the non-chiral S_C mixture ZLI-3234 B doped with 10 per cent of chiral NCBs.

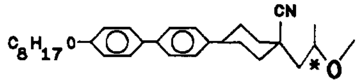
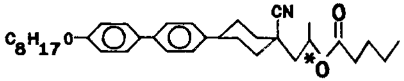
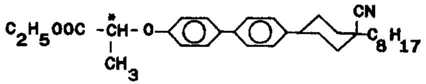
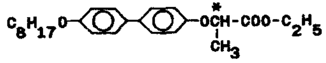
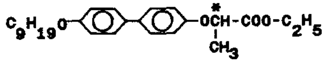
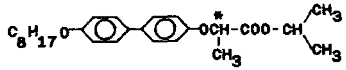
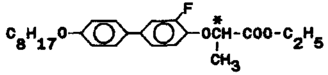
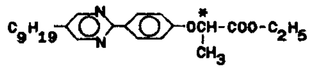
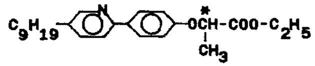
	Dopant	$T_{S_C^*\to S_A}$/°C or $T_{S_C^*\to Ch}$/°C	$T_{S_A\to Ch}$/°C	$T_{Ch\to I}$/°C	P_S/nC cm^{-2}	θ/°	τ/μs
					at 20°C		
3		74	78	99	5·6	33	520
5		75	—	95	17·2	32	140
6		66	72	92	16·1	29	120

Table 4. Physical properties of the non-chiral host ZLI-3234 B doped with 10 per cent of lactate-ether derivatives.

	Dopant	$T_{S_C^* \to S_A}$/°C or $T_{S_C^* \to Ch}$/°C	$T_{S_A \to Ch}$/°C	$T_{Ch \to I}$/°C	P_S/nC cm^{-2}	θ/°	τ/μs
					at 20°C		
7		60	61	86	11·7	29	105
8		62	66	85	11·4	25	150
9		61	64	86	15·3	28	130
10		58	65	86	10·8	26	150
11		63	64	89	10·4	29	160
12		59	—	85	9·6	26	140

see that variation of the chain length, branching of the side chain, lateral fluorination of the core or substitution of a phenyl group by a heterocyclic ring system does not improve the properties of biphenyl-lactate-ether **7**.

4. Cyanoacetate dopants

Subsequently, we have developed new chiral dopants incorporating a more efficient chiral moiety as the source of the dipole moment. They derive from esters of optically active 2-methyl-2-cyano-alkanoic acids [9] and have the general structure shown in the figure. The methyl substituent in the 2-position is necessary, otherwise a hydrogen atom in this position would give rise to racemization due to the acidity of a C–H bond adjacent to two unsaturated electron-withdrawing substituents. Esters of this type can be understood as derivatives of 2,2-disubstituted cyanoacetic acid.

The synthesis of these compounds (see scheme 3) conveniently starts with a Knoevenagel condensation of ethylcyanoacetate with an appropriate aldehyde. In the

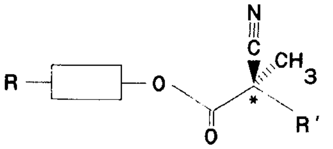
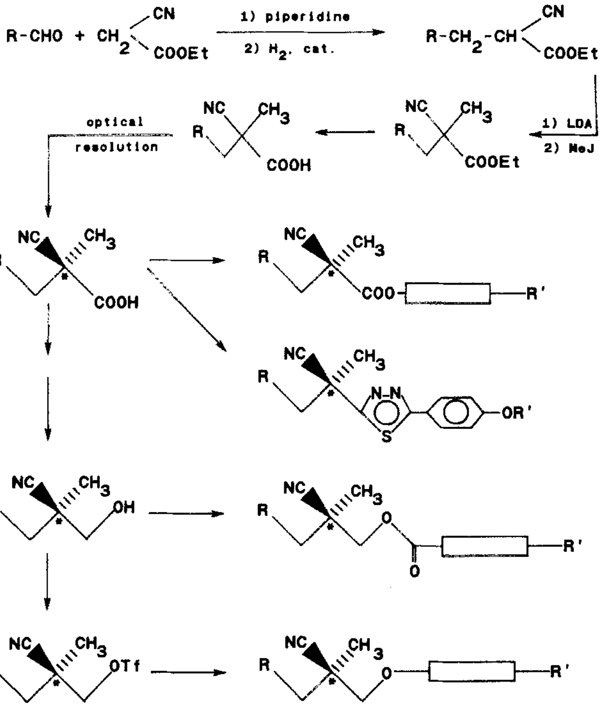


Figure General structure of 2-cyano-2-methylalkanoate dopants (cyanoacetate dopants).



* unknown absolute configuration

Scheme 3. Synthesis of 2-cyano-2-methylalkanoate dopants and their derivatives.

Table 5. Physical properties of the non-chiral S_C mixture ZLI-3234 B doped with 10 per cent of optically active 2-cyano-2-methylcaproic acid derivatives.

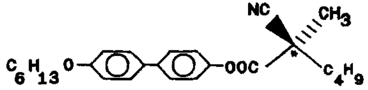
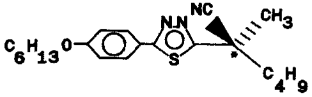
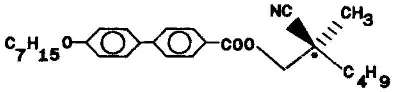
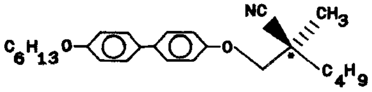
	Dopant	$T_{S_C^*\rightarrow S_A}$/°C	$T_{S_A\rightarrow Ch}$/°C	$T_{Ch\rightarrow I}$/°C	P_S/nC cm^{-2}	θ/°	τ/μs
					at 20°C		
13		61	76	86	25·3	29	65
14		45	64	86	16·0	20	90
15		62	69	90	12·6	27	180
16		62	72	87	14·1	28	100

Table 6. Physical properties of the non-chiral S_C mixture ZLI-3234 B doped with 10 per cent of 2-cyano-2-methylcaproates.

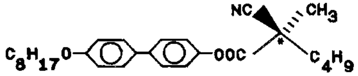
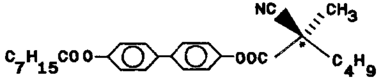
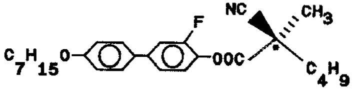
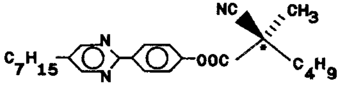
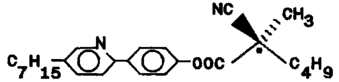
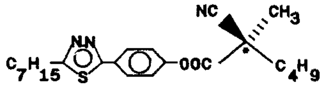
	Dopant	$T_{S_C^* \to S_A}$/°C	$T_{S_A \to Ch}$/°C	$T_{Ch \to I}$/°C	P_S/nC cm^{-2}	θ/°	τ/μs
					at 20°C		
17		66	79	88	24·0	27	70
18		68	78	88	32·0	30	75
19		62	78	87	23·3	25	90
20		58	75	86	15·7	23	95
21		58	73	84	21·1	27	55
22		63	71	84	24·2	29	85

Table 7. Properties of the ferroelectric mixtures ZLI-4000 (lactate-ether dopant) and ZLI-4140 (cyanoacetate dopant).

	ZLI-4000	ZLI-4140
$T_{C\rightarrow S_C^*}/°C$	< -20	< -20
$T_{S_C^*\rightarrow S_A^*}/°C$	64	70
$T_{S_A^*\rightarrow Ch}/°C$	69	76
$T_{Ch\rightarrow I}/°C$	80	80
$P_S/\mathrm{nC\,cm^{-2}}$ at 20°C	10·6	23·6
$\gamma_n/\mathrm{mPa\,s}$ at 20°C	190	240
$\tau_{0\text{-}90\%}$/at 20°C and 15 V	80	50

following steps, the resulting alkylidene cyanoacetic acid ester is hydrogenated or reduced by $NaBH_4$, alkylated with methyl iodide in the presence of a base, and saponified. Optical resolution of the disubstituted cyanoacetic acid is carried out by formation of a diastereomeric salt with an appropriate base, preferably with quinine. In this way we have obtained optically active 2-methyl-2-cyano-caproic acid of unknown absolute configuration with an enantiomeric excess [10] of more than 98 per cent. Without going into further detail we see, from scheme 3, that besides simple cyanoacetates other types of dopants can be made by elaboration of this synthetic route.

The properties of representative dopants are collated in table 5. There is not such a deteriorating effect on the S_C phase range by the sterically crowded chiral centre as might be anticipated, except for the thiadiazole derivative **14**, where this centre is next to the core. The ether derivative **16** in table 5 resembles the lactate-ether dopants with regard to switching time and S_C phase range, but it causes a slightly higher spontaneous polarization. It is apparent that the cyanoacetate **13** is the most promising dopant in this series leading to a switching time of 65 μs.

Structural variation of the 2-cyano-2-methylcaproate dopants (see table 6) shows that elongation of the side chain (**17**) increases the switching time slightly. Replacement of an alkoxy group by an alkanoyloxy group (**18**) causes a substantially enlarged spontaneous polarization, but does not lead to faster switching times. The fluorinated compound **19** and the phenylpyrimidine derivative **20** are unexpectedly slow, whereas the phenylpyridine **21** shows the best switching time but a comparatively low transition temperature.

5. Ferroelectric liquid crystal

Utilizing lactate-ether dopants and cyanoacetate dopants we have developed new ferroelectric liquid crystal mixtures (see table 7). The lactate-ether mixture ZLI-4000 is characterized by a comparatively small polarization of $10{\cdot}6\,\mathrm{nC\,cm^{-2}}$ and a switching time of 80 μs at 20°C and $15\,\mathrm{V\,\mu m^{-1}}$, whereas the cyanoacetate mixture ZLI-4140 exhibits a higher spontaneous polarization and a switching time of 50 μs.

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