Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

Four unit linking groups III. Liquid crystals of negative dielectric anisotropy

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To cite this Article Kelly, S. M.(1991) 'Four unit linking groups III. Liquid crystals of negative dielectric anisotropy', Liquid Crystals, 10: 2, 261 — 272

To link to this Article: DOI: 10.1080/02678299108036430

URL: http://dx.doi.org/10.1080/02678299108036430

LIQUID CRYSTALS, 1991, VOL. 10, NO. 2, 261–272

Four unit linking groups

III. Liquid crystals of negative dielectric anisotropy

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(*Received 30 August 1990; accepted 23 October 1990*)

A series of 1-*n*-alkoxy-2,3-difluoro-4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]-benzenes has been synthesized. Several homologues exhibit an enantiotropic nematic phase of moderately strong negative dielectric anisotropy ($\Delta\varepsilon \approx -5$) at or just above room temperature. An analogous series of three-ring diethers also including some (*E*)-3-allyloxy derivatives possesses enantiotropic, wide range nematic phases also of moderately strong negative dielectric anisotropy, but at elevated temperatures. The synthesis and liquid crystal transition temperatures of these 2,3-difluoroquinone derivatives are described and comparisons are made with the transition temperatures of the corresponding materials incorporating standard central linkages (–, C_2H_4, CH_2O and COO).

1. Introduction

Nematic liquid crystals of negative dielectric anisotropy are required for guest–host displays of positive contrast [1–4] and for displays based on electrically controlled birefringence of nematic layers with homeotropic boundaries [5–11]. A low threshold voltage for these effects is necessary for battery operation and/or because of CMOS compatibility. Since the threshold voltage is proportional to $(-\Delta\varepsilon)^{-1/2}$, a large negative value of $\Delta\varepsilon$, the dielectric anisotropy ($\Delta\varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$), is desirable for these applications. Additionally nematic liquid crystals of negative dielectric anisotropy can be added to nematic mixtures of positive dielectric anisotropy in order to reduce $\Delta\varepsilon/\varepsilon_{\perp}$, thus improving the steepness of the electrooptic contrast curve of supertwisted displays (e.g. SBE, STN, OMI) [12–15]. A steeper contrast curve leads to a higher degree of multiplexability, better contrast or viewing-angle dependency, etc.

Compounds of negative dielectric anisotropy have been prepared by the incorporation of a polar substituent (e.g. F, Cl, Br, CN) into a lateral position of a mesogenic structure [16–19]. The cyano group has been utilized most of all because of its large dipole moment (4 D). However, the large van der Waals volume of the cyano group induces substantial clearing point depressions and a high viscosity, while the induced negative dielectric anisotropy is only moderate (*c.* −4). Materials incorporating two cyano groups in lateral positions exhibit a much greater negative dielectric anisotropy (*c.* −20), because the resultant dipole moment (7 D) is directed perpendicular to the long axis of the molecules. The viscosity does not increase proportionately, whereas the clearing point may be even higher than the corresponding mono cyano substituted derivative [20–27]. Although the magnitude of the dielectric anisotropy of dicyano-substituted materials is sufficiently great to allow the use of small concentrations, these substances may still suffer from the disadvantages of low solubility, high viscosity, thermal or photochemical instability, etc. A variety of 3,6-disubstituted pyridazines,

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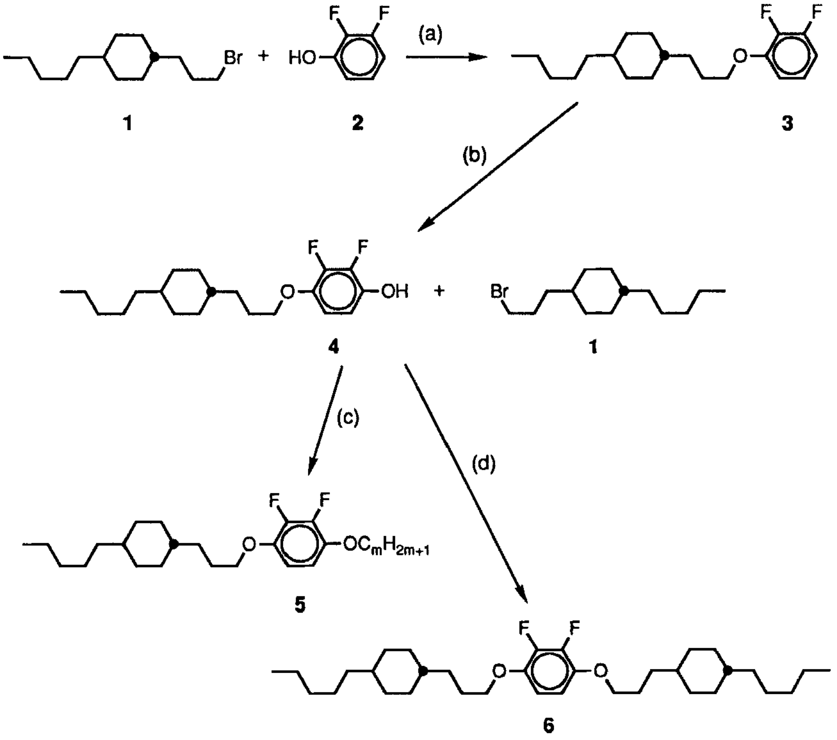
whose lone pair electrons, situated at the nitrogen atoms, give rise to a large dipole moment perpendicular to the long molecular axis, also suffer from the disadvantages of photo-instability [27, 28]. The *trans*, *trans*-4α,4′α-dialkyl-1α,1′α-dicyclohexyl-4β-carbonitriles contain only one cyano group. However, the axial position of this nitrile function on one of the cyclohexane rings locates the dipole moment (4 D) exactly perpendicular to the long molecular axis [29–31]. These materials are chemically, thermally and photochemically stable, exhibit wide range enantiotropic nematic phases at or just above room temperature and their viscosity is much lower than the aromatic, mono cyano substituted compounds [16–19] described previously. These substances appear to be very suitable for guest–host displays of positive contrast. However, the very low birefringence of these axially substituted bicyclohexanes renders them unsuitable for electrooptic displays based on electrically controlled birefringence.

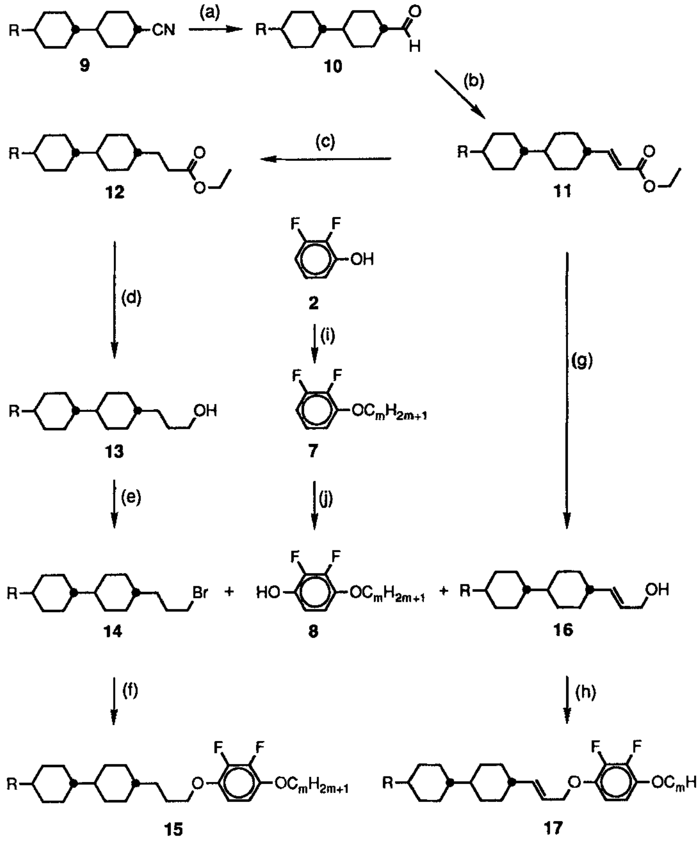
A most promising approach to the synthesis of nematogens of negative dielectric anisotropy involves 2,3-difluorobenzenes [32]. The small van der Waals volume of the fluorine atom and its relatively small dipole moment (1·4 D) lead to materials of relatively low viscosity and weak to moderately strong negative dielectric anisotropy in the nematic phase. If diether derivatives of 2,3-difluoroquinone are prepared, the resultant dipole moment perpendicular to the long molecular axis is enhanced and thus relatively large values of the dielectric anisotropy (*c*. −5) are induced. The scope of these investigations has now been widened to include 2,3-difluoro-substituted quinones incorporating the new four unit linking units 3-propyloxy (C_3H_6O) and allyloxy (C_3H_4O). These new central linkages have been shown recently to be suitable for incorporation in possible mesogenic structures [33].



Scheme 1. (*a*) K_2CO_3/butanone, (*b*) $C_4H_9Li/B(OCH_3)/H_2O_2$/tetrahydrofuran, (*c*) $C_mH_{2m+1}Br/K_2CO_3$/butanone, (*d*) K_2CO_3/butanone.

2. Synthesis

The reaction pathway leading to the asymmetrical, two-ring diethers **5** and the symmetrical, three-ring diether **6** is delineated in scheme 1. The commercially available 2,3-difluorophenol **2** is alkylated in a Williamson ether synthesis by the bromide **1** to yield the monoether **3**. Metallation of the ether **3** with butyl-lithium [32] at low temperature (−78°C) followed by formation of the corresponding dimethyl borate ester and subsequent, *in situ*, oxidation with peroxide yielded the phenol **4**. Williamson ether reactions then yielded the two- and three-ring propyloxy diethers **5** and **6**. The synthesis of the three-ring propyloxy and allyloxy substituted diethers **15** and **17** is depicted in scheme 2. The phenol **8** was first prepared by alkylation of 2,3-difluorophenol **2** to yield the monoether **7**, followed by metallation, borate ester formation and peroxide oxidation to the phenol **8**. Then the nitrile **9** [35] was reduced with diisobutyl aluminium hydride to the aldehyde **10** [36], which is then converted via a Wittig–Horner reaction [37] to the *trans*-acrylate ester **11**, followed by hydrogenation using a palladium catalyst to the propionate ester **12**. Reduction of the ester **12** to the alcohol **13**, followed by conversion using tetrabromomethane [38] to the bromide **14** and subsequent Williamson alkylation with the phenol **8** yielded the propyloxy



Scheme 2. (*a*) DIBAH/hexane, (*b*) $P(OC_2H_5)_2CH_2CO_2C_2H_5$/KOH/tetrahydrofuran, (*c*) Pd/C/ethyl acetate, (*d*) $LiAlH_4$/ether, (*e*) CBr_4/TPP/dichloromethane (*f*) K_2CO_3/butanone, (*g*) DIBAH/hexane, (*h*) DEAD/TPP/tetrahydrofuran, (*i*) $C_mH_{2m+1}Br/K_2CO_3$/butanone, (*j*) $C_4H_9Li/B(OCH_3)_3/H_2O_2$ tetrahydrofuran.

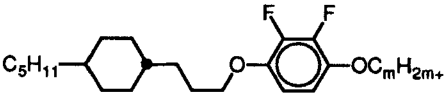
diether **15**. Conversion of the *trans*-acrylate **11** to the corresponding *trans* allylalcohol **16** using diisobutyl aluminium hydride [37, 39] and subsequent alkylation with the phenol **8** in a Mitsunobu reaction [40] yielded the corresponding allyloxy diether **17**.

3. Results

The liquid crystal transition temperatures and enthalpies of fusion of the 1-*n*-alkoxy-2,3-difluoro-4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzenes **5** ($m = 1$–7) are collated in table 1. As can be seen from this table the melting point (C–S_A and C–N) decreases steeply with increasing chain length from being significantly above room temperature (C–I = 44°C) for the shortest chain length possible ($m = 1$) to substantially below room temperature (C–S_A = 8°C) for the longest chain length studied ($m = 7$). Melting points at or just below room temperature are observed for intermediate chain lengths ($m = 2$–6). The normal pattern of alternation is observed. An enantiotropic smectic A mesophase is observed below room temperature for the longest chain length prepared. The consequence of these patterns for the melting point (23°C, on average) and the clearing point (25°C, on average) is a narrow range, enantiotropic nematic mesophase (2°C, on average) for most of the homologues prepared. However, reasonably wide range nematic phases (8–14°C) are exhibited by several homologues ($m = 6$ and 7) with long terminal alkoxy chains. The enthalpies of fusion (ΔH) of the ethers **5** are of a normal magnitude (28·6 kJ mol^{-1}, on average) for nematic materials.

Collated in table 2 are the liquid crystal transition temperatures and some enthalpies of fusion for the 1-alkoxy-2,3-difluoro-4-(3-[*trans*-4-(*trans*-4-alkylcyclohexyl)cyclohexyl]propyloxy)benzenes **15** and 1-alkoxy-2,3-difluoro-4-([(*E*)-3-(*trans*-4-[*trans*-4-alkylcyclohexyl]cyclohexyl)allyl]oxy)benzenes **17**. The two series of ethers **15** and **17** differ only in the length of the alkoxy chain ($m = 2$ or 4), in the length of the alkyl chain or the nature of the central linkage, in both of which a *trans* carbon–carbon bond may be incorporated ($R = C_3H_7$, C_3H_5 and C_5H_{11}). The effect of introducing one *trans*-carbon–carbon double bond into the terminal alkyl chain and then a second one into the central linking unit of the ethers **15** ($R = C_3H_7$; $m = 2$) to produce the ethers **17** ($R = C_3H_7$ and C_3H_5; $m = 2$) on their liquid crystal temperatures is shown by the thermal data for the first three homologues in table 2. The influence of the first double bond ($Z = C_3H_4O$) is to increase the melting point (C–N) moderately (+6°C) and the clearing point (N–I) marginally (+1°C). The second double bond ($R = C_3H_5$) increases

Table 1. Liquid crystal transition temperatures and enthalpies of fusion for the 1-*n*-alkoxy-2,3-difluoro-4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]benzenes **5**.

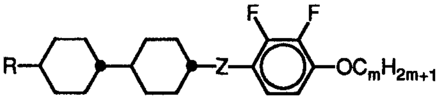


m	$T_{CS_AN/I}$/°C	T_{S_AN}/°C	T_{NI}/°C	ΔH/kJ mol^{-1}
1	44	—	(26)	30·2
2	25	—	26	25·4
3	21	—	(19)	30·1
4	20	—	22	34·6
5	20	—	22	20·3
6	20	—	28	30·9
7	8	14	28	

the melting point still further (+7°C) to a moderate degree and the clearing point substantially (+19°C). Thus the introduction of the two double bonds leads only to a small broadening (+7°C) of the nematic temperature range. An increase of two methylene units (CH_2) in the alkoxy chain of the first three compounds ($m=2$) produces the following three ethers ($m=4$) in table 2. Both the melting point (C–S_A and C–N) and clearing point (N–I) are decreased (−8°C and −10°C, on average) almost equally. An enantiotropic smectic A mesophase is observed for one ether **15** ($Z=C_3H_6O$), which results in a significant decrease (−19°C) in the nematic temperature range. A similar increase in the alkyl chain length to yield the remaining two ethers **15** and **17** ($R=C_5H_{11}$) in table 2 causes a decrease (−12°C, on average) in the melting point and an increase (+3·5°C, on average) in the clearing point. A smectic A mesophase is injected at an elevated temperature for the ether **15** ($Z=C_3H_6O$), while the other ether **17** ($Z=C_3H_4O$) exhibits the broadest nematic range (89°C) of all the compounds in table 2.

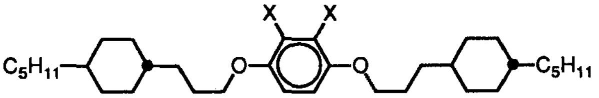
The liquid crystal transition temperatures and some enthalpies of three symmetrical diethers are recorded in table 3. The introduction of two fluorine atoms in a lateral position in the parent, non-substituted material **18** ($X=H$) to create the 2,3-difluorosubstituted substance **6** ($X=F$) induces a decrease in all the liquid crystal transition temperatures. However, the melting point (C–S_A) and the smectic–nematic transition temperature (S_A–N) are decreased more (−66°C and −34°C, respectively)

Table 2. Liquid crystal transition temperatures and some enthalpies of fusion for the diethers **15** and **17** of the structure:



R	*Z*	*m*	$T_{CS_A/N}$/°C	T_{S_AN}/°C	T_{NI}/°C	Δ*H*/kJ mol^{-1}
		2	59	—	135	30·2
		2	65	—	136	24·5
		2	72	—	155	28·3
		4	52	68	125	34·6
		4	54	—	127	24·0
		4	66	—	144	26·8
		2	49	102	138	33·0
		2	51	—	140	—

Table 3. Liquid crystal transition temperatures and some enthalpies of fusion for the symmetrical diethers of the structure:



X	$T_{CS_A/I}$/°C	T_{S_AN}/°C	T_{NI}/°C	Δ*H*/kJ mol^{-1}
H	108	112	115	
F	42	78	92	41·9
CN	204	—	—	

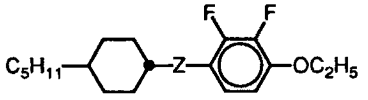
than the clearing point (N–I; −23°C). This leads to an increase (+14°C) in the temperature range of the nematic mesophase. The replacement of the two hydrogen atoms by two cyano-groups **19** (X = CN) leads to an exceptionally large rise (+98°C) in the melting point (C–I) and to the disappearance of all liquid-crystalline properties. The thermal data in table 3 demonstrate once again the advantage of 2,3-difluorosubstitution [32] with respect to 2,3-dicyano-substitution of which there are many examples in the literature [20–27].

4. Discussion

The liquid crystal transition temperature of three 1-ethoxy-2,3-difluoro-4-substituted-quinones differing only in the nature of the central linkage ($Z = CH_2O$, C_3H_6O and C_3H_4O) are listed in table 4. Both the 3-propyloxy and the (E)-3-allyloxy diethers exhibit lower melting points (−13°C and −15°C, respectively) and higher clearing points (+26°C and +5°C, respectively) than the corresponding methylenoxy-diether ($Z = CH_2O$). Thus, while both the (E)-3-allyloxy and the methylenoxy-diethers ($Z = C_3H_4O$ and CH_2O, respectively) possess a strongly monotropic nematic mesophase well below room temperature, the 3-propyloxy derivative exhibits an enantiotropic, very narrow range (1°C) nematic mesophase just above room temperature.

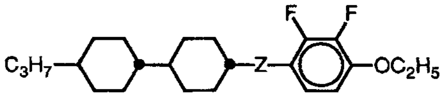
The liquid crystal transition temperatures and some dielectric anisotropies of six three-ring 1-ethoxy-2,3-difluoro-4-substituted-quinones each incorporating a different central linking unit (Z) are collated in table 5. The first four compounds in this table

Table 4. Liquid crystal transition temperatures of the diethers of the structure shown differing only in the nature of the central linkage Z.



Z	$T_{\mathrm{CN/I}}$/°C	T_{NI}/°C	Reference
	38	(0)	[41]
	25	26	
	23	(5)	

Table 5. Liquid crystal transition temperatures and some dielectric anisotropies for the diethers of the structure shown differing only in the nature of the central linkage Z.



Z	$T_{\mathrm{CS_B/S_A/N}}$/°C	$T_{\mathrm{S_BS_A/N}}$/°C	$T_{\mathrm{S_AN}}$/°C	T_{NI}/°C	$\Delta\varepsilon$	Reference
	68	109	—	160	−3·7	[32]
	62	—	—	154	−6·0	[32]
—	76	79	—	186	−4·4	[32]
	87	(81)	98	222	−4·1	[32]
	59	—	—	136	−5·1	[42]
	65	—	—	135		

($Z=C_2H_4$, CH_2O, —, COO) exhibit a clearing point (N–I) at considerably higher temperatures (180°C, on average) than the analogous 3-propyloxy and (*E*)-3-allyloxy compounds (135·5°C, on average), while the melting points (C–S_B, C–S_A and C–N) lie much closer to each other (73°C and 62°C, on average, respectively). Despite the presence of smectic mesophases (S_B and S_A) at elevated temperatures (90°C, on average) for three ($Z=C_2H_4$, —, and COO) of the first four compounds, they still exhibit a broader (+20°C) nematic mesophase range (94°C, on average) than that (74°C, on average) of the corresponding materials incorporating the four-unit-linking-groups ($Z=C_3H_6O$ and C_3H_4O). It is evident from the data in table 5 that two oxygen atoms ($Z=CH_2O$, C_3H_6O and C_3H_4O) are required to produce even a moderately strong negative dielectric anisotropy ($\Delta\varepsilon \leqslant -5$).

5. Conclusions

A homologous series of 1-*n*-alkoxy-2,3-difluoro-4-[3-(*trans*-4-pentylcyclohexyl)-propyloxy]benzenes **5** has been prepared. Several members of this series exhibit enantiotropic, narrow-range nematic mesophases of moderately strong negative dielectric anisotropy ($\Delta\varepsilon \approx -5$) at, just above or just below room temperature. This is significantly higher ($\approx +25$°C) than the clearing point of the corresponding methylenoxy material. Analogous three-ring diethers **15** possess enantiotropic nematic mesophases over a wide temperature range (*c.* 70°C) significantly above room temperature. The corresponding three-ring methylenoxy substance exhibits both a higher (+18°C) clearing point and a wider (+15°C) nematic mesophase temperature range. This may be due to a higher proportion of non-linear conformations in the four-unit-linking-group at elevated temperatures. These new materials **15** with the corresponding (*E*)-3-allyloxy compounds **17** are of commercial interest for certain electrooptic display device applications.

6. Experimental

The liquid crystal transition temperatures of the compounds prepared, recorded in tables 1–3, 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 of 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 (< −20°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 and enthalpies were also determined using a Mettler DTA TA 2000.

The purity of the compounds was determined by thin layer chromatography, gas chromatography and DTA analysis. A Perkin–Elmer 8310 gas chromatograph and GP-100 graphics printer were used. 4×8 cm precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0·25 mm (Macheray-Nagel, Düren, Germany) were utilized.

Column-chromatography was carried out using silica gel 60 (230–400 mesh ASTM). Reaction solvents and liquid reagents were purified by distillation or drying shortly before use. Reactions were carried out under N_2 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.

2,3-Difluoro-4[*3*-(trans-*4-pentylcyclohexyl)propyloxy*]*benzene* **3**. A mixture of 3-(*trans*-4-pentylcyclohexyl)-1-bromopropane **1** [34] (12·7 g, 0·0461 mol), 2,3-difluorophenol **2** (5·0 g, 0·0384 mol), potassium carbonate (21·2 g, 0·1536 mol) and butanone (500 ml) was heated under reflux overnight. The cooled reaction mixture was poured on water (500 ml) and extracted into ether (3 x 75 ml). The combined organic layers were washed with brine (2 x 100 ml), dried ($MgSO_4$), filtered and then evaporated down under slightly reduced pressure. The residue was purified by column chromatography on silica gel using hexane. The liquid residue was pure (99·8 per cent) enough to be used in the next reaction without further purification (yield 11 g, 88 per cent). IR (Film): 2929, 1620, 1513, 1288, 1221, 1085, 768. MS: 324 (M^+), 194.

The ethers

2,3-Difluoro-4-(*ethoxy*)*benzene* **7** ($m = 2$) (yield 82 per cent). IR (Film): 2985, 2903, 1701, 1618, 1515, 1479, 1259, 1075, 815, 766. MS: 158 (M^+).

2,3-Difluoro-4-(*butyloxy*)*benzene* **7** ($m = 4$) (yield 92 per cent). IR (Film): 2937, 2876, 1620, 1479, 1253, 1112, 1082, 766. MS: (M^+) 186 (M^+), 130.

were prepared using the same procedure.

2,3-Difluoro-4-[*3*-(trans-*4-pentylcyclohexyl*)*propyloxy*]*phenol* **4**. A 1·6 M solution of butyl lithium in hexane (17·4 ml, 0·0277 mol) was added dropwise to a solution of 2,3-difluoro-4-[3-*trans*-4-pentylcyclohexyl)propyloxy]benzene (9·0 g, 0·0277 mol) and tetrahydrofuran (100 ml) at −78°C. The reaction solution was stirred at this temperature for 5 hours. A solution of trimethyl borate (5·8 ml, 0·0416 mol) in tetrahydrofuran (20 ml) was added dropwise to the reaction mixture at −78°C and then allowed to reattain room temperature overnight. A 30 per cent hydrogen peroxide solution was added (20 ml) and the reaction mixture heated under gentle reflux for 30 min, allowed to cool and extracted with diethyl ether (4 x 50 ml). The combined organic layers were washed with saturated sodium metabisulphite solution (2 x 25 ml) and brine (2 x 50 ml), dried ($MgSO_4$), filtered and then evaporated down. The residue was purified by column chromatography on silica gel using a 9:1 hexane/ethyl acetate mixture as eluent, followed by recrystallization from hexane to give pure (99·9 per cent) phenol (yield 7·1 g, 76 per cent), m.p., 87–88°C. IR (KBr): 3376, 2917, 2850, 1612, 1527, 1499, 1262, 787. MS: 340 (M^+), 194, 150.

The phenols

2,3-Difluoro-4-(*ethoxy*)*phenol* **8** ($m = 2$) (yield 64 per cent), m.p., 76–77°C. IR (KBr): 3282, 1612, 1497, 1260, 1174, 1076, 795. MS: 174 (M^+), 146.

2,3-Difluoro-4-(*butyloxy*)*phenol* **8** ($m = 4$) (yield 68 per cent), m.p., 61–62°C. IR (KBr): 3376, 1615, 1527, 1503, 1285, 1266, 808. MS: 202 (M^+), 146.

were prepared using the same procedure.

1-Methoxy-2,3-difluoro-4-[*3*-(trans-*4-pentylcyclohexyl*)*propyloxy*]*benzene* **5** ($m = 1$). A mixture of 2,3-difluoro-4-[3-(*trans*-4-pentylcyclohexyl)propyloxy]phenol (0·3 g, 0·001 mol), methyl iodide (0·17 g, 0·0012 mol), potassium carbonate (0·6 g, 0·004 mol) and butanone (50 ml) was heated under reflux overnight. The cooled reaction mixture was poured on water (500 ml) and extracted into ether (3 x 50 ml). The combined organic layers were washed with water (2 x 500 ml) and then dried ($MgSO_4$). The drying agent was filtered off and the filtrate evaporated down under slightly reduced pressure. Purification of the crude product was achieved using column chromatography with toluene as eluent followed by recrystallization from alcohol. The liquid crystal transition temperatures and some enthalpies of fusion of this ether and other ethers prepared using this general method are collated in tables 1–3 IR (KBr): 2921, 1639, 1511, 1270, 704. MS: 354 (M^+), 160.

[trans-4-(trans-*4-Propylcyclohexyl*)*cyclohexane*]*carboxaldehyde* **10** ($R=C_3H_7$). A solution of diisobutyl aluminium hydride (20% v/v) in hexane (60 ml) was added dropwise to a solution of [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexane]carbonitrile **10** [35] (5 g) in toluene (100 ml) at −78°C (dry ice/acetone). After completion of the addition the reaction solution was allowed to regain room temperature slowly and was stirred at this temperature overnight. The reaction solution was cooled to 0°C and cold (10% v/v) sulphuric acid (100 ml) was added carefully. The organic phase was separated off and the aqueous phase extracted into toluene (2 × 100 ml). The combined organic phases were washed with water (500 ml), dilute potassium carbonate solution (2 × 100 ml) and again with water (500 ml), dried ($MgSO_4$), filtered and finally evaporated down under reduced pressure. The residue was purified by column chromatography on silica gel using toluene as eluent. This gave pure (99 per cent) aldehyde (4·5 g, 89 per cent). IR (Nujol): 2922, 2848, 1728, 1666, 1446. MS: 236 (M^+).

The aldehydes

[trans-4-(trans-*4-pentylcyclohexyl*)*cyclohexane*]*carboxaldehyde* **10** ($R=C_5H_{11}$ (yield 45 per cent). IR (Nujol): 1730, 1670, 1444. MS: 264 (M^+).

[trans-4-(trans-*4-*[(*E*)-*1-propenyl*]*cyclohexyl*)*cyclohexane*]*carboxaldehyde* **10** ($R=C_3H_5$) (yield 60 per cent).

were prepared using the same procedure.

Ethyl (*E*)-[trans-4-(trans-*4-propylcyclohexyl*)*cyclohexyl*]*acrylate* **11** ($R=C_3H_7$). A mixture of [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexane]carboxaldehyde (4·5 g, 0·017 mol), triethylphosphonoacetate (5·0 g, 0·020 mol), ground potassium hydroxide (1·9 g, 0·034 mol) and tetrahydrofuran was stirred for 90 min at room temperature. Water (500 ml) was added to the reaction mixture and then extracted into ether (4 × 100 ml). The combined organic layers were washed with brine (2 × 500 ml), dried ($MgSO_4$), filtered and finally evaporated down under slightly reduced pressure. This gave pure (95 per cent) ester (5·2 g, yield 100 per cent, $T_{CN}=32°C$; $T_{NI}=76°C$. IR (Film): 2920, 2847, 1729, 1652, 1270, 984. MS: 306 (M^+), 260.

The esters

Ethyl (*E*)-[trans-4-(trans-*4-pentylcyclohexyl*)*cyclohexyl*]*acrylate* **11** ($R=C_5H_{11}$) (yield 98 per cent), $T_{CN}=27°C$; $T_{S_BN}=49°C$; $T_{NI}=93°C$. IR (KBr): 2920, 2849, 1729, 1652, 1270, 1221, 989. MS: 334 (M^+), 288, 246.

Ethyl (*E*)-[trans-4-(trans-4-[(*E*)-*propenyl*]*cyclohexyl*)*cyclohexyl*]*acrylate* **11** ($R=C_3H_5$ (yield 92 per cent), $T_{CN}=40°C$; $T_{NI}=94°C$. IR (KBr): 2931, 2849, 1709, 1651, 1293, 1271, 965. MS: 304 (M^+), 258, 216.

were prepared using the same procedure.

Ethyl 3-[trans-4-(trans-*4-propylcyclohexyl*)*cyclohexyl*]*propionate* **12** ($R=C_3H_7$). A mixture of ethyl (*E*)-[*trans*-4-(*trans*-4-propylcyclohexyl)acrylate (5·6 g, ethyl acetate (50 ml) and 10 per cent palladium on 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 give pure (99·4 per cent) ester (5·5 g, 96 per cent). $T_{CS_B}=38°C$; $T_{S_BI}=$ 64°C. IR (KBr): 2923, 2847, 1724, 1188, 1139. MS: 308 (M^+), 290, 279, 263.

The ester

Ethyl 3-[trans-4-(trans-*4-pentylcyclohexyl)cyclohexyl]propionate* **12** ($R = C_5H_{11}$) (yield 95 per cent), $T_{CS_B} = 11°C$; $T_{S_BI} = 90°C$. IR (KBr): 2916, 2849, 1738, 1177, 895. MS: 336 (M^+), 307, 291, 273, 249.

was prepared using the same procedure.

3-[trans-4-(trans-*4-Propylcyclohexyl)cyclohexyl]propanol* **13** ($R = C_3H_7$). A solution of ethyl 3-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]propionate (5·0 g, 0·016 mol) and diethyl ether (50 ml) was added dropwise to a mixture of lithium aluminium hydride (1·1 g, 0·028 mol) and diethyl ether (20 ml) at room temperature. An exothermic reaction was observed. The reaction mixture was heated overnight under gentle reflux and then cooled to 0°C. Ethyl acetate (50 ml) and then 25 per cent hydrochloric acid (100 ml) were added carefully. The organic layer was separated off and the aqueous layer extracted with diethyl ether (2 x 50 ml). The combined organic layers were washed with water (50 ml), dilute potassium carbonate solution (2 x 50 ml) and then again with water (50 ml), dried ($MgSO_4$), filtered and evaporated down under slightly reduced pressure. The residue was purified by recrystallization from acetone at $-25°C$ to give pure (99·8 per cent) alcohol (yield 4·0 g, 93 per cent), $T_{CS_B} = 48°C$; $T_{S_BI} = 145°C$. IR (Nujol): 3316, 2923, 2848, 1444, 1056. MS: 266 (M^+), 248, 220, 205.

The alcohol

3-[trans-4-(trans-*4-Pentylcyclohexyl)cyclohexyl]propanol* **13** ($R = C_5H_{11}$) (yield 80 per cent), $T_{CS_B} = 51°C$; $T_{S_BI} = 153°C$. IR (Nujol): 3299, 2929, 2847, 1444, 1058. MS: 276 ($C_{20}H_{36}^+$), 248, 152.

was prepared using the same procedure.

3-[trans-4-(trans-*4-Propylcyclohexyl)cyclohexyl]-1-bromopropane* **14** ($R = C_3H_7$). A solution of tetrabromomethane (7·4 g, 0·0022 mol) in dichloromethane (50 ml) was added dropwise to a solution of 3-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]propanol (5·4 g, 0·002 mol), triphenylphosphine (5·9 g, 0·0022 mol) and dichloromethane (50 ml) at $-15°C$. The reaction mixture was stirred at room temperature overnight, evaporated down, taken up in warm hexane (50 ml), filtered to remove insoluble material (PPh_3O) and then evaporated down again. The residue was purified by column chromatography on silica gel using a 4:1 toluene/ethyl acetate mixture as eluent and recrystallization from acetone at $-25°C$ to give pure (99·8 per cent) bromide (yield 4·4 g, 66 per cent). IR (Film): 2914, 2847, 1742, 1446, 1240. MS: 328, 330 (M^+), 287, 285, 255, 253.

1-Butyloxy-2,3-difluoro-4-(3-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]propyloxy)benzene **15** ($R = C_3H_7$; $m = 4$). A mixture of 3-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]-1-bromopropane (0·5 g, 0·0015 mol), 2,3-difluoro-4-(butyloxy)phenol (0·25 g, 0·0012 mol), potassium carbonate (0·68 g, 0·0050 mol) and butanone was heated under gentle reflux overnight, filtered to remove inorganic material and the filtrate evaporated down. The residue was purified by column chromatography on silica gel using toluene as eluent and recrystallization from alcohol until the liquid crystal transition temperatures were constant. The thermal data for this ether and others prepared using this method are listed in tables 2 and 3. IR (KBr): 2954, 2909, 1640, 1520, 1275, 1078, 702. MS 450 (M^+), 202, 146.

(E)-4-[trans-4-(trans-*4-Propylcyclohexyl)cyclohexyl]allylalcohol* **16** ($R = C_3H_7$). A 20 per cent solution of diisopropyl aluminium hydride in hexane (20 ml) was added dropwise to a solution of ethyl (*E*)-[*trans*-4-(*trans*-4-

propylcyclohexyl)cyclohexyl]acrylate (2·2 g) in hexane (50 ml) at 0°C. After completion of the addition the ice bath was removed and the reaction was stirred at room temperature for a further 3 hours. The reaction mixture was cooled to 0°C and then ethanol (10 ml), 25 per cent hydrochloric acid (250 ml) and then water (250 ml) were added carefully, one after the other. The organic layer was separated off and the aqueous layer was extracted with ether (4 × 50 ml). The combined organic layers were washed with water (250 ml), concentrated potassium carbonate solution (100 ml) and then again with water (250 ml), 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 toluene/ethyl acetate mixture as eluent and recrystallization from acetone at −25°C (yield 1·6 g, 93 per cent), $T_{CS_B} = 63°C$; $T_{S_BI} = 118°C$. IR (KBr): 3314, 2918, 2849, 1664, 1093, 1058, 968. MS: 264 (M^+), 223, 205.

The alcohols

(*E*)-[trans-*4*-(trans-*4-Pentylcyclohexyl*)*cyclohexyl*]*allylalcohol* **16** ($R = C_5H_{11}$) (yield 82 per cent), $T_{CS_B} = 46°C$; $T_{S_BI} = 134°C$. IR (KBr): 3200, 2913, 2846, 1665, 1447, 1005, 968. MS: 292 (M^+), 274, 233.

(*E*)-[trans-*4*-(trans-*4*-[(*E*)-*propenyl*]*cyclohexyl*)*cyclohexyl*]*allylalcohol* **16** ($R = C_3H_5$) (yield 97 per cent), $T_{CS_B} = 56°C$; $T_{S_BN} = 95°C$; $T_{NI} = 113°C$. IR (KBr): 3310, 2913, 2846, 1665, 1450, 1094, 968. MS: 262 (M^+), 244, 203.

were prepared using the same procedure.

1-Ethoxy-2,3-difluoro-4-([(*E*)-*3*-(trans-*4*-[trans-*4-propylcyclohexyl*]*cyclohexyl*)*allyl*] *oxy*)*benzene* **17** ($R = C_3H_7$; $m = 2$). A solution of (*E*)-[*trans-4*-(*trans*-4-propylcyclohexyl)cyclohexyl]allylalcohol (0·26 g, 0·001 mol), 2,3-difluoro-4-(ethoxy)phenol (0·17 g, 0·001 mol), diethyl azodicarboxylate (0·17 g, 0·001 mol), triphenylphosphine (0·26 g, 0·001 mol) and tetrahydrofuran (25 ml) was stirred at room temperature overnight and then evaporated down. The solid residue was taken up in warm hexane (30 ml), filtered to remove precipitated matter (PPh_3O) and evaporated down again. Purification of the residue by column chromatography on silica gel using a 9 : 1 hexane/ethyl acetate mixture as eluent and then recrystallization from a 4 : 1 ethanol/ethyl acetate mixture gave the pure ether (yield 0·2 g, 49 per cent). The liquid crystal transition temperatures and some enthalpies of fusion of this ether and some other ethers **17** prepared using this general method are collated in table 2.

The author expresses his gratitude to Mr. B. Müller, Mr. S. Wehrli, Mr. P. Winiger and Mr. U. Wyss for sound technical assistance in the preparation of the compounds. Dr. W. Arnold (NMR), Mr. W. Meister (MS), Dr. M. Grosjean (IR), Mr. F. Wild and Mr. B. Halm (DTA) are thanked for the measurement and interpretation of the required spectra.

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