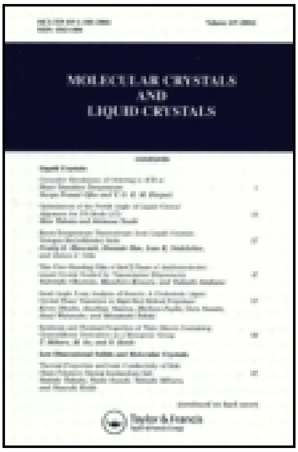

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl18

Liquid Crystals with Polar Substituents Containing Fluorine: Synthesis and Physical Properties

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Version of record first published: 04 Oct 2006.

To cite this article: E. Bartmann, D. Dorsch & U. Finkenzeller (1991): Liquid Crystals with Polar Substituents Containing Fluorine: Synthesis and Physical Properties, Molecular Crystals and Liquid Crystals, 204:1, 77-89

To link to this article: http://dx.doi.org/10.1080/00268949108046596

Mol. Cryst. Liq. Cryst., 1991, Vol. 204, pp. 77-89
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Printed in the United States of America

Liquid Crystals with Polar Substituents Containing Fluorine: Synthesis and Physical Properties

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(Received July 26, 1990)

Liquid crystalline compounds with various polar terminal groups containing fluorine have been prepared (see below formula $\underline{1}$ with Z = $S—CHF_2$, $S—CF_3$, $SO—CHF_2$, $SO—CF_3$, $SO_2—CHF_2$, $SO_2—CF_3$, SO_2F, OCH_2CF_3, $CO—OCH_2CF_3$, $CO—CF_3$, $CO—CF_2Cl$, $CO—CF_2H$, $CO—CF_2—CH_3$, $CO—CF_2—C_3H_7$). The synthesis of these compounds is outlined here and their physical properties (phase transitions, dielectric anisotropy, birefringence, viscosity) are discussed.

Keywords: LCs containing fluorine, nematics

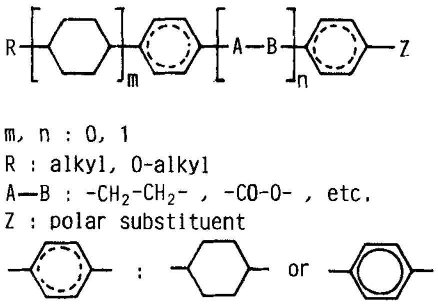
1. INTRODUCTION

There is a continuing search for new, polar or intermediately polar, liquid crystalline compounds with low viscosity, high thermal stability and chemical inertness. These efforts are initiated by the increasingly demanding requirements set by display technologists. Particularly the demand on materials to exhibit a high electrical resistivity (and a high holding ratio) which gives rise to an improved contrast ratio, a longer lifetime and reduced flickering problems of the display[1,2] necessitate studies on new l.c. materials. This is especially true in TFT displays.

The well established liquid crystals containing a cyano group as terminal substituent show relatively high dielectric anisotropy. However, these materials do not have that low viscosity which is desirable in many cases; furthermore, holding ratios are often unsatisfactory.

Other polar substituents (like the isothiocyanato group) or other polar liquid crystalline structures are not completely stable by themselves under more demanding working conditions (resulting in thermal, photolytical or display material catalyzed decomposition).

It is known that the introduction of fluorine often alters certain properties of organic compounds, e.g. thermal and chemical stability, viscosity etc. in a favourable manner. Furthermore, in liquid crystals other characteristic properties, like mesophase range and dielectric anisotropy, can be modified.[3] So we have found that liquid crystals with terminal groups containing fluorine such as trifluoromethyl, trifluoromethoxy and difluoromethoxy[4–7] (formula 1: Z = CF_3, OCF_3, OCF_2H) are highly useful and promising materials; they show interesting mesophase ranges and dielectric properties, low viscosities as well as high stability and holding ratios. In a more systematic approach we have synthesized a broad variety of compounds with other groups containing fluorine. Some of these new substances, their synthesis, and their properties are presented in the following.



1

m, n : 0, 1
R : alkyl, O-alkyl
A—B : $-CH_2-CH_2-$, -CO-O- , etc.
Z : polar substituent

2. RESULTS AND DISCUSSION

2.1 Sulfur Compounds Containing Fluorine

In analogy to the difluoromethoxy and the trifluoromethoxy substituted liquid crystals, the corresponding sulfur compounds also can be prepared. Difluoromethyl thioethers 2 can be synthesized by the well-known reaction of aromatic thiols with difluorocarbene[8,9] generated in situ from chlorodifluoromethane and base (see Scheme I); the trifluoromethylthio compounds 3 can be formed by palladium catalyzed cross-coupling[10–12] of 4-bromophenyl-trifluoromethyl-thioether with phenyl zinc or cyclohexyl zinc derivatives (see Scheme II).

These thioethers containing fluorine can easily be oxidized[13] (see Scheme I and II) to the corresponding sulfoxides and sulfones (4, 5, 6, and 7) which are interesting due to the highly polar nature of these structural elements.

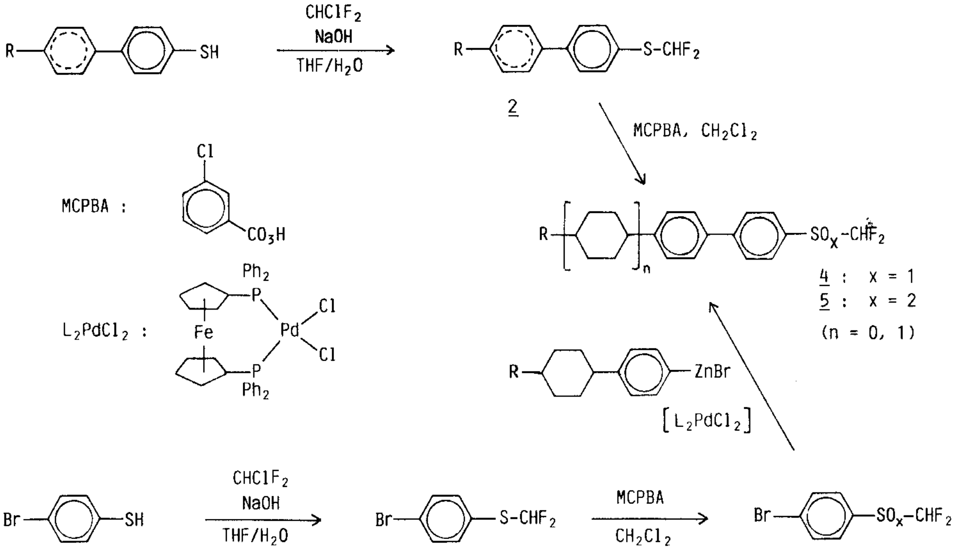
Difluoromethyl sulfoxides and sulfones (4, 5) have also been prepared by a sequence of difluorocarbene addition, oxidation, and cross coupling as outlined in Scheme I. Furthermore, we have synthesized trifluoromethyl sulfones containing carboxylic ester bridges (7b, c) by esterification of p-trifluoromethylsulfonylphenol.

A further highly polar, sulfur based substituent is the fluorosulfonyl group. Sulfonyl fluorides 8 can be prepared by simple metathesis of sulfonyl chlorides with fluoride[14,15] (Equation 1). (In contrast to a frequent assumption, sulfonyl fluorides are very stable compounds which are not even easily hydrolyzable.)

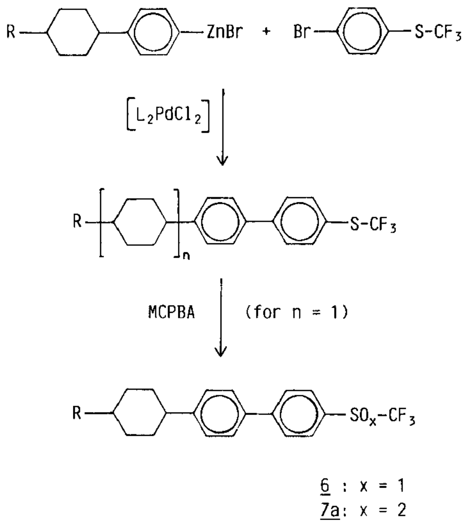
$$R^1-SO_2Cl \xrightarrow[CH_2Cl_2]{Bu_4N^+\ F^-} \underset{\underline{8}}{R^1-SO_2F} \qquad \text{(eq. 1)}$$

(R^1: for detailed structures see table 3)

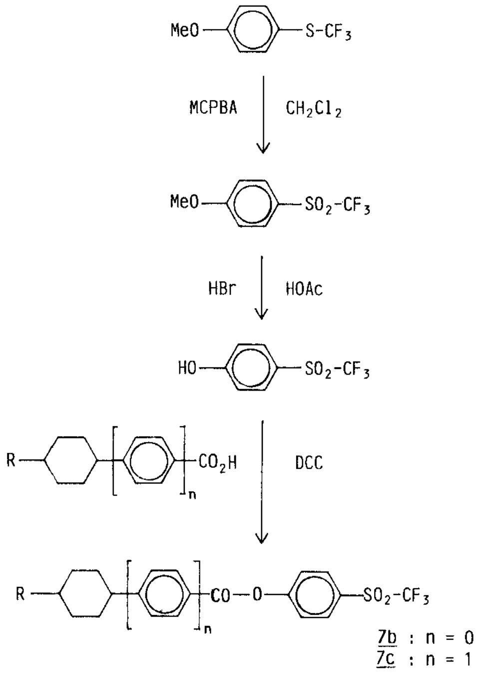
The physical data of the newly synthesized sulfur compounds are shown in Tables I–III. With respect to the dielectric (and also the optical) anisotropy the fluorinated thioethers 2 and 3 are comparable to the corresponding oxo derivatives.[4–6] How-



SCHEME I



SCHEME II



<u>7b</u> : n = 0
<u>7c</u> : n = 1

SCHEME III

ever, with respect to the other properties of interest, the thioethers are inferior to the corresponding oxo compounds: The extrapolated clearing points are 30–40°C lower, and the viscosities are about double.

Consequently, the well-known difference in the properties of liquid crystalline ethers and thioethers also holds for the terminally fluorinated systems. In a similar

TABLE I

Fluorinated thioethers

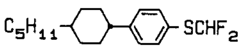
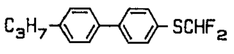
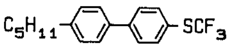
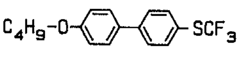
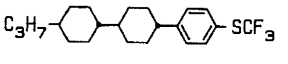
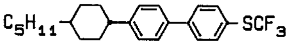
Table 1: Fluorinated thioethers		phase transitions °C	extrp. Clp. °C	$\Delta\varepsilon$ (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm^2/sec (20 °C)
<u>2a</u>		K 7 I	-60	7.2	0.055	14
<u>2b</u>		K 58 I	-70	11.3	0.119	16
<u>3a</u>		K 31 I	-80	8.4	0.093	13
<u>3b</u>		K 82 I	-40	9.9	0.125	24
<u>3c</u>		K 51 N 109.5 I	80	8.6	0.100	29
<u>3d</u>		K 60 SmB 78 N 105.2 I	70	9.4	0.149	39

TABLE II

Fluorinated sulfoxides and sulfones

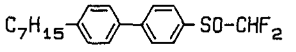
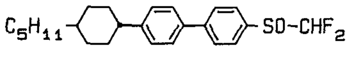
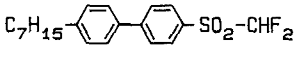
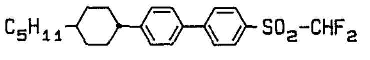
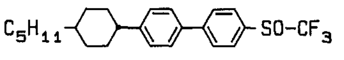
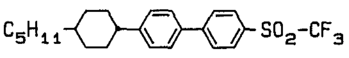
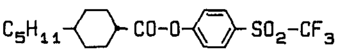
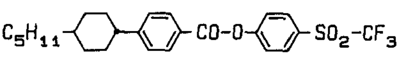
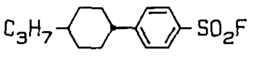
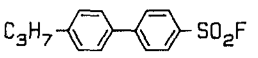
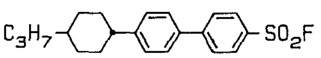
Table 2: Fluorinated sulfoxides and sulfones		phase transitions °C	extrp. Clp. °C	Δε (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm^2/sec (20 °C)
4a		K 72 I	-70	14.8	0.098	200
4b		K 102 N 108.5 I	80	16.3	0.151	350
5a		K 50 I	-110	11.2	0.087	340
5b		K 119 I	40	13.1	0.155	500
6		K 123 I	50	12.5	0.158	180
7a		K 125 I	20	22.9	0.139	310
7b		K 56 I	-90	16.0	0.029	120
7c		K 84 N 183 I	130	32.0	0.097	-

TABLE III

Sulfonyl fluorides

Table 3: Sulfonyl fluorides		phase transitions °C	extrp. Clp. °C	Δε (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm^2/sec (20 °C)
8a		K 72 I	-110	22.4	0.063	48
8b		K 94 I	-100	27.9	0.112	61
8c		K 156 I	60	27.1	0.179	200

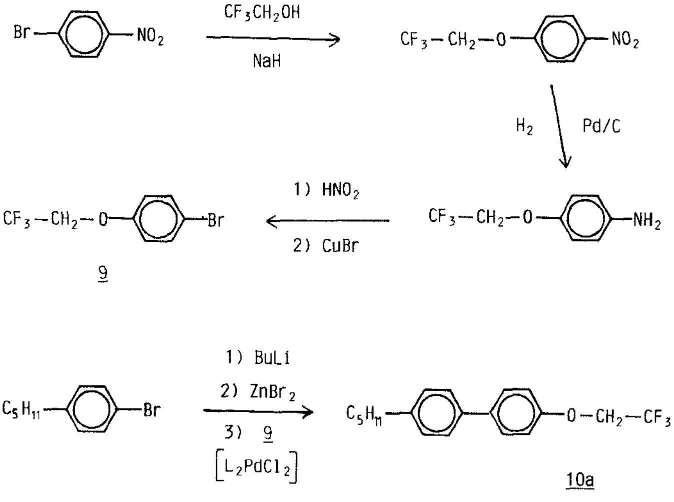
fashion to that observed in the case of the non-fluorinated systems, the liquid crystalline properties are degenerated to an even greater degree by oxidation of the thioether moiety (see Table II) as seen by the fluorinated sulfoxides and sulfones. In particular, the viscosities of these latter compounds are mostly very high. Remarkably, their Δε-values vary over a broad range:

The values for $\Delta\varepsilon$ increase in the following order of substituents SO—CF_3 < SO_2—CHF_2 < SO—CHF_2 < SO_2—CF_3; i.e. in the case of the sulfones the replacement of a terminal difluoromethyl with a trifluoromethyl causes a drastic increase in $\Delta\varepsilon$ (the trifluoromethylsulfones being the most polar compounds of this series, as expected), whereas in the case of the sulfoxides the opposite behaviour is observed with difluoromethylsulfoxide being even more effective than difluoromethylsulfone. In contrast to these somewhat strange effects, the extrapolated clearing points behave in a more predictable manner: They seem to correlate inversely with the sizes of the substituents, the clearing points increasing in the series SO_2CF_3 < SO_2CHF_2 < $SOCF_3$ < (SO_2F) < $SOCHF_2$.

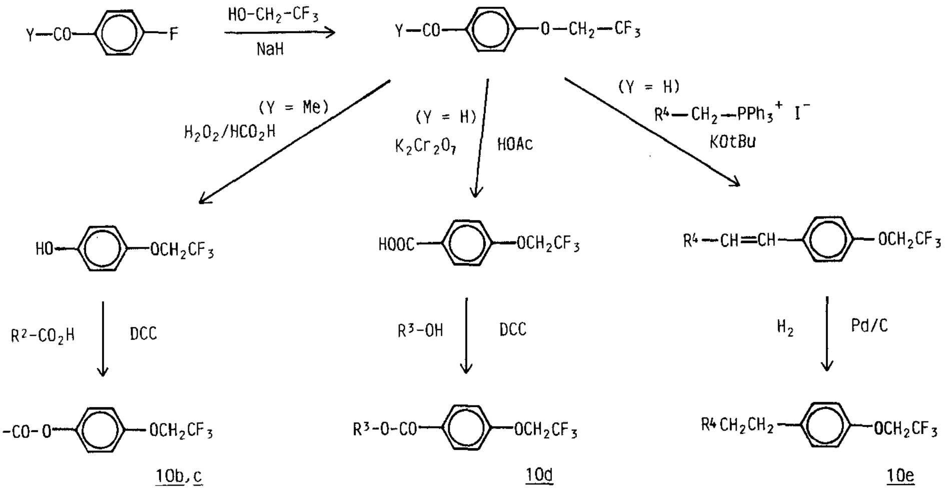
The sulfonyl fluorides 8 (see Table III) do not differ very much from the fluorinated sulfoxides and sulfones in their mesophase ranges, but they have better viscosities (at least as far as the two-ring compounds are concerned). However, they exceed even the trifluoromethylsulfones with respect to the dielectric anisotropy; indeed, the $\Delta\varepsilon$-values found for the SO_2F group are the highest ever observed for liquid crystalline structures with a single polar moiety. (Similar or higher $\Delta\varepsilon$-values can be achieved normally only by a combination of two or more polar structural moieties within a liquid crystalline molecule.)

2.2 Trifluoro-ethoxy Ethers and Esters

Since liquid crystalline compounds containing the trifluoromethoxy substituent (OCF_3) have proven to be particularly useful materials, the preparation and characterization of the homologous 2,2,2-trifluoroethoxy ethers (containing the OCH_2CF_3 group), appeared to offer a further attractive alternative. Synthesis procedures for these latter type of compounds (10) are outlined in Schemes IV and V. The first step of the synthesis of all these aromatic trifluoroethyl ethers consisted in a nucleophilie reaction of sodium trifluoroethoxide with an activated phenyl halide (1-bromo-4-nitrobenzene, p-fluorobenzaldehyde, p-fluoroacetophenone).[16,17] The nitro group was substituted by bromine via reductive hydrogenation to an amino group, dia-



SCHEME IV

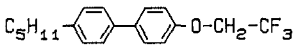
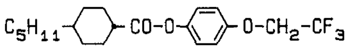
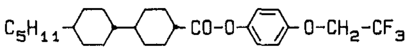
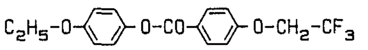
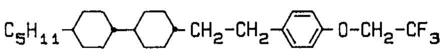


(R², R³, R⁴: detailed structures see table 4)

SCHEME V

TABLE IV

Trifluoro-ethoxy ethers

Table 4: Trifluoro-ethoxy ethers		phase transitions °C	extrp. Clp. °C	Δε (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm²/sec (20 °C)
10a		K 107 I	-30	8.7	0.116	16.0
10b		K 84 I	10	6.8	0.056	47.0
10c		K 84 SmB 178 N 197.4 I	140	7.9	0.097	61.0
10d		K 99 I	10	8.2	-	74.0
10e		K 66 SmB 166 I	120	7.2	0.101	46.0

zotation and Sandmeyer reaction, and then the bromide (9) was converted to the diphenyl derivative 10a via cross-coupling with an aryl zinc (Scheme IV). The CF_3CH_2O substituted acetophenone could be converted to liquid crystalline esters 10b and c by Baeyer-Villiger oxidation and subsequent esterification with cyclohexane carboxylic acid derivatives (Scheme V). The aldehyde was converted either into a liquid crystalline ester 10d via oxidation and esterification with a phenol or into an ethyl linked compound 10e via Wittig olefination and subsequent hydrogenation of the ethylene formed (Scheme V).

The physical properties are shown in Table IV. In comparison to the OCF_3 derivatives, the OCH_2CF_3 derivatives have almost exactly the same values for

TABLE V

Trifluoroethoxy-esters

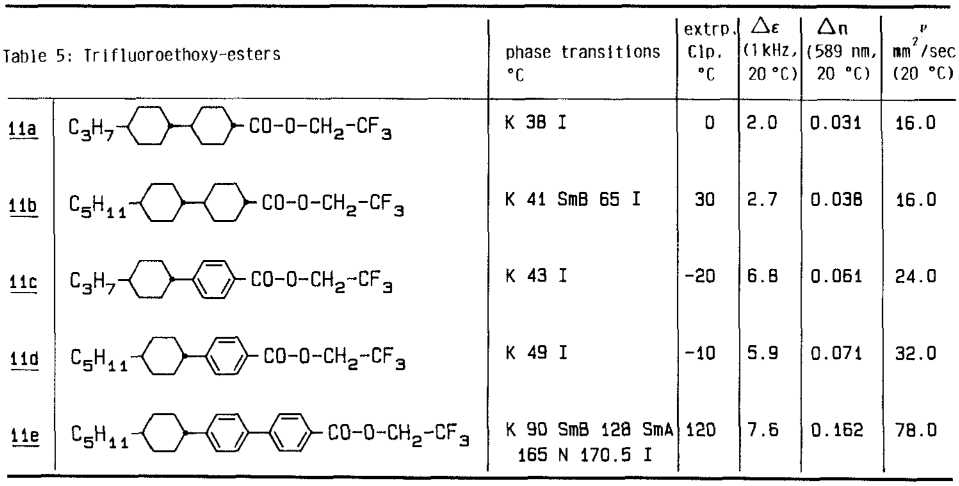


Table 5: Trifluoroethoxy-esters		phase transitions °C	extrp. Clp. °C	$\Delta\varepsilon$ (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm^2/sec (20 °C)
11a	C_3H_7 $CO-O-CH_2-CF_3$	K 38 I	0	2.0	0.031	16.0
11b	C_5H_{11} $CO-O-CH_2-CF_3$	K 41 SmB 65 I	30	2.7	0.038	16.0
11c	C_3H_7 $CO-O-CH_2-CF_3$	K 43 I	-20	6.8	0.061	24.0
11d	C_5H_{11} $CO-O-CH_2-CF_3$	K 49 I	-10	5.9	0.071	32.0
11e	C_5H_{11} $CO-O-CH_2-CF_3$	K 90 SmB 128 SmA 165 N 170.5 I	120	7.6	0.162	78.0

dielectric and optical anisotropy. However, the viscosities are drastically higher, and the OCH_2CF_3 compounds display a increased tendency to form smectic-B-phases; the extrapolated clearing points are 10–20°C higher than those of comparable OCF_3-compounds.

Whereas the synthesis of the trifluoroethoxy ethers require multi-step procedures, trifluoroethoxy esters (11) are prepared simply by esterification of the corresponding acids via the acid chlorides (see Equation 2). Physical data are given in Table V. Compared to corresponding OCF_3 derivatives, these fluorinated esters show similar values for $\Delta\varepsilon$; however, their viscosities are considerably higher. On the other hand, the extrapolated clearing points are in the range of 20–60°C higher than those of comparable structures containing OCF_3.

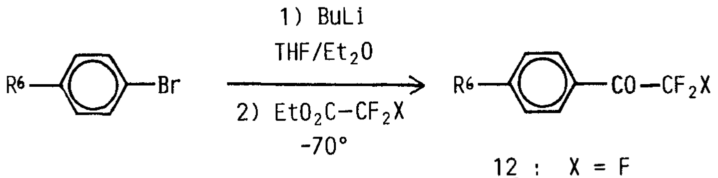
$$R^5{-}CO_2H \xrightarrow[\text{2) } CF_3CH_2OH]{\text{1) } SOCl_2} \underset{\underline{11}}{R^5{-}CO{-}O{-}CH_2{-}CF_3} \qquad \text{(eq. 2)}$$

(R^5: for detailed structures see table 5)

2.3 Fluorinated Ketones

A polar group 'par excellence' containing fluorine is the trifluoroacetyl group. We have synthesized various liquid crystalline compounds with this substituent, as well as with the difluoroacetyl, the homologous difluoropropionyl and difluorovaleroyl, and the chlorodifluoroacetyl groups.

There are several possibilities for the synthesis of these fluorinated ketones; the most convenient one on a laboratory scale consists in bromine-lithium exchange of an aromatic bromide and subsequent reaction with a fluorocarboxylic ester[18] (Equation 3).



(eq. 3)

12 : X = F
13 : H
14 : Cl
15 : Me
16 : Pr

(R^6: for detailed structures see tables 6 and 7)

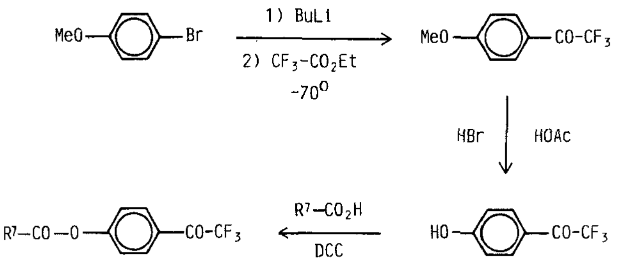
By means of this conversion 4-trifluoroacetyl-phenol also can be prepared, which can be transformed into trifluoromethyl ketones containing a carboxylic ester bridge 12f–12i (see Scheme VI). Using the same phenol also compound 12k containing a CH$_2$—O bridge could be synthesized (via reaction of the sodium phenoxide with the appropriate benzyl chloride).

As shown in Table VI, the trifluoroacetyl derivatives 12 have high dielectric anisotropies; if considered in relation to these high values for Δε, the viscosities are surprisingly low. Furthermore, these compounds exhibit a broad nematic phase range.

The CF$_3$CO compounds take an intermediate position between two important classes of polar liquid crystals, the well established nitriles and the recently introduced fluorinated materials with e.g. OCF$_3$ and CF$_3$ substituents. This is especially true with respect to the mesophase ranges and the viscosities, whereas the Δε values are as high as those of the nitriles.

Substitution of one of the fluorines of the trifluoroacetyl group by chlorine, hydrogen or alkyl changes the properties of the compounds in a more or less expected manner (see Table VII). The introduction of a chlorine atom does not bring any advantage; all physical properties considered here are deteriorated by this transformation (compare compounds 14 and 12c).

Almost the same is true for the replacement of one fluorine by hydrogen (com-



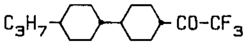
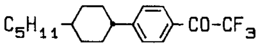
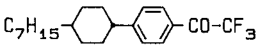
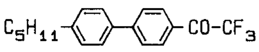
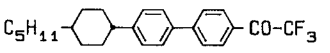
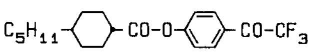
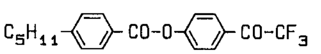
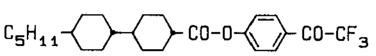
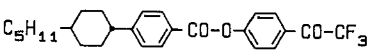
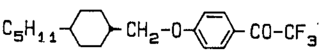
12f-i

(R^7: for detailed structures see table 6)

SCHEME VI

TABLE VI

Trifluoromethyl ketones

Table 6: Trifluoromethyl ketones		phase transitions °C	extrp. Clp. °C	Δε (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm²/sec (20 °C)
12a		K 43 I	0	5.1	0.020	13
12b		K 7 N (-24) I	-30	15.5	0.078	15
12c		K 19 N (-5.1) I	-20	15.5	0.068	20
12d		K 13 I	-40	17.5	0.161	20
12e		K 70 N 141.2 I	110	17.7	0.196	60
12f		K 71 I	0	14.0	0.075	24
12g		K 27 I	-20	26.7	0.089	34
12h		K 84 N 182.8 I	130	11.3	0.097	58
12i		K 87 N 161.7 I	110	26.0	0.150	91
12k		K 60 I	-30	13.7	0.083	26

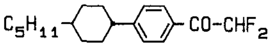
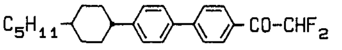
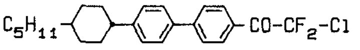
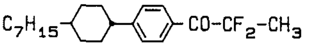
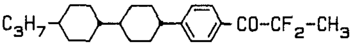
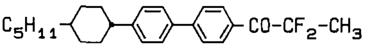
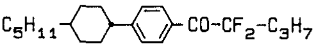
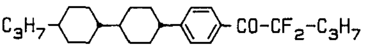
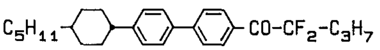
pounds 13a and 13b): The values obtained for the viscosity and for Δε are worse, however, the nematic phase range is slightly extended. On going to the homologous difluoroacyl derivatives (compounds 15 and 16), the clearing points are raised further, but also the tendency to form smectic phases is increased. Δε values are, of course, considerably lower than with the trifluoroacetyl derivatives, however, viscosities are comparable or even better. A potentially unfavourable property of all these alkyl aromatic ketones containing fluorine is a certain sensitivity against UV light (except of the purely aliphatic compound 12a). Nevertheless, these compounds, especially the trifluoromethyl ketones (12), seem to be highly promising materials.

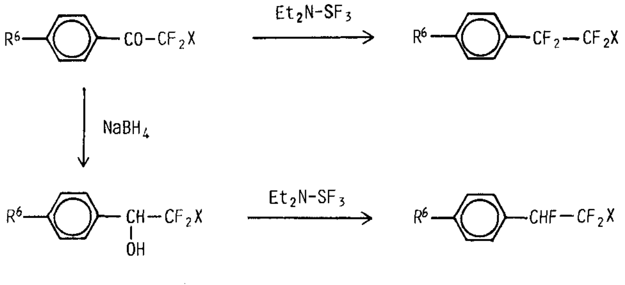
3. OUTLOOK

It is rather obvious that the fluorinated ketones described before can themselves be used as starting materials for the synthesis of many more liquid crystals con-

TABLE VII

Difluoroalkyl ketones

	Table 7: Difluoroalkyl ketones	phase transitions °C	extrp. Clp. °C	Δε (1 kHz, 20 °C)	Δn (589 nm, 20 °C)	ν mm^2/sec (20 °C)
13a		K 39 I	-20	11.1	0.076	21
13b		K 80 N 158 I	120	10.2	0.200	83
14		K 52 N 124 I	100	16.5	0.185	98
15a		K 28 N 43.6 I	30	6.7	0.095	19
15b		K 92 N 197.1 I	150	7.1	0.146	56
15c		K 52 SmB 140 SmA 169 N 190.7 I	150	8.5	0.217	54
16a		K 20 SmB 33 N 53.9 I	20	5.7	0.096	17
16b		K 73 SmB 152 N 199 I	150	7.4	0.142	49
16c		K 159 SmB (158) SmA 189 N 192.8 I	150	8.5	0.204	47



SCHEME VII

taining fluorinated substituents; fluorinating agents (like DAST) easily convert the keto groups, or hydroxymethylene groups generated from the former, into methylene units containing fluorine[19,20]; thus liquid crystalline compounds containing partially (or even fully) fluorinated alkyl substituents are produced (see Scheme VII). Compounds of this latter type and related structures are currently under investigation and will be presented in detail in another publication.

4. EXPERIMENTAL: MEASUREMENT OF THE PHYSICAL PROPERTIES

The methods used to determine the physical properties of the substances synthesized have already been described in detail.[21,22] 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.

Known concentrations of 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_o and n_e of the homeotropically aligned materials were measured in an Abbe refractometer. The viscosities were determined in flow viscosimeters (Hoffmann type). The values of the pure materials were then obtained by linear extrapolation.

Additional Material

^{1}H-NMR and MS data of the prepared compounds are available.

Acknowledgment

We thank Jörg Haas, Andreas Ruhl, and Walter Wetzel for their work in the synthesis of the compounds and Ray Jubb, Heike Prücher and Helga Schubert for the measurement of the physical properties.

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