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S. M. Kelley[a]; A. Germann[a]; M. Schadt[a]
[a] Dept. RLCR, F. Hoffmann-La Roche Ltd., Basle, Switzerland

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The synthesis and liquid crystal transition temperatures of some weakly polar nematic methyl (*E*)-[*trans*-4-substituted-cyclohexyl]-allyl ethers

by S. M. KELLY*, A. GERMANN and M. SCHADT
F. Hoffmann-La Roche Ltd., Dept. RLCR, CH-4002 Basle, Switzerland

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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 of a wide variety of liquid crystalline cyclohexane derivatives to produce a variety of new methyl (*E*)-allyl ethers. The melting points and tendency to form smectic mesophases are often low, while nearly all of the compounds prepared exhibit a nematic phase. Thus, even two-ring derivatives can exhibit nematic phases over a wide temperature range ($\leqslant 80°C$), sometimes starting below room temperature ($T_m \approx 10°C$). 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. Thus many of the new methyl (*E*)-allyl ethers exhibit nematic phases over a wider temperature range than the corresponding materials with an unsubstituted alkyl chain attached to the cyclohexyl ring. The new compounds are easily prepared from known starting materials. Many intermediates are themselves liquid crystalline. This allows investigation of the relationship between liquid crystal transition temperatures and the nature of the terminally substituted alkyl chain (for example, incorporating C=C, OH, $CO_2C_2H_5$ and OCH_3 groups).

1. Introduction

Most commercially available electro-optic liquid crystal displays (LCDs) are based on passively or actively addressed twisted nematic (for example, TN [1], TFT [2], MIM [3], etc.), or super twisted configurations (for example, SBE [4], STN [5], OMI [6], DSTN [7], BW STN [8], etc.), sometimes with dichroic dyes (for example, GH [9], GHSTN [10], etc.). These display types require nematic liquid crystals of positive dielectric anisotropy ($\Delta\varepsilon = \varepsilon_\parallel - \varepsilon_\perp > 0$). As the threshold voltage (V_{10}) for a TN-LCD is given [1, 11–13] by

$$V_{10} \propto (\kappa/\Delta\varepsilon)^{-1/2},$$

it is clear that the dielectric anisotropy should be as great as possible for a low threshold voltage (most LCDs are battery powered). However, the threshold voltage is also dependent on the elastic constants (k_{33}, k_{22} and k_{11}) via the elastic expression [11–13]

$$\kappa = k_{11} + (k_{33} - 2k_{22})/4,$$

κ should also be as low as possible. The response times (switch on, t_{on} and switch off, t_{off} times) should be as short as possible. Apart from the rotational viscosity γ_1, t_{off} is

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*Author for correspondence.

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also strongly affected by the elastic expression κ. A low visco-elastic ratio γ_1/κ leads to short t_{off} times [11–14].

$$t_{off} \propto \gamma_1/\kappa$$

Therefore, nematic liquid crystals are required, whose physical properties allow often contradictory requirements to be overcome efficiently for a given application. As the sophistication of the display device increases, so do the requirements imposed on the nematic mixtures. Thus, although the equations given above are only valid [11–13] for TN-LCDs, the same physical parameters (if not always the same values or ratios) are of similar importance for the electro-optic response of the other display devices mentioned above [2–10].

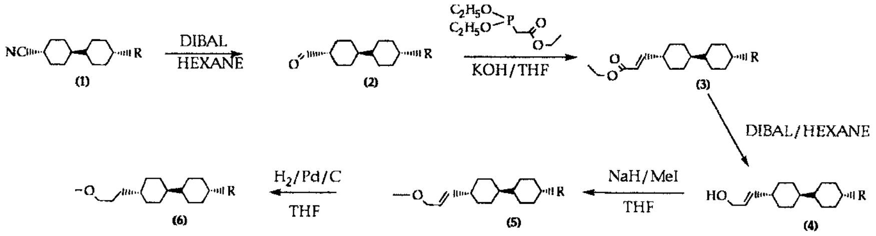
In order to satisfy all the LCD specifications for each individual application, it is necessary to utilize complex mixtures of liquid crystals of both high positive and weak positive or negative dielectric anisotropy. Mesogens of low dielectric anisotropy (weakly polar) often possess low melting and clearing points, viscosity and birefringence. The liquid crystals of high positive dielectric anisotropy (polar) are diluted by weakly polar liquid crystals in order to lower the melting point and viscosity, to modify the eleastic constant ratios and birefringence and to disrupt the degree of interdigitation [11, 14, 15]. However, the clearing point (N–I) of weakly polar liquid crystals is often low [16–19]. This imposes limits on the upper temperature range of the nematic mixture and/or limits the amount of these components that can be used. The presence of ordered smectic phases (for example, S_B) induced at low temperatures is often a problem in such mixtures.

In an attempt to synthesize non-polar liquid crystal materials of low viscosity, smectic tendencies and melting point and, at the same time, having a high clearing point (i.e., with a wide nematic temperature range), a series of the recently reported methyl (*E*)-[*trans*-4-substituted-cyclohexyl]allyl ethers [20] with alkyl/alkoxy substituents has now been synthesized. Nematic liquid crystals with either an oxygen atom [21–24] or a carbon–carbon double bond [25–31] in the terminal aliphatic chain are known. The methyl (*E*)-[*trans*-4-substituted-cyclohexyl]allyl ethers have been shown to exhibit unusual combinations of elastic, dielectric (static) and optical properties [20].

2. Synthesis

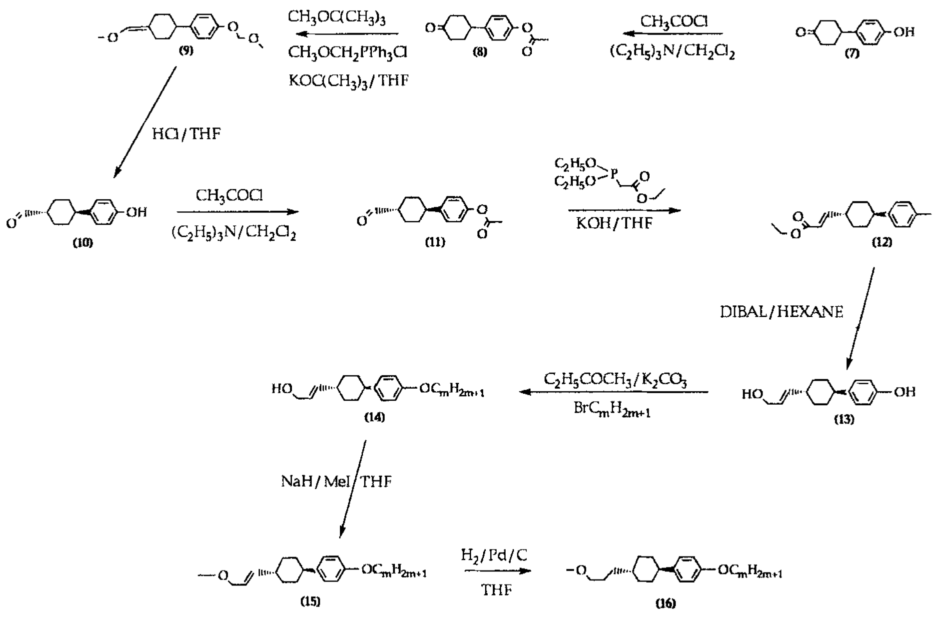
The methods of synthesis of the new methyl (*E*)-[*trans*-4-substituted-cyclohexyl]allyl ethers (**5a–e**, **15** and **27**, $X = \mathrm{H/F}$) with a *trans*-carbon–carbon double bond in the terminal chain are shown in reaction schemes 1–3. The methods of preparation are described in general below and in detail in the experimental section. One homologue (**6** and **16**) of each of the 3-methoxypropyl-substituted compounds (without a carbon–carbon double bond in the alkoxy chain) is included as reference compound. The configuration of the carbon–carbon double bond in the methyl (*E*)-allyl ether chain of the new ethers (**5a–e**, **15** and **27**; $X = \mathrm{H/F}$) 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 infra-red spectroscopy (the *trans*-absorption bands are narrow and exact ≈970–960 cm^{-1}, while *cis*-absorption bands are observed at distinctly different wavelengths ≈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 [32].

The methyl (*E*)-[*trans*-4-(*trans*-4-[alkenyl]cyclohexyl)cyclohexyl]allyl ethers (**5**) were synthesized as depicted in reaction scheme 1 from the known [11] 4-alkenyl-1′-[*trans*-4-cyanocyclohexyl]cylohexanes (**1**) by reduction with DIBAL [33, 34] to the aldehydes (**2**) [35], followed by a Wittig–Horner reaction [36] to yield the acrylic esters (**3a–e**) with a *trans*-configuration at the double bond [35] after recrystallization. The acrylic esters (**3a–e**) were then converted to the corresponding (*E*)-allyl alcohols (**4a–e**) [35] by reduction with DIBAL [33, 34]. Alkylation of the alcohols (**4a–e**) using sodium hydride [37] yielded the desired (*E*)-allyl ethers (**5a–e**). Hydrogenation over a palladium catalyst on active charcoal gave the analogous methyl 3-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]propyl ether (**6**) as a reference compound.



Scheme 1.

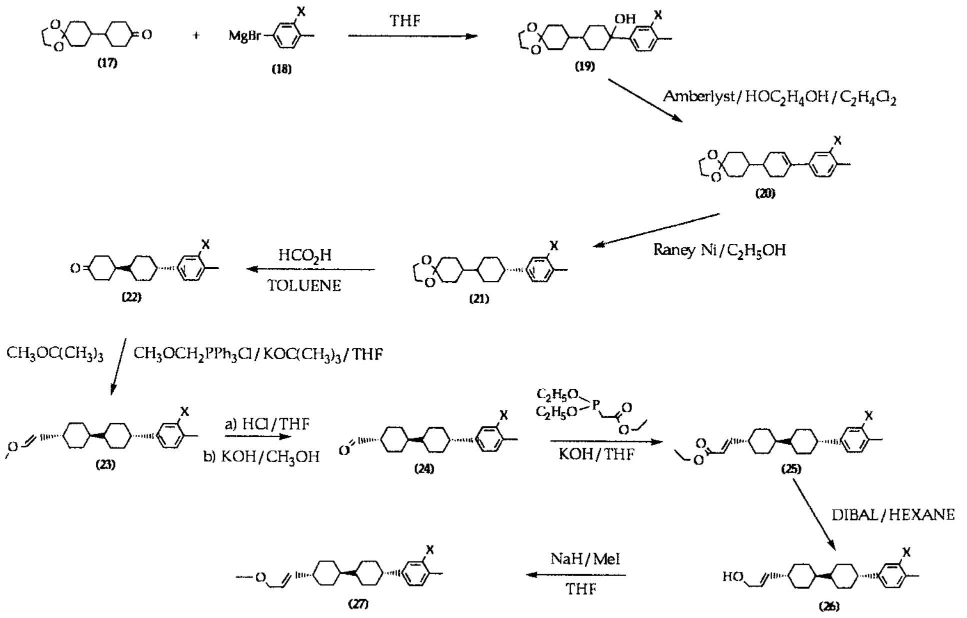
The methyl (*E*)-[*trans*-4-(4-alkoxyphenyl)cyclohexyl]allyl ethers (**15**; $m = 1$–7) were prepared as shown in reaction scheme 2. The acetate (**8**) was first prepared



Scheme 2.

from 4-hydroxyphenylcyclohexanone (**7**) [38] by esterification with acetyl chloride. A Wittig reaction using methoxymethyltriphenylphosphonium chloride yielded the enol ether (**9**) with the phenol group protected as a methoxymethyl ether [39]. The 4-(*trans*-4-formylcyclohexyl)phenol (**10**) was obtained in a predominantly *trans*-form by hydrolysis with hydrochloric acid. Protection as the acetate (**11**) as described above, followed by a Wittig–Horner reaction [36] yielded the unprotected acrylate (**12**) in a pure *trans*-configuration. The allyl alcohol/phenol (**13**) was obtained by reduction with DIBAL [33, 34] and then selectively alkylated in a standard Williamson ether synthesis. The resultant methyl (*E*)-[*trans*-4-(4-alkoxyphenyl)-cyclohexyl]allyl alcohol (**14**) was alkylated using a stronger base (sodium hydride) with commercially available bromo- or iodo-alkanes to yield the desired methyl (*E*)-[*trans*-4-(4-alkoxyphenyl)cyclohexyl]allyl ethers (**15**; $m=1$–7). The reference methyl 3-[*trans*-4-(4-ethoxyphenyl)cyclohexyl]propyl ether (**16**) was prepared by hydrogenation of methyl (*E*)-(*trans*-4-(4-ethoxyphenyl)cyclohexyl]allyl ether (**15**; $m=2$) over a palladium catalyst [35].

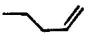
Methyl (*E*)-(*trans*-4-[*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexyl)allyl ether (**27**; $X=H$) and the corresponding 2-fluoro-substituted derivative (**27**; $X=F$) were synthesized as depicted in scheme 3. Reaction of the Grignard reagent (**18**) with the



Scheme 3.

protected cyclohexanone (**17**) [40] yielded the alcohol (**19**). Elimination of the alcohol group using amberlyst 15 yielded the cyclohexene compound (**20**). Hydrogenation over palladium on charcoal gave the *trans*-ketal (**21**). The ketone (**22**), obtained by deprotection with formic acid was used in a Wittig reaction to yield compound (**23**). Hydrolysis using hydrochloric acid gave the aldehyde (**24**), which was isomerised using potassium hydroxide to the pure *trans*-form. The methyl

Table 1. Transition temperatures for the compounds (**3**)

Compound	*R*	C-S_B/N/°C	S_B-N/°C	N-I/°C	$\Delta T_{N\text{-}I}$/°C
3a		2	—	43	41
3b		39	—	94	55
3c		15	—	80	65
3d		34	—	94	60
3e		7	44	70	26

(*E*)-allyl ethers (**27**) were produced in the pure *trans*-form from the aldehyde (**24**) via a Wittig–Horner reaction to produce the ethyl (*E*)-acrylates (**25**), reduction to the allyl alcohols (**26**) using DIBAL and then methylation using sodium hydride. No isomerization of the unsaturated carbon–carbon bond was necessary.

3. Mesomorphic properties

The liquid crystal transition temperatures of the methyl (*E*)-[*trans*-4-(*trans*-4-[alkenyl]cyclohexyl)cyclohexyl]allyl ethers, (**5a–e**) and those of the intermediate acrylic esters (**3a–e**) and allyl alcohols (**4a–e**) are recorded in the tables 1–3, where ΔT_{N-I} represents the nematic phase range.

The melting (C–N) and clearing points (N–I) of the known [11] nitriles (**1**), used as starting materials, are both high [54°C and 79°C, on average, respectively, for the same homologues as the ethers (**5a–e**)]. The nitriles with a *trans*-carbon–carbon double bond exhibit higher clearing points than those of the corresponding nitriles with a double bond in a terminal position The compound (4-pentenyl) with the longest chain with a double bond in a terminal position also exhibits a smectic B phase. These effects are typical for alkenyl-substituted mesogens [11–13, 25–31]. The analogous aldehydes (**2**) are isotropic liquids at room temperature. No attempt was made to produce pure *trans*-isomers as this would have led to low product yields due to the low melting points and good solubility in most organic solvents. The esters (**3a–e**) possess substantially lower (−35°C, on average) melting points and slightly lower (−3°C, on average, comparing only compounds with the same chains)

Table 2. Transition temperatures for the compounds (**4**)

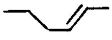
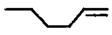
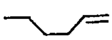
Compound	*R*	C-S_B/°C	S_B-N/I°C	N-I/°C	$\Delta T_{N\text{-}I}$/°C
4a		27	82	—	—
4b		56	95	113	18
4c		55	110	—	—
4d		68	114	118	4
4e		13	124	—	—

Table 3. Transition temperatures for the compounds (**5**)

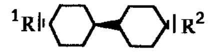
Compound	*R*	C-S_B/N/°C	S_B-N/I/°C	N-I/°C	$\Delta T_{N\text{-}I}$/°C
5a		9	18	36	18
5b		10	—	92	82
5c		−17	67	75	8
5d		39	71	100	29
5e		13	89	—	—

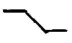
clearing points than the corresponding nitriles (**1**), see table 1. Thus the nematic phase range is broader (+28°C, on average), taking into account the smectic B phase present for the 4-pentenyl derivatives. The esters (**3b** and **3d**) with a *trans*-carbon–carbon double bond exhibit higher clearing points than those of the corresponding esters (**3a**, **3c** and **3e**) with a double bond in a terminal position. The compound (**3e**) with the longest chain with a double bond in a terminal position also exhibits a smectic B phase. The analogous alcohols (**4a–e**) exhibit higher melting points (+28°C, on average), higher smectic B transition temperatures (+80°C for the 4-pentenyl homologue) and clearing points (+22°C comparing two homologues), see table 2. The alcohols are predominantly smectic B in character. This may well be a result of hydrogen bonding between the hydroxy groups [41] giving rise to a number of quasi five-ring dimers in the bulk liquid crystal [42]. The liquid crystal transition temperatures of the methyl (*E*)-*trans*-4-(*trans*-4-[alkenyl]cyclohexyl)-cyclohexyl]allyl ethers (**5a–e**) are collated in table 3. The ethers (**5a–e**) exhibit lower melting points (−33°C, on average), smectic B transition temperatures (−47°C, on average, for four homologues) and clearing points (−20°C, on average, for two homologues) than the allyl alcohols (**4a–e**). The results in an increase in the nematic temperature range (+45°C, on average, for two homologues). The clearing points of some homologues are remarkably high for two-ring systems. The low melting point, high clearing point and wide nematic temperature range of the ether (**5b**) are of particular interest.

A comparison between the transition temperatures of one methyl (*E*)-[*trans*-4-(*trans*-4-[(*E*)-1-propenyl]cyclohexyl)cyclohexyl]allyl ether (**5b**), the corresponding 3-methoxypropyl-substituted ether (**6**) and an intermediate alkyl/alkenyl derivative (**28**) is shown in table 4. The ether (**6**) only exhibits a smectic B phase, while the intermediate alkyl/alkenyl derivative (**7**) exhibits both a smectic B and a nematic mesophase at elevated temperatures. However, the nematic phase for the compound (**28**) is of much narrower range than that of the ether (**5b**), which exhibits a particularly wide nematic temperature range (82°C). This suggests that synergetic effects due to the presence of both an oxygen atom and a carbon–carbon double bond can lead to wide nematic temperature ranges. A more exact comparison of these effects is shown later (see table 6).

The liquid crystal transition temperatures of the methyl (*E*)-[*trans*-4-(4-alkoxyphenyl)cyclohexyl]allyl ethers (**15**; $m = 1$–7) are collated in table 5. Several of the ethers (**15**) exhibit nematic phases at or just above room temperature (for

Table 4. Transition temperatures for the compounds



Compound	R^1	R^2	C-S_B/N/°C	S_B-N/I/°C	N-I/°C	$\Delta T_{N\text{-}I}$/°C
6			25	85	—	—
28			38	73	95	22
5b			10	—	92	82

example, $m=2$ and 4). The two plots of the clearing point (N-I) show a large degree of alternation. The first plot ($m=1$, 3 and 5) rises from low values for short chains and then converges with the second plot ($m=2$, 4 and 6), which descends from a relatively high value with increasing chain length. A smectic B phase is observed for long alkoxy chains ($m=6$ and 7). The smectic B phase replaces the nematic phase for the longest chain length studied ($m=7$).

The effect of an oxygen atom, a carbon-carbon double bond, or a combination of both in the terminal end chain on the liquid crystal transition temperatures of a model system is shown in table 6. The introduction of an oxygen atom into the ether (**29**) [43] to produce the 3-methoxypropyl-substituted ether (**16**) results in a much lower melting point (−34°C) and a lower clearing point (−9°C). However, as the melting point is decreased much more than the clearing point, a relatively broad nematic phase just above room temperature is observed. The incorporation of a carbon-carbon double bond instead of an oxygen atom into the ether (**29**) [43] to produce the 1-pentenyl-substituted ether (**30**) results in a lower melting point (−20°C), but a higher clearing point (+8°C). The result is also a relatively broad nematic phase, but at higher temperatures. The introduction of an oxygen atom and a carbon-carbon double bond into the ether (**29**) [43] to produce the allyl ether (**15**; $n=2$) leads to a nematic phase with the widest temperature range just above room temperature.

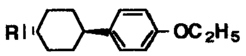
The liquid crystal transition temperatures of the methyl (*E*)-(*trans*-4-[*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexyl)allyl ether (**27**; $X=$H/F) and the intermediate acrylic esters (**25**; $X=$H/F) and allyl alcohols (**26**; $X=$H/F) are recorded in

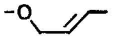
Table 5. The transition temperatures for the compounds (**15**)

m	C-S_B/N/I/°C	S_B-N/I/°C	N-I/°C	$\Delta T_{N\text{-}I}$/°C	ΔH/kJ mol^{-1}
1	24	—	(17)	—	—
2	19	—	46	27	—
3	30	—	(19)	—	21·0
4	23	—	40	17	—
5	30	—	31	1	17·4
6	16	30	38	8	15·1
7	14	38	—	—	9·3

( ) Represents a monotropic transition temperature.

Table 6. The transition temperatures for the compounds



Compound	*R*	C-N/I/°C	N-I/°C	$\Delta T_{N\text{-}I}$/°C
29		52	(47)	—
16		18	38	20
30		32	55	23
15 (*n* = 2)		19	46	27

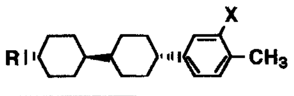
( ) Represents a monotropic transition temperature.

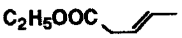
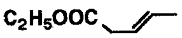
table 7. The melting (C-S_B and C-N) and clearing (N/I) points of the allyl alcohols (**26**; *X* = H/F) are higher (+37°C and +14°C, on average, respectively) than those of the corresponding acrylic esters (**25**; *X* = H/F) as could have been expected on the basis of the previous results. However, the differences are not so great, due to the dilution effect of the third six-membered ring. The allyl ethers (**27**; *X* = H/F) exhibit the lowest melting (69°C, on average) and clearing points (177°C, on average). The fluorine atom totally suppresses the smectic B phase for the allyl alcohol (**26**; *X* = F) and the allyl ether (**27**; *X* = F). Although unusually large, this effect is consistent with previous results [41–47].

4. Experimental

The liquid crystal transition temperatures of the compounds prepared and recorded in tables 1–7 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 values (extrapolated) had to be determined. When necessary, the Mettler stage could be cooled (−50°C) by allowing N_2 gas, cooled by

Table 7. The transition temperatures for the compounds (**25–27**; *X* = H/F)



Compound	*R*	C-S_B/N/°C	S_B-N/°C	N-I/°C
(**25**; *X* = H)		83	—	201
(**25**; *X* = F)		92	—	185
(**26**; *X* = H)		123	140	222
(**26**; *X* = F)		127	—	196
(**27**; *X* = H)		79	99	193
(**27**; *X* = F)		58	—	160

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 chromatography 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 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 under nitrogen unless water was present as solvent or reagent. All temperatures were measured externally unless otherwise stated. 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 on a MS9 (AEZ Manchester) spectrometer.

4.1. *Methyl (E)-[*trans*-4-(trans-4-[(E)-1-propenyl]cyclohexyl)cyclohexyl]allyl ether* (**5b**)

A solution of (*E*)-[*trans*-4-(*trans*-4-[(*E*)-1-propenyl]cyclohexyl)cyclohexyl]allyl alcohol (0·5 g, 2 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension (50 w/w per cent in mineral oil) of sodium hydride (0·2 g, 4·1 mmol) in tetrahydrofuran (50 cm^3) at room temperature. After stirring for 4 h, methyl iodide (0·4 g, 26 mmol) was added dropwise and the reaction mixture stirred overnight. Methanol (10 cm^3) and then water (50 cm^3) were added and the product extracted into 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 9·1 hexane/ethyl acetate mixture as eluent and recrystallization from acetone at −25°C to yield the pure (99·8 per cent) ether (**5b**) (yield 0·35 g, 66 per cent); IR (KBr) ν_{max}: 2919, 2850, 1669, 1446, 1119, 968 cm^{-1}. MS *m/z*: 276 (M^+), 244 ($C_{18}H_{28}$). ^1H NMR ($CDCl_3$): 1·01 (10 H, overlapping peaks), 1·57–1·62 (3 H, d), 1·64 (10 H, overlapping peaks), 3·31 (3 H, s), 3·63–3·86 (2 H, d), 5·35–5·37 (2 H, t), 5·45–5·69 (2 H, overlapping peaks). The liquid crystal transition temperatures of this ether (**5b**) and other homologues (**5a**, **c**–**e**) prepared using this general method are collated in table 3.

4.2. *Methyl 3-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]propyl ether* (**6**)

A mixture of methyl (*E*)-[*trans*-4-(*trans*-4-[(*E*)-1-propenyl]cyclohexyl)-cyclohexyl]allyl ether (**5b**) (0·5 g, 19 mmol), ethyl acetate (50 cm^3) and 10 per cent palladium on active charcoal (1 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 recrystallization from acetone at −25°C to yield the pure (99·9 per cent) ether (**6**) (yield 0·17 g, 33 per cent); MS *m/z*: 280 (M^+), 248 ($C_{18}H_{32}^+$). NMR ($CDCl_3$): 0·83–1·76 (32 H, overlapping peaks), 3·31–3·37 (5 H, t). The liquid crystal transition temperatures of this ether (**6**) are given in table 4.

4.3. *4-(4-Acetoxyphenyl)cyclohexanone* (**8**)

Acetyl chloride (10·1 g, 142 mmol) was added dropwise at 0°C to a solution of 4-(4-hydroxyphenyl)cyclohexanone (**7**) [38] (25·8 g, 135 mmol), triethylamine (19·8 cm^3

142 mmol) and dichloromethane (400 cm^3). The reaction mixture was stirred for 1 h at room temperature and then added to water (1000 cm^3). The organic layer was separated off and the aqueous layer shaken with dichloromethane (2 × 30 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 dichloromethane as eluent and recrystallization from acetone at −25°C to yield the pure (99·8 per cent) ester (**8**) (yield 24·7 g, 79 per cent); MS *m/z*: 232 (M^+).

4.4. *1-Methoxymethylidene-4-(4-[methoxymethyl]phenyl)cyclohexane* (**9**)

Potassium tert-butylate (26·5 g, 234 mmol) was added portion wise to a mixture of 4-(4-acetoxyphenyl)cyclohexanone (**8**) (25·9 g, 111 mmol), methoxymethyltriphenylphosphonium chloride (80·1 g, 234 mmol) and tetrahydrofuran (500 cm^3). After completion of the addition, the reaction mixture was stirred for 1 h 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 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 ether (**9**) (yield 30 g, quantitative); MS *m/z*: 262 (M^+).

4.5. *trans/cis-4-(4-Hydroxyphenyl)cyclohexane-1-carboxaldehyde* (**10**)

A mixture of (*E*/*Z*)-1-methoxymethylidene-4-(4-[methoxymethyl]phenyl)-cyclohexane (**9**) (30·7 g, 118 mmol), tetrahydrofuran (325 cm^3) and 1 M-hydrochloric acid (110 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 × 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 1:1 hexane/ethyl acetate mixture as eluent to yield the pure (97·9 per cent; *E*/*Z*: 5·5:1) phenol (**10**) (yield 18·0 g, 75 per cent); MS *m/z*: 204 (M^+).

4.6. *trans/cis-4-(4-Acetoxyphenyl)cyclohexane-1-carboxaldehyde* (**11**)

Acetyl chloride (6·6 cm^3, 92 mmol) was added dropwise at 0°C to a solution of *trans/cis*-4-(4-hydroxyphenyl)cyclohexane-1-carboxaldehyde (**10**) (18·0 g, 88 mmol), triethylamine (12·9 cm^3 92 mmol) and dichloromethane (350 cm^3). The reaction mixture was stirred for 1 h at room temperature and then added to water (1000 cm^3) The organic layer was separated off and the aqueous layer shaken with dichloromethane (2 × 30 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 dichloromethane as eluent and recrystallization from acetone at −25°C to yield the pure (99·8 per cent) aldehyde (**11**) (yield 16·6 g, 77 per cent); MS *m/z*: 246 (M^+).

4.7. *Ethyl(E)-[trans-4-(4-Hydroxyphenyl)cyclohexyl]acrylate* (**12**)

Potassium hydroxide (7·6 g, 135 mmol) was added portionwise to a mixture of *trans/cis*-4-(4-acetoxyphenyl)cyclohexane-1-carboxaldehyde (**11**) (16·6 g, 67·4 mmol), ethyl diethylphosphonoacetate (18·2 g, 80·8 mmol) and tetrahydrofuran (500 cm^3). After completion of the addition, the reaction mixture 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 ether (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 and recrystallization from ethyl acetate to yield the pure (98·6 per cent; > 1 per cent *cis*) acrylate (**12**) (yield 17·6 g, 83 per cent); m.p. 90°C; MS *m/z*: 274 (M^+), 228 ($C_{14}H_{17}O$), 201 ($C_{15}H_{16}O_2$).

4.8. *(E)-[trans-4-(4-Hydroxyphenyl)cyclohexyl]allyl alcohol* (**13**)

20 per cent Diisobutylaluminium hydride in hexane (150 cm^3) was added dropwise to a solution of ethyl (*E*)-[*trans*-4-(4-hydroxyphenyl)cyclohexyl]acrylate (**12**) (17·6 g, 55 mmol) in toluene (350 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, then poured on to water (1000 cm^3) and organic material extracted into 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 96:4 dichloromethane/methanol mixture as eluent and recrystallization from ethyl acetate to yield the pure (100 per cent) allyl alcohol (**13**) (yield 6·4 g, 50 per cent); MS *m/z*: 232 (M^+), 133 (C_9H_9O), 120 (C_8H_8O).

4.9. *(E)-[trans-4-(4-Methoxyphenyl)cyclohexyl]allyl alcohol* (**14**)

A mixture of methyl iodide (0·4 g, 26 mmol), (*E*)-[*trans*-4-(4-hydroxyphenyl)-cyclohexyl]allyl alcohol (**13**) (0·5 g, 22 mmol), potassium carbonate (1·4 g, 103 mmol) and ethyl methyl ketone (50 cm^3) was heated under gentle reflux overnight. The reaction mixture was added to water (1000 cm^3) and then shaken with ether (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 1:1 hexane/ethyl acetate mixture as eluent and recrystallization from hexane to yield the pure (99·8 per cent) allyl alcohol (**14**) (yield 0·3 g, 57 per cent); m.p. 79–80°C; IR (KBr) ν_{max}: 3309, 2919, 2847, 1665, 1609, 1514, 1445, 1259, 1029, 971, 827 cm^{-1}. MS *m/z*: 246 (M^+), 134 ($C_8H_{10}O$). ^1H NMR ($CDCl_3$): 1·31 (5 H, overlapping peaks), 1·89 (5 H, overlapping peaks), 4·11 (2 H, d), 5·64–5·68 (2 H, t), 6·82–6·85 (2 H, d), 7·11–7·14 (2 H, d).

4.10 *Methyl (E)-[trans-4-(4-methoxyphenyl)cyclohexyl]allyl ether* (**15**; *m* = *1*)

A solution of (*E*)-[(*trans*-4-(4-methoxyphenyl)cyclohexyl]allyl alcohol (**14**) (0·28 g, 1·1 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension (50 w/w per cent in mineral oil) of sodium hydride (0·03 g, 1·3 mmol) in tetrahydrofuran (25 cm^3) at room temperature. After stirring for 4 h, methyl iodide (0·2 g, 14 mmol) was added dropwise and the reaction mixture stirred overnight. The reaction mixture was worked up and purified as described above for methyl (*E*)-[*trans*-4-(*trans*-4-[(*E*)-1-propenyl]cyclohexyl)cyclohexyl]allyl ether (**5b**) to yield the pure (100 per cent) ether (**15**; *m* = 1) (yield 0·14 g, 47 per cent). IR (KBr) ν_{max}:

2922, 2849, 1669, 1611, 1512, 1446, 1429, 1118, 1038, 972 cm^{-1}. MS *m*/*z*: 260 (M^+), 134 ($C_8H_{10}O$). ^1H NMR ($CDCl_3$): 1·01 (5 H, overlapping peaks), 1·57 (4 H, d), 1·87 (4 H, d), 3·33 (3 H, s), 3·78 (3 H, s), 3·79–3·90 (2 H, d), 6·82–6·86 (2 H, d), 7·11–7·17 (2 H, d). The liquid crystal transition temperatures of this ether (**15**; $m=1$) and other homologues (**15**; $m=2$–7) prepared using this general method are collated in table 5.

4.11. *Methyl 3-[trans-4-(4-ethoxyphenyl)cyclohexyl]propyl ether* (**16**)

A mixture of methyl (*E*)-[*trans*-4-(4-ethoxyphenyl)cyclohexyl]allyl ether (**15**; $m=2$) (0·5 g, 18 mmol) ethyl acetate (50 cm^3) and 10 per cent palladium on active charcoal (1 g) was hydrogenated until no more hydrogen was taken up. The catalyst was filtered off and the filtrate evaporated. The residue was purified by recrystallization from acetone at $-25°C$ to yield the pure (99·7 per cent) ether (**16**) (yield 0·18 g, 35 per cent); MS *m*/*z*: 276 (M^+). NMR ($CDCl_3$): 0·83–1·58 (12 H, overlapping peaks), 1·84–1·88 (4 H, d), 3·34–3·40 (5 H, t), 3·96–4·04 (2 H, q), 6·80–6·83 (2 H, d), 7·09–7·12 (2 H, d). The liquid crystal transition tempeatures of this ether (**16**) are recorded in table 6.

4.12 *4-[4-(4-Methylphenyl)-4-hydroxy-cyclohexenyl]cyclohexanone ethylene ketal* (**19**; *X* = *H*)

A solution of Grignard reagent (**18**; $X=H$) [produced as usual from 4-bromotoluene (45·6 g, 267 mmol), magnesium turnings (6·1 g, 249 mmol and tetrahydrofuran (125 cm^3)] was added dropwise to a mixture of 4-oxacyclohexyl-4-cyclohexanone ethylene ketal (**17**) [40] (47·7 g, 200 mmol) in tetrahydrofuran (200 cm^3) at 0°C and then stirred overnight at room temperature. 10 per cent ammonium chloride solution was added dropwise to the reaction mixture at 0°C, which was then shaken with 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 reduced pressure to yield (**19**; $X=H$) (yield 63·5 g, 94 per cent); MS *m*/*z*: 330 (M^+).

4-[4-(3-Fluoro-4-methylphenyl)-4-hydrocyclohexenyl]cyclohexanone ethylene ketal (**19**; $X=F$) was prepared using the same procedure (yield 99 per cent); MS *m*/*z*: 348 (M^+).

4.13 *4-[4-(4-Methylphenyl)-3,4-cyclohexenyl]cyclohexanone ethylene ketal* (**20**; *X* = *H*)

A mixture of 4-[4-(4-methylphenyl)-4-hydroxycyclohexenyl]cyclohexanone ethylene ketal (**19**; $X=H$) (63·5 g, 200 mmol), ethylene chloride (700 cm^3), ethylene glycol (10 cm^3) and amberlyst 15 (9·5 g) was heated under reflux overnight and 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 ($MgSO_4$), filtered and then evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using a 49:1 hexane/ethyl acetate mixture as eluent and recrystallization from a 1:3·5 ethyl acetate/iso-propanol mixture to yield pure (99·8 per cent) ketal (**20**; $X=H$) (yield 34·6 g, 58 per cent); m.p. 124–125°C; MS *m*/*z*: 312 (M^+).

4-[4-(3-Fluoro-4-methylphenyl)-3,4-cyclohexenyl]cyclohexanone ethylene ketal (**20**; $X=F$) was prepared using the same procedure (yield 71 per cent); MS *m*/*z*: 330 (M^+).

4.14 *4-[trans-4-(4-Methylphenyl)cyclohexyl]cyclohexanone ethylene ketal* (**21**; *X* = *H*)

A mixture of 4-[4-(4-methylphenyl)-3,4-cyclohexenyl]cyclohexanone ethylene ketal (**20**; X = H). (33·9 g, 108 mmol), ethanol (4000 cm^3) and Raney nickel (7·4 g) was hydrogenated at 50°C and 0·1 atmosphere 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 49:1 hexane/ethyl acetate mixture as eluent and recrystallization from a 1:3·5 ethyl acetate/iso-propanol mixture to yield pure (99·8 per cent) ketal (**21**; X = H) (yield 23·3 g, 68 per cent); MS *m*/*z*: 314 (M^+).

4-[*trans*-4-(3-Fluoro-4-methylphenyl)cyclohexyl]cyclohexanone ethylene ketal (**21**; X = F) was prepared using the same procedure (yield 75 per cent); MS *m*/*z*: 332 (M^+).

4.15. *4-[trans-4-(4-Methylphenyl)cyclohexyl]cyclohexanone* (**22**; *X* = *H*)

A mixture of 4-[*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexanone ethylene ketal (**21**; X = H) (23·3 g, 76 mmol), toluene (325 cm^3) and formic acid (80 cm^3) was stirred overnight at room temperature and then added to water (1000 cm^3). The organic layer was separated off and the organic material extracted into ether (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 (99·9 per cent) ketone (**22**; X = H; *E*/*Z*: 135:1) (yield 20·9 g, quantitative); MS *m*/*z*: 270 (M^+).

4-[*trans*-4-(3-Fluoro-4-methylphenyl)cyclohexyl]cyclohexanone (**22**; X = F) was prepared using the same procedure (yield quantitative); MS *m*/*z*: 288 (M^+).

4.16. *1-Methoxymethylidene-4-[trans-4-(4-methylphenyl)cyclohexyl]cyclohexane* (**23**; *X* = *H*)

Potassium tert-butylate (8·9 g, 78·8 mmol) was added portionwise to a mixture of 4-[*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexanone (**22**; X = H) (14·2 g, 53 mmol), methoxymethyltriphenylphosphonium chloride (27·0 g, 78·8 mmol) and tetrahydrofuran (230 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 a 39:1 hexane/ethyl acetate mixture as eluent to yield the relatively pure (97·2 per cent) ether (yield 16·6 g, quantitative); IR (KBr) ν_{max}: 2945, 2914, 2846, 1691, 1514, 1448, 1248, 1135, 981, 812 cm^{-1}. MS *m*/*z*: 298 (M^+), 118 (C_9H_{10}).

1 - Methoxymethylidene - 4 - [*trans* - 4 - (3 - fluoro - 4 - methylphenyl)cyclohexyl]-cyclohexane (**23**; X = F) was prepared using the same procedure (yield 99 per cent); MS *m*/*z*: 316 (M^+).

4.17. *trans-4-[trans-4-(4-Methylphenyl)cyclohexyl]cyclohexyl-1-carboxaldehyde* (**24**; X = *H*)

A mixture of 1-methoxymethylidine-4-[*trans*-4-(4-methylphenyl)cyclohexyl]-cyclohexane (**23**; X = H) (15·5 g, 52 mmol), tetrahydrofuran (150 cm^3) and 1 M hydrochloric acid (13 cm^3) and water (26 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 x 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 x 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 relatively pure (97·9 per cent) aldehyde (**24**; $X=$H) as a (5:1) *trans/cis*-mixture. A mixture of the aldehyde (13·8 g, 49 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 organic product extracted into dichloromethane (3 x 50 cm^3). The combined organic layers were washed with dilute sodium carbonate solution (2 x 100 cm^3), dried ($MgSO_4$), filtered and then evaporated down under reduced pressure. Recrystallization from iso-propanol yielded pure (100 per cent) aldehyde (**24**; $X=$H; *trans/cis*: 132:1) (yield 9·9 g, 67 per cent); IR (KBr) ν_{max}: 2923, 2851, 2717, 1723, 1572, 1514, 1445, 981, 812 cm^{-1}. MS *m/z*: 284 (M$^+$), 131 ($C_{10}H_{11}$), 118 (C_9H_{10}).

trans - 4 - [*trans* - 4 - (3 - Fluoro - 4 - methylphenyl)cyclohexyl]cyclohexyl - 1 - carboxaldehyde (**24**; $X=$F) was prepared using the same procedure (yield 99 per cent); MS *m/z*: 302 (M$^+$).

4.18. *Methyl (E)-(trans-4-[4-methylphenyl)cyclohexyl]cyclohexyl)acrylate (**25**; X=H)*

Potassium hydroxide (1·9 g, 34 mmol) was added portionwise to a mixture of *trans*-4-([*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexyl)-1-carboxaldehyde (**24**; $X=$H) (4·9 g, 17 mmol), ethyl diethylphosphonoacetate (4·6 g, 20·5 mmol) and tetrahydrofuran (500 cm^3). After completion of the addition the reaction mixture was stirred overnight at room temperature. The reaction mixture was worked up and purified as described above for ethyl (*E*)-[trans-4-(4-hydroxyphenyl)cyclohexyl]-acrylate (**12**) to yield the acrylate (**25**; $X=$H) (yield 5·4 g, 90 per cent); IR (KBr) ν_{max}: 2916, 2848, 1717, 1650, 1515, 1448, 1368, 1188, 1168, 1034, 986, 813 cm^{-1}. MS *m/z*: 354 (M$^+$), 118 (C_9H_{10}). ^{1}H NMR ($CDCl_3$): 1·15–1·32 (11 H, overlapping peaks), 1·56–1·81 (10 H, overlapping peaks), 2·31 (3 H, s), 4·14 (2 H, q), 5·74–5·80 (2 H, overlapping peaks), 6·87–6·96 (4 H, s), 7·09 (4 H, s). The liquid crystal transition temperatures of this acrylate (**24**; $X=$H) are recorded in table 7.

Methyl (*E*)-(*trans*-4-[*trans*-4-(3-fluoro-4-methylphenyl)cyclohexyl]cyclohexyl)-acrylate (**25**; $X=$F) was prepared using the same procedure (yield 93 per cent); IR (KBr) ν_{max}: 2924, 2851, 1718, 1652, 1580, 1512, 1446, 1367, 1272, 1168, 1034, 985, 815 cm^{-1}. MS *m/z*: 327 (M$^+$), 136 (C_9H_9F), 123 (C_8H_9F). ^{1}H NMR ($CDCl_3$): 1·14–1·32 (14 H, overlapping peaks), 1·61 (10 H, overlapping peaks), 2·22 (3 H, s), 4·14–4·20 (2 H, q), 5·74 (1 H, d), 5·80 (1 H, d), 6·86–6·93 (3 H, overlapping peaks), 7·09 (1 H, t). The liquid crystal transition temperatures of this acrylate (**25**; $X=$F) are recorded in table 7.

4.19. *(E)-(trans-4-[trans-4-(4-Methylphenyl)cyclohexyl]cyclohexyl)allyl alcohol (**26**; X=H)*

20 Per cent diisobutylaluminium hydride in hexane (22·5 cm^3) was added dropwise to a solution of ethyl (*E*)-(*trans*-4-[*trans*-4-(4-methylphenyl)cyclohexyl]-cyclohexyl)acrylate (**25**; $X=$H) (5·3 g, 15 mmol) in toluene (100 cm^3) at 0°C and stirred at room temperature overnight. The reaction mixture was worked up and

purified as described above for (*E*)-[*trans*-4-(4-hydroxyphenyl)cyclohexyl]allyl alcohol (**13**) to yield the allyl alcohol (yield 3·9 g, 82 per cent); IR (KBr) ν_{max}: 3312, 2920, 2845, 1665, 1625, 1515, 1449, 1336, 1003, 975, 812 cm^{-1}. MS *m*/*z*: 312 (M$^+$), 294 ($C_{22}H_{30}$). ^{1}H NMR ($CDCl_3$): 1·07–1·14 (12 H, overlapping peaks), 1·56–1·79 (9 H, overlapping peaks), 2·31 (3 H, s), 4·08 (2 H, d) 5·61–5·64 (2 H, overlapping peaks), 7·09 (4 H, s), 7·25 (3 H, s). The liquid crystal transition temperatures of this allyl alcohol (**26**; $X = H$) are collated in table 7.

(*E*)-(*trans*-4-[*trans*-4-(3-Fluoro-4-methylphenyl)cyclohexyl]cyclohexyl)allyl alcohol (**26**; $X = F$) was prepared using the same procedure (yield 46 per cent); IR (KBr) ν_{max}: 3278, 2922, 2850, 1667, 1626, 1582, 1511, 1447, 1378, 1252, 1118, 1006, 970, 815 cm^{-1} MS *m*/*z*: 330 (M$^+$), 136 (C_9H_9F), 123 (C_8H_9F). ^{1}H NMR ($CDCl_3$): 1·07–1·79 (20 H, overlapping peaks), 2·22 (3 H, s), 4·08–4·10 (2 H, d), 5·62 (1 H, d), 5·63 (1 H, d) 6·82–6·88 (2 H, overlapping peaks), 7·06 (1 H, t). The liquid crystal transition temperatures of this allyl alcohol (**26**; $X = H$) are collated in table 7.

4.20. *Methyl (E)-(trans-4-[trans-4-(4-methylphenyl)cyclohexyl]cyclohexyl)allyl ether* (**27**; *X = H*)

A solution of (*E*)-(*trans*-4-[*trans*-4-(4-methylphenyl)cyclohexyl]cyclohexyl) allyl alcohol (**26**; $X = H$) (3·8 g, 12 mmol) in tetrahydrofuran (10 cm^3) was added dropwise to a suspension (50 w/w per cent in mineral oil) of sodium hydride (0·75 g 1·3 mmol) in tetrahydrofuran (100 cm^3) at room temperature. After stirring for 4 h, methyl iodide (2·6 g, 18 mmol) was added dropwise and the reaction mixture stirred overnight. The reaction mixture was worked up and purified as described above for methyl (*E*)-[*trans*-4-(*trans*-4-[(*E*)-1-propenyl]cyclohexyl)cyclohexyl]allyl ether (**5b**) to yield the pure (100 per cent) ether (yield 2·4 g, 60 per cent); IR (KBr) ν_{max}: 2915, 2849, 1669, 1631, 1515, 1449, 1384, 1122, 972, 813 cm^{-1}. MS *m*/*z*: 326 (M$^+$), 294 ($C_{22}H_{30}$). ^{1}H NMR ($CDCl_3$): 1·08–1·14 (11 H, overlapping peaks), 1·56–1·79 (10 H overlapping peaks), 2·31 (3 H, s), 3·33 (3 H, s), 3·84–3·87 (3 H, d), 5·53–5·64 (2 H, overlapping peaks), 7·10 (4 H, s), 7·25 (3 H, s). The liquid crystal transition temperatures of this methyl (*E*)-allyl ether (**27**; $X = H$) are collated in table 7.

Methyl(*E*)-(*trans*-4-[*trans*-4-(3-fluoro-4-methylphenyl)cyclohexyl]cyclohexyl)allyl ether (**27**; $X = F$) was prepared using the same procedure (yield 66 per cent); IR (KBr) ν_{max}: 2922, 2854, 1660, 1662, 1577, 1512, 1446, 1247, 1097, 975, 825 cm^{-1}. MS *m*/*z*: 344 (M$^+$). 312 ($C_{22}H_{29}F$), 136 (C_9H_9F), 123 (C_8H_9F). ^{1}H NMR ($CDCl_3$): 1·07–1·79 (19 H, overlapping peaks), 2·22 (3 H, s), 3·32 (3 H, s), 3·87 (2 H, d), 5·62 (1 H, d), 5·63 (1 H, d), 6·82–6·88 (2 H, overlapping peaks), 7·06 (1 H, t). The liquid crystal transition temperatures of this methyl (*E*)-allyl ether (**27**; $X = F$) are collated in table 7.

5. Conclusions

The melting points and smectic transition temperatures of the new methyl (*E*)-[*trans*-4-cyclohexyl-substituted]allyl ethers are often low, while the nematic transition temperatures are mostly high. Synergetic effects between the oxygen atom and the carbon–carbon double bond lead to broad nematic phases. The new methyl (*E*)-[*trans*-4-cyclohexyl-substituted]allyl ethers are easy to synthesise as pure *trans*-isomers from known aldehydes. Many intermediates are themselves liquid crystalline. The new compounds are useful components for nematic mixtures, especially where a wide temperature range is required. The greater rigidity and linearity of the methyl (*E*)-[*trans*-4-cyclohexyl-substituted]allyl ether chain is probabily responsible for these effects.

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