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The influence of the liquid crystalline core geometry on the mesogenicity of novel chiral 2-(4-substituted-phenoxy)propanonitriles

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The synthesis and characterization of seven novel (*R*)-2-(4-substituted-phenoxy)propanonitriles are described. The propanonitriles were prepared to evaluate their potential use as thermochromics and ferroelectric dopants, as well as to determine their twist sense properties. The materials exhibit smectic and chiral nematic phases of high thermal stability; the mesogenic behaviour of the nitriles is directly related to the type of two-ring core unit employed. The effects of the different molecular geometries and polarizabilities of the liquid crystalline cores on mesophase stability are discussed, particularly in relation to other members of this series. The chiral nematic phase of the propanonitriles is assigned as having a left-handed twist sense from contact preparation studies, and this is in agreement with rules relating absolute configuration and molecular structure to helical twist sense.

1. Introduction

The cyano group is probably one of the most widely used terminal groups in liquid crystal chemistry [1, 2] and it owes its extraordinary utility to its highly polar nature and its stability. Firstly, a terminal, electron-withdrawing cyano moiety attached to an aromatic core leads to conjugation with the aromatic nucleus, and thereby forms a region of extended π–π orbital overlap giving an increase in anisotropy of molecular polarizability relative to non-cyano systems and generally leading to an increase in thermal stability of a mesophase [3]. Secondly, the dipole moment associated with the electron-withdrawing cyano group may correlate in an antiparallel fashion with the dipoles of neighbouring molecules, and this also leads to increased phase stability [4, 5]. The dipole moment of the cyano group has frequently been used to modulate the dielectric anisotropy ($\Delta\varepsilon$) of materials for use in mixtures for electro-optic applications, by use as a terminal or lateral moiety [6–9]. More recently, chiral cyano materials have been investigated for use as chiral dopants in ferroelectric applications; these materials are characterized by the dipolar cyano substituent being situated at a chiral point close

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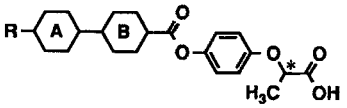
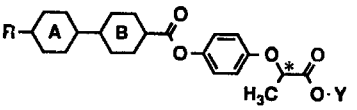
to the liquid crystalline core and they frequently lead to materials with a high spontaneous polarization (P_s) [10–13].

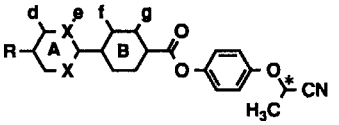
A variety of (*R*)-2-(4-substituted-phenoxy)propanoic acids (**1**) were available from previous work which involved the characterization of (*R*)-2-(4-substituted-phenoxy)propanoate esters as potential thermochromic compounds (**2**) [14], and offered the opportunity of synthesizing a series of novel chiral aliphatic nitriles (**3**) in order to assess their potential as thermochromic materials or ferroelectric dopants, as well as to determine their twist sense behaviour according to established rules [15, 16]. The earlier studies revealed the ineffectiveness of single-ring core acids, such as *trans*-4-pentylcyclohexane-1-carboxylic acid, in generating chiral mesophases in the propanoate and propanonitrile systems [14]. As a consequence, a variety of two-ring liquid crystalline cores was selected to establish systematically the influence of alicyclic–alicyclic, alicyclic–aromatic, aromatic–aromatic, heteroaromatic–aromatic and twisted fluoro-substituted aromatic–aromatic cores on mesophase formation in this class of compound.



1; where *A* and *B* = alicyclic or aromatic unit.



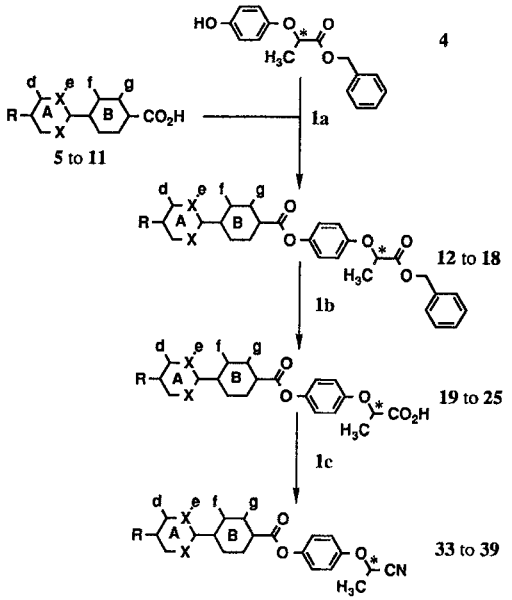
2; where *A* and *B* are as for **1**; *Y* = alkyl, alicyclic or aromatic unit.



3; where *A* and *B* are as for **1**; *R* = pentyl or heptyl;
X = carbon or nitrogen, *d*, *e*, *f*, *g* = H_2, H, F or no substituent.

2. Experimental discussion

The (*R*)-2-(4-substituted-phenoxy)propanonitriles (compounds **33** to **39**) were prepared as shown in the scheme. The first step involves the esterification of (*R*)-benzyl 2-(4-hydroxyphenoxy)propanoate (**4**) [14] with the appropriate two-ring core acid (compounds **5** to **11**) using dicyclohexylcarbodiimide and 4-*N*,*N*-dimethylaminopyridine or 4-(*N*-pyrrolidino)pyridine as catalyst to give the benzyl protected esters (compounds **12** to **18**) in good yields [17]. (Certain two-ring core acids were supplied by Merck Ltd (Poole) (**5–8** and **11**), or were synthesized (**9** and **10**) as described previously [18].) The benzyl group was removed by mild hydrogenolysis using palladium-on-charcoal as catalyst in ethyl acetate at room temperature to give the appropriate propanoic acids (compounds **19** to **25**) [19]. Compounds **19** to **25** were then converted to their amides (compounds **26** to **32**) via their acid chlorides, and dehydrated using thionyl chloride in *N*,*N*-dimethylformamide at room temperature to furnish the propanonitriles as crystalline solids in moderate yields [14].



								Compound number		
R	*A*†	*B*†	*X*	*d*	*e*	*f*	*g*	Ester	Acid	Nitrile
C_5H_{11}	CH	CH	C	H_2	H_2	H_2	H_2	**12**	**19**	**33**
C_5H_{11}	CH	Ph	C	H_2	H_2	H	H	**13**	**20**	**34**
C_5H_{11}	Ph	Ph	C	H	H	H	H	**14**	**21**	**35**
C_5H_{11}	Ph	Ph	C	F	H	H	H	**15**	**22**	**36**
C_5H_{11}	Ph	Ph	C	H	F	H	H	**16**	**23**	**37**
C_5H_{11}	Ph	Ph	C	H	H	F	F	**17**	**24**	**38**
C_7H_{15}	Py	Ph	N	H	–	H	H	**18**	**25**	**39**

† CH = *trans*-1,4-cyclohexyl, Ph = 1,4-phenyl, Py = 2,5-pyrimidinyl.

1a DCC, DMAP or 4-PP, dry CH_2Cl_2, RT.
1b H_2, 5 or 10 per cent Pd–C, EtOAc, RT.
1c (i) $(COCl)_2$, trace DMF, C_6H_6, RT;
(ii) NH_3 (aq), diglyme, RT;
(iii) $SOCl_2$, DMF, RT.

Scheme: The synthetic route to the (*R*)-2-(4-substituted-phenoxy)propanonitriles.

3. Experimental

3.1. *Analysis*

^{1}H NMR spectra were obtained using a JEOL GX NM270 FT-NMR spectrometer; tetramethylsilane was used as the internal standard unless stated otherwise. Infrared spectra were recorded using a Perkin–Elmer 783 spectrometer and mass spectra using a Finnigan 1020 GC-MS spectrometer. Specific optical rotations, were determined at room temperature (22–24°C) using an Optical Activity Ltd AA-10 Automatic Polarimeter. All phase transitions were recorded using a Mettler FP 52 hot stage, Mettler FP 5 temperature controller and either an Olympus model BH-2 or Zeiss Universal polarizing microscope, and by DSC using a Perkin–Elmer DSC7 calorimeter, TAC 7/PC instrument controller linked to IBM personal system/2 model 50 Z computer.

Thin layer chromatography was performed using aluminium-backed silica gel plates (60 F254 Merck) and developed using iodine. Column chromatography was performed using Fisons 60–120 mesh silica gel and flash chromatography using May and Baker Sorbsil® C60 40–60 H micron silica gel as described by Clark Still [20]. The purity of all key intermediates and final products was shown to be in excess of 99 per cent by HPLC or by GC. HPLC was carried out using a Kontron Instruments HPLC pump 420, Chrompack (MUST) multiport stream switch, Perkin–Elmer ISS-100 Autosampler, Spectroflow 757 absorbance detector and a Chessel Ltd chart recorder; either a Microsorb C18 or Si column was used with May and Baker Chromanorm™ acetonitrile as the mobile phase. GC was carried out using a Perkin–Elmer 8320 Capillary Gas Chromatograph with QC2/BP1–1·0 SGE (12 m) capillary column.

(*R*)-Benzyl 2-(4-hydroxyphenoxy)propanoate (**4**) was prepared from (*R*)-2-(4-hydroxyphenoxy)propanoic acid [14], as supplied by Zeneca FCMO (formerly ICI FCMO (Huddersfield)). The intermediates **5** to **8** and **11** were obtained from Merck Ltd (Poole) and were used without further purification. All solvents were dried, distilled and stored as described by Perrin and Armarego [21].

Attempts to measure the spontaneous polarization were made using 1·4 or 1·5 μm thick cells (Electronics Chemicals High Technology Group, Japan) with an active area of indium–tin oxide electrodes of 0·25 cm^2, previously treated with unidirectionally buffed polyimide alignment layers. The cells were filled by capillary action with 10 per cent (w/w) mixtures of the appropriate propanonitrile in the ferroelectric host H1 (Merck Ltd). Good alignment was obtained by slowly cooling each mixture from the isotropic liquid into the respective smectic A and smectic C* states. Cooling rates were of the order of 0·2°C min^{-1}. Once filled the cells were connected to an a.c. frequency generator (5 or 10 V peak to peak at 60 Hz), a dual trace oscilloscope and a Diamant Bridge [22].

3.2. *Synthesis of* **12–18**

3.2.1. (R)-*Benzyl 2-{4-[trans-4-(trans-4-pentylcyclohexyl)cyclohexylcarbonyloxy]-phenoxy}propanoate* (**12**)

Dicyclohexylcarbodiimide (8·80 g, 42·65 mmol) was added to a stirred solution of *trans*-4-(*trans*-4-pentylcyclohexyl)cyclohexane-1-carboxylic acid (**5**) (10·30 g, 36·79 mmol), compound **4** (10·00 g, 36·77 mmol), 4-(*N*-pyrrolidino)pyridine (1·65 g, 11·10 mmol) in dry dichloromethane (200 ml) at room temperature. The mixture was stirred for a further 18 h, before removal of the precipitated *N,N'*-disubstituted urea by filtration through 'Hyflo supercel'. The organic solution was then successively washed with water (50 ml), 5 per cent (v/v) acetic acid solution (2 × 50 ml) and water (50 ml) before being dried ($MgSO_4$), refiltered and evaporated to give a solid. The crude product was then purified by column chromatography [silica gel; dichloromethane] to give a pale yellow solid which was dried *in vacuo* ($CaCl_2$, 0·50 mmHg, RT, 4 h). Yield = 13·18 g (67 per cent); m.p. 109–110°C. ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·88 (5 H, t), 1·08 (9 H, m), 1·25 (6 H, m), 1·52 (2 H, d), 1·61 (3 H, d), 1·76 (6 H, d), 2·13 (2 H, d), 2·42 (1 H, sextet), 4·75 (1 H, q), 5·20 (2 H, s), 6·82 (2 H, d), 6·92 (2 H, d), 7·30 (5 H, m). IR ν_{max} (KCl) 2930, 2850, 1750, 1600, 1505, 1250, 765, 705, 605, 520 cm^{-1}. *m/z* 534 (M^+, 4 per cent), 257 (16), 182 (100), 136 (13), 109 (24), 91 (13).

The following compounds (**13–18**) were prepared in a similar manner to compound **12**.

3.2.2. (R)-*Benzyl 2-{4-[4-(trans-4-pentylcyclohexyl)benzoyloxy]phenoxy}-propanoate* (**13**)

Yield = 9·68 g (72 per cent); m.p. 147–151°C. ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·89 (3 H, d), 1·09 (2 H, q), 1·29 (10 H, m), 1·49 (2 H, q), 1·63 (3 H, d), 1·90 (4 H, d), 2·56 (1 H, sextet), 4·77 (1 H, q), 5·19 (2 H, s), 6·88 (2 H, d), 7·02 (2 H, d), 7·31 (6 H, m), 8·10 (2 H, d). IR ν_{max} (KCl) 2930, 2850, 1750, 1735, 1610, 1505, 1260, 1245, 1195, 1180, 1145, 1105, 1075, 1015, 750, 710 cm^{-1}. *m/z* 530 (M^+, 6 per cent), 257 (20), 131 (10), 91 (80). $[\alpha]_D = +5{\cdot}3°$ (*c* 0·0755 g ml^{-1}; $CHCl_3$).

3.2.3. (R)-*Benzyl 2-[4-(4'-pentylbiphenyl-4-carbonyloxy)phenoxy]propanoate* (**14**)

Yield = 15·79 g (67 per cent). ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (4 H, t), 1·35 (5 H, m), 1·65 (6 H, m), 2·65 (2 H, t), 4·77 (1 H, q), 5·20 (2 H, s), 6·90 (2 H, d), 7·15 (2 H, d), 7·35 (4 H, m), 7·58 (2 H, d), 7·72 (2 H, d), 8·24 (2 H, d). IR ν_{max} (KCl) 2930, 2870, 1770, 1755, 1730, 1610, 1510, 1455, 1405, 1385, 1315, 1275, 1245, 1195, 1120, 1080, 1005, 880, 870, 850, 815, 770, 750, 745, 725, 695, 550 cm^{-1}. *m/z* 524 (M^+, 10 per cent); 251 (40), 91 (100). $[\alpha]_D = +8{\cdot}5°$ (*c* 0·0071 g ml^{-1}; $CHCl_3$).

3.2.4. (R)-*Benzyl 2-[4-(3'-fluoro-4'-pentylbiphenyl-4-carbonyloxy)phenoxy]-propanoate* (**15**)

Yield = 13·50 g (68 per cent); m.p. 60–63°C. ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·92 (3 H, t), 1·36 (4 H, m), 1·64 (5 H, d), 2·69 (2 H, t), 4·79 (1 H, q), 5·20 (2 H, s), 6·90 (2 H, d), 7·11 (2 H, d), 7·32 (8 H, m), 7·70 (2 H, d), 8·25 (2 H, d). IR ν_{max} (KBr) 3070, 2960, 2940, 1765, 1740, 1610, 1505, 1360, 1350, 1300, 1200, 1060, 1015, 870, 770, 750, 700 cm^{-1}. *m/z* 540 (M^+, 4 per cent), 269 (100), 183 (5), 91 (20). $[\alpha]_D = +8{\cdot}0°$ (*c* 0·0375 g ml^{-1}; $CHCl_3$).

3.2.5. (R)-*Benzyl 2-[4-(2'-fluoro-4'-pentylbiphenyl-4-carbonyloxy)phenoxy]-propanoate* (**16**)

Yield = 0·80 g (74 per cent). ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·92 (3 H, t), 1·36 (4 H, m), 1·64 (5 H, m), 2·66 (2 H, t), 4·79 (1 H, q), 5·20 (2 H, s), 6·90 (2 H, d), 7·10 (3 H, m), 7·34 (7 H, m), 7·69 (2 H, q), 8·25 (2 H, d). IR ν_{max} (KBr) 2960, 2940, 2870, 1760, 1745, 1505, 1275, 1245, 1195, 1150, 1075, 875, 815, 775, 750, 700 cm^{-1}. *m/z* 540 (M^+, 10 per cent), 269 (100), 183 (20), 91 (31).

3.2.6. (R)-*Benzyl 2-[4-(2,3-difluoro-4'-pentylbiphenyl-4-carbonyloxy)phenoxy]-propanoate* (**17**)

Yield = 0·44 g (59 per cent). ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·91 (3 H, t), 1·36 (4 H, m), 1·64 (5 H, m), 2·68 (2 H, t), 4·79 (1 H, q), 5·20 (2 H, s), 6·90 (2 H, d), 7·13 (2 H, d), 7·32 (8 H, m), 7·60 (2 H, q), 7·88 (1 H, t). IR ν_{max} (KBr) 2950, 2920, 2870, 1735, 1625, 1500, 1460, 1405, 1300, 1210, 1185, 1120, 1010, 895, 860, 770, 750, 695, 515 cm^{-1}. *m/z* 558 (M^+, 13 per cent), 287 (100), 202 (41), 183 (12), 91 (30).

3.2.7. (R)-*Benzyl 2-{4-[4-(5-heptylpyrimidin-2-yl)benzoyloxy]phenoxy}-propanoate* (**18**)

Yield = 1·03 g (48 per cent); m.p. 82–83°C. ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (3 H, t), 1·35 (8 H, d), 1·65 (5 H, m), 2·70 (2 H, t), 4·80 (1 H, q),

5·20 (2 H, s), 6·90 (2 H, d), 7·13 (2 H, d), 7·32 (5 H, m), 8·30 (2 H, d), 8·57 (2 H, d), 8·68 (2 H, s). IR ν_{max} (KBr) 2960, 2930, 2860, 1750, 1730, 1505, 1440, 1270, 1250, 1200, 1190, 1135, 1075, 760, 695 cm^{-1}. *m/z* 552 (M^+, trace), 281 (100 per cent), 168 (10), 91 (40).

3.3. *Synthesis of* **19–25**

3.3.1. (R)-2-{*4*-[trans-*4*-(trans-*4-Pentylcyclohexyl*)*cyclohexylcarbonyloxy*]-*phenoxy*}*propanoic acid* (**19**)

Compound **12** (17·41 g, 32·60 mmol) was dissolved in ethyl acetate (200 ml) and a slurry of 5 per cent palladium-on-charcoal (1·00 g) and ethyl acetate (50 ml) was added with stirring. The mixture was then degassed under reduced pressure (water pump) and then stirred under a hydrogen atmosphere for 18 h. After degassing the mixture, the catalyst was removed by filtration through 'Hyflo supercel', and the solution was dried ($MgSO_4$), refiltered and evaporated to give a white solid. Yield = 11·40 g (79 per cent); m.p. 196–200°C. ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (5 H, m), 1·05 (9 H, m), 1·25 (6 H, m), 1·52 (2 H, q), 1·75 (9 H, m), 2·13 (2 H, d), 2·43 (1 H, sextet), 4·75 (1 H, q), 6·85 (2 H, d), 6·98 (2 H, d), (carboxylic acid H not detected). IR ν_{max} (KCl) 3420, 2930, 2860, 1750, 1715, 1515, 1245, 1205, 1040, 855, 525 cm^{-1}. *m/z* 444 (M^+, 4 per cent), 257 (16), 182 (100), 136 (13), 109 (24), 97 (21), 83 (31), 74 (5), 67 (23). $[\alpha]_D = +12{\cdot}3°$ (*c* 0·0137 g ml^{-1}; $CHCl_3$).

The following compounds (**20–25**) were prepared in a similar manner to compound **19**.

3.3.2. (R)-2-{*4*-[*4*-(trans-*4-Pentylcyclohexyl*)*benzoyloxy*]*phenoxy*}*propanoic acid* (**20**)

Yield = 7·23 g (90 per cent); m.p. 158–161°C. ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (3 H, m), 1·10 (2 H, q), 1·30 (10 H, m), 1·50 (2 H, q), 1·70 (3 H, d), 1·90 (3 H, d), 2·55 (1 H, t), 4·80 (1 H, q), 6·95 (2 H, d), 7·15 (2 H, d), 7·33 (2 H, d), 8·10 (2 H, d), (carboxylic acid H not detected). IR ν_{max} (KCl) 3440, 2920, 2850, 1735, 1715, 1615, 1505, 1270, 1245, 1195, 1180, 1075, 705 cm^{-1}. *m/z* 438 (M^+, 3 per cent), 384 (4), 257 (100), 131 (10), 91 (19).

3.3.3. (R)-2-[*4*-(*4'-Pentylbiphenyl-4-carbonyloxy*)*phenoxy*]*propanoic acid* (**21**)

Yield = 12·58 g (97 per cent). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (3 H, t), 1·35 (5 H, m), 1·70 (4 H, m), 2·65 (2 H, t), 4·80 (1 H, q), 6·97 (2 H, d), 7·17 (2 H, d), 7·29 (2 H, d), 7·57 (2 H, d), 7·71 (2 H, d), 8·23 (2 H, d), (carboxylic acid H not detected). IR ν_{max} (KCl) 3160, 2960, 2930, 2860, 1730, 1610, 1505, 1455, 1425, 1400, 1380, 1275, 1250, 1190, 1135, 1100, 1075, 1015, 1005, 935, 875, 815, 765, 750, 695, 630, 580, 555, 525 cm^{-1}. *m/z* 432 (M^+, 7 per cent), 251 (100), 165 (20), 57 (14). $[\alpha]_D = +8{\cdot}5°$ (*c* 0·0071 g ml^{-1}; $CHCl_3$).

3.3.4. (R)-2-[*4*-(*3'-Fluoro-4'-pentylbiphenyl-4-carbonyloxy*)*phenoxy*]*propanoic acid* (**22**)

Yield = 10·18 g (93 per cent); m.p. 154–158°C. ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·92 (3 H, t), 1·36 (4 H, m), 1·69 (5 H, m), 2·68 (2 H, t), 4·80 (1 H, q), 6·96 (2 H, d), 7·16 (2 H, d), 7·29 (3 H, d), 7·68 (2 H, d), 8·23 (2 H, d), 8·70 (1 H, s, broad). IR ν_{max} (KBr) 3440, 2960, 2930, 2870, 1735, 1730, 1610, 1505, 1400, 1275, 1250, 1195, 1075, 765, 525 cm^{-1}. *m/z* 450 (M^+, 5 per cent), 269 (100), 183 (20). $[\alpha]_D = +9{\cdot}4°$ (*c* 0·0638 g ml^{-1}; $CHCl_3$).

3.3.5. (R)-*2*-[*4*-(*2'-Fluoro-4'-pentylbiphenyl-4-carbonyloxy*)*phenoxy*]*propanoic acid* (**23**)

Yield = 0·56 g (84 per cent). ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 60·95 (3 H, t), 1·35 (4 H, m), 1·65 (5 H, m), 2·65 (2 H, m), 4·80 (1 H, q), 6·96–7·16 (6 H, m), 7·38 (1 H, t), 7·65 (2 H, d), 8·25 (2 H, d), (carboxylic acid H not detected). IR ν_{max} (KBr) 3420, 2950, 2920, 2850, 1735, 1725, 1500, 1265, 1245, 1190, 1075, 865, 815, 765 cm^{-1}. *m/z* 450 (M^+, 9 per cent), 269 (100).

3.3.6. (R)-*2*-[*4*-(*2,3-Difluoro-4'-pentylbiphenyl-4-carbonyloxy*)*phenoxy*]*propanoic acid* (**24**)

Yield = 0·34 g (94 per cent). ^{1}H NMR (270 MHz); solvent $CDCl_3$; standard TMS) δ 0·90 (3 H, t), 1·35 (4 H, m), 1·65 (5 H, m), 2·65 (2 H, t), 4·80 (1 H, q), 5·45 (1 H, s, broad), 6·95 (2 H, d), 7·18 (2 H, d), 7·30 (3 H, m), 7·50 (2 H, d), 7·88 (1 H, t). IR ν_{max} (KBr) 3450, 2960, 2935, 2860, 1730, 1510, 1465, 1410, 1310, 1220, 1195, 1120, 775 cm^{-1}. *m/z* 468 (M^+, trace), 287 (100 per cent), 109 (14).

3.3.7. (R)-*2*-{*4*-[*4*-(*5-Heptylpyrimidin-2-yl*)*benzoyloxy*]*phenoxy*}*propanoic acid* (**25**)

Yield = 0·80 g (95 per cent); m.p. 133–134°C. ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·89 (3 H, t), 1·30 (8 H, m), 1·70 (5 H, m), 2·68 (2 H, t), 4·81 (1 H, q), 6·97 (2 H, d), 7·18 (2 H, d), 8·22 (2 H, d), 8·44 (2 H, d), 8·72 (2 H, s), (carboxylic acid H not detected). IR ν_{max} (KCl) 3430, 2930, 2860, 1750, 1730, 1510, 1440, 1270, 1245, 1200, 1180, 1140, 1075, 1020, 870, 810, 760, 695, 660 cm^{-1}. *m/z* 462 (M^+, 4 per cent), 100 (100), 167 (23).

3.4. *Synthesis of* **33–39**

3.4.1. (R)-(+)-*2*-{*4*-[trans-*4*-(trans-*4-Pentylcyclohexyl*)*cyclohexylcarbonyloxy*]-*phenoxy*}*propanonitrile* (**33**)

Oxalyl chloride (0·73 g, 5·75 mmol) in dry benzene (20 ml) was added dropwise at room temperature to a stirred suspension of compound **19** (1·20 g, 2·70 mmol) in dry benzene (20 ml) containing 5-drops of dry *N,N*-dimethylformamide (DMF). The mixture was stirred for 18 h before the excess of oxalyl chloride and benzene was removed under reduced pressure (water pump) to give the crude acid chloride. The residue was redissolved in dry diglyme (25 ml) and added slowly to a stirred solution of ammonia (35 per cent solution, 70 ml). The mixture was cooled and the precipitate filtered off, washed (water) and dried *in vacuo* (P_2O_5, 0·60 mmHg, 50°C, 4·5 h). Yield = 1·06 g (88 per cent). Thionyl chloride (2·79 g, 23·5 mmol) in dry DMF (5 ml) was added dropwise at room temperature to a stirred suspension of the amide (1·04 g, 2·35 mmol) in dry DMF (10 ml). The mixture was stirred for a further 24 h before pouring on to ice (50 g) and water (50 ml) with stirring. The product was extracted using dichloromethane (3 × 20 ml); the combined extracts were washed successively with water (20 ml), saturated sodium bicarbonate (3 × 20 ml) and finally water (20 ml). The organic phase was dried ($MgSO_4$), filtered and evaporated to give an orange oil which was purified by flash chromatography [fine mesh silica gel; 9 : 1 dichloromethane-petrol (b.p. 40–60°C)], recrystallized (ethyl acetate) and dried *in vacuo* (P_2O_5, 0·25 mmHg, 50°C, 5 h). Yield = 0·47 g (47 per cent); C 82·5 S_A 146·9 N* 179·6 I (°C). ^{1}H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·88 (5 H, t), 1·00 (3 H, d), 1·11 (7 H, m), 1·25 (3 H, m), 1·55 (3 H, t), 1·79 (10 H, m), 2·14 (2 H, d), 2·44 (1 H, sextet), 4·84 (1 H, q), 7·20 (4 H, 2xd). IR ν_{max} (KCl) 2960, 2920, 1850, 1745, 1505, 1235, 1200, 1140,

525 cm^{-1}. *m/z* 425 (M^+, 15 per cent), 262 (53), 235 (23), 210 (25), 163 (38). $[\alpha]_D = +34.9°$ (*c* 0·0063 g ml^{-1}; $CHCl_3$).

The following compounds (**34–39**) were prepared in a similar manner to compound **33** using the appropriate acids (**20–25**).

3.4.2. (R)-(+)-*2*-{*4*-[*4*-(trans-*4-Pentylcyclohexyl)benzoyloxy*]*phenoxy*}-*propanonitrile* (**34**)

Yield = 0·63 g (56 per cent); C 122·3 (S_A 92·9) N* 151·6 I (°C). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (3 H, t), 1·09 (2 H, t), 1·27 (9 H, m), 1·51 (3 H, m), 1·81 (3 H, d), 1·91 (3 H, d), 2·56 (1 H, sextet), 4·87 (1 H, q), 7·06 (2 H, d), 7·18 (2 H, d), 7·34 (2 H, d), 8·11 (2 H, d). IR ν_{max} (KCl) 2970, 2920, 2850, 1740, 1505, 1265, 1190, 1180, 1075, 1015, 770, 705 cm^{-1}. *m/z* 419 (M^+, trace), 257 (100 per cent), 131 (5), 91 (5). $[\alpha]_D = +40.6°$ (*c* 0·0069 g ml^{-1}; $CHCl_3$).

3.4.3. (R)-(+)-*2*-[*4*-(*4'-Pentylbiphenyl-4-carbonyloxy*)*phenoxy*]*propanonitrile* (**35**)

Yield = 0·61 g (44 per cent); C 120·7 S_A 155·4 N* 166·6 I (°C). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·91 (3 H, t), 1·35 (4 H, m), 1·54 (1 H, s), 1·67 (1 H, quint), 1·82 (3 H, d), 2·67 (2 H, t), 4·99 (1 H, q), 7·08 (2 H, d), 7·22 (2 H, d), 7·30 (2 H, d), 7·58 (2 H, d), 7·73 (2 H, d), 8·24 (2 H, d). IR ν_{max} (KBr) 2970, 2920, 2880, 2850, 1730, 1610, 1505, 1400, 1385, 1290, 1235, 1180, 1100, 1075, 1045, 1015, 930, 850, 820, 770, 750 cm^{-1}. *m/z* 413 (M^+, trace), 350 (2 per cent), 251 (100), 165 (24), 152 (17), 109 (11). $[\alpha]_D = +42.2°$ (*c* 0·0045 g ml^{-1}; $CHCl_3$).

3.4.4. (R)-(+)-*2*-[*4*-(*3'-Fluoro-4'-pentylbiphenyl-4-carbonyloxy*)*phenoxy*]-*propanonitrile* (**36**)

Yield = 1·53 g (80 per cent); C 112·3 S_A 125·8 N* 137·0 I (°C). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·91 (3 H, t), 1·37 (4 H, m), 1·65 (2 H, t), 1·82 (3 H, d), 2·69 (2 H, t), 4·89 (1 H, q), 7·08 (2 H, d), 7·30 (5 H, m), 7·71 (2 H, d), 8·28 (2 H, d). IR ν_{max} (KBr) 2970, 2940, 2880, 1740, 1610, 1510, 1400, 1270, 1195, 1135, 1100, 1080, 1045, 1015, 930, 765 cm^{-1}. *m/z* 431 (M^+, 5 per cent), 269 (100), 183 (16). $[\alpha]_D = +74.1°$ (*c* 0·0216 g ml^{-1}; $CHCl_3$).

3.4.5. (R)-(+)-*2*-[*4*-(*2'-Fluoro-4'-pentylbiphenyl-4-carbonyloxy*)*phenoxy*]-*propanonitrile* (**37**)

Yield = 0·36 g (78 per cent); C 45·7 S_A 83·1 N* 123·1 I (°C). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·91 (3 H, t), 1·36 (5 H, m), 1·67 (2 H, quint), 1·82 (3 H, d), 2·66 (2 H, t), 4·89 (1 H, q), 7·05 (4 H, m), 7·22 (2 H, d), 7·40 (1 H, t), 7·70 (1 H, q), 8·25 (2 H, d). IR ν_{max} (KBr) 2960, 2930, 2860, 1735, 1505, 1270, 1240, 1195, 1190, 1075, 870, 770, 700 cm^{-1}. *m/z* 431 (M^+, 1 per cent), 269 (100), 183 (21), 94 (62). $[\alpha]_D = +77.7°$ (*c* 0·0196 g ml^{-1}; $CHCl_3$).

3.4.6. (R)-(+)-*2*-[*4*-(*2,3-Difluoro-4'-pentylbiphenyl-4-carbonyloxy*)*phenoxy*]-*propanonitrile* (**38**)

Yield = 0·17 g (68 per cent); C 72·9 (S_A 72·4) N* 125·1 I (°C). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·92 (3 H, t), 1·36 (4 H, m), 1·67 (2 H, quint), 1·82 (3 H, d), 2·67 (2 H, t), 4·89 (1 H, q), 7·08 (2 H, d), 7·28 (5 H, m), 7·52 (2 H, q), 7·89 (1 H, septet). IR ν_{max} (KBr) 2960, 2930, 2870, 2850, 1735, 1625, 1500, 1460, 1405, 1375,

1305, 1215, 1185, 1120, 1195, 1045, 1010, 770 cm^{-1}. *m/z* 449 (M^+, 5 per cent), 287 (100), 202 (32), 58 (21). $[\alpha]_D = +67{\cdot}7°$ (*c* 0·0133 g ml^{-1}; $CHCl_3$).

3.4.7. (R)-(+)-2-{*4-[4-(5-Heptylpyrimidin-2-yl)benzoyloxy]phenoxy*}-*propanonitrile* (**39**)

Yield = 0·28 g (49 per cent); C 123·1 S_A 124·7 N* 138·5 I (°C). ^1H NMR (270 MHz; solvent $CDCl_3$; standard TMS) δ 0·90 (3 H, t), 1·35 (8 H, d), 1·65 (2 H, m), 1·82 (3 H, d), 2·67 (2 H, t), 4·89 (1 H, q), 7·08 (2 H, d), 7·24 (2 H, d), 8·30 (2 H, d), 8·57 (2 H, d), 8·68 (2 H, s). IR ν_{max} (KBr) 2960, 2940, 2860, 1730, 1510, 1440, 1270, 1195, 1180, 1020, 880, 760 cm^{-1}. *m/z* 443 (M^+, 1 per cent), 281 (100). $[\alpha]_D = +64{\cdot}7°$ (*c* 0·0201 g ml^{-1}; $CHCl_3$).

4. Results

The phase sequences of compounds **33** to **39** were determined by optical microscopy and are given in the table. On cooling from the isotropic liquid, all the compounds formed the characteristic iridescent *Grandjean* texture associated with the chiral nematic phase (N*). Further cooling revealed, for all compounds, the formation of the focal-conic fan texture of the smectic A phase (S_A) which was characterized by optical discontinuities shown as crosses; compounds **34** and **38** both exhibited monotropic smectic A phases. Cooling the S_A phase still further resulted in crystallization and no other phases were observed. The trends in the transition temperature for this group of nitriles is more clearly seen in the bar chart in figure 1.

Inspection of the transition temperatures listed in the table shows a direct correlation between the geometry and polarizability of the liquid crystalline core and mesophase stability. Firstly, the effects of a sequential increase in the rigidity of the liquid crystalline core are seen in the transition temperatures of compounds **33**, **34** and **35**; these effects are directly related to the ability of the mesogenic core unit to pack efficiently with favourable intermolecular interactions between the molecular orbitals of neighbouring molecules (i.e. sp^3–sp^3 interactions in the case of compound **33** or π–π (sp^2–sp^2) aided by conjugation of aromatic rings in the case of compound **35**) [3, 23–25].

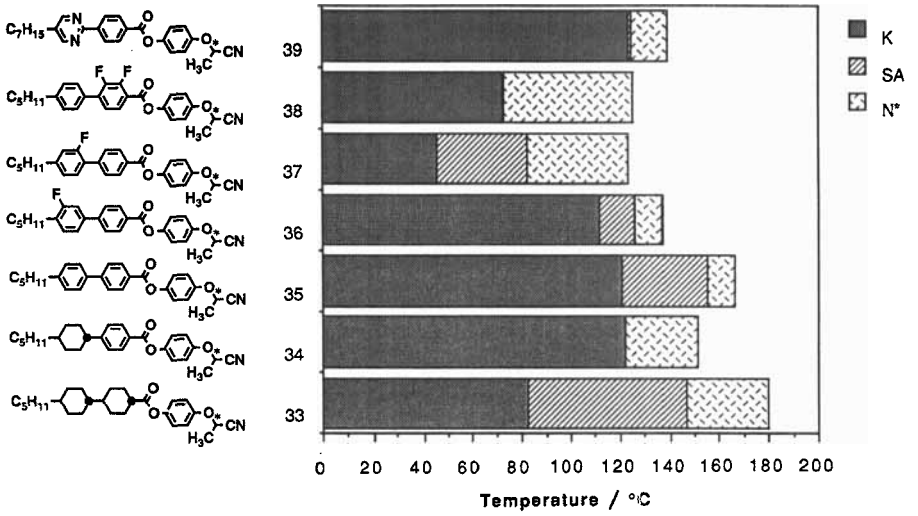
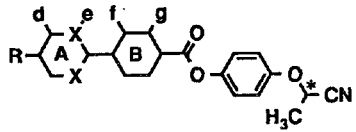


Figure 1. The transition temperatures of the (*R*)-2-(4-substituted-phenoxy)propanonitriles (the monotropic smectic A phases of compounds **34** and **38** are not shown).

The transition temperatures and related thermodynamic data for the (*R*)-2-(4-substituted-phenoxy)propanonitriles.



Compound number	*R*	*A*†	*B*†	*X*	*d*	*e*	*f*	*g*	Transition temperatures/°C‡ C		S_A		N*		I
33	C_5H_{11}	CH	CH	C	H_2	H_2	H_2	H_2	•	82·5 [21·8]§	•	146·9 [1·9]	•	179·6 [0·3]	•
34	C_5H_{11}	CH	Ph	C	H_2	H_2	H	H	•	122·3 [23·7]	(•	92·9)‖¶	•	151·6 [0·3]	•
35	C_5H_{11}	Ph	Ph	C	H	H	H	H	•	120·7 [23·8]	•	155·4 [1·8]	•	166·6 [0·6]	•
36	C_5H_{11}	Ph	Ph	C	F	H	H	H	•	112·3 [22·9]	•	125·8 [0·1]	•	137·0 [0·1]	•
37	C_5H_{11}	Ph	Ph	C	H	F	H	H	•	45·7 [13·1]	•	83·1 [0·2]	•	123·1 [0·5]	•
38	C_5H_{11}	Ph	Ph	C	H	H	F	F	•	72·9 [10·6]	(•	72·4)‖[0·5]	•	125·1 [0·5]	•
39	C_7H_{15}	Py	Ph	N	H	–	H	H	•	123·1 [21·7]	•	124·7 [1·2]	•	138·5 [0·7]	•

† CH = *trans*-1,4-cyclohexyl, Ph = 1,4-phenyl, Py = 2,5-pyrimidinyl; ‡ recorded by thermal optical microscopy at 2°C min^{-1}; § figures in square brackets denote enthalpies of transition (kJ mol^{-1}); ‖ figures in round brackets denote a monotropic phase transition; ¶ enthalpy too small to measure.

Compounds **36**, **37** and **38** illustrate the use of fluoro-substituents to depress the stability of melting points and the $T_{S_A-N^*}$ and T_{N^*-I} transitions relative to one another and the non-fluoro-substituted parent (**35**). The use of interannular fluoro-substituents (for example, compounds **37** and **38**) is believed to dramatically depress transition temperatures by further reducing π–π conjugation (and therefore polarizability) between core rings by virtue of increasing the interannular torsion angle [3, 26–28]. The following order of the decreasing effect of the three kinds of fluoro-substitution patterns applies to these propanonitrile materials and compares well to other published data [29, 30]:

$$2'\text{-fluoro} \approx 2,3\text{-difluoro} > 3'\text{-fluoro}$$

(in order of decreasing destabilizing influence).

In the case of the (5-pyrimidin-2-yl)benzoate ester (**39**), the localized polarity and polarizability of the nitrogen atoms in the pyrimidyl ring may also have a pronounced effect on intermolecular attractions and therefore the packing of the molecules [24, 30, 31].

5. Helical twist sense studies

Using a modified form of Gray and McDonnell's rules [15, 16], the handedness of the twist sense of the chiral nematic phase for the chiral propanonitriles **33** to **39** may be predicted since all compounds have the following features,

(*R*)- absolute configuration,
e even parity or position of the chiral centre from the core,
(-*I*) a negatively inductive nitrile group at the chiral centre.

Therefore compound **37** might be expected to have a left-handed helical twist sense. This was later confirmed during detailed miscibility and twist sense studies carried out on binary mixtures of compound **37** and a related chiral 1-alkoxypropane [32]; the exact experimental details are reported elsewhere [33]. Although the chiral nematic phases of all of the propanonitriles were iridescent (indicating a pitch length of *c.* 0·5 μm), pitch length measurements were not possible because no dechiralization lines could be clearly observed in planar aligned samples.

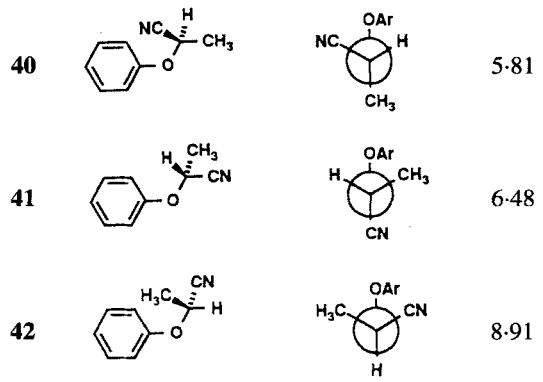


Figure 2. Extreme conformational structures caused by rotation about the O–C_1 bond in chiral propanonitriles and relative energy barriers (kcal).

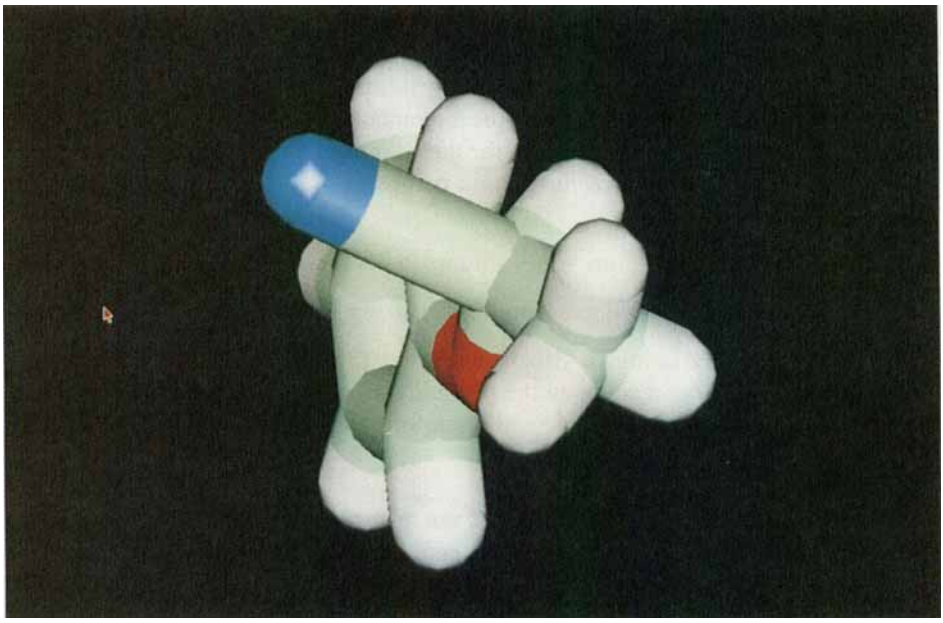


Figure 3. A molecular model of the energetically preferred conformer **40**.

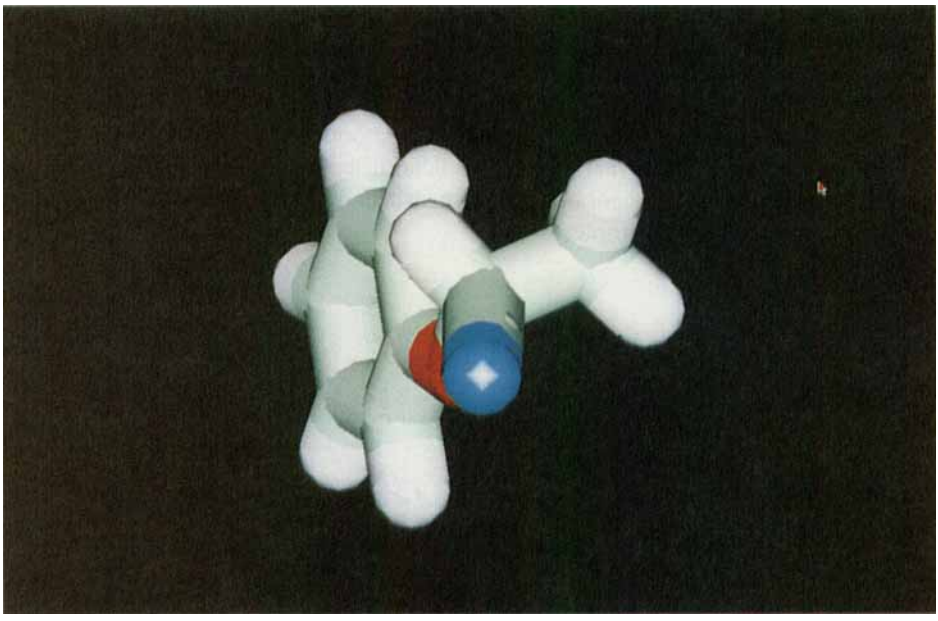


Figure 4. A molecular model of conformer **41**.

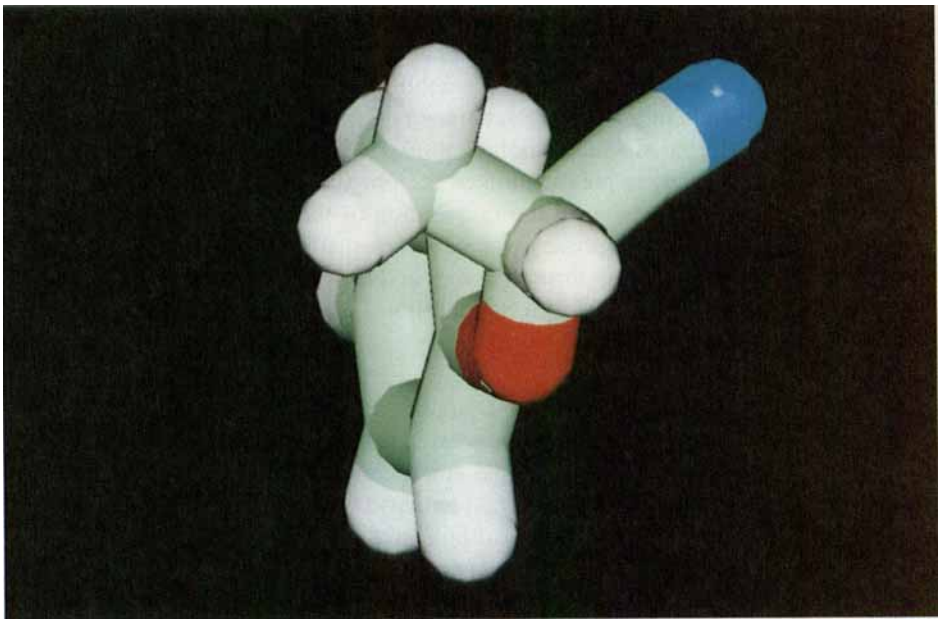


Figure 5. A molecular model of conformer **42**.

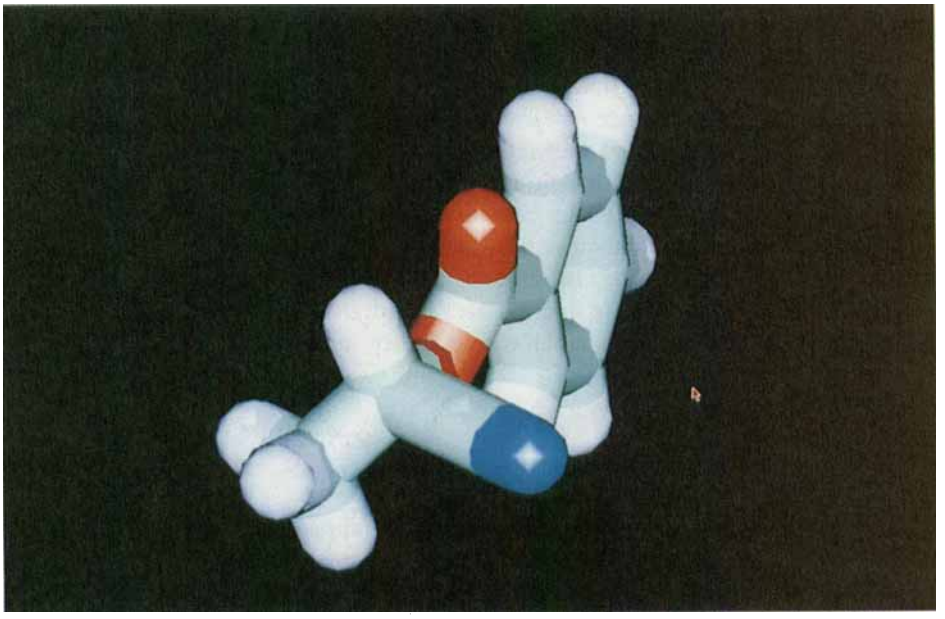


Figure 6. A molecular model of the lowest energy conformation of (*S*)-1-cyanoethyl benzoate ester [model for M71ac (**43**)].

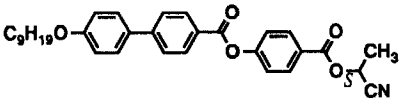
6. Spontaneous polarization studies

Compounds **33–39** failed to show smectic C* phases and therefore their ferroelectric spontaneous polarizations could only be measured by formulating them as dopants in a suitable smectic C host (10 per cent [w/w] in H1 [Merck Ltd]). However, despite obtaining good alignment and switching (observable at low frequency, i.e. 15 Hz), all compounds failed to give satisfactory hysteresis loops thus preventing the measurement of the spontaneous polarization. This is believed to be due to the inherently low spontaneous polarization of the propanonitrile system.

It is of interest to note that in the preparation of these ferroelectric mixtures the presence of induced TGB A phases was observed mediating the smectic A to chiral nematic transitions of these mixtures of compounds **33–39**. This is further confirmation of the high twisting powers of the propanonitriles which has already been observed in other binary systems [33].

7. Discussion

The low value of the spontaneous polarization in these chiral systems may be attributed to a smearing out of the dipole at the chiral centre caused by the relatively free rotation about the oxygen–carbon (asymmetric atom) bond. This results in a weak coupling between the lateral molecular dipole and the chiral centre dipole. Thus, it is possible that the polar cyano group will spend as much time positioned along the axis of the molecule as pointing away from the side of it. For example, if we consider the extreme conformational structures shown in figure 2 for rotations about the O–C_1 bond in (*R*)-2-(phenoxy)propanonitrile, we can see that the lateral dipoles in structures **40** and **42**, where the cyano group is positioned on opposite sides of the axis, almost cancel one another. Structure **42**, would be expected to be just slightly more polar than **40** because of the donor methyl group. Structure **41** has only a weak lateral dipole because the cyano group points along the molecular long axis. The distribution of conformers should, therefore, not make much difference to the overall or average dipole, which is expected to be weak and hence will lead to low spontaneous polarization. This contrasts to the compound (*S*)-(−)-1-cyanoethyl 4-(4′-nonyloxybiphenyl-4-carbonyloxy) benzoate (M71ac; **43**) [13] which appears to owe its spontaneous polarization of 70 nC cm^{-2} (measured as a 10 per cent w/w mixture in H1) to the cyano group being located in conformations lateral with respect to the long molecular axis. These facts appear to be supported by results obtained by molecular modelling on the simplified (*R*)-2-(phenoxy)propanonitrile and (*S*)-1-cyanoethyl benzoate systems; the energetically preferred conformations obtained are shown in figures 3, 4, 5 and 6 [34].



M71ac; **43**

The steric sizes of the methyl and cyano groups appended to the chiral centre differ considerably with the cyano group protruding more than the methyl, particularly when arranged so that it is located in a lateral position relative to the long axis, i.e., structures **40** and **42**. As a result the steric packing requirements of the various conformers will differ markedly. For instance, consider first conformer **41**; this structure is likely to be high energy, and therefore will not be represented to a great degree in the overall time averaged structure. Moreover, the two lateral substituents in structure **42** will have competing steric effects and thereby will tend to compensate for one another. If we

compare structures **41** and **40**, these can interconvert simply by rotation about the O–C_1 bond to give the steric bulk of the lateral group on the same side of the molecule. Furthermore, molecular modelling shows that structure **40** is the more stable configuration, which would be expected to lead to a low P_S, but because of the lateral methyl group would conversely support a tight pitch mesophase.

In this discussion we have only considered, so far, rotations about the C_1–O bond. However, it is also important to recognize that rotations about adjacent bonds could also play a significant part in determining phase morphology and properties. In the context of the two systems under investigation, we have also examined rotations about the O–phenyl bond and the effect on the relative energies of the conformers depicted in figure 2. However, in this particular case, the relative energy levels remain the same for the minimized structures. Therefore, although the minimum energy conformers produced by rotations about the O–phenyl bond may be important to the overall structure, they do not change the relative energies of the conformers described earlier. Rotations about other bonds peripheral to the cores are obviously of no importance in this case, i.e. methyl, cyano and hydrogen rotations are isotropic about the bond linking them to the asymmetric centre.

Finally, we note that these arguments would have to be modified accordingly to take into account dipolar and quadrupolar coupling of the dipoles in the system, particularly in the case of the nitrile group. Such an investigation would rely on a detailed understanding of the self-assembled nature of the mesophase. Our present studies are, however, confined to gas phase analysis, and therefore these models have reduced importance in the mesomorphic state. Rather they serve simply as an illustration of possible interactions in the liquid crystal state in order to aid interpretation of the data.

8. Conclusions

The chiral (*R*)-2-(4-substituted-phenoxy)propanonitriles discussed all display smectic A and chiral nematic phases; the chiral nematic phases are highly twisting and obey the modified Gray and McDonnell's rules [16] relating molecular structure to twist sense. The effect of different geometries and polarizabilities caused by modification to the liquid crystalline core is clearly evident in the transition temperatures of compounds **33**, **34** and **35**. The lateral fluoro-substituents demonstrate their value in being able to increase the inter-annular twist of the rigid core and in inducing a loss of either, or both, the anisotropy of geometry or polarizability; this is reflected in the depressions (or an increase in one case) in the transition temperatures of compounds **36**, **37** and **38**. However, the potential use of these compounds as thermochromic materials is limited because of their high mesophase thermal stability and the instability of the chiral centre towards racemization [14, 32]; additionally the materials proved to be poor ferroelectric dopants.

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[34] The results published were generated using the programs CHARMm and QUANTA. These programs have been developed by Molecular Simulations, Inc.