The synthesis and liquid crystal transition temperatures of some weakly polar nematic *trans*-4-substituted-cyclohexyl (*E*)-alk-2-enoates

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The effect on the liquid crystal transition temperatures of introducing various groups (for example incorporating C=C, O, CO_2 and CO) into the terminal alkyl chain of a weakly polar model compound 1-[*trans*-4-(*trans*-4-propylcyclo-hexyl)cyclohexyl]pentane has been investigated systematically. Only the compound containing both an ester function and a *trans*-carbon–carbon double bond exhibited a wide-range nematic mesophase at elevated temperatures. Therefore, a wide variety of *trans*-4-substituted-cyclohexyl (*E*)-alk-2-enoates incorporating a carbon double bond with a *trans*-configuration (*E*) in the terminal alkyl chain has been synthesized. Nearly all the two-ring esters prepared exhibit a nematic phase over a wide temperature range (≤ 100°C) at elevated temperatures (≤ 200°C). The tendency to form smectic mesophases is often low. Comparisons with the corresponding derivatives incorporating either just a carboxy group (COO) or just a carbon–carbon double bond (C=C) in the same positions indicate that synergetic effects lead to broader nematic phases than would otherwise have been expected. The new compounds are easily prepared from known starting materials.

1. Introduction

Nematic mixtures of positive dielectric anisotropy, which satisfy the twisted nematic and supertwisted nematic display device (TN-LCD) [1–10]) specifications (for example, low threshold voltage [11–13], short response times [11–14], etc.) for various applications are usually multicomponent mixtures of mesogens of both high positive and weakly positive or negative dielectric anisotropy. Liquid crystal materials of low dielectric anisotropy (weakly polar) usually exhibit low melting and clearing points, viscosity and birefringence. Such liquid crystal components usually contain at least one and often two *trans*-1,4-disubstituted cyclohexane rings with an unbranched alkyl group (often propyl or pentyl), as such mesogens have been shown to exhibit advantageous values for the above properties (see for example, table 1). The weakly polar liquid crystal materials are used to dilute liquid crystal materials of high positive dielectric anisotropy (polar) in order to lower the melting point and viscosity, to modify the elastic constant ratios and birefringence by dilution effects and by disrupting the degree of interdigitation [11, 14, 15]. However, due to the low clearing point (N–I) and the presence of ordered smectic phases (for example, S_B induced at low temperatures) of weakly polar mesogens [16–20], the upper temperature range of the nematic mixture and/or the amount of these components that can be used is limited.

Many attempts have been made to synthesize weakly polar nematic mesogens with an advantageous combination of properties for LCDs. This has been achieved, for example, by introducing either an oxygen atom [20–24] or a carbon–carbon double

Table 1.   Transition temperatures for the compounds:

R—⟨ ⟩—⟨ ⟩—

Compound	R	C–S_B/N/I /°C	S_B–N/I /°C	N–I /°C	ΔT_{N-I} /°C	Reference
1		23	96	—	—	
2		32	74	—	—	[24]
3		15	42	—	—	
4		25	85	—	—	[34, 35]
5		− 16	89	—	—	[32]
6		44	75	96	21	[32]
7		60	—	(47)†	—	[32]
8		30	70	73	3	[34, 35]
9		55	96	—	—	[37, 38]
10		56	92	—	—	
11		65	84	—	—	
12		41	69	73	4	[39]
13		77	—	172	95	

† ( ) Represents a monotropic transition temperature.

bond [25–33] or both [32, 34–36] in certain well-defined positions and configurations in the terminal aliphatic chain of various liquid crystal systems. Some typical examples of these attempts to synthesize weakly polar liquid crystal materials of low viscosity and birefringence and, at the same time, a high clearing point (i.e. with a wide nematic temperature range) are shown in table 1. Oxygen atoms (for example, compounds 2–4) [24, 32, 34, 35] and carbon–carbon double bonds (for example, compounds 5 and 6) [32] or both (for example, compounds 7 and 8) [32, 34, 35] have been incorporated in various positions into the non-polar 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]pentane (1) [37]. Oxygen atoms in the form of a ketone group have also been introduced (for example, compounds 9–11) [38]. As can be seen from the table most of the compounds exhibit a smectic B phase at elevated temperatures. Only the bicyclohexanes incorporating either an ester group (for example, compound 12) [39], a carbon–carbon double bond (for example, compound 6) [32], or an oxygen atom *and* a carbon–carbon

double bond (for example, compounds **7** and **8**) [32, 34, 35], possess a nematic phase (either monotropic or above a smectic B phase).

It has recently been shown that pyrimidinylphenyl esters of (*E*)-alk-2-enoic acids exhibit high nematic transition temperatures [40] for two-ring systems. This effect has already been observed for a limited number of other aromatic esters [41, 42] and has been explained in terms of a high degree of planarity and stiffness of the carboxy group and aliphatic chain due to conjugation of these groups with the benzene ring. Similar, although smaller, effects have recently been observed for a related range of aromatic phenylpyrimidine and phenylpyridine ethers [43–45]. Therefore, it seemed of interest to synthesize analogues containing both a carbon–carbon double bond and an ester group. Initial results with (*E*)-but-2-enoic (crotonic) acid were very promising (for example, compound **13**, see table 1).

2. Synthesis

The desired substituted cyclohexyl alkenoates could be synthesized via a normal esterification of mostly known *trans*-4-substituted cyclohexanols [24, 39, 46–48] prepared according to literature methods and (*E*)-alk-2-enoic acids (either commercially available or prepared according to literature methods [40]) and various octenoic acids [40] (with the double bond in defined positions and configurations) using DCC and DMAP [49]. The *trans*-4-substituted cyclohexanols include *trans*-4-(*trans*-4-*n*-alkylcyclohexyl)cyclohexanols [24], *trans*-4-[(*trans*-4-*n*-alkylcyclohexyl)ethyl]cyclohexanols [39], *trans*-4-propylcyclohexanol [46], *trans*, *trans*-[1,1′-bicyclohexyl]-4,4′-diol [47], *trans*-4-(*trans*-4-hydroxycyclohexyl)-phenol [47], and *trans*-4-(4-propylphenyl)cyclohexanol [48]. The *trans*-4-(4-*n*-alkoxyphenyl)cyclohexanols and *trans*-4-[*trans*-4-(4-ethoxyphenyl)-cyclohexyl]-cyclohexanol are described in detail in the Experimental section. The totally aliphatic reference compound 1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]pentane (**1**) was prepared by a Wolff–Kischner reduction of the ketone (**10**) formed by a Grignard reaction of commercially available propyl magnesium bromide and [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]acetonitrile [50]. The ether (**3**) was prepared by alkylation of [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]methanol [50] with propyl bromide and potassium *tert*-butoxide. The ketone (**11**) was synthesized in a Grignard reaction using commercially available ethyl magnesium bromide and [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]proprionitrile formed by hydrogenation of the corresponding [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]acrylonitrile, produced from [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]carboxaldehyde [51] and diethyl cyanomethylphosphonate (Fluka) in a Wittig–Horner reaction [52].

3. Results and discussion

3.1. *Alicyclic* (E)-*2-alkenoates*

The influence of chain length on the transition temperatures of a short homologous series (*n* = 3–5) of the (*trans*-4-*n*-alkylcyclohexyl)cyclohexyl (*E*)-but-2-enoates (**13–15**) is shown by reference to table 2. The difference between the clearing point of the propyl (*n* = 3) and that of the butyl and pentyl homologues (*n* = 4 and 5) is large (40–50°C). The melting points are similar. Consequently, large differences in the nematic range are observed. No smectic mesomorphism could be determined despite significant supercooling below the melting point ($\approx 25°$C).

Table 2.　Transition temperatures for the compounds:
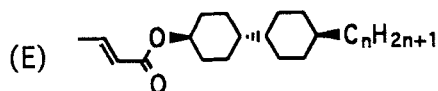
Ester	n	C–N /°C	N–I /°C	ΔT_{N-I} /°C	ΔH /kJ mol^{-1}
13	3	77	172	95	
14	4	67	122	45	26·7
15	5	74	131	57	29·4

Table 3.　Transition temperatures for the compounds:
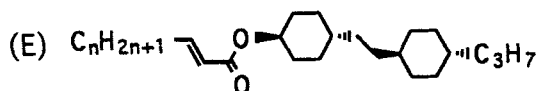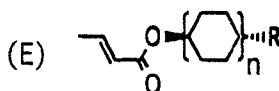

Ester	n	C–S$_B$/N /°C	S$_B$–N /°C	N–I /°C	ΔT_{N-I} /°C	ΔH /kJ mol^{-1}
16	1	44	——	109	65	26·3
17	2	46	62	86	24	17·3
18	3	43	69	89	20	17·6
19	4	25	71	78	7	15·7
20	5	39	72	83	11	10·7

Table 4.　Transition temperatures for the compounds:

Ester	R	n	C–N/I /°C	N–I /°C	ΔT_{N-I} /°C
21	C_3H_7	1	< 25	—	—
13	C_3H_7	2	77	172	95
22	$CH_3CH=CHCO_2$	1	93	—	—
23	$CH_3CH=CHCO_2$	2	168	202	34

　　　The effect of introducing the dimethylene linkage between the cyclohexyl rings of the ester (**13**) to produce the ester (**16**) is to reduce the melting point (-34°C), the clearing point (− 63°C) and the nematic range (− 30°C) significantly—see table 3. This may well be due to the added flexibility of the dimethylene linkage and the reduced length/breadth ratio due to the displacement of the two cyclohexane rings from a common collinear axis. Increasing the length of the carbon chain in the alkenoic acid part of the molecules results in the appearance of a smectic B phase at relatively elevated temperatures (68·5°C, on average) and a lower nematic–isotropic transition temperature (84°C, on average). As the melting point does not change greatly, this results in a substantial decrease (− 50°C, on average) in the nematic temperature range compared to that of the first member of the series.

　　　The data collated in table 4 reveal that despite the very high clearing point (172°C)
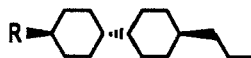
Table 5. Transition temperatures for the compounds:
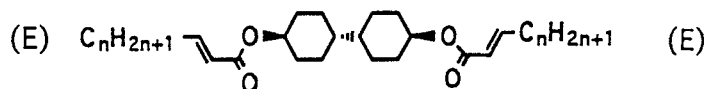
Ester	n	C–S_B/N /°C	S_B–I /°C	N–I /°C	ΔT_{N-I} /°C
23	1	168	—	202	34
24	2	146	—	153	7
25	3	122	—	153	31
26	4	87	—	129	42
27	5	100	—	126	26
28	6	78	100	—	—
29	7	100	113	—	—

of the two-ring ester (**13**) the one ring *trans*-4-propylcyclohexyl (*E*)-but-2-enoate (**21**) and *trans*-4-[(*E*)-but-2-enoyloxy]cyclohexyl (*E*)-but-2-enoate (**22**) do not exhibit mesomorphic behaviour. The replacement of the propyl chain in the two-ring mono ester (**13**) by an (*E*)-but-2-enoyloxy chain to yield the diester 4′-*trans*-[1,1′-bicyclo-hexyl]-4-*trans*- di-(*E*)-but-2-enoate (**23**) results in an increase (+ 30°C) in the already high clearing point. This would suggest that a central core of at least two rings is necessary for mesophase formation above room temperature. However, compounds with no ring at all or with only one ring have been found to exhibit mesomorphic behaviour. The nematic phases observed for simple unsaturated aliphatic acids (with two *trans*-double bonds and no rings [53]) and the smectic phases determined for one ring esters with polyfluorinated chains [54] can be rationalized by invoking stabilization effects due to increased rigidity of the terminal chain. Hydrogen bonding between the two hydroxy groups of two neighbouring acid molecules simulates one ring, while the *trans*-double bonds in a diene configuration impose a semi-rigid half-ring structure on the rest of the chains (thus, resulting in a very conformationally mobile, quasi three-ring structure. The same effect results from the perfluorinated chains, which are very rigid [54, 55], due to the large size of the fluorine atoms (thus, simulating a two-ring structure). However, on the basis of these explanations a mesophase could have been expected for at least one of the one-ring (*E*)-2-butenoates (**21** and **22**).

The data collated in table 5 for a homologous series of symmetrical 4′-*trans*-[1,1′-bicyclohexyl]-4-*trans*- di-(*E*)-alk-2-enoates (**23–29**) reveal that the very high values for the clearing point decrease with increasing chain length. This may be due to the higher number of non-linear conformations allowed as the chains become longer. These effects will be greater at high temperatures due to the large amount of kinetic energy available for conformation changes. The proportion of non-planar boat conformations of the cyclohexane rings should be the same for each diester. The esters (**13–15**) and the diesters (**23–29**) exhibit the highest clearing points and widest nematic ranges of any two-ring mesogens known to the author.

The diesters (**23–29**) are symmetrical and the dielectric anisotropy may be assumed to be close to zero. The resultant dipole of the carboxy group of the other aliphatic (mono) esters (**13–21**) is at an angle to the molecular axis [56, 57]. Therefore, the dielectric anisotropy will also be close to zero and may even be negative. Thus, the very high clearing points and wide nematic ranges of these esters are very difficult to explain using the Maier–Saupe theory of the nematic phase [58]. Hard rod theories [59] which

Table 6.   Transition temperatures for the compounds:

Ester	R	C–S_B/N/I /°C	S_B–N/I /°C	N–I /°C	ΔT_{N-I} /°C	Reference
1		23	96	—	—	
2		32	74	—	—	[24]
10		56	92	—	—	
6		44	75	96	21	[32]
13		77	—	172	95	

neglect all attractive forces would not explain the differences in clearing point for isomers incorporating oxygen atoms at different positions in the chain which are almost identical in shape (see table 1). Combined theories may be more appropriate [60–63]. This is illustrated by reference to table 6, where the effect of systematically introducing oxygen atoms (O) and double bonds (C=O and C=C) into the fully aliphatic 1-[trans-4-(trans-4-propylcyclohexyl)cyclohexyl]pentane (1) to yield the intermediate products (2, 6 and 10) and finally the trans-4-trans-4-propylcyclohexyl)cyclohexyl (E)-but-2-enoate (13). Increasing the polarity of the chain by introducing an oxygen atom or a ketone group (C=O) does not induce a nematic phase. The added stiffness (i.e. the reduced number of non-linear conformations) and increased dispersion forces due to the presence of the carbon–carbon double bond in the chain result in a nematic phase at elevated temperatures. However, a smectic B phase is still present, also at high temperatures. Only the combination of all these elements to produce the (E)-but-2-enoate (13) yields a very high clearing point and a wide nematic phase without smectogenic character. The effects of individual building blocks (for example, oxygen atoms, double bonds, etc.) on the liquid crystal temperatures are clearly not additive. Therefore, some cooperative effects due to the combination of exactly these groups in these positions and configurations must be responsible. No conjugation between the ester group and the cyclohexane ring is possible. Thus, the explanations given for the aromatic alkenoates [40–42] which invoke a high degree of conjugation between the double bond, the ester function and the adjacent benzene ring cannot be valid for alicyclic (for example, cyclohexyl) alkenoates.

3.2. *Alicyclic/aromatic* (E)-2-alkenoates

The effect of replacing one of the cyclohexane rings in the trans-4-(trans-4-propyl-cyclohexyl)cyclohexyl (E)-but-2-enoate (13) with a benzene ring to produce the trans-4-(4-propylphenyl)cyclohexyl (E)-but-2-enoate (30) is shown clearly in table 7. Although the melting points are similar, the clearing point of the phenyl substituted ester (30) is drastically lower (− 122°C) resulting in the formation of a monotropic nematic phase. Increasing the polarity by replacing one methylene unit in the propyl chain by an oxygen atom to yield the trans-4-(4-ethoxyphenyl)cyclohexyl (E)-but-2-enoate (31)
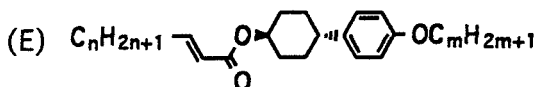
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trans-4-Substituted-cyclohexyl (E)-alk-2-enoates 217

Table 7. Transition temperatures for the compounds:
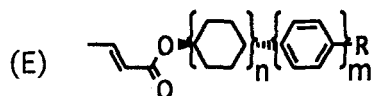
Ester	R	n	m	C–N/I /°C	N–I /°C	ΔT_{N-I} /°C	ΔH /kJ mol^{-1}
30	C_3H_7	1	1	71	(47)†	—	24·5
13	C_3H_7	2	0	77	172	95	
31	OC_2H_5	1	1	78	110	32	27·9
32	OC_2H_5	2	1	86	275	190	29·3

† ( ) Represents a monotropic transition temperature.

Table 8. Transition temperatures for the compounds:

Ester	n	m	C–N/I /°C	N–I /°C	ΔT_{N-I} /°C	ΔH /kJ mol^{-1}
33	1	1	74	89	15	23·7
31	1	2	78	110	32	27·9
34	1	3	65	87	22	18·2
35	1	4	71	92	21	23·0
36	1	5	75	79	4	26·7
37	1	6	67	80	13	30·6
38	1	7	61	74	13	36·6
39	2	2	84	(80)†	—	39·8
40	3	2	53	86	33	21·4
41	4	2	46	68	22	16·1
42	5	2	55	72	17	20·0

† ( ) Represents a monotropic transition temperature.

Table 9. Transition temperatures for the compounds:
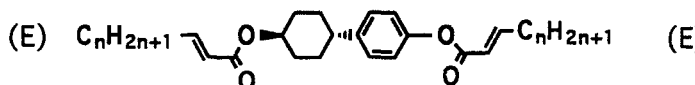
Ester	n	C–N/I /°C	N–I /°C	ΔT_{N-I} /°C	ΔH /kJ mol^{-1}
43	1	117	185	68	21·5
44	2	123	129	6	
45	3	136	(135)†	—	
46	4	96	105	9	
47	5	105	113	8	
48	6	80	90	10	
49	7	98	100	2	32·9

† ( ) Represents a monotropic transition temperature.

leaves the melting point almost unchanged, but increases the clearing point considerably (+ 63°C), resulting in an enantiotropic nematic phase. The effect is usual [16–20], but unusually large. Introduction of an additional cyclohexane ring into the two-ring *trans*-4-(4-ethoxyphenyl)cyclohexyl (*E*)-but-2-enoate (**31**) to yield the three-ring *trans*-4-[*trans*-4-(4-ethoxyphenyl)cyclohexyl]cyclohexyl (*E*)-but-2-enoate (**32**) increases the melting point slightly (+ 8°C), but increases the clearing point drastically (+ 165°C). No smectic mesomorphism could be observed. Thus, an unusually wide-range nematic phase is produced (190°C).

The data collected in table 8 for two homologous series of esters (**31, 33–38** and **31, 39–42**) where, for each series, one chain length is kept constant, while the other is varied, show that even increasing the chain length significantly ($n = 1$–7) does not produce smectic mesomorphism. The melting point, clearing point and nematic range generally tend to decrease gradually with increasing chain length for either series. This contrasts strongly with the large differences seen for the related *trans*-4-(*trans*-4-*n*-alkylcyclohexyl)cyclohexyl (*E*)-but-2-enoates (**13–15**), see table 2.

The data collated in table 9 for a homologous series of *trans*-4-(4-[(*E*)-alk-2-enoyl-oxy]phenyl)cyclohexyl (*E*)-but-2-enoates (**43–49**) show that the very high value for the clearing point and the width of the nematic phase observed for the (*E*)-but-2-enoate (**43**) decreases sharply for the homologues (**44–49**) with longer chains. The nematic ranges of the other diesters are remarkably narrow.

The liquid crystal transition temperatures of the *trans*-4-(4-[ethoxy]phenyl)-cyclohexyl octenoates (**42** and **51–55**) and those of the analogous *trans*-4-(4-[ethoxy]phenyl)cyclohexyl octanoate (**50**) are collated in table 10. The position of the carbon–carbon double bond is varied systematically from the beginning to the end of the terminal octenoyloxy chain. The configuration at the double bond is alternately *trans* and *cis* (*E* and *Z*). The 7-octenyloxy chain incorporating a double bond in a terminal position is neither *trans* nor *cis* due to the equivalence of the two hydrogen atoms on the end carbon atom.

The clearing point (N–I) of the (*E*)-oct-2-enoate (**42**) is much higher (+ 41°C) than that (31°C) of the corresponding octanoate (**50**) without a double bond in the octanoyloxy chain. The *trans*-double bond in one (6) of the other two possible positions in the chain (4 and 6) leads to transition temperatures of the octenoate (**54**) which do not differ significantly from those of the octanoate (**50**). A double bond in the remaining possible position (4) leads to the formation of a monotropic nematic phase for the octenoate (**52**). The introduction of a double bond with a *cis*-configuration into either the 3- or 5-position depresses the transition temperatures strongly. The octenoate (**51**) with a *cis*-double bond in the 3-position does not exhibit liquid crystal behaviour at all (at least above the recrystallization temperature). The octenoate (**52**) with a *cis*-double bond in the 5-position only exhibits a monotropic nematic phase at relatively low temperatures (− 20°C). The double bond in a terminal position also depresses the liquid crystal transition temperatures strongly. The ester (**55**) is not mesomorphic and is a liquid at room temperature. These results show the strong effect of the configuration and conformation of the terminal chain on the mesomorphic behaviour of very similar compounds (in this case isomers). They are consistent with those observed for pyrimidinylphenyl and pyridinylphenyl octenoates prepared for chiral smectic C applications [40].

The physical properties of representative *trans*-4-substituted (*E*)-alk-2-enoates will be reported elsewhere [64].

Table 10. Transition temperatures for the compounds:

Ester	R	C–N/I /°C	N–I /°C	ΔT_{N-I} /°C	ΔH /kJ mol^{-1}
50		46	(31)†	—	45·2
42		55	72	17	20·0
51		10	—	—	18·9
52		46	(19)	—	
53		24	(−20)	—	19·0
54		53	(30)	—	26·3
55		<25	—	—	—

† ( ) Represents a monotropic transition temperature.

4. Experimental

4.1. *Analysis*

The configuration of the carbon–carbon double bond in the alkenyl chain of the new esters (**13–49, 51–55**) was confirmed by ^{1}H NMR spectroscopy (the *trans*-olefinic coupling constants $\approx$ 12–18 Hz are larger than those of the corresponding *cis*-olefinic coupling constants $\approx$ 7–11 Hz) and by infrared spectroscopy (the *trans*-absorption bands are narrow and exact $\approx$ 970–960 cm^{-1}, while the *cis*-absorption bands are observed at distinctly different wavelengths $\approx$ 730–675 cm^{-1}). The structural and isometric purity was determined by differential thermal analysis and capillary gas chromatography as usual and, where necessary, on liquid crystal packed columns [65].

The liquid crystal transition temperatures of the esters prepared and recorded in tables 1–10 were determined by optical microscopy using a Leitz Otholux 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) has 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 capillary gas chromatograph and GP-100 graphics printer were used. 4 cm × 8 cm

precoated TLC plates, SiO_2 SIL G/UV_{254}, layer thickness 0·25 mm (Machery–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 a reagent or solvent. 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.

4.2. *1-[trans-4-(trans-4-Propylcyclohexyl)cyclohexyl]pentane* (1)

A mixture of 1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]pentan-2-one (10) (0·5 g, 19 mmol) and 98–100 per cent hydrazine hydrate (20 cm^3) was heated under gentle reflux for 5 h. Potassium hydroxide (3·4 g, 60 mmol) and ethylene glycol (50 cm^3) were added to the cooled reaction mixture and the temperature of the reaction solution raised to 210°C, in the process distilling off the excess of hydazine hydrate. The solution was heated at this temperature until the evolution of hydrogen had ceased. The cooled reaction mixture was added to water and the resultant mixture extracted using 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 20 : 1 hexane/ethyl acetate mixture as eluent and recrystallization from acetone at − 25°C to yield the pure (99·9 per cent) ether (1) (yield 0·17 g, 33 per cent); C–S_B, 23°C; S_B–I, 96°C; IR (KBr) νmax: 2918, 2848, 1447 cm^{-1}. MS m/z: 278 (M^+). NMR ($CDCl_3$): 0·83–1·28 (30 H, overlapping peaks), 1·66–1·80 (8 H, overlapping peaks).

4.3. *1-([trans-4-(trans-4-Propylcyclohexyl)cyclohexyl]-methoxy)propane* (3)

A mixture of [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]methanol (1·0 g, 4·2 mmol), toluene-4-sulphonic acid propyl ester (3·0 g, 13·8 mmol), potassium *tert*-butoxide (1·4 g, 12·6 mmol) and 1,2-dimethoxyethane (50 cm^3) was stirred overnight at room temperature. Water (100 cm^3) was added and the resultant mixture extracted using 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 20 : 1 hexane/ethyl acetate mixture as eluent and recrystallization from acetone at − 25°C to yield the pure (99·8 per cent) ether (yield 0·35 g, 30 per cent); C–S_B, 15°C; S_B–I, 42°C; IR (KBr) νmax: 2918, 2848, 1447, 1377, 1109 cm^{-1}. MS m/z: 220 ($C_{16}H_{28}O$), 191 ($C_{14}H_{23}O$). ^1H NMR ($CDCl_3$): 0·83–1·32 (20 H, overlapping peaks), 1·51–1·83 (12 H, overlapping peaks), 3·18–3·20 (2 H, d), 3·32–3·37 (2 H, t).12

4.4. *1-[trans-4-(trans-4-Propylcyclohexyl)cyclohexyl]-pentan-2-one* (10)

A solution of propyl magnesium iodide (produced as usual from 1-bromopropane (8·0 g, 65 mmol), magnesium turnings (1·6 g, 65 mmol) and diethyl ether (25 cm^{-3})) was added dropwise to a mixture of [*trans*-4-(*trans*-4-propylcyclohexyl)cyclo-hexyl]acetonitrile (4·0 g, 16 mmol) [50] in diethyl ether (30 cm^{-3} at 0°C and then heated overnight under gentle reflux. 1 M sulphuric acid (25 cm^3) was added dropwise to the cooled reaction mixture, which was stirred for 0·5 h and then extracted using 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. The residue

was purified by recrystallization from acetone to yield the pure (99·8 per cent) ketone (yield 63·5 g, 94 per cent); C–S_B, 56°C; S_B–I, 92°C; IR (KBr) νmax: 2952, 2908, 2848, 1700, 1446, 1408, 1376 cm^{-1}. MS m/z: 292 (M$^+$). ^{1}H NMR (CDCl$_3$): 0·83–1·70 (22 H, overlapping peaks), 2·23–2·26 (2 H, d), 2·32–3·38 (2 H, t).

4.5. *1-[trans-4-(trans-4-Propylcyclohexyl)cyclohexyl]-pentan-3-one* (11)

A solution of ethyl magnesium iodide (produced as usual from 1-iodoethane (45·6 g, 267 mmol), magnesium turnings (6·1 g, 249 mmol) and tetrahydrofuran (125 cm^3)) was added dropwise to a mixture of 1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]propionitrile (47·7 g, 200 mmol) in tetrahydrofuran (200 cm^3) at 0°C and then heated overnight under gentle reflux. The reaction mixture was worked up and purified as described above to yield the pure (99·8 per cent) ketone (yield 63·5 g, 94 per cent); C–S_B, 65°C; S_B–I, 84°C; IR (KBr) νmax: 2940, 2906, 2845, 1711, 1444, 1417, 1374, 1116 cm^{-1}. MS m/z: 292 (M$^+$). ^{1}H NMR (CDCl$_3$): 0·83–1·75 (22 H, overlapping peaks), 2·27–2·44 (4 H, q).

4.6. *1-[trans-4-(trans-4-Propylcyclohexyl)cyclohexyl]propionitrile*

A mixture of 1-[*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]acrylonitrile (8·4 g), toluene (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 down. The residue was purified by recrystallization from hexane at $-25°C$ to yield the pure (99·8 per cent) nitrile (yield 8·4 g, 98 per cent); C–S_B, 15°C; S_B–I, 97°C; IR (KBr) νmax: 2916, 2847, 2247, 1448 cm^{-1}. MS m/z: 261 (M$^+$), 232 (C$_{16}$H$_{26}$N) 218 (C$_{15}$H$_{24}$N). ^{1}H NMR (CDCl$_3$): 0·64–1·75 (28 H, overlapping peaks), 2·32–2·37 (2 H, t), 7·26 (1 H, s).

4.7. *1-[trans-4-(trans-4-Propylcyclohexyl)cyclohexyl]acrylonitrile*

Potassium hydroxide (4·8 g, 85 mmol) was added portion-wise to a mixture of [*trans*-4-(*trans*-4-propylcyclohexyl)cyclohexyl]carboxaldehyde [51] (10·0 g, 43 mmol), diethyl cyanomethylphosphonate (9·1 g, 51 mmol) and tetrahydrofuran (100 cm^3). After completion of the addition, the reaction mixture was stirred overnight at room temperature and then added to water (500 cm^3). The organic layer was separated off and the aqueous layer extracted using diethyl ether (3 × 100 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 toluene as eluent and recrystallization from hexane to yield the pure (98·6 per cent) acrylonitrile (yield 9·4 g, 86 per cent); m.p., 86°C; IR (KBr) νmax: 2918, 2849, 2220, 1625, 1507, 1444, 965, 897, 763 cm^{-1}. MS m/z: 259 (M$^+$), 231 (C$_{16}$H$_{25}$N) 214 (C$_{15}$H$_{20}$N). ^{1}H NMR (CDCl$_3$): 1·02 (10 H, overlapping peaks), 1·57–1·64 (3 H, overlapping peaks), 1·72–1·78 (14 H, overlapping peaks), 2·55 (1 H, s), 6·24–6·32 (1 H, t), 7·26 (1 H, s).

4.8. *trans-4-[trans-4-(4-Ethoxyphenyl)cyclohexyl]cyclohexyl (E)-but-2-enoate* (32)

A solution of N,N-dicyclohexylcarbodiimide (1·07 g, 5·2 mmol) in dichloromethane (50 cm^3) was added slowly to a solution of *trans*-4-[*trans*-4-(4-ethoxyphenyl)-cyclohexyl]cyclohexanol (1·05 g, 3·5 mmol), (E)-but-2-enoic acid (Fluka) (0·45 g, 5·2 mmol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (25 cm^3) cooled in an ice bath under an atmosphere of nitrogen. The reaction mixture was worked up and purified as described above to yield the pure ester (yield 0·85 g, 66 per cent). C–N,

86°C; N–I, 275°C. ^{1}H NMR (CDCl$_3$): 1·13–1·42 (13 H, overlapping peaks), 1·85–1·89 (12 H, overlapping peaks), 2·13 (1 H, overlapping peaks), 3·96–4·02 (2 H, q), 5·80 (1 H, d), 5·85 (1 H, d), 6·80–6·91 (2 H, d), 6·91 (1 H, overlapping peaks), 7·26 (1 H, s). νmax: 2913, 2852, 1710, 1654, 1511, 1245, 1020, 976, 830 cm^{-1}. m/z: 370 (M$^+$), 161 (C$_{11}$H$_{13}$O$^+$).

4.9. trans-4-[trans-4-(4-Ethoxyphenyl)cyclohexyl]cyclohexanone

A mixture of ethyl iodide (2·1 g, 13 mmol), *trans*-4-[*trans*-4-(4-hydroxyphenyl)-cyclohexyl]cyclohexanone [66] (3·0 g, 11 mmol), potassium carbonate (6·5 g, 44 mmol) and butan-2-one (50 cm^3) was heated under reflux overnight, then filtered to remove inorganic material. The reaction mixture was worked up and purified as described above to yield the pure ether (2·0 g, 60 per cent); m.p., 114–115°C; ^{1}H NMR (CDCl$_3$): 1·17–1·59 (14 H, overlapping peaks), 1·85–1·95 (4 H, overlapping peaks), 2·05 (2 H, overlapping peaks), 2·38 (1 H, overlapping peaks), 3·96–4·02 (2 H, q), 6·80–6·84 (2 H, d), 7·09–7·13 (2 H, d) 7·26 (1 H, s). IR (KBr) νmax: 3441, 2918, 2850, 1712, 1515, 1448, 1252, 1179, 1048, 841 cm^{-1}. MS m/z: 300 (M$^+$), 161 (C$_{11}$H$_{13}$O$^+$).

4.10. trans-4-[trans-4-(4-Ethoxyphenyl)cyclohexyl]cyclohexanol

A solution of *trans*-4-[*trans*-4-(4-ethoxyphenyl)cyclohexyl]cyclohexanone (1·5 g, 5 mmol) and a mixture of 9 : 1 methanol/ether (25 cm^3) was added dropwise to a freshly prepared mixture of sodium borohydride (1·4 g, 10 mmol) and a mixture of 9 : 1 methanol/ether (25 cm^3) at 0°C. After the addition was complete, the reaction mixture was stirred overnight at room temperature. A 25 per cent hydrochloric acid solution was added carefully to the reaction mixture, which was extracted using ethyl acetate (3 × 50 cm^3). The combined organic extracts were washed with water (2 × 500 ml) and dilute sodium carbonate solution (2 × 500 ml), dried (MgSO$_4$), filtered and then evaporated down. 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 alcohol (1·2 g, 77 per cent). ^{1}H NMR (CDCl$_3$): 1·03–1·75 (19 H, overlapping peaks), 2·3 (1 H, t), 2·49–2·50 (2 H, t), 3·33 (1 H, s), 3·92–4·00 (2 H, t), 4·44–4·45 (1 H, d), 6·78–6·81 (2 H, d), 7·07–7·10 (2 H, d). IR (KBr) νmax: 3420, 2920, 2852, 1612, 1513, 1452, 1248, 1178, 1051, 825 cm^{-1}. MS m/z: 302 (M$^+$), 161 (C$_{11}$H$_{13}$O$^+$).

4.11. trans-4-(4-Methoxyphenyl)cyclohexyl (E)-but-2-enoate (33)

A solution of *N,N*-dicyclohexylcarbodiimide (0·24 g, 0·12 mmol) in dichloro-methane (50 cm^3) was added slowly to a solution of *trans*-4-(4-methoxyphenyl)-cyclohexanol (0·20 g, 0·01 mmol), (*E*)-but-2-enoic acid (Fluka) (0·08 g, 0·01 mmol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (25 cm^3) cooled in an ice bath under an atmosphere of nitrogen. After filtration to remove precipitated material, the filtrate was 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 (yield 0·18 g, 68 per cent) of the pure ester. ^{1}H NMR (CDCl$_3$): 1·52–1·57 (4 H, overlapping peaks), 1·87–1·90 (5 H, overlapping peaks), 2·13 (2 H, overlapping peaks), 2·50 (1 H, overlapping peaks), 3·78 (3 H, s), 5·82–5·88 (2 H, d), 6·82–6·85 (2 H, d), 6·93–7·00 (1 H, overlapping peaks), 7·02–7·14 (2 H, d). νmax: 2946, 2860, 1707, 1651, 1512, 1245, 1032, 979, 830 cm^{-1}. m/z: 274 (M$^+$), 188 (C$_{13}$H$_{16}$O), 173 (C$_{12}$H$_{13}$O). The liquid crystal transition

temperatures of this ester (**33**) and similar esters (**31** and **34–42**) prepared using this general method are collated in tables 1–10.

4.12. trans-*4-(4-Methoxyphenyl)cyclohexanol*

A mixture of methyl iodide (0·44 g, 3·1 mmol), 4-(*trans*-4-hydroxycyclohexyl)phenol [47] (0·50 g, 3·1 mmol), potassium carbonate (1·40 g, 10·4 mmol) and butan-2-one (25 ml) was heated under reflux overnight, then filtered to remove inorganic material. The filtrate was diluted with water (500 ml) and then extracted using diethyl ether (3 × 100 ml). The combined organic extracts were washed with water (2 × 500 ml), dried (MgSO$_4$), filtered and then evaporated down. 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 ether (0·24 g, 45 per cent); m.p., 142–143°C; ^{1}H NMR (CDCl$_3$): 1·38–1·53 (5 H, overlapping peaks), 1·88 (2 H, overlapping peaks), 2·11 (2 H, overlapping peaks), 2·45 (1 H, overlapping peaks), 2·65 (1 H, overlapping peaks), 3·77–3·78 (3 H, s), 6·82–6·85 (2 H, d), 7·10–7·26 (2 H, d). IR (KBr) νmax: 3430, 2919, 2852, 1614, 1514, 1452, 1249, 1177, 1058, 823 cm^{-1}. MS *m/z*: 206 (M$^+$), 188 (C$_{13}$H$_{16}$O$^+$), 173 (C$_{12}$H$_{15}$O$^+$).

4.13. trans-*4-(4-[(E)-But-2-enoyloxy]phenyl)cyclohexyl* (E)-*but-2-enoate* (**43**)

A solution of *N,N*-dicyclohexylcarbodiimide (0·19 g, 0·9 mmol) in dichloromethane (10 cm^3) was added slowly to a solution of 4-(*trans*-4-hydroxycyclohexyl)phenol (0·25 g, 0·8 mmol), (*E*)-but-2-enoic acid (Fluka) (0·14 g, 0·8 mmol), 4-(dimethylamino)pyridine (0·04 g) and dichloromethane (25 cm^3) cooled in an ice bath under an atmosphere of nitrogen. The reaction mixture was worked up and purified as described above to yield *trans*-4-(4-[(*E*)-but-2-enoyloxy]phenyl)cyclohexyl (*E*)-2-butenoate (0·32 g, 84 per cent). ^{1}H NMR (CDCl$_3$): 0·89–0·90 (6 H, overlapping peaks), 1·28 (28 H, overlapping peaks), 1·77 (2 H, q), 1·91 (4 H, t), 2·60–2·66 (3 H, t), 7·26–7·34 (2 H, t), 8·29–8·32 (2 H, d), 8·61 (2 H, s). νmax: 2920, 2850, 1768, 1546, 1429, 1232, 1133, 857 cm^{-1}. MS m/z: 328 (M$^+$).

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