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New liquid-crystalline compounds with negative dielectric anisotropy

V. Reiffenrath[a]; J. Krause[a]; H. J. Plach[a]; G. Weber[a]
[a] Industrial Chemicals Division, Department of Organic Research, E. Merck, Darmstadt, F. R. Germany

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New liquid-crystalline compounds with negative dielectric anisotropy

by V. REIFFENRATH, J. KRAUSE, H. J. PLACH and G. WEBER
E. Merck, Industrial Chemicals Division, Department of Organic Research,
Frankfurter Straße 250, D-6100 Darmstadt, F.R. Germany

Until now, liquid-crystalline compounds with high negative dielectric anisotropy were usually realized by a lateral cyano group. A drawback to these cyano substituted liquid crystals, namely the considerable increase in the viscosity and the reduction of the thermodynamic stability of the mesophase, has been circumvented by preparing 2,3-difluorobenzene derivatives. A universal method to prepare a variety of classes of liquid-crystalline compounds containing the 2,3-difluorophenylene moiety has been developed. The new materials are characterized by high negative $\Delta\varepsilon$ values of up to -6, and viscosities comparable with the non-fluorinated compounds. The introduction of the two fluorine atoms also leads to an increase in K_{33}/K_{11}. They also suppress higher ordered smectic phases and transform S_A into S_C phases. The new compound classes are promising materials for liquid crystal mixtures for various applications as electrically controlled birefringent, supertwisted nematic and ferroelectric liquid crystal displays.

1. Introduction

Most of the liquid crystal displays (LCDs) produced today are based on the principle of the twisted nematic cell (TNC) [1]. They require liquid-crystalline compounds with positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$). However, there is still a marked interest in liquid crystal materials either with negative $\Delta\varepsilon$ or with high values of $\varepsilon_{\perp}$. Supertwisted nematics (STN) [2, 3], SBE [4] and OMI [5] applications represent recent developments allowing LCDs with higher information densities at acceptable contrast [6]. In these applications a steep electro-optic contrast curve can be achieved by materials with small values of $\Delta\varepsilon/\varepsilon_{\perp}$ [7–9]. For electrically controlled birefringence (ECB) [10–12], positive contrast quest-host (GH) [13–15] and ferroelectric liquid crystal (FLC) [16] displays liquid crystal materials with negative $\Delta\varepsilon$ are needed.

A material with negative $\Delta\varepsilon$ or with high $\varepsilon_{\perp}$ can be achieved by the introduction of a lateral, polar substituent into the mesogenic molecule. Preferably the polar substituent should form an angle of 90° with the long axis of the molecule. However, this is difficult to realize in molecules consisting mainly of hexagonal ring systems. The substituent that has widely been used to introduce a negative $\Delta\varepsilon$ is the cyano group [17–20]. As shown in table 1, this particular substituent, having a larger van der Waals volume, leads to a significant deterioration of the clearing point as well as to a significant increase in the kinematic viscosity, ν, of the materials **1** and **2**. Two cyano groups in the 2,3-positions **3** of the aromatic ring are much more effective, in regard to increasing $\Delta\varepsilon$, as a strong lateral dipole oriented at 90° to the molecular long axis results. The major drawbacks of these 2,3-dicyanohydroquinone derivatives are, besides their high viscosity, the poor solubility in liquid crystal hosts and insufficient photostability [20]. The 3,6-pyridazines **4** [21], whose lone pair electrons, located at the nitrogen atoms, form a dipole orthogonal to the long axis of the molecules, exhibit lower viscosities but are also not photostable [22].

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Table 1. Conventional materials with a negative $\Delta\varepsilon$.

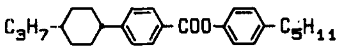
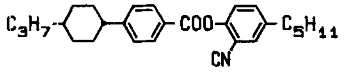
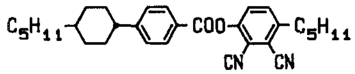
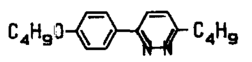
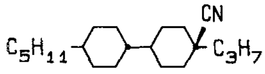
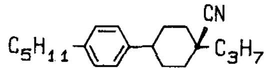
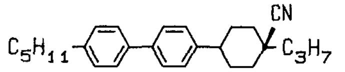
No.	Chemical structure	Phase X T_{XY}/°C phase Y	$\Delta\varepsilon$	ν/mm^2 s^{-1}
1		C 87 S_A (80) N 176 I	0·6	41
2		C 57 N 111 I	−4	200
3		C 138 N 148 I	−20	
4		C 100 S_B N 107 I	−6	100

Table 2. Materials with an axial cyano group.

No.	Chemical structure	Phase X T_{XY}/°C phase Y	$\Delta\varepsilon$	ν/mm^2 s^{-1}	Δn
5		C 32 S_B (24) N 42 I	−7·7	71	0·03
6		C −50 I	−4·7	130	0·15
7		C 73 N 135 I	−4·7	130	0·15

Initial progress has been achieved by the synthesis of dialkylbicyclohexane derivatives **5** with an axial cyano group [23]. These substances have reasonably high negative $\Delta\varepsilon$ values and an acceptable viscosity (compare table 2). However, the optical anisotropy of these materials is too small for some applications. Especially for ECB applications a larger value of Δn is of great interest. The attempt to increase Δn of the substances, e.g. by introducing aromatic rings into the molecules, leads to a deterioration of the clearing points and the viscosities **6**, **7**. Compound **6** has no mesophase at temperatures above −50°C. We have extrapolated the clearing point from a nematic host, $T_{NI,extrap}$, to be −110°C.

This problem has been circumvented by introducing a fluorine atom as a lateral polar substituent in the aromatic core of mesogenic molecules [24]. Having a small van der Waals volume, a fluorine atom affects both the clearing point [25] and the viscosity much less than the cyano group. However, to the smaller dipole moment of a fluorine atom compared with a cyano group, a single fluorine atom does not induce a sufficiently negative $\Delta\varepsilon$.

2. Experimental

2.1. *Organic synthesis*

We have developed a universal method to synthesize 1,4-disubstituted 2,3-difluorobenzene derivatives. The metallation of fluorobenzene has been reported by Gilman and Soddy [26]. The reaction of this compound with *n*-butyl-lithium (BuLi)

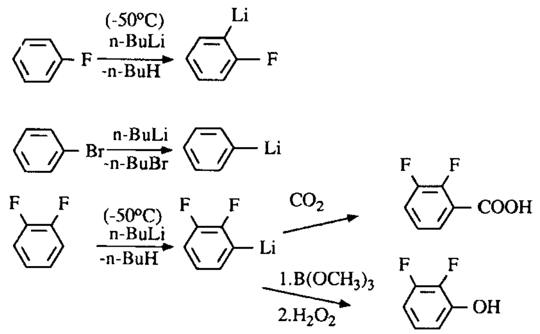


Figure 1. Reaction scheme for the first metallation.

in tetrahydrofuran (THF) at low temperatures yields *o*-lithiofluorobenzene. This is in contrast to the halogen–metal exchange observed for bromo- and iodoaromatics [27] (compare figure 1). The metallation of the fluoroaromatics is mediated by the activation of the vicinal hydrogen atoms via the $-I$ effect of the strongly bound fluorine. To avoid the competing formation of arines, by elimination of LiF, the temperature must not exceed − 50°C. Roe *et al.* [28] have shown that *o*-difluorobenzene can also be metallated in the vicinal position. By conversion of the resulting metallated compound with an electrophile, such as CO_2 or trimethoxyborate ($B(OCH_3)_3$), difluorobenzene derivatives, like 2,3-difluorobenzoic acid and 2,3-difluorophenol, which are not easily prepared by other reactions, are accessible.

Our investigations showed that after introduction of the first substituent the same process can be repeated with the second vicinal hydrogen atom. This reaction opens the way to 1,4-disubstituted 2,3-fluorobenzenes, perfectly suited as liquid-crystalline materials. The 2,3-difluorobenzene derivative prepared in the first step is metallated again in the activated 4-position of the aromatic ring and subsequently can be reacted with another electrophile. This is illustrated in figure 2. Obviously, the substituent introduced in the first step should be selected in a way so as not to react with BuLi itself and to be of smaller ortho-directing strength than fluorine. Applying this restriction, the whole range of known structures for mesogenic molecules is accessible with this new aromatic core.

The scope of this method is shown in figure 3. Alkoxybenzoic acids as well as alkoxyphenols have been important building blocks of mesogenic molecules. The new corresponding 2,3-difluorophenol, prepared by the first metallation step, is alkylated and subsequently metallated in the 4-position. The product of this second metallation is an intermediate to several interesting compounds. Whereas the reaction with CO_2

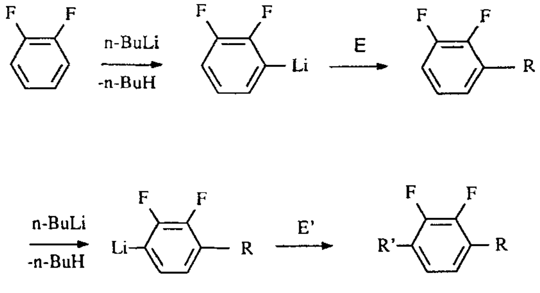
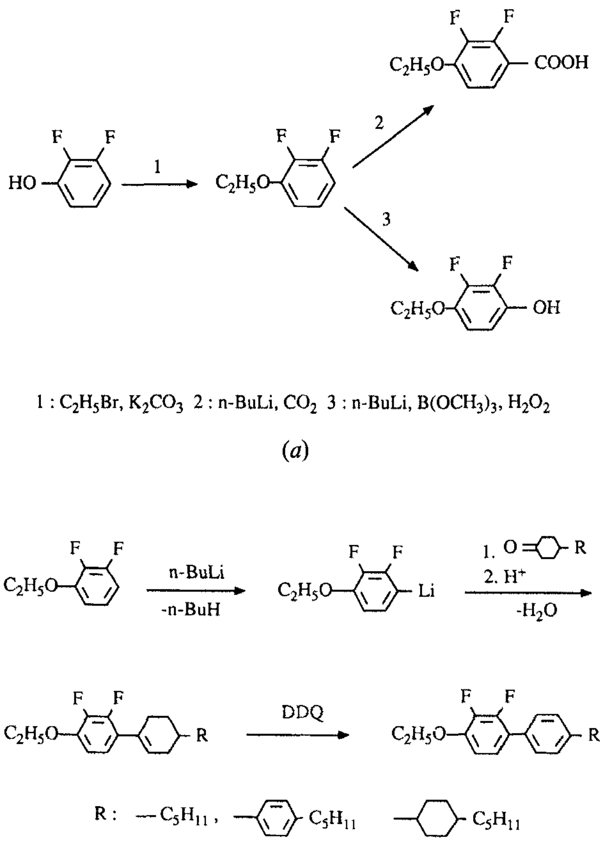


Figure 2. Scheme of the overall synthesis; *E* and *E′* represent electrophiles.



1 : C_2H_5Br, K_2CO_3 2 : n-BuLi, CO_2 3 : n-BuLi, $B(OCH_3)_3$, H_2O_2

(*a*)

(*b*)

Figure 3. Reaction paths from the first metallated product.

yields the alkoxybenzoic acid, the conversion with trimethoxyborate and subsequent oxidation with H_2O_2 leads to the monoalkylated 2,3-difluorohydroquinone. Biphenyl, cyclohexylbiphenyl and terphenyl derivatives are obtained by conversion of the metallated difluorobenzene derivatives with 4-substituted cyclohexanones. The alcohol formed is dehydrated and the resultant cyclohexane derivative is aromatized with dichlorodicyanoquinone (DDQ). The metallated difluorobenzene can be alkylated by the reaction with *n*-alkylbromides or iodides, as shown for the first metallation step in figure 4. These alkylations proceed readily when a mixture of BuLi and

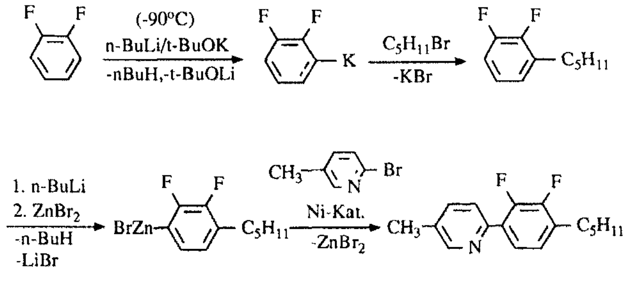


Figure 4. Scheme for the alkylation and for the coupling reaction.

potassium-*t*-butoxide has been used as metallization agent. This Schlosser base [29] presumably leads to a potassium organic compound. Reacting the lithium difluorobenzene derivative with $ZnBr_2$ leads to a zinc organic compound that is more stable at increased temperatures and is suited for coupling reactions with arylbromides and iodides catalysed by nickel organic compounds. We have used this method, for example, in the synthesis of difluorophenylpyridine derivatives.

2.2. *Physical properties*

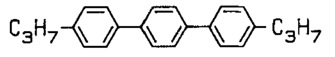
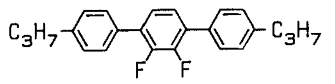
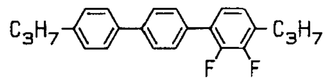
The methods used to determine the physical properties of the substances synthesised have already been described in detail [30, 31]. We only briefly mention here the determination of some relevant physical properties. The mesogenic phases of the substances have been assigned using a polarizing microscope equipped with a hot stage. The corresponding transition temperatures have been determined by differential scanning calorimetry (D.S.C.). The purities of the substances have been confirmed to be better than 99·5 per cent by gas chromatography (G.C.), high-performance liquid chromatography (H.P.L.C.) and D.S.C.

The substances were dissolved in a dielectrically neutral nematic host and the dielectric properties, optical anisotropies and flow viscosities of the resultant mixtures were determined. The dielectric permittivities $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ have been derived from the capacitance of liquid crystal samples aligned homeotropically and homogeneously in test cells, respectively. The refractive indices n_0 and n_e of the homeotropically aligned materials were measured in an Abbe refractometer. The viscosities were determined in flow viscosimeters (Hoffmann type). The Frank elastic constants K_{11}, K_{22} and K_{33} of selected compounds have been determined by optically monitoring electrically and magnetically induced director deformations [32]. The U.V. and temperature stability were also investigated in these mixtures. In the following we base our discussion of the characteristics of the new substances on the physical properties extrapolated from these mixtures.

3. Results and discussion

We have prepared homologues of several compound classes containing the 2,3-difluoro-1,4-phenylene moiety. The properties of these substances are compared with those of the corresponding non- or monofluorinated substances. The influence of the double fluorine substitution on the mesogenic phase range is illustrated in table 3. The substitution of the two hydrogens in the central ring of 4,4″-dipropyl-1,1′:4′,1″-terphenyl **8** leads to a significant decrease in the melting point as well as of the

Table 3. Dialkylterphenyls.

No.	Chemical structure	Phase X	T_{XY}/°C	phase Y			$\Delta\varepsilon$	ν/mm^{2}s^{-1}	Δn
8		C	221	S	228	I			
9		C	96	N	132	I	−1·7	31	0·25
10		C	132	N	148	I	−1·9	33	0·25

clearing point **9**, cf. **10**. At the same time, the higher ordered smectic phase is substituted by the nematic phase. A similar effect, for monofluorination, was observed by Chan *et al.* [33]. The strong influence of fluorination might be due to the increase of the torsional angle between the phenyl rings, caused by substitution in the 2′,3′-positions. The increased torsional angle affects the packing of the molecules [34] and thus the phase range and the structural ordering of the phases.

For the 2,3-difluoroalkylalkoxyterphenyl **12** the S_C phase replaces both the S_A and the S_E phases of the unsubstituted molecule **11** (see table 4). Here, the influence of the clearing point is less pronounced. The value of $\Delta\varepsilon$ of this compound is more than twice that of the corresponding difluorinated dialkycompound. This indicates the influence of the oxygen in the *ortho* position to one of the fluorine atoms. The substitution of one **13** or two **14** of the aromatic rings by cyclohexane rings leads to materials with high clearing points and almost the same $\Delta\varepsilon$, but with markedly decreased optical anisotropy.

To investigate this effect we have prepared a series of 2,3-difluorobenzene derivatives linked to an alkylbicyclohexane moiety by different bridging groups (compare table 5). For example, compound **15** is linked by an ethylenic bridge ($-C_2H_4-$) and has no further substituent and so only a small negative dielectric anisotropy ($\Delta\varepsilon = -1{\cdot}3$) is observed. Introducing an alkoxy group into this molecule **16** leads, besides an increased clearing point, to a marked increase in the absolute value of $\Delta\varepsilon$ ($\Delta\varepsilon = -3{\cdot}7$). A similar value ($\Delta\varepsilon = -3{\cdot}4$) is observed for compound **17** where the oxygen atom, in the *ortho* position to the fluorine atom, forms a part of the central link. The largest negative value ($\Delta\varepsilon = -6{\cdot}0$) is found for the diether compound **18** having two oxygen atoms, each vicinal to one of the fluorine atoms. This compound is a very promising component for nematic mixtures. It combines a wide nematic range with a large negative dielectric anisotropy. Also, taking into account the high clearing point, the viscosity is acceptable.

If the methoxy bridge ($-CH_2O-$) is replaced by an ester link **19**, the clearing point is increased significantly ($T_{NI} = 222°C$), whereas the dielectric anisotropy is decreased ($\Delta\varepsilon = -4{\cdot}1$). This may be due to the carbonyl oxygen preferring an antiparallel orientation to the fluorine atoms in order to minimize the intramolecular dipolar interaction energy. Contrasting the equivalent dicyano compound, the new substance is found to be photostable and sufficiently soluble in the nematic host. As the clearing point of this substance is rather high it is obviously an interesting component for the development of liquid crystal mixtures.

Of comparable interest are the cyclohexane carboxylic acid esters of monoalkyldifluorohydroquinones (compare table 6). The introduction of the two fluorine atoms **22**, compared with the unsubstituted compound **20**, leads to a decrease in the clearing point of 23°C to a T_{NI} of 63°C. Remarkably, the viscosity is not significantly altered. Compared with the monofluorinated dihydroquinone compound **21** the clearing point is reduced less and the viscosity is also more favourable.

To determine the influence of the fluorine substitution on the elastic constants we have prepared 2,3-difluoro-4-pentylphenylic esters of pentylcyclohexylcarbonic acid **25**. Both the corresponding monofluorinated compounds **24** [35] and the non-fluorinated product **23** [36] are well known. For these compounds the elastic constants have already been determined [37]. At a reduced temperature, T_{red}, of 0·98 the elastic constants of the new difluoro compounds are compared with the other values in table 7. Upon monofluorination the ratio K_{33}/K_{11} increases from 0·85 to 1·11, whereas the second fluorination increases the value of the non-fluorinated compound to 1·00 only.

Table 4. 2,3-Difluorophenol ethers.

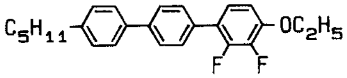
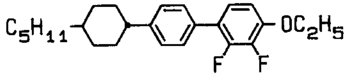
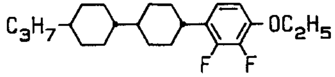
No.	Chemical structure	Phase X T_{XY}/°C phase Y	Δε	ν/mm^2 s^{-1}	Δ*n*
11		C 234 S_E 237 S_A 242 N 248 I			
12		C 105 S_C 135 N 185 I	−4·2	49	0·27
13		C 68 S_A 87 N 172 I	−4·1	46	0·18
14		C 76 S_B 79 N 186 I	−4·4	39	0·13

Table 5. Influence of the *ortho* oxygen atom on $\Delta\varepsilon$.

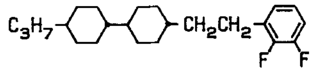
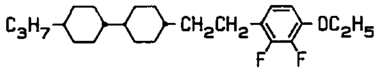
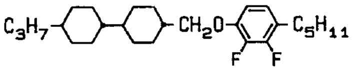
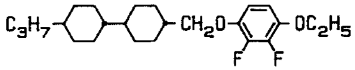
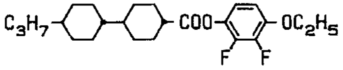
No.	Chemical structure	Phase X T_{XY}/°C phase Y	$\Delta\varepsilon$	ν/mm^2 s^{-1}	Δn
15		C 42 S_B 81 N 96 I	−1·3	29	0·07
16		C 68 S_B 109 N 160 I	−3·7	34	0·12
17		C 35 S_A 66 N 118 I	−3·4	39	0·09
18		C 62 N 154 I	−6·0	36	0·12
19		C 87 S_B (81) S_A 98 N 222 I	−4·1	37	0·11

Table 6. Cyclohexanecarboxylates of fluorinated hydroquinones.

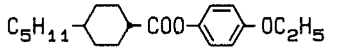
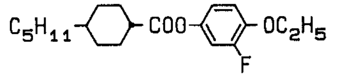
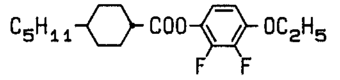
No.	Chemical structure	Phase X	T_{XY}/°C	phase Y	Δε	ν/mm^{2}s^{-1}	Δ*n*
20		C	57 N 86	I	−1·2	19	
21		C	49 N 59	I	−1·9	21	
22		C	51 N 63	I	−4·6	18	0·09

Table 7. Cyclohexanecarboxylates of fluorinated hydroquinones.

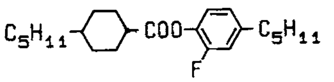
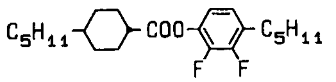
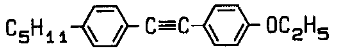
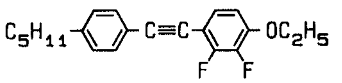
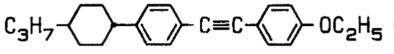
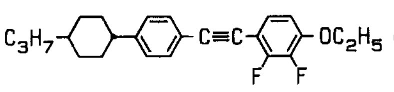
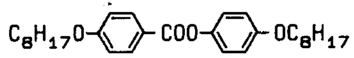
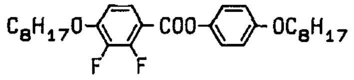
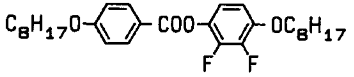
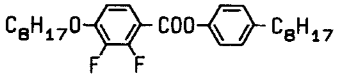
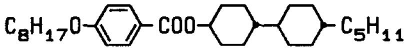
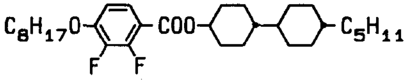
No.	Chemical structure	Phase X	T_{XY}/°C	phase Y	Δε	ν/mm^{2}s^{-1}	K_{33}/K_{11}
23		C	37 S_A (29) N 47	I			0·90
24		C	17 N 37	I	−0·9	14	1·11
25		C	13 N 29	I	−2·1	24	1·00

Table 8. Fluorinated tolanes.

No.	Chemical structure	Phase X	T_{XY}/°C	phase Y	Δε	ν/mm^{2}s^{-1}	Δ*n*
26		C	61 N 89	I	0·2	20	0·28
27		C	57 N 61	I	−4·4	17	0·25
28		C	110 N 253	I	0	36	0·32
29		C	84 N 229	I	−4·1	27	0·29

Difluorinated esters of this kind show a small optical anisotropy. To prepare materials with high optical anisotropies and negative dielectric anisotropies we have introduced the 2,3-difluoro-1,4-phenylene moiety into the tolane structure (see table 8). The extrapolated viscosities of these compounds **27** and **29** are significantly lower than those of the non-fluorinated materials **26** and **28**. The Δε values are in the range characteristic of compounds having an oxygen atom in the *ortho* position to one of the fluorine atoms. The three ring compound has a wide nematic phase range and a high clearing point. Compounds of this type are particularly well suited for nematic mixtures for ECB applications.

Table 9. Fluorinated esters exhibiting smectic phases.

No.	Chemical structure	Phase X T_{XY}/°C phase Y	Δε	ν/mm^2 s^{-1}	Δ*n*
30		C 63 S_C 74 N 91 I			
31		C 48 S_C 71 N 82 I	−2·7	120	0·13
32		C 54 S_C (39) N 60 I			
33		C 54 S_A 64 N 66 I	0·4	70	0·11
34		C 37 S_C 49 N 57 I	−2·7	82	0·11
35		C 80 S_A 140 N 182 I	−0·8	82	0·13
36		C 90 S_C 98 N 170 I	−2·1	82	0·12

The mesomorphic properties of aromatic alkoxybenzoic acid esters are already well known [38]. Dialkoxy compounds with long side chains, for example compound **30** in table 9, exhibit an S_C phase. We have substituted the hydrogen atoms of the aromatic rings by fluorine atoms in the acid part **31**, as well as in the hydroquinone part **32**, of the molecule. We find that the introduction of the fluorine atoms in the acid part decreases the temperature of the smectic to nematic transition much less than fluorination in the quinone part **32**. For the difluorobenzoic acid derivative **31** the melting point is decreased even more than the smectic to nematic transition temperature, so the S_C phase range is increased.

The enhancement of S_C phase formation is observed also for alkylphenyl esters of difluoroalkoxybenzoic acids (compare table 9). These esters, for example compound **33**, without fluorination, would exhibit nematic and S_A phases only. After fluorine substitution **34** the S_A phase is replaced by the S_C phase. The same effect is observed in compound **35**, having only one aromatic ring and hence not showing an S_C phase. Here the S_A phase is also converted into the S_C phase upon fluorination **36**.

4. Conclusions

The introduction of the 2,3-difluorobenzene ring into mesogenic molecules has made possible the preparation of promising new substance classes for nematic and ferroelectric liquid crystal mixtures. The new compounds show very interesting combinations of physical properties. In particular a high $\varepsilon_\perp$ value and so a highly negative dielectric anisotropy $\Delta\varepsilon$ or a low value of $\Delta\varepsilon/\varepsilon_\perp$ are feasible without markedly decreasing the desired phase range or increasing the viscosity even at high Δn values. So a major improvement of mixtures for highly twisted and especially for ECB applications can be anticipated. Also a pronounced enhancement of the S_C phase is observed in some molecules, leading to dielectrically negative compounds for FLC mixtures.

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