152. The Synthesis and Liquid-Crystal Transition Temperatures of Some Fluoro-Substituted Benzonitriles

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Various laterally fluoro-substituted benzonitriles have been prepared containing a *trans*-4-(*n*-alkyl)cyclohexane ring linked to the 4-position of the benzonitriles either through a methyleneoxy (–CH_2O–) or an ethylene (–CH_2CH_2–) bridge. The bridging group links the benzonitrile and cyclohexane rings either directly or through an additional 1,4-bonded cyclohexane or benzene ring. The synthesis and liquid-crystal transition temperatures of these new compounds are described. In several cases the nematic-isotropic transition temperatures of F-substituted benzonitriles are found to be *higher* than those of the non-laterally substituted analogues.

Introduction. – The synthesis, liquid-crystal transition temperatures [1–3], and some other physical properties [4] [5] of a wide variety of substituted phenyl esters bearing a terminal CN function *and* a lateral substituent on the phenyl ring have recently been reported. The esters were constituted from 1,4-disubstituted rings, *i.e.*, benzene [2], *trans*-cyclohexane and bicyclo[2.2.2]octane [3]. Some of the esters are useful as components of nematic mixtures for electrooptic display devices [4] [5]. Many of the esters with a lateral F-atom exhibit higher, sometimes substantially higher, nematic-isotropic transition temperatures (N–I) than the corresponding unsubstituted esters (with an H- instead of the F-atom).

To investigate the effect of different central linking units on the physical properties of such laterally substituted benzonitriles, we have synthesised similar materials incorporating a methyleneoxy group (–CH_2O–) or an ethylene group (–CH_2CH_2–) in place of the ester linkage (–CO.O–) of some of the compounds above [3]. All of the compounds synthesised incorporate the *trans*-1,4-disubstituted cyclohexane ring. This is because several classes of cyclohexyl benzonitriles possess advantagous combinations of physical properties for electrooptical display devices (such as low viscosity, high nematic-isotropic transition temperatures, low melting point) [6–9]. It was hoped, therefore, that the cyclohexyl-2-F-substituted-benzonitriles synthesised would also be of commercial interest, especially for twisted nematic devices with multiplexed addressing [5]. Only benzonitriles containing a lateral F-atom were prepared, because compounds containing larger lateral substituents (such as Cl, CN, Br) exhibit much lower nematic-isotropic transition temperatures [2] [3] [10–14].

Results and Discussion. – The ethers **5** were synthesised *via* alkylation of 2-fluoro- or 3-fluoro-4-hydroxybenzonitrile **4** [2] with the appropriate substituted bromides **3** (see *Scheme 1*), which were prepared by bromination of the alcohols **2** produced by reduction of the readily available acids **1** [3] (see *Exper. Part*).

Scheme 1

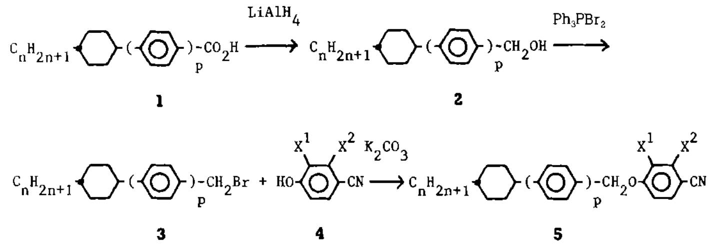
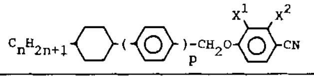


Table 1. *Transition Temperatures (°C) for* **5**


5

C_nH_{2n+1}	p	X^1	X^2	C–S_A/N/I	S_A–N/I	N–I[a])	ΔT_{N-I} (H→F)
C_3H_7	0	F	H	55.5	–	[15]	–21
C_5H_{11}	0	F	H	57.5	–	(45.5)	–3
C_7H_{15}	0	F	H	69.5	–	(51)	–2.5
C_3H_7	0	H	F	66.5	–	[–10]	–46
C_5H_{11}	0	H	F	80	–	[8]	–40.5
C_7H_{15}	0	H	F	37.5	–	(24.5)	–29
C_3H_7	1	F	H	111.5	–	(95.5)	
C_5H_{11}	1	F	H	102	–	103	
C_7H_{15}	1	F	H	98	108	–	
C_3H_7	1	H	F	104	–	(74.5)	
C_5H_{11}	1	H	F	105	–	(82)	
C_7H_{15}	1	H	F	72.5	73.5	85	

[a]) ( ) Indicates a monotropic transition temp.; [ ] indicates a 'virtual' transition temp.

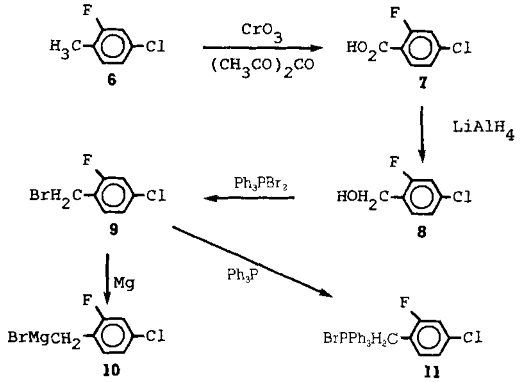
The liquid-crystal transition temperatures of the compounds **5** are recorded in *Table 1*. Additionally the differences between the clearing points (N–I) of the F-substituted compounds **5** (p = 0) and those of the analogous homologues of the corresponding non-F-substituted compounds (with an H- instead of the F-atom) are listed in the eighth column.

The clearing points of the two-ring nitriles **5** (p = 0) are all monotropic or 'virtual' transition temperatures (see *Exper. Part*), and increase (from very low values for the Pr homologues) with increasing C-chain length as usual for cyclohexane derivatives [3]. The clearing points of the 3-F-substituted ethers **5** (p = 0, X^1 = F, X^2 = H) are higher than those of the 2-F-substituted ethers **5** (p = 0, X^1 = H, X^2 = F). The clearing points of the F-substituted nitriles are lower than those of the corresponding unsubstituted nitriles with an H- in place of the F-atom [8], see the eight column of *Table 1*. No smectic phases were observed at or above r.t.

The melting points (C–S_A/N/I) and clearing points of the analogous three-ring nitriles **5** (p = 1) are significantly higher than those of the two-ring nitriles **5** (p = 0). Two homologues possess enantiotropic nematic phases. Smectic phases (S_A) are observed for the longest C-chains prepared (n = 7), one of which is purely smectic (X^1 = F, X^2 = H).

The preparation of the reaction-intermediates **10** and **11** required to synthesise the 1,2-disubstituted *ethane* analogues **15** *(cf. Scheme 3)* and/or **20** *(cf. Scheme 4)* of the 3-F-substituted methoxy compounds **5** (p = 0 or 1) is shown in *Scheme 2*. 4-Chloro-2-

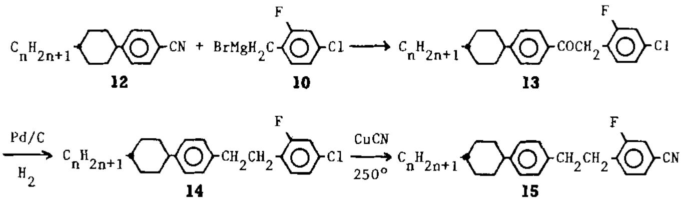
Scheme 2



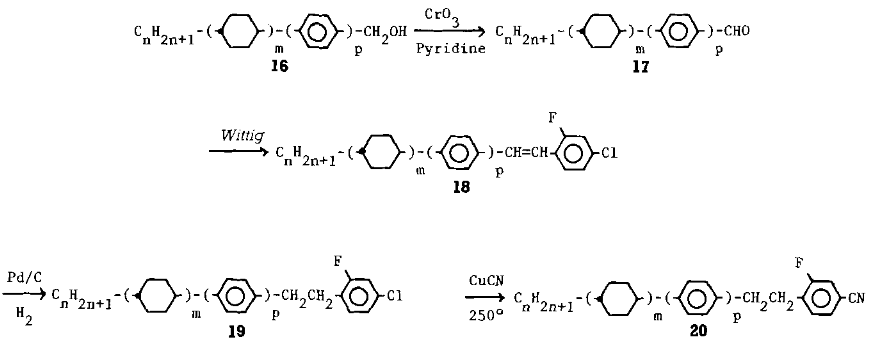
fluorobenzyl bromide (**9**) was prepared from the commercially available 4-chloro-2-fluorotoluene (**6**) using two different procedures. The first involved bromination of **6** with Br_2 without a solvent to yield the bromide **9**. In the second, **6** was oxidised to 4-chloro-2-fluorobenzoic acid (**7**); reduction yielded the benzyl alcohol **8**, which was brominated to yield **9**. The raw product was pure enough (98%) to be used in the next reaction without further purification. The benzyl bromide **9** was either converted to the *Grignard* reagent **10** and used as shown in *Scheme 3* or converted to the phosphonium salt **11** and used as depicted in *Scheme 4*.

The 1,2-disubstituted ethane analogues **15** of the 3-F-substituted methoxy compounds **5** ($p = 1$, $X^1 = F$, $X^2 = H$) were synthesised according to *Scheme 3*. The reaction

Scheme 3



Scheme 4

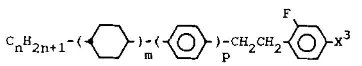


of **10** with the commercially available benzonitriles **12** yielded the ketones **13**. Catalytic hydrogenation yielded the 1,2-disubstituted ethanes **14**. Cyanation of **14** to yield the nitriles **15** required higher temperatures (250°) than usual, due to the low reactivity of chlorobenzenes. The latter reactions were carried out in sealed glass ampoules in an autoclave (see *Exper. Part*).

The pentyl homologue of **15** was prepared a second time according to *Scheme 4*. The product obtained (**20**; n = 5, m = p = 1) was identical with **15** (n = 5). The liquid-crystal transition temperatures of this homologue and the other homologues of **14** and **15** are recorded in *Table 2*.

The nitriles **20** (m = 1 or 2, p = 0) containing one or two cyclohexane rings were prepared as shown in *Scheme 4*. The known *trans*-4-substituted-cyclohexane-1-carboxylic acids [3] [6] [8] were reduced to the alcohols **16**. Oxidation yielded the aldehydes **17**, which were used in *Wittig* reactions to yield the ethenes **18**. The raw product **18** consisting of *cis*- and *trans*-isomers, was catalytically hydrogenated to yield the 1,2-substituted ethanes **19**. Cyanation, as described above, yielded the nitriles **20**.

Table 2. *Transition Temperatures* (°C) *for* **19** *and* **20**



14, 15, 19 and 20

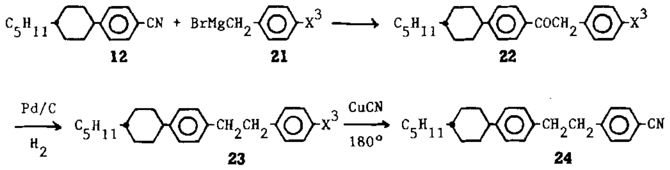
C_nH_{2n+1}	m	p	X^3	C–N	S_A–N[a])	N–I
C_5H_{11}	1	0	CN	45	–	54
C_7H_{15}	1	0	CN	43.5	–	56
C_3H_7	1	1	Cl	64	–	69
C_5H_{11}	1	1	Cl	57.5	–	85
C_7H_{15}	1	1	Cl	58.5	–	83
C_3H_7	1	1	CN	90	–	115.5
C_5H_{11}	1	1	CN	77.5	–	119.5
C_7H_{15}	1	1	CN	75	(74)	115
C_5H_{11}	2	0	Cl	69	–	149
C_5H_{11}	2	0	CN	115	–	187

[a]) ( ) Indicates a monotropic transition temperature.

The liquid-crystal transition temperatures of **14**, **15**, **19**, and **20** are collected in *Table 2*. In contrast to the analogous methoxy compounds **5**, all of the ethanes **14**, **15**, **19**, and **20** exhibit enantiotropic nematic phases. The two-ring ethanes **20** (m = 1, p = 0) exhibit the lowest melting points (C–N) and lowest clearing points (N–I) of the ethanes listed. Narrow-range enantiotropic nematic phases are observed. The corresponding ethanes **15** containing an additional benzene ring (m = p = 1) possess higher melting and clearing points and also wider-range nematic phases (*ca.* 25–45°) as is usually observed [1] [10]. The highest clearing points are exhibited by the **19** and **20** (m = 2, p = 0) with the nitrile exhibiting the highest. This is consistent with the observation that liquid crystals containing the *trans*-1,4-disubstituted-cyclohexane ring generally exhibit higher nematic-isotropic transition temperatures than the analogous 1,4-disubstituted-benzene derivatives [6–9] [15].

The 1,2-disubstituted ethanes **23** (X^3 = F, Cl, Br) and **24** (X^3 = CN) were synthesised as shown in *Scheme 5*. The reduction of the ketone **22** (X^3 = Br) was carried out *via* the

Scheme 5

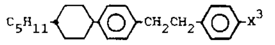


Huang-Minlon modification of the *Wolff-Kishner* reaction to avoid hydrogenolysis of the C–Br bond. The bromobenzene **23** (X^3 = Br) could be cyanated as usual [2] to yield **24**.

The effect of the terminal substituents on the clearing points of **23** (X^3 = F, Cl, Br) and **24** (X^3 = CN) is demonstrated in *Table 3*. The liquid-crystal transition temperatures increase with increasing magnitude of the terminal dipole as is usually the case [10] [16] [17]. The clearing point (131°) of **24** is higher than that of the corresponding laterally F-substituted nitrile **15** (n = 5) as expected on the basis of previous results [2] [3].

The compounds reported in *Tables 1* and *2*, along with other F-substituted benzonitriles reported in [3] [14] allow comparisons with a number of analogous non-laterally-substituted benzonitriles [6–9]. The liquid-crystal transition temperatures of eight different *trans*-4-heptyl-substituted benzonitriles, some with a lateral F-atom, incorporating the linking unit Z, are listed in *Table 4*. The differences in the nematic-isotropic transition temperatures of the F-substituted compounds (X^1 = F) and those of the corresponding non-F-substituted materials (X^1 = H) are recorded in the fifth column. The molecular structures of the compounds in *Table 4* differ only in the type of central linkage Z or in the presence or absence of a lateral F-atom (X^1 = H or F).

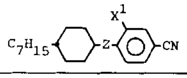
Table 3. *Transition Temperatures* (°C) *for* **23** *and* **24**



23 and 24

X^3	C–N	N–I
F	57	79
Cl	76.5	110
Br	88.5	112
CN	96	131

Table 4. *Transition Temperatures* (°C) *for Compounds of Structure*



Z	X^1	C–N	N–I[a])	ΔT_{N-I} (H→F)	Ref.
–	H	30	59	–	[7]
CH_2O	H	48	53.5	–	[8]
CH_2CH_2	H	45	54.5	–	[9]
CO.O	H	54.5	80.5	–	[6]
–	F	40	59	0	[14]
CH_2O	F	57.5	(45.5)	–8	–
CH_2CH_2	F	43.5	56	+1.5	–
CO.O	F	75.5	93.5	+13.5	[3]

[a]) ( ) Indicates a monotropic transition temperature.

Considering the non F-substituted compounds first (X^1 = H), the materials with a non-rigid central linkage ($-CH_2O-$ and $-CH_2CH_2-$) possess higher melting points and marginally lower clearing points than those of the corresponding material with a direct linkage (Z = –). The effect of the greater length/breadth ratio due to the central linkage of the first two compounds (which would be expected to give rise to substantially higher clearing points [5] [10]) may be cancelled out by the higher degree of flexibility introduced by the linking unit and/or by a lower degree of association of dimer pairs [5] [18]. The liquid crystal transition temperatures of the ester (Z = CO.O) are the highest of the series. The high clearing point is probably due to a combination of the greater degree of polarisability and conjugation as well as to the greater rigidity of the ester [6] [10]. The degree of association in dimer pairs of the benzonitriles with or without an ester linkage (Z = CO.O or) is approximately equal [18].

Considering now the laterally F-substituted materials in *Table 4*, it is observed that the melting points of these compounds (X^1 = F) are substantially higher in three cases and almost the same in one (Z = CH_2CH_2) compared with the corresponding non-F-substituted materials. This contrasts with the (often substantially) lower melting points observed for a wide variety of laterally F-substituted compounds with an alkyl- or alkoxy-C-chain instead of the CN group [10–13] [15] [16].

With few exceptions [11], the large majority of alkyl/alkoxy laterally F-substituted liquid crystals reported in [10–13] [15–17] possess lower nematic-isotropic transition temperatures than those of the corresponding non-laterally substituted analogues. This has been attributed principally to intermolecular steric interactions [10–12]. The laterally F-substituted benzonitriles in *Table 4* exhibit either lower, equal, or *higher* clearing points, *i.e.* no uniform trend can be observed. For substituted benzonitriles molecular association contributes to the nematic-isotropic transition temperature [5] [18], which is not the case for alkyl/alkoxy-substituted liquid crystals. Determinations of the degree and kind of association of these benzonitriles are required before satisfactory explanations could be proposed for the observed differences between the nematic-isotropic transition temperatures [5].

In conclusion, with respect to the two linking units under study, the methyleneoxy linkage appears to give rise to a combination of higher melting points and lower clearing points, compared with those of the corresponding benzonitriles with no linkage, whereas the ethylene linkage seems to cause the smallest changes in the liquid-crystal transition temperatures. This appears to be valid for non-laterally substituted and F-substituted benzonitriles.

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Experimental Part

General. The purity, structure, and liquid-crystal transition temp. of the compounds **1**–**24** were determined using the instruments and methods described in [2]. The 'virtual' nematic-isotropic transition temp. given in *Table 1* were determined in the usual manner [2] [3]. The methods used to synthesise **5**, **15**, **20**, and **24** are illustrated below for one homologue (n = 5). Similar reactions were used to yield the other homologues recorded in *Tables 1* and *2*.

*4-(*trans*-4-Pentylcyclohexyl)benzyl Alcohol* (**2**; *n = 5, p = 1*). A soln. of 10.0 g (0.037 mol) of *4-(*trans*-4-pentylcyclohexyl)benzoic acid* (**1**; n = 5, p = 1) and anh. THF (150 ml) was added dropwise to a mixture of $LiAlH_4$ (2.4 g, 0.064 mol) and anh. THF (50 ml) under anh. conditions. The resultant mixture was heated under reflux overnight. After decomposition of the complex and excess of hydride in the normal way, the org. layer was separated off and the aq. layer was shaken with Et_2O (2 × 50 ml). The combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under vacuum to yield pure (98%) product: 9.5 g (99%), m.p. 49–50°. MS: 260 (M^+). Anal. calc. for $C_{18}H_{28}O$ (260.40): C 83.02, H 10.84; found: C 83.07, H 10.87.

*4-(*trans*-4-Pentylcyclohexyl)benzyl Bromide (***3***; $n = 5, p = 1$).* Br_2 (3.2 g, 0.020 mol) was added dropwise to a soln. of Ph_3P (5.3 g, 0.020 mol) and MeCN (50 ml) maintained between 0 and 10° throughout the addition under anh. conditions. A white emulsion was formed which was stirred at r.t. for a further 1 h. A soln. of 5.0 g (0.019 mol) of **2** (n = 5, p = 1) and MeCN (50 ml) was added. The white precipitate disappeared almost immediately and the resultant soln. was stirred for a further 30 min at r.t. The MeCN was then distilled off and a temp. of 120° maintained for 15 min. H_2O (100 ml) was added to the cooled reaction soln. and the resultant mixture shaken with CH_2Cl_2 (3 × 200 ml). The combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under slightly reduced pressure to yield an org. phase and a solid residue (Ph_3PO). Hexane was added and the mixture filtered to remove more inorg. material. The solvent was removed under slightly reduced pressure to yield raw product which was taken up in a minimum of solvent and eluted from a silica-gel column with toluene to yield pure (95%) bromide: 4.0 g (64%), m.p. 28–29°. MS: 322, 324 (M^+). Anal. calc. for $C_{18}H_{27}Br$ (323.32): C 66.86, H 8.42, Br 24.72; found: C 66.69, H 8.64, Br 24.68.

*3-Fluoro-4-[4-(*trans*-4-pentylcyclohexyl)benzyloxy]benzonitrile (***5***; $n = 5, p = 1, X^1 = F, X^2 = H$).* A mixture of 0.2 g (0.0015 mol) of *3-fluoro-4-hydroxybenzonitrile* (**4**; $X^1 = F$, $X^2 = H$), 0.5 g (0.0016 mol) of **3** (n = 5, p = 1), anh. K_2CO_3 (0.8 g, 0.0058 mol), and dry $CH_3COC_2H_5$ (20 ml) was heated under reflux overnight under anh. conditions. The cooled mixture was added to H_2O (100 ml) and shaken with $CHCl_3$ (3 × 50 ml). The combined org. layers were washed with H_2O (2 × 250 ml) and dried ($MgSO_4$). After removal of the solvent under reduced pressure, the crude product was eluted down a silica-gel column using toluene as eluent. Single-spot fractions containing the ether were combined and evaporated together to yield required product, which was crystallised from AcOEt until constant transition temp. were obtained (see *Table 1* for the liquid-crystal transition temp. of this and other nitriles **5** prepared by this method). IR (KBr): 2215 (CN), 1300 (C–O), 1120, 815 (phenyl). MS: 379 (M^+). Anal. calc. for $C_{25}H_{30}FNO$ (379.50): C 79.12, H 7.79, F 5.01, N 3.69; found: C 79.29, H 7.79, F 5.24, N 3.75.

4-Chloro-2-fluorobenzoic Acid (**7**). CrO_3 (28 g, 0.277 mol) was added portionwise to a stirred soln. of 4-chloro-2-fluorotoluene (10 g, 0.069 mol), glacial AcOH (250 ml), Ac_2O (170 ml) and conc. H_2SO_4 (30 ml) cooled *via* an ice-bath. The addition was so made that the internal temp. did not excede 10°. The soln. was left stirring overnight and allowed to attain r.t., poured into ice (1000 g) and stirred for a further 30 min. The precipitate was filtered off, washed with a little H_2O and pressed dry. Crystallisation from EtOH yielded pure acid: 5.0 g (41%), m.p. 206–207°. MS: 174, 176 (M^+).

4-Chloro-2-fluorobenzyl Alcohol (**8**). A soln. of 5 g (0.029 mol) of *4-chloro-2-fluorobenzoic acid* (**7**) and dry Et_2O (25 ml) was added dropwise to a mixture of $LiAlH_4$ (1.9 g, 0.050 mol) and dry Et_2O (25 ml) under anh. conditions. The resultant mixture was heated under reflux for 2 h and worked up as described in the preparation of **2** (n = 5, p = 1) to yield 3.2 g (71%) of pure alcohol **8**. MS: 160, 162 (M^+).

4-Chloro-2-fluorobenzyl Bromide (**9**). Br_2 (3.4 g, 0.019 mol) was added dropwise to a soln. of Ph_3P (4.9 g, 0.019 mol) and MeCN (40 ml) maintained between 0 and 10° during the addition under a dry atmosphere. The resultant white emulsion was stirred at r.t. for a further 1 h. A soln. of 3 g (0.019 mol) of **8** and MeCN (40 ml) was then added. The resultant soln. was stirred for a further 30 min at r.t. and then the MeCN was distilled off and a final temp. of 120° maintained for 15 min. The mixture was worked up and purified in the same way as **3** to yield pure (98%) bromide (2.5 g, 60%) which was used in the next reaction without further purification.

(4-Chloro-2-fluorobenzyl)triphenylphosphonium Bromide **11**. A soln. of 4.3 g (0.019 mol) of *4-chloro-2-fluorobenzyl bromide* (**9**), Ph_3P (5.0 g, 0.019 mol) and anh. xylene (50 ml) was heated under gentle reflux for 2 h. A precipitate was observed on cooling. Hexane (100 ml) was added to the cooled mixture and the precipitate filtered off, washed with hexane and dried under vacuum. The phosphonium salt (9.0 g, 97%) thus obtained was used in the next reaction without further purification.

*α-(4-Chloro-2-fluorophenyl)-4-(*trans*-4-pentylcyclohexyl)acetophenone (***13***; $n = 5$).* A soln. of 2.5 g (0.010 mol) of **12** (n = 5) and dry Et_2O (20 ml) was added to 0.016 mol of the *Grignard* reagent **10** ($X^1 = F$, $X^2 = Cl$; prepared in the usual way) and dry Et_2O (20 ml) under N_2. The resultant soln. was heated overnight under gentle reflux. A precipitate was formed. The cooled mixture was decomposed with ice and conc. H_2SO_4 and the Et_2O distilled off. After heating for a further 6 h to ensure hydrolysis of the ketimine, **13** was extracted into Et_2O (4 × 100 ml). The combined org. layers were washed with brine (2 × 1000 ml) and dried ($MgSO_4$). The crude product, obtained after filtration and removal of the solvent under slightly reduced pressure, was taken up in a minimum of solvent and eluted down a silica-gel column using toluene as eluent. Crystallisation from EtOH yielded pure (97%) ketone: 2.4 g (58%), m.p. 147–148°. IR (KBr): 1685 (C=O), 1605, 1495, 1450, 850 (phenyl). MS: 400, 402 (M^+). Anal. calc. for $C_{25}H_{30}ClFO$ (400.95): C 74.89, H 7.54, Cl 8.84, F 4.74; found: C 75.00, H 7.67, Cl 8.85, F 4.82.

*1-(4-Chloro-2-fluorophenyl)-2-[4-(*trans*-4-pentylcyclohexyl)phenyl]ethane (***14***; n = 5).* A mixture of 0.5 g (0.0012 mol) of **13** (n = 5), Pd/C (10%; 0.15 g) and AcOEt (40 ml) was stirred at r.t. under an atmosphere of dry H_2 until the uptake of H_2 was complete. The mixture was filtered to remove catalyst and the resultant soln. evaporated down under reduced pressure to yield raw product, which was further purified using column chromatography on silica-gel using hexane as eluent. The product **14** obtained was crystallised from hexane until constant transition temp. were observed (see *Table 2* for the liquid-crystal transition temp. of this and other ethanes **14** produced using this method). The yield of pure ethane was 0.3 g (60%). IR (KBr): 1610, 1490, 1400, 900 (phenyl). MS: 386, 388 (M^+). Anal. calc. for $C_{25}H_{32}ClF$ (386.5): C 77.59, H 8.34, Cl 9.16, F 4.91; found: C 77.46, H 8.20, Cl 9.41, F 5.08.

*4-(*trans*-4-Pentylcyclohexyl)benzaldehyde (***17***; n = 5, m = p = 1).* CrO_3 (22 g, 0.219 mol) was added portionwise to a stirred soln. of anh. pyridine (34.6 g, 0.438 mol) and dry CH_2Cl_2 cooled *via* an ice-bath and maintained under anh. conditions. The resultant mixture was stirred for a further 15 min at r.t., then 9.5 g (0.0365 mol) of **16** (n = 5, m = p = 1) was added. The mixture was stirred for 2 h and then the org. phase was decanted off. The solid residue was washed with Et_2O (4 × 50 ml) and the combined org. layers washed with 5% aq. NaOH (3 × 100 ml), 5% *aq.* HCl (1 × 100 ml), 5% *aq.* $NaHCO_3$ (1 × 100 ml), brine (2 × 100 ml) and then dried ($MgSO_4$). The filtered soln. was evaporated under reduced pressure and the raw product taken up in a minimum of solvent and eluted from a silica-gel column with toluene. The crude product thus obtained was crystallised from hexane (2×) to yield pure (96%) aldehyde: 5.5 g (58%) m.p. 29–30°. IR (KBr): 1700 (C=O), 1605, 1450, 825 (phenyl). MS: 258 (M^+). Anal. calc. for $C_{18}H_{26}O$ (258.39): C 83.66, H 12.12; found: C 83.56, H 10.28.

*1-(4-Chloro-2-fluorophenyl)-2-[4-(*trans*-4-pentylcyclohexyl)phenyl]ethylene (***18***; n = 5, m = p = 1).* A 1.6M soln. of BuLi in hexane (2.4 ml) was added to a suspension of 1.9 g (0.0039 mol) of the phosphonium salt **11** and anh. toluene (50 ml) under N_2. An orangey-red colour was immediately observed. The resultant mixture was stirred for 1 h, then 1.0 g (0.0039 mol) of **17** (n = 5, m = p = 1) in dry toluene (5 ml) was added, and then stirred for a further 2 h. H_2O (500 ml) was added and the org. layer separated off. The aq. layer was shaken with toluene (2 × 50 ml) and the combined org. layers were washed with H_2O (2 × 500 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under vacuum and the raw product was taken up in a minimum of solvent and eluted down a silica-gel column using toluene as eluent. The stilbene **18** obtained (0.8 g, 54%) was a mixture of *cis-* and *trans-*isomers and was used in the next reaction without further purification. IR (KBr): 1605, 965 (C=C). MS: 384, 386 (M^+). Anal. calc. for $C_{25}H_{30}ClF$ (384.95): C 78.00, H 7.86, Cl 9.21, F 4.94; found: C 78.17, H 7.98, Cl 9.39, F 4.99.

*1-(4-Chloro-2-fluorophenyl)-2-[4-(*trans*-4-pentylcyclohexyl)phenyl]ethane (***19***; n = 5, m = p = 1).* A mixture of 5.0 g (0.013 mol) of **18** (n = 5, m = p = 1), Pd/C (10%, 1.0 g), and AcOEt (250 ml) was stirred at r.t. under an atmosphere of dry H_2 until uptake was complete. The mixture was worked up and purified as above to yield pure (99%) **19** (3.0 g, 60%) with identical liquid-crystal transition temp. (see *Table 2*) and other physical properties to those of **14** (n = 5). IR (KBr): 1600, 1490, 1400, 900 (phenyl). MS: 386, 388 (M^+). Anal. calc. for $C_{25}H_{32}ClF$ (386.97): C 77.59, H 8.34, Cl 9.16, F 4.91; found: C 77.63, H 8.42, Cl 9.09, F 4.82.

*3-Fluoro-4-{2-[4-(*trans*-4-pentylcyclohexyl)phenyl]ethyl}benzonitrite (***20***; n = 5, m = p = 1).* A soln. of 3.0 g (0.0078 mol) of **19** (n = 5; m = p = 1), anh. CuCN (1.7 g, 0.0194 mol) and anh. 1-methyl-2-pyrrolidinone (20 ml) in a sealed ampoule in an autoclave was heated at an internal temp. of 250° for 3 h. The cooled mixture was added to a soln. of anh. $FeCl_3$ (2 g) and conc. HCl (1 ml) in H_2O (20 ml) and stirred at 50–60° for 30 min. The resultant mixture was shaken with Et_2O (4 × 100 ml) and the combined org. layers were washed with brine (2 × 1000 ml) and dried ($MgSO_4$). The filtered soln. was evaporated under slightly reduced pressure to yield raw product, which was purified by column chromatography using silica-gel and a toluene/hexane 1:1. The nitrile thus obtained was crystallised from AcOEt until constant transition temp. were obtained (see *Table 2* for the liquid-crystal transition temp. of this compound and those of the other nitriles prepared using this method). The yield of pure nitrile was 1.0 g (34%). IR (KBr): 2215 (CN). MS: 377 (M^+). Anal. calc. for $C_{26}H_{32}FN$ (377.53): C 82.71, H 8.48, F 5.03, N 3.71; found: C 82.64, H 8.35, F 5.17, N 3.82.

*α-(4-Bromophenyl)-4-(*trans*-4-pentylcyclohexyl)acetophenone (***22***; X^3 = Br).* A soln. of 10 g (0.039 mol) of **12** (n = 5) and anh. Et_2O (80 ml) was added to 0.063 mol of the *Grignard* reagent **21** (X^3 = Br; prepared in the usual way) and anh. Et_2O (100 ml) under N_2. The resultant soln. was heated overnight under gentle reflux and worked up as described for **13** (n = 5). The crude product was crystallised from AcOEt to yield pure (99%) ketone: 6.5 g (38%), m.p. 169–170°. IR (KBr): 1690 (C=O). MS: 426, 428 (M^+).

*1-(4-Bromophenyl)-2-[4-(*trans*-4-pentylcyclohexyl)phenyl]ethane (***23***; X^3 = Br).* A soln. of 2 g (0.0047 mol) of **22** (X^3 = Br) and 98–100% hydrazine hydrate (6 ml) was heated under reflux for 6 h. Diethylene glycol (50 ml) and KOH (1.3 g, 0.0234 mol) were added to the cooled soln. and the temp. raised gradually to 220°, in the process distilling off the excess hydrazine hydrate. The soln. was heated at this temp. until the evolution of N_2 had ceased. The cooled mixture was added to H_2O (500 ml) and shaken with Et_2O (3 × 50 ml). The combined org. extracts were washed with 15% HCl (2 × 50 ml), brine (2 × 500 ml), and dried ($MgSO_4$). Column chromatography on silica-gel using hexane as eluent was carried out and the product thus obtained was crystallised from AcOEt until constant transition temp. were obtained (see *Table 3* for the liquid-crystal transition temp. of this compound). The yield of pure ethane was 1.3 g (67%). IR (KBr): 1600, 1475, 1390 (phenyl). MS: 412, 414 (M^+).

*4-{2-[4-(*trans*-Pentylcyclohexyl)phenyl]ethyl}benzonitrite* (**24**). A soln. of 1.2 g (0.003 mol) of **23** (X^3 = Br), anh. CuCN (0.7 g, 0.007 mol), and anh. 1-methyl-2-pyrrolidinone (20 ml) was heated at an oil-bath temp. of 180° for 2.5 h. The mixture was worked up and purified in the same way as **20** (n = 5, m = p = 1). The yield of **24** was 0.5 g (48%). IR (KBr): 2220 (CN). MS: 359 (M^+). See *Table 3* for the liquid-crystal transition temp.

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