Polar nematic methyl (*E*)-[*trans*-4-cyclohexyl-substituted]allyl ethers: Synthesis, liquid crystal transition temperatures and some physical properties

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Polar nematic methyl (*E*)-[*trans*-4-cyclohexyl-substituted]allyl ethers: synthesis, liquid crystal transition temperatures and some physical properties

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We have introduced an oxygen atom and a carbon–carbon double bond with a *trans*-configuration (*E*) into the terminal alkyl chain attached to the cyclohexyl ring of a variety of two- and three-ring nematic liquid crystals of positive dielectric anisotropy. The new polar two-ring methyl (*E*)-allyl ethers often possess low melting points, but are not mesomorphic in general. The related three-ring methyl (*E*)-allyl ethers exhibit high clearing points and wide nematic ranges. Comparisons with the corresponding derivatives incorporating either just an oxygen atom or just a carbon–carbon double bond in the same position indicate that synergetic effects lead to broader nematic phases than would otherwise have been expected. This is partially due to the low smectic transition temperatures observed for the methyl (*E*)-allyl ethers. Selected physical properties of three binary mixtures of a weakly polar standard nematic liquid crystal and three difluoro-substituted (polar) liquid crystals (including the new ethers) differing only in the nature of the terminal chain show that, although some of the methyl (*E*)-allyl ethers exhibit longer switch-off times in TN cells than those of analogous liquid crystals incorporating either a methyl propyl ether or a 1-(*E*)-propenyl chain instead of the methyl (*E*)-allyl ether chain, they are still useful components for nematic mixtures, especially where a wide temperature range is required.

1. Introduction

Polar nematic liquid crystals of positive dielectric anisotropy for commercial electro-optic liquid crystal displays (LCDs) [1–11] normally consist of two to four 1,4-disubstituted six-membered rings, a polar end group, linking units and terminal alkyl/alkoxy chains [11–16]. Attempts have been made to optimize the physical properties (for example, the liquid crystal transition temperatures, elastic constants, viscosity, etc.) of these nematic liquid crystals by systematically varying many of their structural elements. Several aliphatic and aromatic 1,4-disubstituted rings with axial symmetry and linearity have been introduced (for example, benzene, cyclohexane, pyrimidine, etc. [17–20]). In order to obtain a positive dielectric anisotropy, at least one electron rich and polarizable benzene ring has normally been substituted with at least one polar terminal substituent (for example, F, Cl, CN, OCF_3, etc. [17–24]). The two or three rings are normally linked directly or by two or four atom units (for example, C_2H_4, C_4H_8, etc. [23–28]). More recently the terminal aliphatic chains have been varied by the introduction of hetero atoms (for example, S, N, Si, O, for example [29–32]) and carbon–carbon double bonds (for example, [33–41]). The position of the hetero atom or the carbon–carbon double bond is of critical importance [29–41].

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However, there are very few reports of liquid crystals incorporating two different functional groups in the terminal chains [11–16]. Therefore, as a first step in a systematic study, it was decided to introduce two of these groups (i.e., an oxygen atom and a double bond) into the side chains of a variety of polar, potentially mesomorphic structures, as well as into weakly polar materials (see accompanying publication [42]) in order to determine their effect on liquid crystal transition temperatures and some other physical properties of relevance to LCDs.

2. Synthesis

The methods of synthesis and chemical structures of the new methyl (*E*)-allyl ethers (**11a–n, 22a–e, 24a–e** and **33a–f**) with a *trans*-carbon–carbon double bond and oxygen atom in the terminal chain are shown in the reaction schemes 1–4. The methods of preparation are described in general below and then in detail in the experimental section for a representative (trifluoromethoxy-substituted) member of each series (**11k, 22c, 24e** and **33e**). The configuration of the carbon–carbon double bond in the methyl (*E*)-allyl ether chain of the new ethers (**11a–n, 22a–e, 24a–e** and **33a–f**) and reaction intermediates was confirmed by ^{1}H NMR spectroscopy (the *trans*-olefinic coupling constants ≈ 12–18 Hz are larger than those of the corresponding *cis*-olefinic coupling constants ≈ 7–11 Hz) and by infrared spectroscopy (the *trans*-absorption bands are narrow and exact ≈ 970–960 cm^{-1}, while the *cis*-absorption bands are observed at distinctly different wave lengths ≈ 730–675 cm^{-1}). Traces of undesired isomers formed during the preparation of the various reaction intermediates could be removed by recrystallization (see the experimental section). The structural and isomeric purity was determined by differential thermal analysis and capillary gas chromatography as usual and, where necessary, on liquid crystal packed columns [43].

The variously substituted two- and three-ring methyl (*E*)-[*trans*-4-(4-substituted-phenyl)cyclohexyl]allyl ethers (**11a–n**) were synthesized as depicted in scheme 1. Reaction of the Grignard reagent (**2**) with the protected cyclohexanone (**1**) [44] yielded
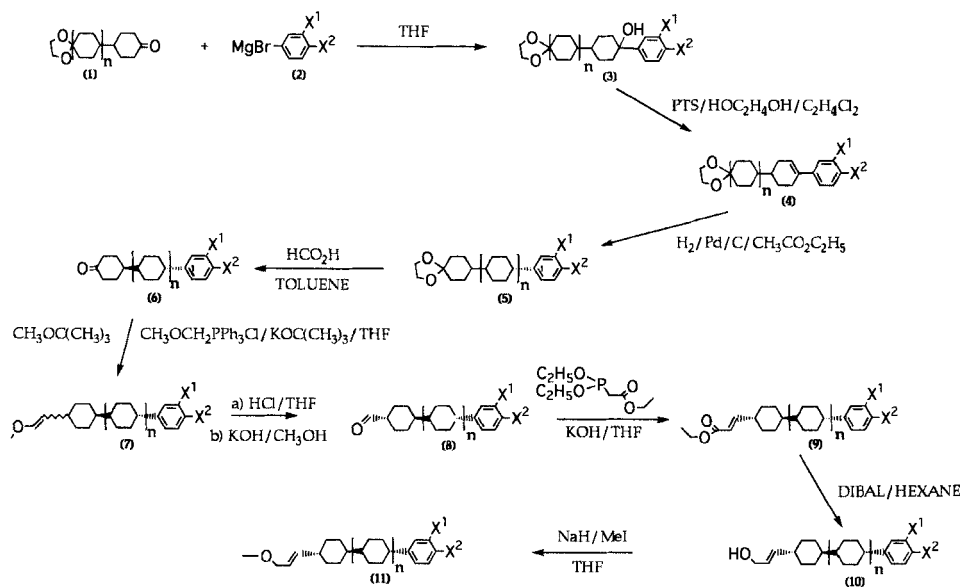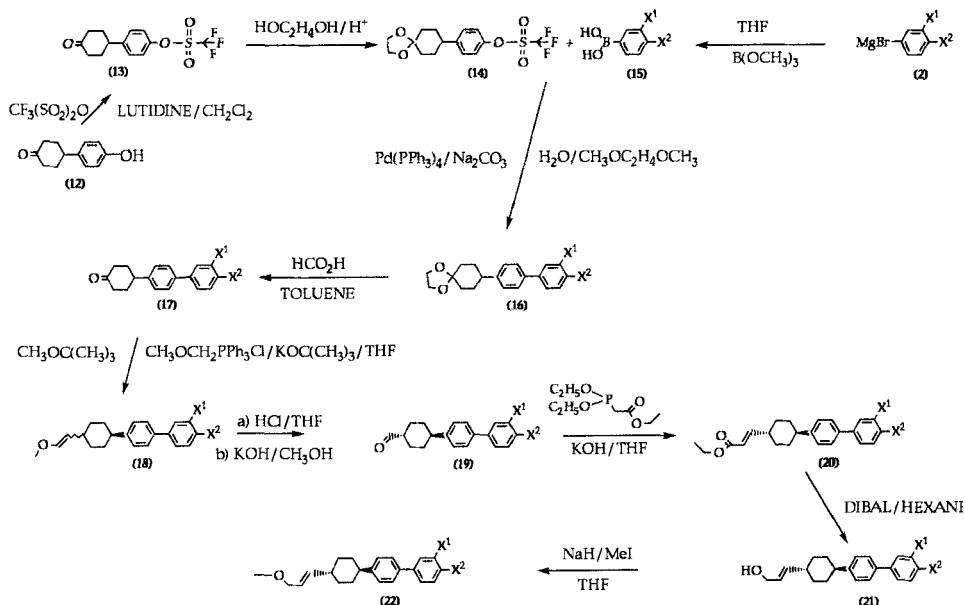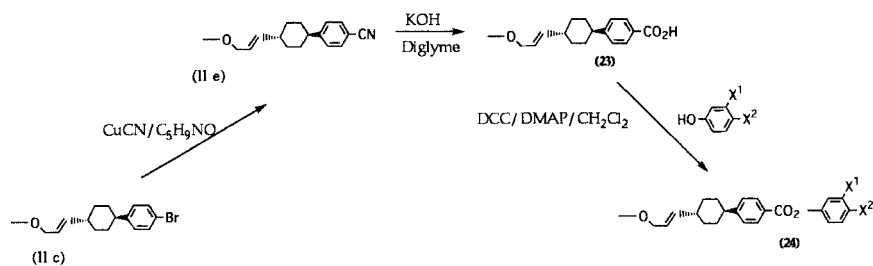

Scheme 1.

Scheme 2.

the alcohol (3) as a *trans-/cis*-mixture. Elimination of the alcohol group using *p*-toluene sulphonic acid yielded the cyclohexene compound (4). Hydrogenation over palladium on charcoal gave the *trans*-ketal (5). The ketone (6), obtained by deprotection with formic acid was used in a Wittig reaction to yield the methoxymethyl substituted compound (7). Hydrolysis using hydrochloric acid gave the aldehyde (8), which was isomerized using potassium hydroxide to the pure *trans*-form. The methyl (E)-allyl ethers (11) were produced in the pure *trans*-form from the aldehyde (8), via a Wittig–Horner [45] reaction to produce the ethyl (E)-acrylates (9), reduction to the allyl alcohols (10) using DIBAL [46, 47] and then methylation using sodium hydride [48]. No isomerization of the carbon–carbon bond was necessary.

The ethers (22a–e) were synthesized via the reaction pathway shown in scheme 2. The starting material 4-(4-hydroxyphenyl)cyclohexanone (12) prepared in three steps [49] from commercially available phenylcyclohexanone) was first converted into the triflate (13) and then protected as usual as the ketal (14). Reaction with commercially available boronic acids (15) (or made from the Grignard reagents (2) as usual [50]) in an aryl–aryl coupling reaction [51, 52] yielded the desired substituted biphenyls (16). Deprotection as described above resulted in the corresponding cyclohexanones (17), which were converted into the methoxymethyl compounds (18) via a Wittig reaction. Hydrolysis using hydrochloric acid and isomerization using potassium hydroxide gave the aldehyde (19) in the pure *trans*-form. The methyl (E)-allyl ethers (22a–e) were produced from the aldehyde (19) via the acrylates (20) and the allyl alcohols (21) as described above.

The variously substituted phenyl benzoates (24a–e) with a methyl (E)-allyl ether chain were synthesized by a normal esterification using DCC and DMAP [53] of the benzoic acid (23) and commercially available phenols, see scheme 3. The benzoic acid (23) resulted from saponification with potassium hydroxide of the analogous benzo-nitrile (11e) produced from the corresponding bromide (11c) using copper (I) cyanide [17, 54], see scheme 1 and table 1.

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Scheme 3.

Table 1. The transition temperatures and some enthalpies of fusion for the methyl (*E*)-allyl ethers (**11a–g**).

Ether	X^1	X^2	C–I/°C	N–I/°C	ΔH/kJ mol^{-1}
11a	H	F	27	—	
11b	H	Cl	40	—	12·4
11c	H	Br	47	—	8·4
11d	H	OCF$_3$	6	—	17·3
11e	H	CN	66	(59)†	16·3
11f	F	F	24	—	18·1
11g	F	Cl	23	—	

† Represents a monotropic transition temperature.
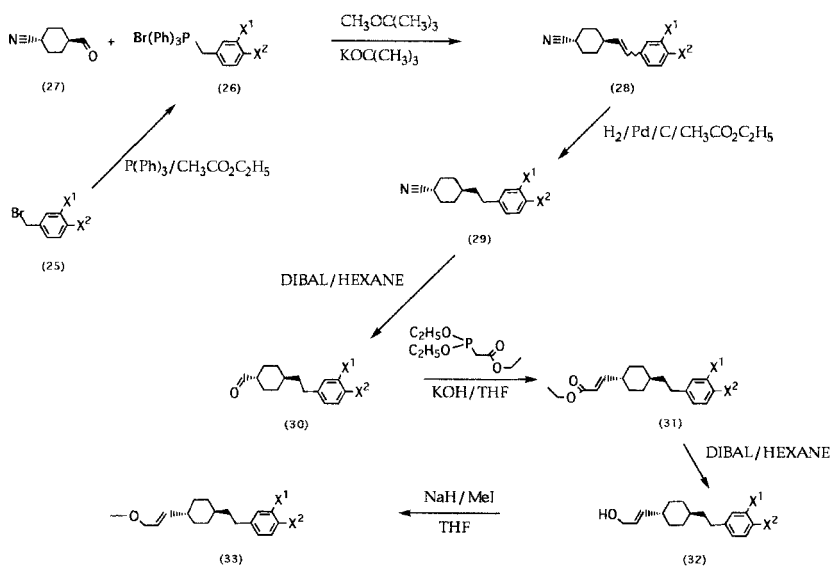
Scheme 4.

The method of synthesis of the methyl (*E*)-allyl ethers with an ethyl linkage (**33a–f**) is depicted in scheme 4. The *trans*-1-cyano-4-formylcyclohexane (**27**) [55] is converted to the ethane (**28**) as a *trans-/cis-(E/Z)* mixture via a Wittig reaction using Wittig salts (**26**), either commercially available or made from the substituted benzyl bromides (**25**) [49]). Hydrogenation over palladium on active charcoal yielded the ethane (**29**), which was reduced by DIBAL [46, 47] to the aldehyde (**30**). A standard Wittig–Horner reaction gave the acrylates (**31**), which were converted using DIBAL to the allyl alcohols (**32**). Methylation using sodium hydride and methyl iodide resulted in the desired methyl (*E*)-allyl ethers (**33a–f**).

3. Mesomorphic properties

The mono- and di-substituted two-ring methyl (*E*)-allyl ethers (**11a–g**) are not mesomorphic in general, see table 1. A monotropic nematic phase could only be determined for the benzonitrile (**11e**). The melting points vary greatly (6–66°C). This is the usual behaviour observed for two-ring compounds [12–16, 21–24].

The introduction of a second 1,4-disubstituted cyclohexane ring into the ethers (**11a–g**) to produce the three-ring methyl (*E*)-allyl ethers (**11h–n**) leads to the formation of broad nematic phases at elevated temperatures, see table 2. The melting point is increased substantially (+52°C, on average comparing only ethers with the same substituents). The clearing point (N–I) of the mono-substituted ethers (**11h–l**) rises with increasing polarity of the end group. Thus the nitrile (**11l**) exhibits the highest clearing point and also the broadest nematic phase. This is normal behaviour for nematics. The other ethers exhibit remarkably similar temperature ranges, see table 2 and figure 1, although the melting points are irregular as usual. Only one ether (**11k**) exhibits an enantiotropic smectic B phase. The melting and clearing points of the disubstituted ethers (**11m** and **11n**) are lower (−33°C and −42°C, on average, respectively) that those of the corresponding mono-substituted ethers (**11h** and **11i**), as expected due to the broadening effect of the lateral substituents.

The replacement of a 1,4-disubstituted cylohexane ring in the compounds (**11h–n**) by a 1,4-disubstituted benzene ring to yield the substituted biphenyls (**22a–e**) does not change the liquid crystal temperatures substantially, see table 3. Only smectic B and nematic phases are observed. The melting point is increased (+5°C, on average, comparing only substances with the same substituents). The smectic B transition temperature (observed for the same substituent, OCF_3) is increased more substantially

Table 2. The transition temperatures and some enthalpies of fusion for the methyl (*E*)-allyl ethers (**11h–n**).

Ether	X^2	X^1	$C–S_B/N/°C$	$S_B–N/°C$	$N–I/°C$	$\Delta H/\text{kJ mol}^{-1}$
11h	H	F	83	—	170	23·0
11i	H	Cl	99	—	204	
11j	H	Br	120	—	207	
11k	H	OCF_3	71	83	170	
11l	H	CN	109	—	265	14·4
11m	F	F	47	—	133	21·0
11n	F	Cl	69	—	168	15·4
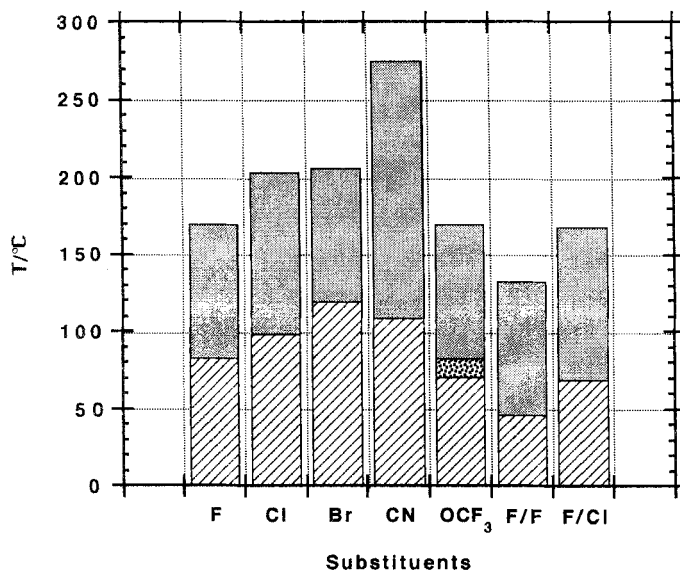
Figure 1. Plot of the transition temperatures against the nature of the substituent of the three-ring methyl (*E*)-allyl ethers (**11h–n**). ▨, Crystal; ▦, S_B; ▩, Nematic.

Table 3. The transition temperatures and some enthalpies of fusion for the methyl (*E*)-allyl ethers (**22a–e**).
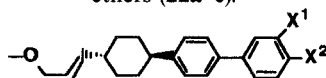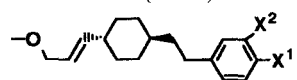
Ether	X^1	X^2	$C-S_B/N/°C$	$S_B-N/°C$	$N-I/°C$	$\Delta H/\text{kJ mol}^{-1}$
22a	H	F	111	—	174	
22b	H	Cl	140	—	208	16·5
22c	H	OCF$_3$	63	113	163	12·0
22d	F	F	91	—	107	16·3
22e	F	Cl	105	—	153	17·6

($+30°C$). The clearing point (N–I) is decreased by a smaller amount ($-8°C$, on average, comparing only substances with the same substituents). This results in a large decrease ($-44°C$, on average) in the nematic phase range.

The introduction of a carboxy group (COO) between the two rings of the substituted biphenyls (**22a–e**) to produce the phenyl benzoates (**24a–e**) results in an increase ($+15°C$, on average, comparing only substances with the same substituents) in the nematic phase range, see table 4, primarily due to the absence of a smectic B phase. The melting and clearing points rise to an almost equal degree ($+28°C$ and $+26°C$, on average, respectively). These increases can probably be ascribed to the greater degree of polarizability and conjugation for the esters (**24a–e**) compared to the directly bonded biphenyl (**22a–e**).

Table 4. The transition temperatures and some enthalpies of fusion for the methyl (*E*)-allyl ethers (**24a–e**).

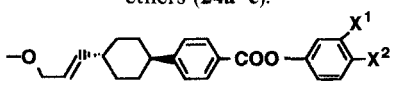| Ether	X^1	X^2	C–N/°C	N–I/°C	ΔH/kJ mol^{-1}
24a	H	F	129	187	30·0
24b	F	F	99	149	25·5
24c	H	CN	147	253	26·1
24d	F	CN	94	214	26·4
24e	H	OCF$_3$	120	187	22·7

Table 5. The transition temperatures and some enthalpies of fusion for the methyl (*E*)-allyl ethers (**33a–f**).

Ether	X^1	X^2	C–I/°C	ΔH/kJ mol^{-1}
33a	H	F	28	13·4
33b	H	Cl	37	28·8
33c	H	Br	46	
33d	H	CF$_3$	40	19·3
33e	H	OCF$_3$	−1	14·8
33f	F	Cl	37	

The variously substituted ethanes (**33a–f**) with a methyl (*E*)-allyl ether chain do not exhibit mesomorphism. The melting points are slightly lower (– 5°C, on average, comparing only substances with the same substituents) than those of the corresponding ethers (**11a–g**) with a direct carbon–carbon bond between the two benzene rings instead of the dimethylene linkage, see table 5. This is often the case due to the added flexibility introduced by the dimethylene linkage [23–28].

The effect of introducing an oxygen atom or a double bond and then both in the same position into the standard difluoro-substituted material with a normal pentyl chain is shown in table 6 and figure 2. The melting and clearing points of all the substances are similar (79°C and 169°C, on average, respectively). However, the methyl (*E*)-allyl ether (**11h**) does not exhibit a smectic phase in contrast to the smectic B behaviour observed at high temperatures (81°C, on average) for the other compounds.

Many three-ring intermediates (i.e., acrylates, **9a–l**, **20a–e**, and **31a–f** and allyl alcohols, **10a–l**, **21a–e** and **32a–f**) are themselves liquid crystalline, see tables 7 and 8. In general, they show the same trends as the corresponding methyl (*E*)-allyl ethers (**11a–n**, **22a–e**, **24a–e** and **33a–f**), see tables 1–5. The relationships between the mesomorphic transition temperatures of such systems are dealt with in detail in the accompanying publication [42].

Table 6. The transition temperatures for the compounds.

$$R\text{---}\langle\text{---}\rangle\text{---}\langle\text{---}\rangle\text{---}\langle\text{---}\rangle\text{---}F$$
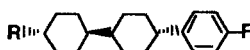
Code	R	C–S_B/N/°C	S_B–N/°C	N–I/°C
5CCPF		68	75	157
103CCPF		75	89	159
3d$_1$CCPF		80	(73)	177
101d$_1$CCPF		83	(⩽25)†	170

†( ) Represents a monotropic transition temperature.
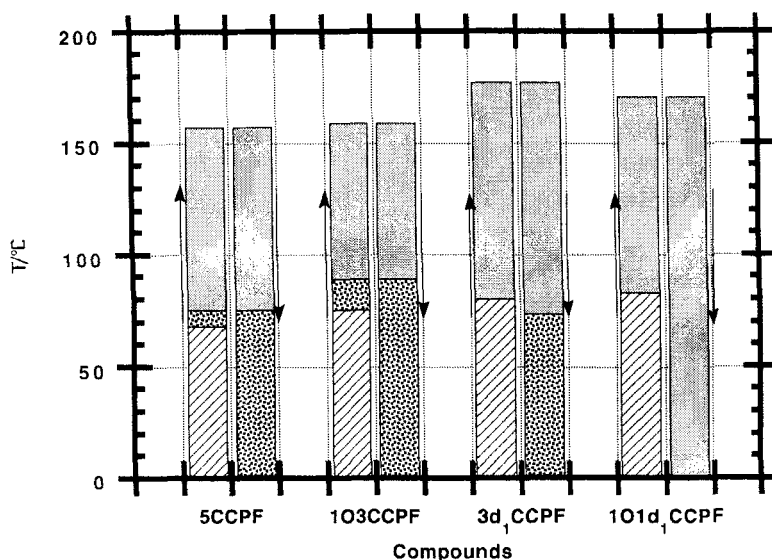
Figure 2. Plot of the transition temperatures against the nature of the terminal chain of the compounds coded 5CCPF; 1d$_1$CCPF, 103CCPF and 101d$_1$CCPF. The arrows represent heating or cooling cycles. ▨, Crystal; ▦, S$_B$; ▢, Nematic.

4. Physical properties

Selected physical properties of three binary mixtures of a weakly polar standard nematic liquid crystal (*E*)-3-pentenyl 4-(*trans*-4-propylcyclohexyl)phenyl ether [41] (code; 3CPOd$_3$1)] and three difluoro-substituted (polar) liquid crystals have been evaluated and compared, see figures 3–9. The three difluoro-substituted liquid crystal materials incorporate the methyl (*E*)-allyl ether (**11m**; code 101d$_1$CCP$_F$F), the methyl propyl ether (code; 103CCP$_F$F) [56, 57] or a 1-(*E*)-propenyl chain (code; 1d$_1$CCP$_F$F) [41]. The two reference compounds 103CCP$_F$F and 1d$_1$CCP$_F$F are important components of (commercially available) nematic mixtures [56, 57] for LCDs. The three binary mixtures exhibit broadly similar plots of the elastic constants ($k_{ii} = k_{33}$, k_{22} and k_{11}) against the reduced temperature (T/T_{NI}), see figure 3. It is therefore, not surprising that the plots of the ratios k_{33}/k_{11} and k_{22}/k_{11} against T/T_{NI} for the binary mixtures are also similar, see figures 4 and 5. However, for the pure methyl (*E*)-allyl ether 101d$_1$CCP$_F$F, the value of k_{33} is large, k_{22} is average, while k_{11} is low compared to the

Table 7. The transition temperatures for the intermediate acrylates (**9a–l**, **20a–e** and **31a–f**) as shown by the general formula.
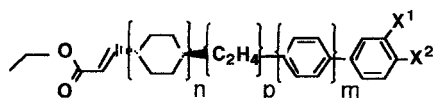
Acrylate	n	m	p	X^1	X^2	C–N/I/°C	N–I/°C
9a	1	0	0	H	F	90	—
9b	1	0	0	H	Cl	46	—
9c	1	0	0	H	Br	140	—
9d	1	0	0	H	ODF_3	46	—
9e	1	0	0	F	F	73	—
9f	1	0	0	F	Cl	74	—
9g	2	0	0	H	F	91	179
9h	2	0	0	H	Cl	95	218
9i	2	0	0	H	Br	108	214
9j	2	0	0	H	OCF_3	88	190
9k	2	0	0	F	F	79	160
9l	2	0	0	F	Cl	76	193
20a	1	1	0	H	F	153	182
20b	1	1	0	H	Cl	167	219
20c	1	1	0	H	OCF_3	104	130
20d	1	1	0	F	F	100	148
20e	1	1	0	F	Cl	123	180
31a	1	0	1	H	F	<25	—
31b	1	0	1	H	Cl	59	—
31c	1	0	1	H	Br	78	—
31d	1	0	1	H	CF_3	38	—
31e	1	0	1	H	OCF_3	31	—
31f	1	0	1	F	Cl	60	—

corresponding elastic constants for the binary mixtures. The high values of k_{33}/k_{11} and k_{22}/k_{11} for the pure component $101d_1CCP_FF$ and the still relatively high values for the standard material $3CPOd_31$ show that these ratios are not additive. This non-linear behaviour could be used to obtain steep voltage-transmission characteristics in supertwisted nematic displays (STN-LCDs), where high values of k_{33}/k_{11} are required [40]. The plots of the elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ against T/T_{NI} for the binary mixtures are similar, although the compound $1d_1CCP_FF$ exhibits the highest absolute values, see figure 6. The plot for the pure ether $101d_1CCP_FF$ is also high and relative flat, indicating a low temperature dependence. This is of advantage for LCD applications, where a small temperature dependence of the electro-optic response is required. The plot of the rotational viscosity γ_1 against T/T_{NI} for the binary mixture containing the methyl (E)-allyl ether $101d_1CCP_FF$ lies somewhat higher than those of the other two binary mixtures, see figure 7. This may be due to the added stiffness or linearity of the methyl (E)-allyl ether chain resulting in a larger rotational viscosity. The plots of the visco-elastic ratio γ_1/κ for all the binary mixtures are very similar in shape, see figure 8. The alkenyl compound $1d_1CCP_FF$ exhibits the lowest absolute values, primarily due to the shorter chain (3 C atoms). The values for the methyl (E)-allyl ether $101d_1CCP_FF$ lie slightly higher than those of the methyl propyl ether $103CCP_FF$. This must be due to the double bond, as this is the only difference between the two structures. The ratio γ_1/κ basically determines the switch off times $t_{off} \propto \gamma_1/\kappa$ in twisted nematic (TN-LCDs) cells. γ_1/κ and thus t_{off}, are similar for the two binary mixtures

Table 8. The transition temperatures for the intermediate allyl alcohols (**10a–l, 21a–e** and **32a–f**) as shown by the general formula.
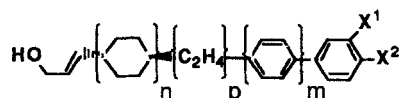
Alcohol	n	m	p	X^1	X^2	C–N/I/°C	N–I/°C
10a	1	0	0	H	F	<25	—
10b	1	0	0	H	Cl	92	—
10c	1	0	0	H	Br	105	—
10b	1	0	0	H	OCF_3	43	—
10d	1	0	0	F	F	<25	—
10f	1	0	0	F	Cl	73	—
10g	2	0	0	H	F	125	198
10h	2	0	0	H	Cl	143	242
10i	2	0	0	H	Br	156	245
10j	2	0	0	H	OCF_3	136	193
10k	2	0	0	F	F	91	167
10l	2	0	0	F	Cl	120	204
21a	1	1	0	H	F	187	201
21b	1	1	0	H	Cl	216	230
21c	1	1	0	H	OCF_3	149	170
21d	1	1	0	F	F	141	—
21e	1	1	0	F	Cl	168	182
32a	1	0	1	H	F	59	—
32b	1	0	1	H	Cl	68	—
32c	1	0	1	H	Br	82	—
32d	1	0	1	H	CF_3	76	—
32e	1	0	1	H	OCF_3	58	—
32f	1	0	1	F	Cl	68	—

containing the compounds $101d_1CCP_FF$ and $103CCP_FF$ with oxygen in the chain (see figures 8 and 9). The response times of the alkenyl compound $1d_1CCP_FF$ are shorter due to the shorter chain. Threshold voltages for binary mixtures, containing the methyl (*E*)-allyl ether $101d_1CCP_FF$ are slightly higher than those of other binary mixtures incorporating the other two reference compounds. This is due to a marginally lower value of the dielectric anisotropy for the former.

Thus, the new methyl (*E*)-allyl ethers show broadly comparable physical properties and electro-optical characteristics to those of some analogous components of commercially available nematic mixtures for LCDs [56, 57]. However, the broad nematic phases, low melting and smectic B transition temperatures and high clearing points of some of the new methyl (*E*)-allyl ethers can simplify the design of nematic mixtures of positive dielectric anisotropy.

The methods for determining the physical properties, especially the elastic constants, have been previously described [58].

5. Experimental

The liquid crystal transition temperatures of the new compounds (tables 1–8) were determined by optical microscopy using a Leitz Ortholux II POL BK microscope in conjunction with a Mettler FP 82 heating stage and FP 80 control unit. All the monotropic liquid crystal phases could be observed using a microscope and no virtual
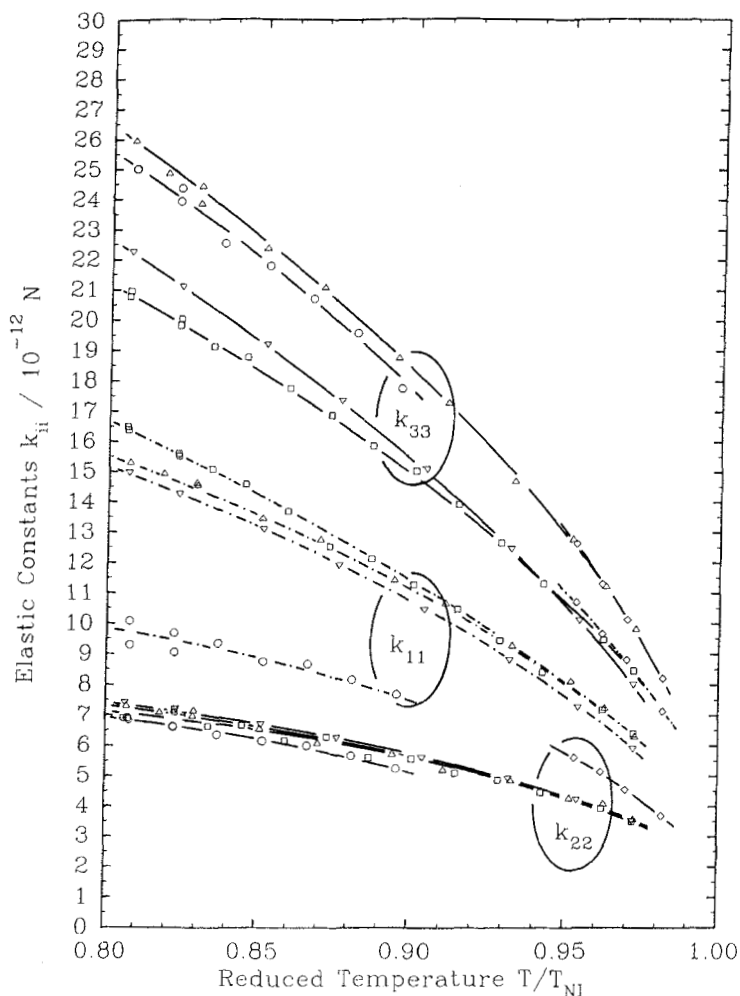
Figure 3. Plots of the elastic constants k_{ii} against reduced temperature T/T_{NI} for the pure compounds 101d$_1$CCPF ($\bigcirc$) and 3CPOd$_3$1 ($\diamond$) and the binary mixtures 1d$_1$CCPF/3CPOd$_3$1 ($\triangle$), 103CCPF/3CPOd$_3$1 ($\square$) and 101d$_1$CCPF/3CPOd$_3$1 ($\triangledown$).

values (extrapolated) had to be determined. When necessary, the Mettler stage could be cooled ($-50°$C) by allowing N$_2$ gas, cooled by liquid N$_2$, to pass through the stage at a controlled rate. The liquid crystal transition temperatures were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin layer chromatography (TLC), gas chromatography (GC) and differential thermal analysis DTA. A Perkin–Elmer 8310 gas capillary chromatograph equipped with a 25 m OV 61 column and GP-100 graphics printer was used. TLC plates (4 cm × 8 cm) coated with SiO$_2$ SIL/G/UV$_{254}$ (Machery–Nagel, Düren, Germany) were utilized. The purity of the final liquid crystalline products (**11, 22, 24** and **33**) was > 99·7 per cent by GC and DTA. Column chromatography was carried out using silica gel 60 (330–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out using a nitrogen atmosphere unless water was present as solvent or reagent. All temperatures were measured externally unless otherwise stated.
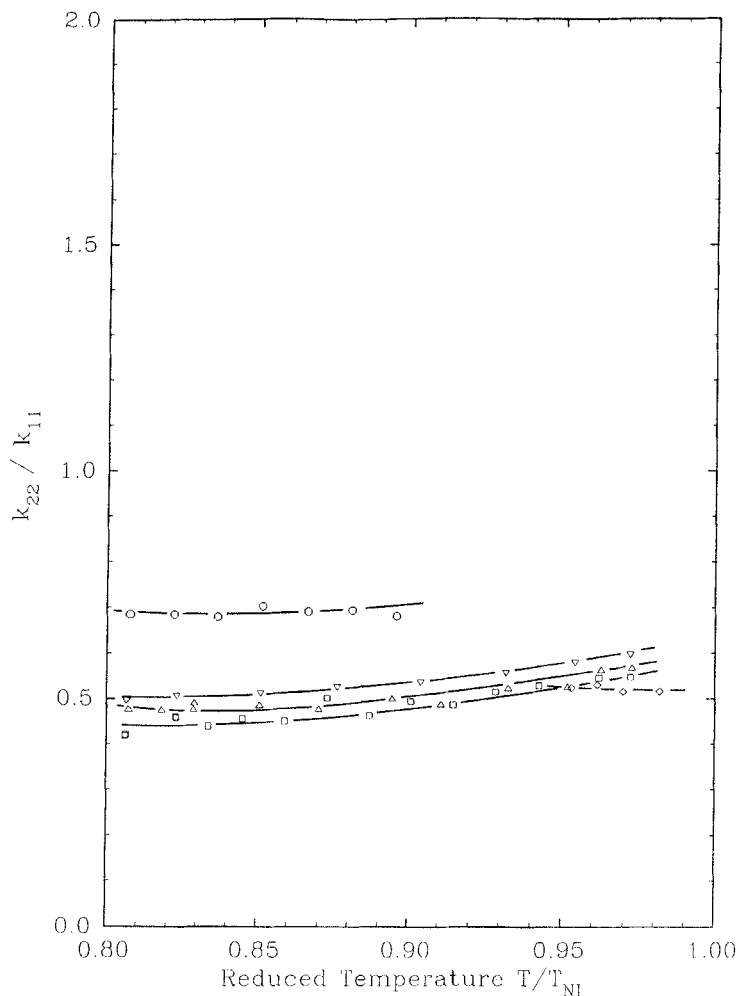
Figure 4. Plots of the elastic constant ratio k_{22}/k_{11} against reduced temperature T/T_{NI} for the
pure compounds $101d_1CCPF$ (○) and $3CPOd_31$ (◇) and the binary mixtures
$1d_1CCPF/3CPOd_31$ (△), $103CCPF/3CPOd_31$ (□) and $101d_1CCPF/3CPOd_31$ (▽).

The ^1H NMR spectra were recorded at 60 MHz (Varian T-60), 80 MHz (Bruker WP-
80) or 270 MHz (Bruker HX-270). Mass spectra were recorded using a MS9 (AEZ
Manchester) spectrometer.

5.1. *4-[4-(4-Trifluoromethoxyphenyl)-4-hydroxycyclohexenyl]cyclohexanone ethylene ketal (3; n = 1; $X^1 = H$; $X^2 = OCF_3$)*

A solution of Grignard reagent (produced as usual from 1-bromo-4-
trifluoromethoxybenzene (41·0 g, 170 mmol), magnesium turnings (4·1 g, 170 mmol)
and tetrahydrofuran (125 cm³)) was added dropwise to a mixture of 4-oxacyclohexyl-4-
cyclohexanone ethylene ketal [44] (30·0 g, 126 mmol) in tetrahydrofuran (200 cm³) at
0°C and then stirred overnight at room temperature. Acetic acid (10 per cent) was
added dropwise to the reaction mixture at 0°C, which was then shaken with ethyl
acetate (3 × 50 cm³). The combined organic layers were washed with brine (2
× 100 cm³), dried (MgSO₄), filtered and then evaporated down under reduced pressure.
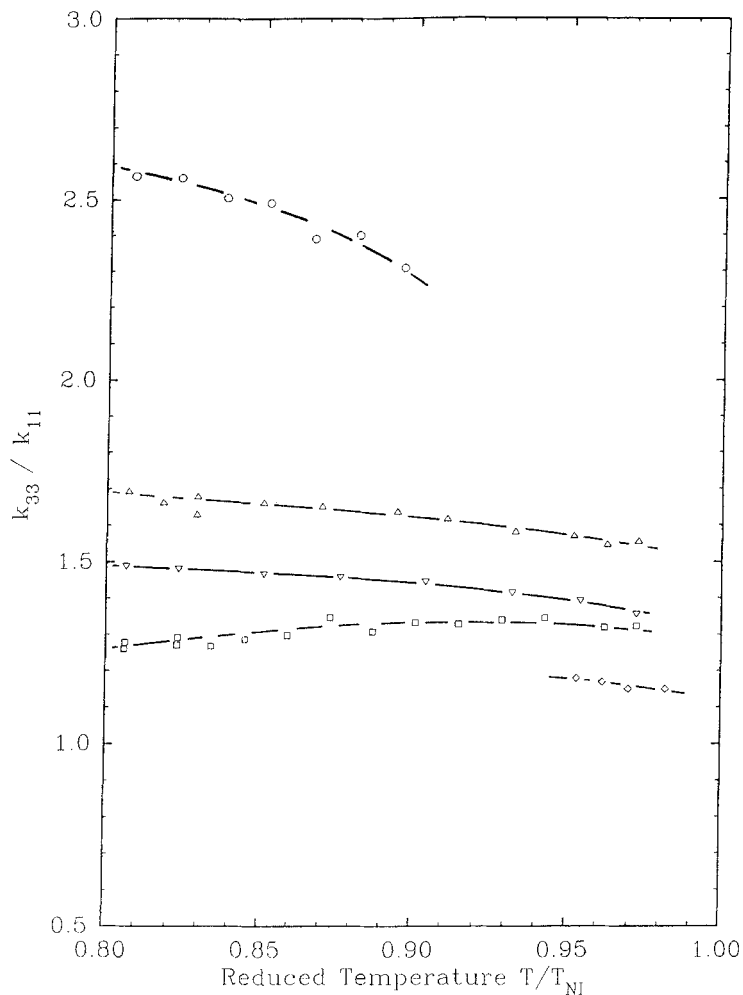
Figure 5.   Plots of the elastic constant ratio k_{33}/k_{11} against reduced temperature T/T_{NI} for the pure compounds $101d_1CCPF$ (○) and $3CPOd_31$ (◇) and the binary mixtures $1d_1CCPF/3CPOd_31$ (△), $103CCPF/3CPOd_31$ (□) and $101d_1CCPF/3CPOd_31$ (▽).

The residue was purified by column chromatography on silica gel using a 3:1 hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield (**3**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (yield 50 g, 99 per cent); IR (KBr) v_{max}: 3478, 2935, 2856, 1508, 1440, 1228, 1154, 914, 852 cm^{-1}. MS m/z: 400 (M$^+$).

5.2.   4-[4-(4-Trifluoromethoxyphenyl)-3,4-cyclohexenyl]cyclohexanone ethylene ketal (**4**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$)

A mixture of 4-[4-(4-trifluoromethoxyphenyl)-4-hydroxycyclohexanyl]cyclohexanone ethylene ketal (**3**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (50·0 g, 125 mmol), o-xylene (400 cm^3), ethylene glycol (15 cm^3) and p-toluene sulphonic acid (1·5 g) was heated at 170°C for 2 h and the water produced distilled off continuously. The reaction mixture was then added to water (1000 cm^3). The organic layer was separated off and the aqueous layer shaken with dichloromethane (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$),
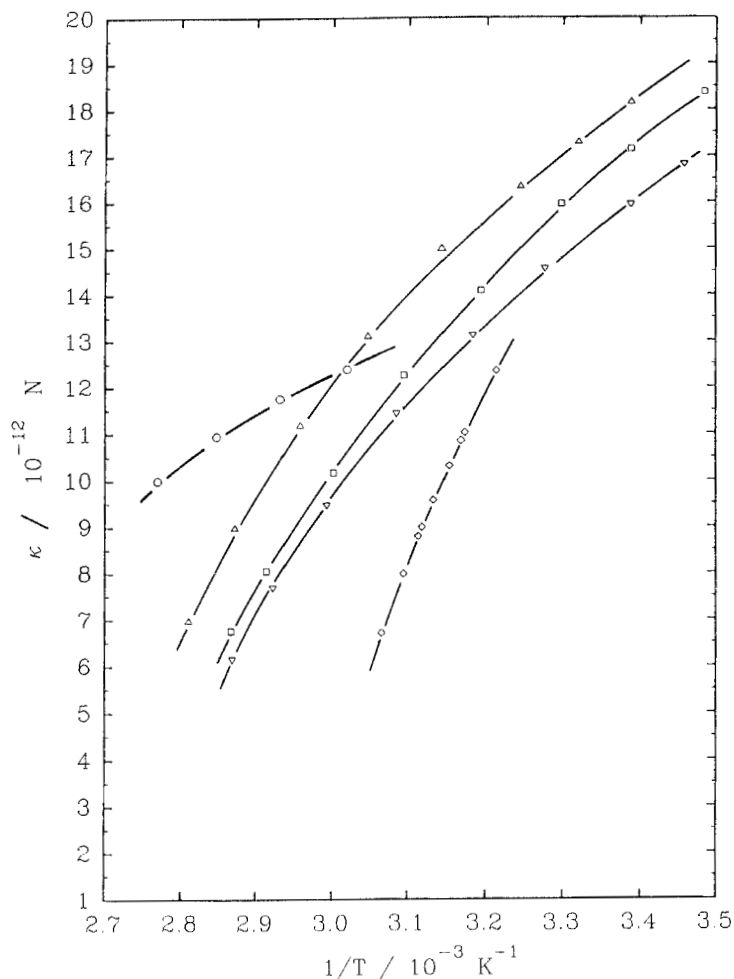
Figure 6. Plots of the elastic expression $\kappa = k_{11} + (k_{33} - 2k_{22})/4$ against the temperature reciprocal for the pure compounds $101d_1CCPF$ ($\bigcirc$) and $3CPOd_31$ ($\diamond$) and the binary mixtures $1d_1CCPF/3CPOd_31$ ($\triangle$), $103CCPF/3CPOd_31$ ($\square$) and $101d_1CCPF/3CPOd_31$ ($\triangledown$).

filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a $8:2$ hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield ketal (**4**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (yield 42·9 g, 90 per cent); IR (KBr) ν_{max}: 3441, 2932, 2874, 1510, 1437, 1226, 1150, 929, 802 cm^{-1}. MS m/z: 382 (M^+), 320 ($C_{19}H_{19}F_3O$), 291 ($CH_{17}H_{14}F_3O$).

5.3. *4-[trans-4-(4-Trifluoromethoxyphenyl)cyclohexyl]cyclohexanone ethyl ketal* (**5**; *n = 1; $X^1 = H$; $X^2 = OCF_3$*)

A mixture of 4-[4-(4-trifluoromethoxyphenyl)-3,4-cyclohexenyl]cyclohexanone ethylene ketal (**4**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$). (42·5 g, 111 mmol), ethyl acetate (1000 cm^3) and palladium on active charcoal (5 g) was hydrogenated until no more hydrogen was taken up. The catalyst was filtered off and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using a $8:2$ hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield ketal

Figure 7. Plots of the rotational viscosity γ_1 against the temperature reciprocal for the pure compounds 101d$_1$CCPF (○) and 3CPOd$_3$1 (◇) and the binary mixtures 1d$_1$CCPF/3CPOd$_3$1 (△), 103CCPF/3CPOd$_3$1 (□) and 101d$_1$CCPF/3CPOd$_3$1 (▽).

(**5**; $n = 1$; $X^1 = H$; $X^1 = OCF_3$) (yield 42 g, 99 per cent); IR (KBr) v_{max}: 3434, 2932, 2851, 1511, 1445, 1227, 1151, 1103, 920, 849 cm^{-1}. MS m/z: 384 (M$^+$), 322 (C$_{19}$H$_{17}$F$_3$O).

5.4. *4-[trans-4-(4-Trifluoromethoxyphenyl)cyclohexyl]cyclohexanone* (**6**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$)

A mixture of 4-[*trans*-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexanone ethylene ketal (**5**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (42 g, 111 mmol), toluene (400 cm^3) and formic acid (200 cm^3) was stirred overnight at room temperature and then added to water (1000 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 4:1 hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield the relatively pure (97·1 per cent) ketone (**6**; $n = 1$;
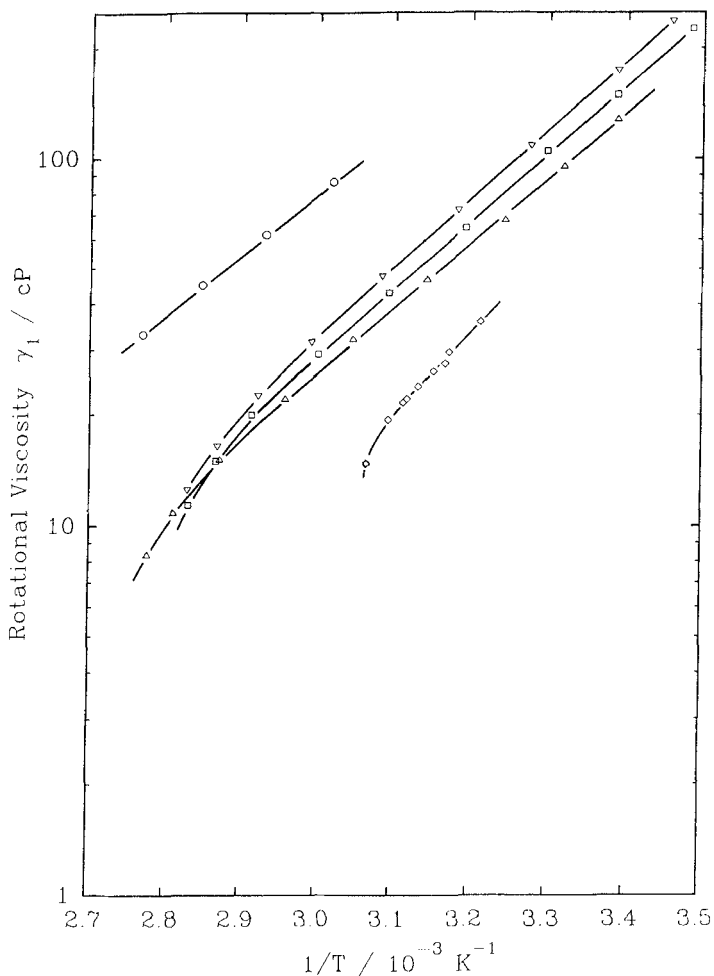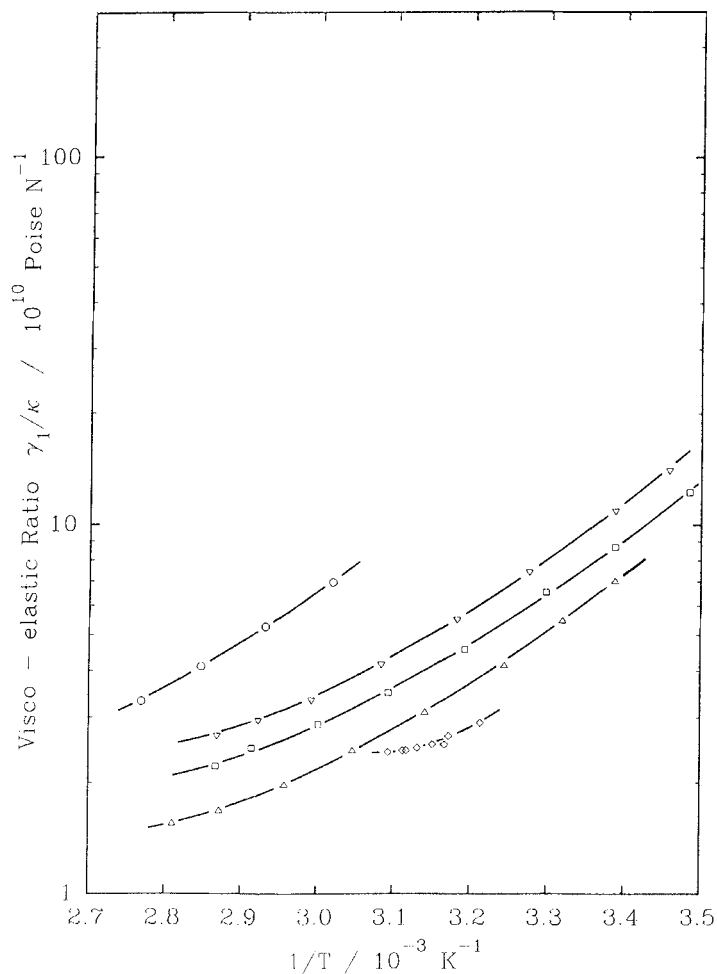
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Figure 8.   Plots of the visco-elastic ratio γ_1/κ against the temperature reciprocal for the pure compounds $101d_1CCPF$ ($\bigcirc$) and $3CPOd_31$ ($\diamond$) and the binary mixtures $1d_1CCPF/3CPOd_31$ ($\triangle$), $103CCPF/3CPOd_31$ ($\square$) and $101d_1CCPF/3CPOd_31$ ($\triangledown$).

$X^1 = H$; $X^1 = OCF_3$) as a (13 : 1) *trans-/cis*-mixture (yield 35·8 g, 96 per cent); m.p., 73–74°C; IR (KBr) v_{max}: 2927, 2859, 1717, 1632, 1500, 1452, 1267, 1195, 1018, 982, 846 cm^{-1}. MS m/z: 340 (M$^+$), 188 ($C_9H_7F_3O$) 175 ($C_8H_6F_3O$). ^1H NMR (CDCl$_3$): 1·47 (8 H, overlapping peaks), 1·92 (2 H, overlapping peaks), 2·39 (5 H, s), 7·10–7·26 (4 H, overlapping peaks).

5.5.   (E/Z) 1-Methoxymethylidene-4-[trans-4-(4-trifluoromethoxyphenyl)cyclo-hexyl]cyclohexane (7; n = 1; X¹ = H; X² = OCF₃)

Potassium tert-butylate (15·2 g, 135 mmol) was added portionwise to a mixture of 4-[*trans*-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexanone (6; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (30·8 g, 90 mmol), methoxymethyltriphenylphosphonium chloride (46·5 g, 135 mmol) and tetrahydrofuran (140 cm^3) at 0°C. After completion of the addition the reaction mixture was stirred overnight at room temperature and saturated sodium bicarbonate solution (250 cm^3) was added dropwise. The organic layer was separated off and the aqueous layer shaken with ethyl acetate (3 × 50 cm^3). The combined organic
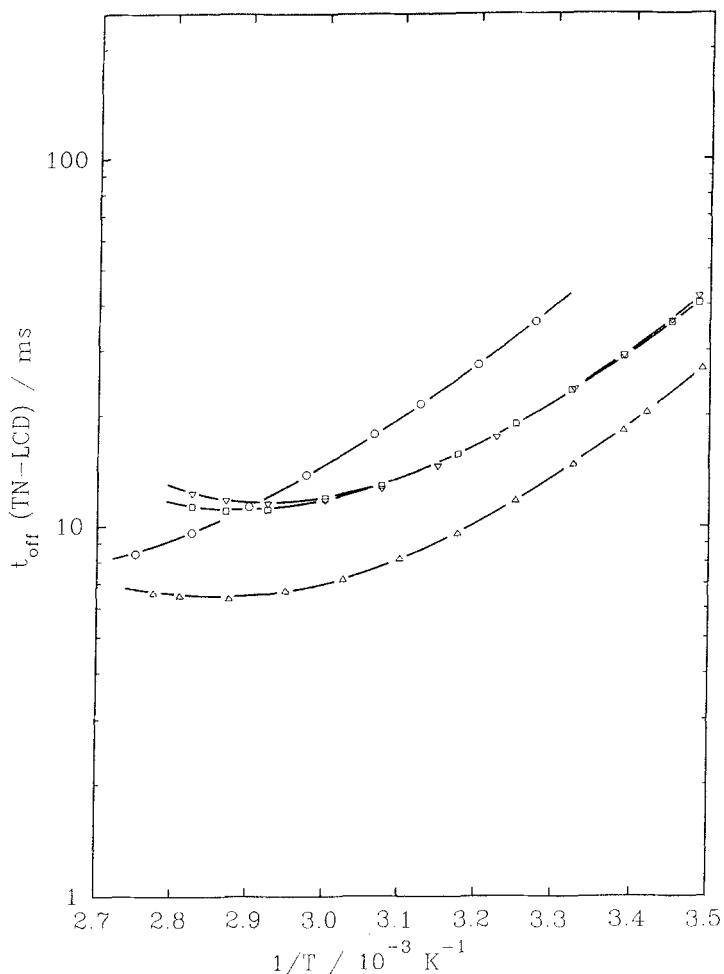
Figure 9. Plots of the switch off times t_{off} against the temperature reciprocal for the pure compound $101d_1CCPF$ (O) and the binary mixtures $1d_1CCPF/3CPOd_31$ ($\triangle$), $103CCPF/3CPOd_31$ ($\square$) and $101d_1CCPF/3CPOd_31$ ($\triangledown$).

layers were washed with brine ($2 \times 100\,cm^3$), dried ($MgSO_4$), filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 8:2 hexane/ethyl acetate mixture as eluent to yield the relatively pure (96·0 per cent) ether (7; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) as a (1:1·6) *trans-/cis-(E/Z)* mixture (yield 33·5 g, quantitative); IR (KBr) ν_{max}: 2922, 2853, 1686, 1509, 1448, 1261, 1156, 1132, $837\,cm^{-1}$. MS m/z: 368 (M^+).

5.6. *trans-4-[trans-4-(4-Trifluoromethoxyphenyl)cyclohexyl]cyclohexyl-1-carbox-aldehyde* (8; $n = 1$; $X^1 = H$; $X^2 = OCF_3$)

A mixture of 1-methoxymethylidene-4-[*trans*-4-(4-trifluoromethoxyphenyl) cyclohexyl]cyclohexane (7; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (33·5 g, 91 mmol), tetrahydrofuran ($330\,cm^3$) and 1 M-hydrochloric acid ($90\,cm^3$) was heated at 55°C for 4 h. The reaction mixture was added to water ($1000\,cm^3$). The organic layer was separated off and the aqueous layer shaken with dichloromethane ($3 \times 50\,cm^3$); the combined organic layers were washed with dilute sodium carbonate solution ($2 \times 100\,cm^3$), dried

(MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography of silica gel using a 20 : 1 hexane/ethyl acetate mixture as eluent to yield the relatively pure (97·9 per cent) aldehyde (**8**; $n = 1$; X^1 = H; X^2 = OCF$_3$) as a *trans-/cis*-mixture (1 : 1·5). A mixture of the aldehyde (30·2 g, 91 mmol), potassium hydroxide (1·8 g, 32 mmol) and methanol (280 cm^3) was then stirred at 10°C for 2·5 h. The reaction mixture was added to water (1000 cm^3) and shaken with dichloromethane (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under reduced pressure. Recrystallization from hexane yielded pure (100 per cent) *trans*-aldehyde (**8**; $n = 1$; X^1 = H; X^2 = OCF$_3$) (yield 18·2 g, 56 per cent); IR (KBr) v_{max}: 2926, 2856, 1725, 1690, 1509, 1449, 1260, 1188, 1222, 844 cm^{-1}. MS m/z: 354 (M$^+$), 188 (C$_9$H$_7$F$_3$O) 175 (C$_8$H$_6$F$_3$O).

5.7. *Ethyl (E)-(trans-4-[trans-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexyl) acrylate (9; n = 1; X¹ = H; X² = OCF₃)*

Potassium hydroxide (0·75 g, 11 mmol) was added portionwise to a mixture of *trans*-4-([*trans*-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexyl)-1-carboxaldehyde (**8**; $n = 1$; X^1 = H; X^2 = OCF$_3$) (2·0 g, 7 mmol), ethyl diethylphosphonoacetate (1·5 g, 7 mmol) and tetrahydrofuran (50 cm^3). After completion of the addition, the reaction mixture was stirred overnight at room temperature and then added to water (100 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate (4 × 50 cm^3). The combined organic layers were washed with brine (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 20 : 1 hexane/ethyl acetate mixture as eluent and recrystallization from ethyl acetate to yield the pure (100 per cent) acrylate (yield 1·5 g, 62 per cent; IR (KBr) v_{max}: 3049, 2985, 2919, 2854, 1708, 1652, 1507, 1446, 1332, 1239, 985, 805 cm^{-1}. MS m/z: 424 (M$^+$), 188 (C$_9$H$_7$F$_3$O) 175 (C$_8$H$_6$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·10–1·32 (3 H, overlapping peaks), 1·55–1·83 (8 H, overlapping peaks), 1·88 (1 H, overlapping peaks), 4·14–4·28 (2 H, q), 5·74–5·80 (2 H, d), 6·87–6·96 (4 H, q), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). The transition temperatures of this acrylate (**9**; $n = 1$; X^1 = H; X^2 = OCF$_3$) and other acrylates (**9**; $n = 0, 1$; X^1 = H, F; X^2 = H, F, Cl, Br, CN) prepared using this general method are collated in table 7.

5.8. *(E)-(trans-4-[trans-4-(4-Trifluoromethoxyphenyl)cyclohexyl]cyclohexyl)allyl alcohol (10; n = 1; X¹ = H; X² = OCF₃)*

Diisobutylaluminium hydride in hexane (20 per cent, 10 cm^3) was added drop-wise to a solution of ethyl (E)-(*trans*-4-[*trans*-4-(4-trifluoromethoxyphenyl)cyclo-hexyl]cyclohexyl)acrylate (**9**; $n = 1$; X^1 = H; X^2 = OCF$_3$) (1·4 g, 3 mmol) in toluene (30 cm^3) at 0°C and stirred at room temperature overnight. 1 M-sulphuric acid was added dropwise to the cooled reaction solution (0°C), which was stirred for 30 min at room temperature and then poured into water (1000 cm^3) and shaken with ethyl acetate (4 × 50 cm^3). The combined organic layers were washed with brine (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 7 : 3 hexane/ethyl acetate mixture as eluent and recrystallization from ethyl acetate to yield the allyl alcohol (yield 0·85 g, 68 per cent); IR (KBR) v_{max}: 3424, 2922, 2851, 1509, 1448, 1258, 1224, 972, 845 cm^{-1}. MS m/z: 382 (M$^+$), 188 (C$_9$H$_7$F$_3$O) 175 (C$_8$H$_6$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·07–1·14 (12 H, overlapping peaks), 1·79 (10 H, overlapping peaks),

2·48 (1 H, t), 4·08 (2 H, d), 5·61–5·63 (2 H, overlapping peaks), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). The transition temperatures of this allyl alcohol (**10**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) and other allyl alcohols (**10**; $n = 0, 1$; $X^1 = H$, F; $X^2 = H$, F. Cl, Br, CN) prepared using this general method are collated in table 8.

5.9. *Methyl (E)-(trans-4-[trans-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclo-hexyl)allyl ether* (**11**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$)

A solution of (*E*)-(*trans*-4-[*trans*-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclo-hexyl)allyl alcohol (**10**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) (0·8 g, 2·1 mmol) in tetrahydrofuran (10 cm³) was added dropwise to a suspension (50 w/w per cent in mineral oil) of sodium hydride (0·2 g, 4·2 mmol) in tetrahydrofuran (50 cm³) at room temperature. After stirring for 4 h, methyl iodide (0·6 g, 4·2 mmol) was added dropwise and the reaction mixture stirred overnight. Methanol (10 cm³) and then water (50 cm³) were added and the resultant mixture shaken with ethyl acetate (3 × 50 cm³). The combined organic layers were washed with brine (2 × 100 cm³), dried (MgSO₄), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent and recrystallization from ethanol to yield the pure (99·7 per cent) ether (yield 0·7 g, 85 per cent); IR (KBr) v_{max}: 2922, 2851, 1509, 1448, 1265, 1221, 972, 848 cm⁻¹. MS *m/z*: 396 (M⁺), 364 ($C_{22}H_{27}F_3O$), 188 ($C_9H_7F_3O$) 175 ($C_8H_6F_3O$). ¹H NMR (CDCl₃): 1·07–1·14 (10 H, overlapping peaks), 1·55–1·78 (9 H, overlapping peaks), 2·48 (1 H, overlapping peaks), 3·32 (3 H, s), 3·85–3·87 (2 H, d) 5·53–5·64 (2 H, overlapping peaks), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). The transition temperatures of this allyl ether (**11**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) and other allyl ethers (**11**; $n = 0, 1$; $X^1 = H$, F; $X^2 = H$, F, Cl, Br, CN) prepared using this general method are collated in tables 1 and 2.

5.10. *4-(4-Trifluoromethylsulphonyloxyphenyl)cyclohexanone* (**13**)

A solution of trifluoromethane sulphonic acid anhydride (21 cm³, 126 mmol) in dichloromethane (500 cm³) was added slowly to a solution of 4-(4-hydroxyphenyl)cyclohexanone (**12**) (20 g, 105 mmol), 2,6-lutidine (21 cm³, 126 mmol), and dichloromethane (100 cm³) at 0°C. The reaction mixture was then added to water (1000 cm³). The organic layer was separated off and the aqueous layer shaken with dichloromethane (3 × 50 cm³). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm³), dried (MgSO₄), filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using an 8 : 2 hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield the relatively pure (98·8 per cent) triflate (**14**) (yield 23 g, 68 per cent); MS *m/z*: 322 (M⁺).

5.11. *4-(4-Trifluoromethylsulphonyloxyphenyl)cyclohexanone ethylene ketal* (**14**)

A mixture of 4-(4-trifluoromethylsulphonyloxyphenyl)cyclohexanone (**13**) (16·1 g, 50 mmol), ethylene chloride (200 cm³), ethylene glycol (3 cm³, 144 mmol) and amberlyst 15 (1·1 g) was heated at 115°C for 18 h and the water produced distilled off azeotropically. The reaction mixture was then added to water (200 cm³). The organic layer was separated off and the aqueous layer shaken with dichloromethane (3 × 50 cm³). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm³), dried (MgSO₄), filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel

using an 8 : 2 hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield ketal (**14**) (yield 11·6 g, 63 per cent); MS m/z: 366 (M$^+$).

5.12. *4-(4-Trifluoromethoxybiphenyl-4-yl)cyclohexyl ethylene ketal* (**16**; $X^1 = H$; $X^2 = OCF_3$)

A mixture of 4-(4-trifluoromethylsulphonyloxyphenyl)cyclohexyl ethylene ketal (**14**) (11·56 g, 36 mmol), 4-trifluoromethoxyphenyl boronic acid (**15**) (7·45 g, 36 mmol), tetrakis(triphenylphosphine)palladium(0) (0·5 g), 2 M-sodium carbonate solution (140 cm^3) and 1,2-dimethoxyethane (200 cm^3) was heated at 90°C for 5 h. The reaction mixture was added to water (200 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using an 8 : 2 hexane/dichloromethane mixture as eluent and recrystallization from ethanol to yield the pure (99·8 per cent) biphenyl (**16**; $X^1 = H$; $X^2 = OCF_3$) (yield 5·0 g, 37 per cent); IR (KBr) v_{max}: 2938, 2866, 1712, 1632, 1496, 1273, 1229, 1184, 1004, 848 cm^{-1}. MS m/z: 334 (M$^+$), 277 ($C_{16}H_{12}F_3O$), 188 ($C_9H_7F_3O$) 175 ($C_8H_6F_3O$). ^{1}H NMR (CDCl$_3$): 2·00 (2 H, overlapping peaks), 2·25 (2 H, overlapping peaks), 2·51–2·54 (4 H, overlapping peaks), 3·15 (1 H, overlapping peaks), 3·85–3·87 (2 H, d), 5·53–5·64 (2 H, overlapping peaks), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t).

5.13. *4-(4-Trifluoromethoxybiphenyl-4'-yl)cyclohexanone* (**17**)

A mixture of 4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexyl ethylene ketal (**16**) (5·0 g, 13 mmol), toluene (100 cm^3) and formic acid (20 cm^3) was stirred overnight at room temperature and then added to water (1000 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure to yield the pure ketone (**17**) (yield 4·4 g, 96 per cent); m.p., 101–102°C; IR (KBr) v_{max}: 3023, 2938, 2866, 1712, 1632, 1496, 1451, 1273, 1229, 1164, 1004, 832 cm^{-1}. MS m/z: 334 (M$^+$), 277 ($C_{16}H_{11}F_3O$). ^{1}H NMR (CDCl$_3$): 1·08–1·14 (11 H, overlapping peaks), 2·00 (2 H, overlapping peaks), 2·30 (2 H, overlapping peaks), 2·50 (2 H, overlapping peaks), 3·33 (1 H, overlapping peaks), 7·50–7·60 (4 H, overlapping peaks.

5.14. *(E/Z)1-Methoxymethylidene-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexane* (**18**)

Potassium tert-butylate (2·2 g, 19·7 mmol) was added portionwise to a mixture of 4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexanone (**17**) (4·4 g, 13·2 mmol), methoxymethyltriphenylphosphonium chloride (6·8 g, 19·7 mmol) and tetrahydrofuran (50 cm^3) at 0°C. After completion of the addition the reaction mixture was stirred overnight at room temperature, saturated sodium bicarbonate solution (250 cm^3) was added dropwise and then the reaction mixture was added to water (1000 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate (3 × 50 cm^3). The combined organic layers were washed with brine (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using an 8 : 2 hexane/ethyl acetate mixture as eluent to yield the ether (**18**) (yield 3·4 g, 72 per cent); IR (KBr) v_{max}: 2930, 2839, 1690, 1423, 1249, 1271, 1249, 1218, 1162, 1132, 1006, 835 cm^{-1}. MS m/z: 362 (M$^+$), 330 ($C_{20}H_{17}F_3O$).

5.15. *trans-4-(4-Trifluoromethoxybiphenyl-4'-yl)cyclohexyl-1-carboxaldehyde* (**19**; $X^1 = H$; $X^2 = OCF_3$)

A mixture of 1-methoxymethylidene-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexane (**18**; $X^1 = H$; $X^2 = OCF_3$) (3·3 g, 9 mmol), tetrahydrofuran (35 cm^3) and 1 M-hydrochloric acid (9 cm^3) was heated at 55°C for 4 h. The reaction mixture was added to water (100 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 2 : 1 hexane/dichloromethane mixture as eluent to yield the aldehyde (**19**; $X^1 = H$; $X^2 = OCF_3$) as a (4 : 1) *trans-/cis*-mixture. A mixture of the aldehyde (3·3 g, 9 mmol), potassium hydroxide (1·8 g, 32 mmol) and methanol (400 cm^3) was then stirred at 10°C for 2·5 h. The reaction mixture was added to water (1000 cm^3) and shaken with ethyl acetate (3 × 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under reduced pressure. Recrystallization from ethanol yielded (purity 94·6 per cent) the aldehyde (**19**, $X^1 = H$; $X^2 = OCF_3$) as a (32 : 1) *trans-/cis*-mixture (yield 3·0 g, 94 per cent); IR (KBr) ν_{max}: 2932, 2722, 1728, 1632, 1496, 1263, 1226, 1153, 836, 808 cm^{-1}. MS *m/z*: 348 (M$^+$). ^{1}H NMR (CDCl$_3$): 1·08–1·14 (11 H, overlapping peaks), 1·56–1·79 (8 H, overlapping peaks), 2·21 (4 H, overlapping peaks), 2·40 (1 H, t), 2·40 (1 H, t), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t).

5.16. *Ethyl (E)-(trans-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexyl)acrylate* (**20**; $X^1 = H$; $X^2 = OCF_3$)

Potassium hydroxide (0·95 g, 14·3 mmol) was added portionwise to a mixture of *trans*-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexyl-1-carboxaldehyde (**19**; $X^1 = H$; $X^2 = OCF_3$) (2·5 g, 7·1 mmol), ethyl diethylphosphonoacetate (2·0 g, 8·6 mmol) and tetrahydrofuran (500 cm^3). After completion of the addition, the reaction mixture was stirred overnight at room temperature and then worked up and purified as described above for methyl *(E)-(trans-4-[trans-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexyl)acrylate* (**9**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) to yield the acrylate (**20**; $X^1 = H$; $X^2 = OCF_3$) (yield 2·5 g, 84 per cent); IR (KBr) ν_{max}: 2984, 2930, 2853, 1712, 1650, 1495, 1447, 1255, 1223, 1173, 1006, 829 cm^{-1}. MS *m/z*: 418 (M$^+$), 372 (C$_{22}$H$_{19}$F$_3$O$_2$), 344 (C$_{21}$H$_{19}$F$_3$O), 264 (C$_{15}$H$_{11}$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·27–1·34 (8 H, overlapping peaks), 2·00 (4 H, t), 2·25 (1 H, overlapping peaks), 2·60 (1 H, t), 4·16–4·25 (2 H, q), 5·80–5·86 (1 H, d), 6·93–7·01 (1 H, q), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). The liquid crystal transition temperatures of this acrylate (**20**; $X^1 = H$; $X^2 = OCF_3$) and other homologues (**20**; $X^1 = H$, F; $X^2 = F$, Cl) prepared using this general method are collated in table 7.

5.17. *(E)-(trans-4-(4-Trifluoromethoxybiphenyl-4'-yl)cyclohexly)allyl alcohol* (**21**; $X^1 = H$; $X^2 = OCF_3$)

Diisobutylaluminium hydride in hexane (20 per cent, 9 cm^3) was added dropwise to a solution of ethyl *(E)-(trans-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexyl)acrylate* (**20**; $X^1 = H$; $X^2 = OCF_3$) (1·3 g, 3·1 mmol) in toluene (30 cm^3) at 0°C and stirred at room temperature overnight and then worked up and purified as described above for *(E)-(trans-4-[trans-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexyl)allyl* alcohol (**10**; $n = 1$; $X^1 = H$; $X^1 = OCF_3$) to yield the allyl alcohol (yield 0·75 g, 65 per cent); IR (KBr) ν_{max}: 3376, 2922, 2851, 1665, 1612, 1495, 1447, 1252, 1164, 1002, 968, 827 cm^{-1}. MS *m/z*:

376 (M$^+$), 264 (C$_{15}$H$_{11}$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·31 (5 H, overlapping peaks), 1·94 (5 H, overlapping peaks), 2·31 (1 H, t), 4·11 (2 H, d), 5·67–5·69 (2 H, d), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). The liquid crystal transition temperatures of this allyl alcohol (21; X^1 = H; X^2 = OCF$_3$) and other allyl alcohols (21; X^1 = H, F; X^2 = F, Cl) prepared using this general method are collated in table 8.

5.18. *Methyl (E)-(trans-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexyl)allyl ether* (22; X^1 = H; X^2 = OCF$_3$)

A solution of (*E*)-(*trans*-4-(4-trifluoromethoxybiphenyl-4'-yl)cyclohexyl)allyl alcohol (21; X^1 = H; X^2 = OCF$_3$) (0·7 g, 1·9 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension (50 w/w per cent in mineral oil) of sodium hydride (0·18 g, 3·7 mmol) in tetrahydrofuran (50 cm^3) at room temperature. After stirring for 4 h, methyl iodide (0·5 g, 3·7 mmol) was added dropwise and the reaction mixture stirred overnight and then worked up and purified as described above for methyl (*E*)-(*trans*-4-[*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexyl)allyl ether (11; n = 1; X^1 = H; X^2 = OCF$_3$) to yield the pure (99·7 per cent) ether (yield 0·3 g, 42 per cent); IR (KBR) v_{max}: 2926, 2849, 1669, 1627, 1495, 1447, 1259, 1225, 1160, 1115, 971, 828 cm^{-1}. MS *m/z*: 390 (M$^+$), 358 (C$_{22}$H$_{21}$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·40 (2 H, q), 1·94 (4 H, t), 2·10 (1 H, overlapping peaks), 2·50 (1 H, t), 3·34 (1 H, s), 3·38–3·91 (2 H, d), 5·60 (1 H, overlapping peaks), 5·75 (1 H, overlapping peaks), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). The liquid crystal transition temperatures of this allyl ether (22; X^1 = H; X^2 = OCF$_3$) and other homologues (22; X^1 = H, F; X^2 = F, Cl) prepared using this general method are collated in table 3.

5.19. *4-(trans-4-[(E)-3-Methoxypropenylcyclohexyl]benzonitrile* (11; n = 0; X^1 = H; X^2 = CN)

A solution of methyl (*E*)-(*trans*-4-(4-bromophenyl)cyclohexyl)allyl ether (11; n = 0; X^1 = H; X^2 = Br) (2·3 g, 7·5 mmol), copper (I) cyanide (1·7 g, 18·6 mmol) and 1-methyl-2-pyrrolidinone (45 cm^3) was heated at 185°C for 2·5 h. The cooled mixture was poured into 15 per cent NaOH solution, stirred for 40 min and then shaken with diethyl ether (3 × 50 cm^3). The combined organic layers were washed with brine (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 7 : 3 hexane/ethyl acetate mixture as eluent and recrystallization from ethanol to yield the pure (100 per cent) ether (yield 2·4 g, 60 per cent); IR (KBr) v_{max}: 2927, 2852, 1672, 1606, 1508, 1446, 1118, 973, 832 cm^{-1}. MS *m/z*: 223 (C$_{16}$H$_{17}$NO), 129 (C$_9$H$_7$N), 116 (C$_8$H$_6$N), 71 (C$_4$H$_7$O). ^{1}H NMR (CDCl$_3$): 1·25–1·29 (2 H, q), 1·47–1·60 (10 H, overlapping peaks), 1·90–1·94 (5 H, d), 2·50 (1 H, t), 3·33 (3 H, s), 3·87–3·89 (3 H, d), 5·59–5·68 (2 H, overlapping peaks), 7·26–7·32 (2 H, t), 7·56–7·59 (2 H, d). The liquid crystal transition temperatures of this benzonitrile (11; n = 0; X^1 = H; X^2 = CN) and the other benzonitrile (11; n = 1; X^1 = H; X^2 = CN) prepared using this general method are collated in tables 1 and 2.

5.20. *4-(trans-4-[(E)-3-Methoxypropenyl]cyclohexyl)benzoic acid* (23)

A solution of 4-(*trans*-4-[(*E*)-3-methoxypropenyl]cyclohexyl)benzonitrile (11; n = 0; X^1 = H; X^2 = CN) (0·58 g, 2·3 mmol), potassium hydroxide (1·5 g, 22·7 mmol) and diethylene glycol (20 cm^3) was heated at 185°C for 2·5 h. The cooled mixture was poured into water (100 cm^3), washed with dichloromethane (2 × 50 cm^3), and the aqueous layer acidified with (pH 1) concentrated hydrochloric acid (2·5 cm^3); it was

then shaken with dichloromethane ($3 \times 50 \, \text{cm}^3$). The combined organic layers were washed with brine ($2 \times 100 \, \text{cm}^3$), dried ($\text{MgSO}_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by recrystallization from ethanol to yield the desired benzoic acid (yield 0·65 g, quantitative); MS m/z: 274 (M^+).

5.21. *4-Trifluoromethoxyphenyl 4-(trans-4-[(E)-3-methoxypropenyl]cyclohexyl) benzoate (24; $X^1 = H$; $X^2 = OCF_3$)*

A solution of N,N-dicyclohexylcarbodiimide (0·23 g, 0·0011 mol) in dichloromethane (10 cm^3) was added slowly to a solution of 4-trifluoromethoxyphenol (0·25 g, 0·0009 mol), 4-*(trans*-4-[*(E)*-3-methoxypropenyl]cyclohexyl)benzoic acid **(23)** (0·13 g, 0·0009 mol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (25 cm^3) cooled at 0°C. The reaction mixture was stirred at room temperature overnight, filtered to remove precipitated material and the filtrate evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent followed by recrystallization from ethanol to yield the pure (99·7 per cent) ester **(24;** $X^1 = H$; $X^2 = OCF_3$); IR (KBr) ν_{max}: 2992, 2927, 2849, 1737, 1610, 1504, 1446, 1269, 1175, 1069, 843 cm^{-1}. MS m/z 396 (M^+), 272 ($C_{17}H_{24}N_2O$), 125 ($C_8H_{13}O$). ^{1}H NMR (CDCl$_3$): 1·40 (2 H, q), 1·94 (4 H, t), 2·10 (1 H, overlapping peaks), 2·50 (1 H, t), 3·34 (1 H, s), 3·38–3·91 (2 H, d) 5·60 (1 H, overlapping peaks), 5·57 (1 H, overlapping peaks), 7·09–7·13 (1 H, d), 7·19–7·26 (1 H, t). 8·09–8·10 (2 H, d). The transition temperatures of this ester **(24;** $X^1 = H$; $X^2 = OCF_3$) and other benzoate esters **(24;** $X^1 = H$, F; $X^2 = F$, CN) prepared using this general procedure are given in table 4.

5.22. *4-Trifluoromethoxybenzyltriphenylphosphonium bromide (26; $X^1 = H$; $X^2 = OCF_3$)*

A solution of 4-trifluoromethoxybenzyl bromide **(25;** 50 g, 196 mmol) in ethyl acetate (150 cm^3) was added slowly to a solution of triphenylphosphine (50 g, 196 mmol) and ethyl acetate (330 cm^3). The reaction mixture was stirred for 48 h at room temperature and 2 h at 0°C; then the precipitate was filtered off, washed with small portions of cold ethyl acetate, and then dried under vacuum to yield the Wittig salt **(26;** $X^1 = H$; $X^2 = OCF_3$) (yield 86·2 g, 85 per cent); IR (KBr) ν_{max}: 3048, 3007, 2844, 1588, 1438, 1257, 1165, 1111, 1194, 996, 863 cm^{-1}. MS m/z: 437 (M^+). ^{1}H NMR (CDCl$_3$): 5·66–5·72 (2 H, d), 6·91–6·99 (2 H, d), 7·59–7·60 (6 H, overlapping peaks), 7·72–7·82 (9 H, overlapping peaks).

5.23. *(E/Z)-1-(4-Trifluoromethoxyphenyl)-2-(trans-4-cyanocyclohexyl)ethene (28; $X^1 = H$; $H^2 = OCF_3$)*

Potassium tert-butylate (14·7 g, 131 mmol), was added portionwise to a mixture of *trans*-4-cyanocyclohexyl-1-carboxaldehyde **(27)** [49] (15·0 g, 109 mmol), 4-trifluoromethoxybenzyltriphenylphosphonium bromide **(26;** $X^1 = H$; $X^2 = OCF_3$) (67·9 g, 131 mmol) and *tert*-butyl methyl ether (300 cm^3) at 0°C. After completion of the addition, the reaction mixture was stirred for 3 h at room temperature and then added to water (500 cm^3). The organic layer was separated off and the aqueous layer shaken with ethyl acetate ($3 \times 50 \, \text{cm}^3$). The combined organic layers were washed with water ($2 \times 100 \, \text{cm}^3$), dried ($\text{MgSO}_4$), filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent to yield the ethene **(28;** $X^1 = H$; $X^2 = OCF_3$) as a

(2·7:1) *trans-/cis-(E/Z)* mixture (yield 30·5 g, 94 per cent); IR (KBr) v_{max}: 2941, 2866, 2238, 1690, 1652, 1507, 1263, 1160, 960, 821 cm^{-1}. MS m/z: 295 (M$^+$), 267 ($C_{15}H_{14}F_3O$), 188 ($C_9H_7F_3O$) 175 ($C_8H_6F_3O$).

5.24. *1-(4-Trifluoromethoxyphenyl)-2-(trans-4-cyanocyclohexyl)ethane* (**29**; $X^1 = H$; $X^2 = OCF_3$)

A mixture of *(E/Z)*-1-(4-trifluoromethoxyphenyl)-2-(*trans*-4-cyanocyclohexyl)ethene (**28**; $X^1 = H$; $X^2 = OCF_3$) (30·4 g, 103 mmol), ethyl acetate (300 cm^3) and palladium on active charcoal (1·5 g) were hydrogenated until no more hydrogen was taken up. The catalyst was filtered off and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using an 8:2 hexane/ethyl acetate mixture as eluent and recrystallization from ethanol to yield pure (99·9 per cent) ethane (**29**; $X^1 = H$; $X^2 = OCF_3$) (yield 31 g, 99 per cent); m.p., 42–43°C; IR (KBr) v_{max}: 2938, 2863, 2239, 1626, 1500, 1452, 1268, 1195, 1159, 1121, 852 cm^{-1}. MS m/z: 297 (M$^+$), 188 ($C_9H_7F_3O$) 175 ($C_8H_6F_3O$).

5.25. *trans-4-[2-(4-Trifluoromethoxyphenyl)ethyl]cyclohexyl-1-carboxaldehyde* (**30**; $X^1 = H$; $X^2 = OCF_3$)

Diisobutylaluminium hydride in hexane (20 per cent, 165 cm^3) was added dropwise to a solution of 1-(4-trifluoromethoxyphenyl)-2-(*trans*-4-cyanocyclohexyl)ethane (**29**; $X^1 = H$; $X^2 = OCF_3$) (30·4 g, 102 mmol) in toluene (300 cm^3) at 0°C and stirred at room temperature overnight. 1 M-sulphuric acid was added dropwise to the cooled reaction solution at 0°C, which was stirred for 30 min at room temperature and then poured on to water (1000 cm^3). After shaking with ethyl acetate (4 × 50 cm^3), the combined organic layers were washed with brine (2 × 100 cm^3), dried (MgSO$_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent to yield the relatively pure (97·2 per cent) aldehyde (yield 25·3 g, 83 per cent); IR (KBr) v_{max}: 2928, 2855, 2710, 1725, 1595, 1508, 1451, 1336, 1262, 1223, 1162, 1003, 975, 812 cm^{-1}. MS m/z: 300 (M$^+$), 282 ($C_{16}H_{17}$).

5.26. *Ethyl (E)-(trans-4-[2-(4-trifluoromethoxyphenyl)ethyl]cyclohexyl)acrylate* (**31**; $X^1 = H$; $X^2 = OCF_3$)

Potassium hydroxide (10·9 g, 168 mmol) was added portionwise to a mixture of *trans*-4-[2-(4-trifluoromethoxyphenyl)ethyl]cyclohexyl-1-carboxaldehyde (**30**; $X^1 = H$; $X^2 = OCF_3$) (25·2 g, 84 mmol), ethyl diethylphosphonoacetate (22·6 g, 100 mmol) and tetrahydrofuran (300 cm^3). After completion of the addition the reaction mixture was stirred overnight at room temperature and then worked up and purified as described above for methyl *(E)-(trans*-4-[*trans*-4-(4-trifluoromethoxyphenyl)cyclohexyl)acrylate (**9**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) to yield the acrylate (yield 5·4 g, 90 per cent); IR (KBr) v_{max}: 2923, 2852, 1719, 1651, 1509, 1448, 1260, 1224, 1163, 1039, 984, 853 cm^{-1}. MS m/z: 370 (M$^+$), 324 ($C_{18}H_{20}F_3O$), 188 ($C_9H_7F_3O$) 175 ($C_8H_6F_3O$). ^{1}H NMR (CDCl$_3$): 1·03–1·32 (10 H, overlapping peaks), 1·53–1·55 (2 H, overlapping peaks), 1·84 (4 H, t), 2·10 (1 H, overlapping peaks), 2·59 (2 H, t), 4·14 (2 H, q), 5·74–5·80 (2 H, d), 6·86–6·96 (4 H, s), 7·12–7·26 (4 H, q). The transition temperatures of this acrylate (**31**; $X^1 = H$; $X^2 = OCF_3$) and other acrylates (**31**; $X^1 = H$, F; $X^2 = F$, Cl, Br, CF$_3$) prepared using this general method are collated in table 7.

5.27. *(E)-(trans-4-[2-(4-Trifluoromethoxyphenyl)ethyl]cyclohexyl)allyl alcohol* (**32**; $X^1 = H$; $X^2 = OCF_3$)

Diisobutylaluminium hydride in hexane (20 per cent, 47 cm^3) was added dropwise to a solution of ethyl *(E)-(trans*-4-[2-(4-trifluoromethoxyphenyl)ethyl]cyclohexyl)acrylate (**31**; $X^1 = H$; $X^2 = OCF_3$) (5·8 g, 15·6 mmol) in toluene (150 cm^3) at 0°C and stirred at room temperature overnight and then worked up and purified as described above for *(E)-(trans*-4-[*trans*-4-(4-trifluoromethoxyphenyl)cyclohexyl]cyclohexyl)allyl alcohol (**10**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) to yield the allyl alcohol (yield 2·8 g, 55 per cent); IR (KBr) ν_{max}: 3376, 2922, 2851, 1669, 1595, 1508, 1449, 1258, 1226, 967, 846 cm^{-1}. MS *m/z*: 328 (M$^+$), 310 (C$_{18}$H$_{21}$F$_3$O), 287 (C$_{15}$H$_{18}$F$_3$O$_2$), 188 (C$_9$H$_7$F$_3$O) 175 (C$_8$H$_6$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·06 (6 H, overlapping peaks), 1·45–1·54 (2 H, overlapping peaks), 1·74–1·80 (5 H, t), 2·59–2·65 (2 H, t), 4·08 (2 H, d), 5·60–5·63 (2 H, overlapping peaks), 7·09–7·25 (4 H, overlapping peaks). The transition temperatures of this allyl alcohol (**32**; $X^1 = H$; $X^2 = OCF_3$) and other allyl alcohols (**32**; $X^1 = H$, F; $X^2 = F$, Cl, Br, CF$_3$) prepared using this general method are collated in table 8.

5.28. *Methyl (E)-(4-trans-4-[2-(trifluoromethoxyphenyl)ethyl]cyclohexyl)allyl ether* (**33**; $X^1 = H$; $X^2 = OCF_3$)

A solution of *(E)-(trans*-4-[2-(4-trifluoromethoxyphenyl)ethyl]cyclohexyl)allyl alcohol (**32**; $X^1 = H$; $X^2 = OCF_3$) (2·0 g, 6·1 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension (50 w/w per cent in mineral oil) of sodium hydride (0·58 g, 12·2 mmol) in tetrahydrofuran (100 cm^3) at room temperature. After stirring for 4 h, methyl iodide (1·7 g, 12·2 mmol) was added dropwise and the reaction mixture stirred overnight and then worked up and purified as described above for methyl *(E)-(trans*-4-[*trans*-4-(4-methylphenyl)cyclohexyl)allyl ether (**11**; $n = 1$; $X^1 = H$; $X^2 = OCF_3$) to yield the pure (100 per cent) ether (yield 1·6 g, 76 per cent); IR (KBr) ν_{max}: 2921, 2850, 1669, 1595, 1509, 1449, 1261, 1222, 1163, 1120, 970, 850 cm^{-1}. MS *m/z*: 310 (C$_{18}$H$_{21}$F$_3$O) 287 (C$_{15}$H$_{18}$F$_3$O$_2$), 188 (C$_9$H$_7$F$_3$O) 175 (C$_8$H$_6$F$_3$O). ^{1}H NMR (CDCl$_3$): 1·00–1·13 (5 H, overlapping peaks), 1·45–1·56 (2 H, overlapping peaks), 1·87 (4 H, t), 2·58–2·64 (2 H, t), 3·33 (3 H, s), 3·84–3·87 (3 H, d), 5·53–5·64 (2 H, overlapping peaks), 7·09–7·26 (4 H, q). The liquid crystal transition temperatures of this allyl ether (**33**; $X^1 = H$; $X^2 = OCF_3$) and other analogues (**33**; $X^1 = H$, F; $X^2 = F$, Cl, Br, CF$_3$) prepared using this general method are collated in table 5.

6. Conclusions

The new polar two-ring methyl *(E)*-allyl ethers often exhibit low melting points, but are not generally mesomorphic. The corresponding three-ring methyl *(E)*-allyl ethers exhibit higher melting points, but synergetic effects due to the presence of both an oxygen atom and a carbon–carbon double bond lead to broad nematic phases (strong suppression of smectic phases). The new methyl *(E)*-allyl ethers are easy to synthesize as pure *trans*-isomers (no isomerization of the carbon–carbon double bond is necessary). Many three-ring intermediates (acrylates and allyl alcohols) are themselves liquid crystalline. Although some of the methyl *(E)*-allyl ethers exhibit longer switch-off times in TN cells than those of analogous liquid crystals incorporating either a methyl propyl ether or a 1-*(E)*-propenyl chain instead of the methyl *(E)*-allyl ether chain, they are still useful components for nematic mixtures, especially where a wide temperature range is required. The greater rigidity and linearity of the methyl *(E)*-allyl ether chain is probably responsible for these effects.

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