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Synthesis and mesomorphic behaviour of wedge-shaped nematic liquid crystals with flexoelectric properties

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The synthesis and mesomorphic behaviour of a series of wedge-shaped liquid crystals and some reference compounds are reported. These unusual liquid crystals possess smectic C, smectic A and nematic phases. These new wedge-shaped materials with a high degree of shape anisotropy and a large dipole moment can be used to induce an increase in the flexoelectric effects of nematic guest–host mixtures as dopants at low concentrations.

1. Introduction

The deformations or curvature strains that are known to take place in the nematic phase, splay, twist and bend, do not have a centre of symmetry. This means that, in principle, each of these deformations could be associated with a local polarization. However, the twist deformation is not connected with a localized polarisation of a medium, because there is always an axis of rotation perpendicular to the helix axis of the twist. The effect of this is that any polarization along the twist axis averages out to zero. It was postulated by R. B. Meyer that if, along with a permanent dipole moment, a molecule has a shape polarity then by introducing deformations into the director field a polarization of the bulk phase would follow and that this could be coupled to an applied electric field in a new kind of LCD [1]. It was further suggested that the molecules required to display this effect should be wedge-, pear- or banana-shaped molecules along with any intermediate forms. Wedge-shaped molecules in particular can efficiently pack to show a splay formation, see figure 1. Shape polarity, such as a wedge shape, leads to both a molecular order that fits the deformation and a preferred direction of the molecular dipole moment, which leads to a local polarization of the phase [1–4]. When wedge-shaped molecules align with the thick ends of the molecules in the direction of the splay the ensuing polarization orientates along the longitudinal part of the molecules, parallel to the director.

A combination of splay and bend deformations brings about a flexoelectric polarization of a nematic phase [1, 2]. The flexoelectric polarization, \mathbf{P} , in a nematic material can be represented as:

$$\mathbf{P} = e_{11}n(\nabla \cdot n) + e_{33}n(\nabla \times n)$$

where e_{11} and e_{33} are the flexoelectric coefficients associated with the splay and bend deformations and n is the nematic director. A range of sub-millisecond LCDs based on the flexoelectric effect in chiral nematic [5–8] and nematic liquid crystals [9–11] are being developed, which exhibit a range of advantageous properties for the next generation of LCDs, such as bistability, ultra fast switching, high contrast and recovery from direct mechanical distortion. However, one of the major constraints on the development of bistable nematic displays is the absence of liquid crystal

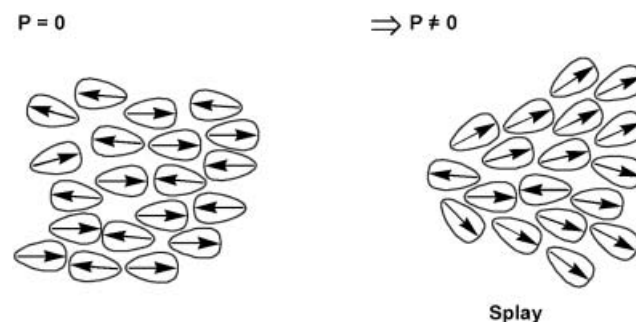


Figure 1. Schematic representation of the splay deformations that give rise to the flexoelectric effect for wedge-shaped molecules in a nematic phase.

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mixtures specifically designed and optimized for the flexoelectric effect.

The flexoelectric effect was measured using a standard room temperature nematic MBBA [12]. Unfortunately, many different values for the same compound, mostly MBBA and K15, have been reported. However, more reliable methods for measuring the flexoelectric coefficients have been reported in the meantime [13–18]. Surprisingly, only a few nematic liquid crystals have been specifically synthesized for use in bistable nematic LCDs based on the flexoelectric effects [19–21]. New nematic liquid crystals with large flexoelectric coefficients are required to facilitate the commercialization of this new class of ultra-fast LCD. A range of theoretical models attempt to correlate molecular structure to the flexoelectric effect [22–29]. However, these models differ in the relative emphasis they place on the importance of shape anisotropy as well as dipolar and quadrupolar effects. Therefore, there is no real guide to the design and synthesis of new flexoelectric nematic materials with the desired physical property spectrum for this new generation of ultra-fast bistable nematic LCDs. Some initial reports describe the flexoelectric coefficients of a swallow-tail mesogen with a wedge-like shape in an apolar nematic host [3, 4]. Therefore, we now report the synthesis of a series of wedge-shaped liquid crystals in order to investigate their mesomorphic behaviour and their flexoelectric properties.

2. Experimental

2.1. Synthesis

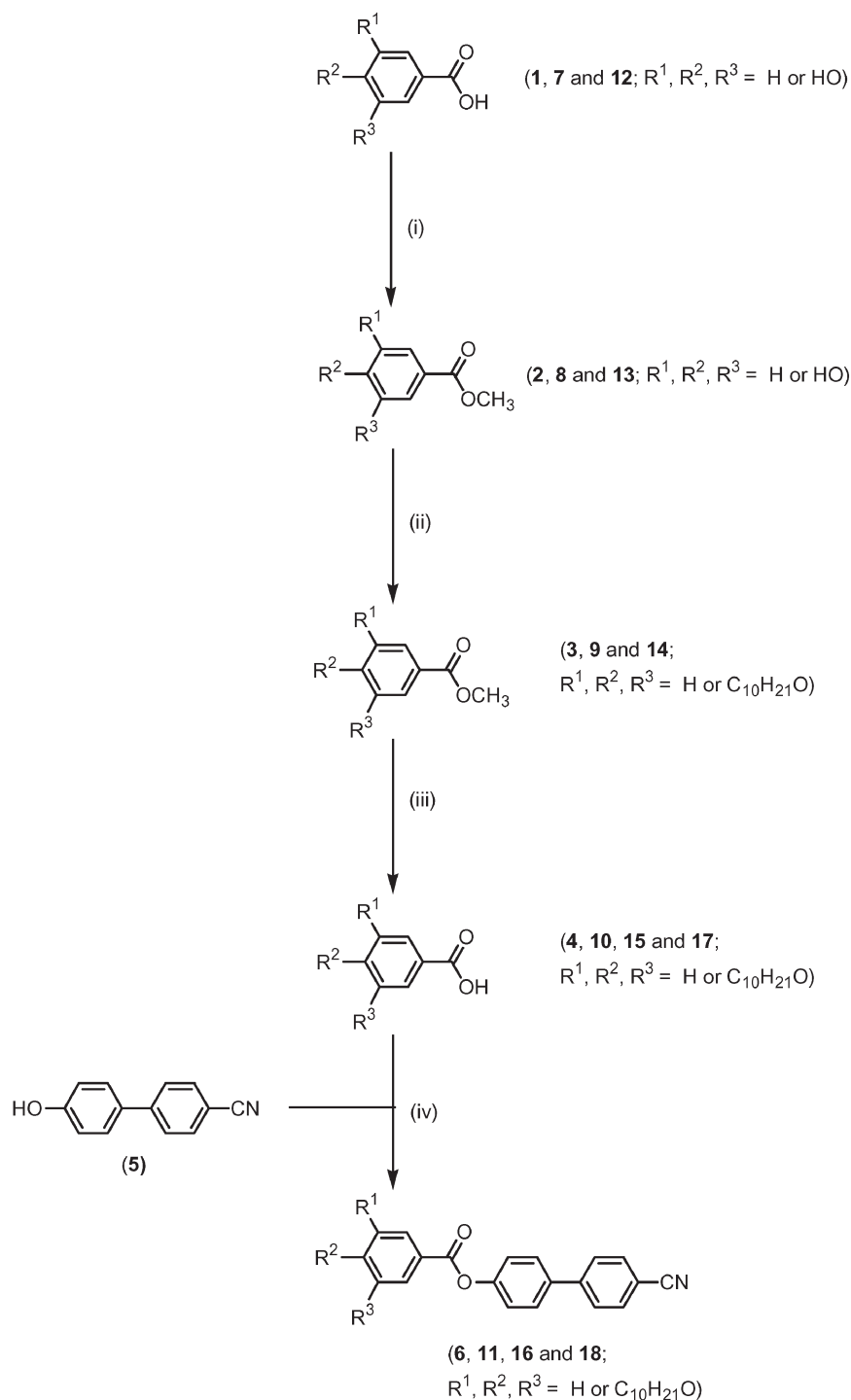
The method of synthesis of the model esters (**6**, **11**, **16**, **18**) is shown in scheme 1 and is based on modified literature procedures [30–39]. In order to produce the necessary alkoxy acids to synthesize final compounds (**6**, **11**, **16**) variously substituted esters (**2**, **8**, **13**) were prepared by the esterification of various commercially available, hydroxy-substituted benzoic acids (**1**, **7** and **12**) using methanol and concentrated sulphuric acid [30]. These methyl hydroxybenzoates were then alkylated using 1-bromodecane and potassium carbonate in a Williamson ether synthesis to produce the methyl esters (**3**, **9**, **14**) [30, 31]. The final stage of the alkoxy acid preparation is the saponification of the methyl esters (**3**, **9**, **14**) using a mixture of sodium hydroxide, water and ethanol to produce the corresponding sodium salt. This is converted to the acid using aqueous hydrochloric acid to yield the benzoic acids (**4**, **10**, **15**) [32–36]. The final products (**6**, **11**, **16**, **18**) were produced by the esterification of commercially available 4-cyano-4'-hydroxybiphenyl (**5**) with the decyloxybenzoic acids (**4**, **10**, **15**, **17**)

using *N,N*-dicyclohexylcarbodiimide (DCC) and *N,N*-dimethylaminopyridine (DMAP) [37–40].

The 4-decyloxybenzoic acid (**17**) was commercially available. The 4'-cyanobiphenyl-4-yl benzoates (**22**, **25**, **28**, **31**) were synthesized as shown in scheme 2. The various benzaldehydes (**20**, **23**, **26**, **29**) were synthesized using an esterification reaction using DCC [39], DMAP [40], commercially available 4-hydroxybenzaldehyde (**19**) and variously substituted decyloxybenzoic acids (**4**, **10**, **15**, **17**) [32–36]. These benzaldehydes were oxidized to form the corresponding benzoic acids (**21**, **24**, **27**, **30**) using Jones reagent (chromium trioxide, sulphuric acid, acetone and water) [32]. The 4'-cyanobiphenyl-4-yl benzoates (**22**, **25**, **28**, **31**) were produced via DCC/DMAP esterification from the 4-(decyloxybenzoyloxy)benzoic acids (**21**, **24**, **27**, **30**) and 4-cyano-4'-hydroxybiphenyl (**5**) [40]. The final compounds (**68–79**) were synthesized analogously with decyloxy acids being replaced by 4-methoxy to 4-dodecyloxy benzoic acids (**4**, **32–42**) and 3,4-hydroxybenzaldehyde (**43**) being utilized instead of 4-hydroxybenzaldehyde, see scheme 3. This produced the aldehydes (**44–55**), which were oxidized to the benzoic acids (**56–67**) [32]. Esterification with 4-cyano-4'-hydroxybiphenyl (**5**) as usual yielded the esters (**68–79**) [40]. The 4-cyanophenyl 3,4-di(4-decyloxybenzoyloxy)benzoate (**81**) was prepared in an analogous manner using 3,4-bis(4-decyloxybenzoyloxy)benzoic acid (**65**) and 4-cyanophenol (**80**) instead of 4-hydroxybenzaldehyde [41]. The synthesis of 4'-cyanobiphenyl-4-yl 3,4-di(4-pentylbenzoyloxy)benzoate (**85**) used 4-pentylbenzoic acid (**82**) to produce the aldehyde (**83**), which was oxidized to the benzoic acid (**84**) in a similar manner to that shown in scheme 3 [32]. Esterification of the benzoic acid (**84**) and 4-cyano-4'-hydroxybiphenyl (**5**) in the usual way yielded the ester (**85**). The synthesis of the ester (**89**) involves esterification of 4-decyloxybenzoic acid (**4**) with 3-hydroxybenzaldehyde (**86**) in the standard way shown in scheme 3 with Jones reagent to produce the aldehyde (**87**), followed by oxidation to produce the benzoic acid (**88**), which is esterified with 4-cyano-4'-hydroxybiphenyl (**5**) in the usual way to produce the desired final product (**89**).

2.2. Experimental Procedures

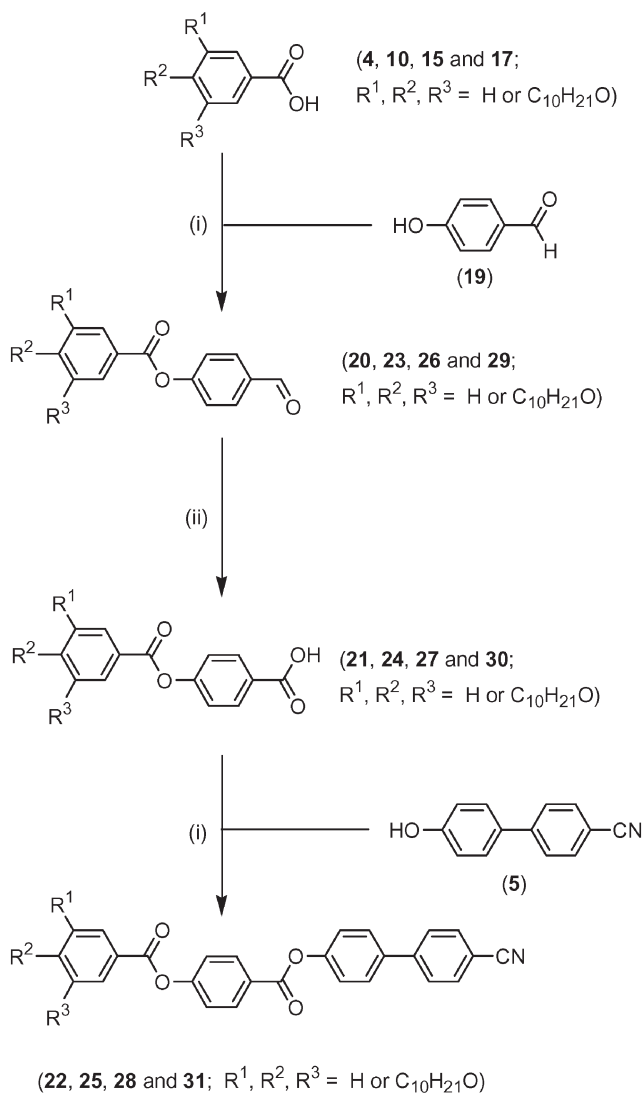
The synthesis, purification and characterization of the intermediates and final products are described in detail in the supplementary information. All commercially available starting materials, reagents and solvents were used as supplied, unless otherwise stated, and were obtained from Aldrich, Strem Chem. Inc., Acros or Lancaster Synthesis. Tetrahydrofuran was pre-dried with sodium wire, then distilled over sodium wire under



Scheme 1. Reagents and conditions: (i) CH_3OH , H_2SO_4 , (ii) $\text{C}_{10}\text{H}_{21}\text{Br}$, K_2CO_3 , $\text{CH}_3\text{COC}_2\text{H}_5$, (iii) a) KOH , H_2O , $\text{C}_2\text{H}_5\text{OH}$ b) HCl_{aq} , (iv) DCC , DMAP , CH_2Cl_2 . The first number for each intermediate and final compound refers to the 4-alkoxy-substituted derivative, the second number to the 3,4-dialkoxy-substituted derivative, the third number to the 3,5-dialkoxy-substituted derivative and the last number to the 3,4,5-trialkoxy-substituted derivative (see supplementary information).

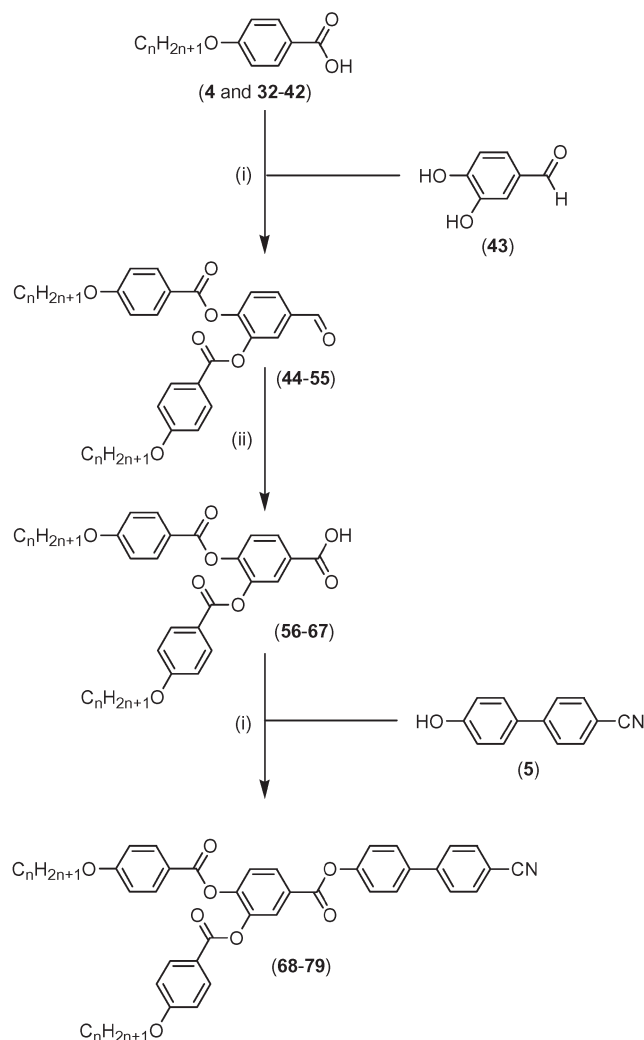
nitrogen with benzophenone indicator when required; it was not stored. All reactions were carried out using a dry nitrogen atmosphere unless water was

present as solvent or reagent and temperatures were measured externally. For compounds with $\text{RMM} < 800 \text{ g mol}^{-1}$, mass spectra were recorded using a



Scheme 2. Reagents and conditions: (i) DCC, DMAP, CH₂Cl₂, (ii) CrO₃, H₂SO₄, H₂O, CH₃COCH₃. The first number for each intermediate and final compound refers to the 4-alkoxy-substituted derivative, the second number to the 3,4-dialkoxy-substituted derivative, the third number to the 3,5-dialkoxy-substituted derivative and the last number to the 3,4,5-trialkoxy-substituted derivative (see supplementary information).

Gas Chromatography/Mass Spectrometer (GC/MS)-QP5050A Shimadzu with Electron Impact (EI) at a source temperature of 200°C. For compounds with RMM > 800 g mol⁻¹, mass spectra were analysed using a Bruker, reflex IV, matrix assisted laser desorption/ionization (MALDI), time of flight (TOF) MS. A 384 well microlitre plate format was used with a scout target. Samples were dissolved in DCM with HABA [2-(4-hydroxyphenylazo)benzoic acid] matrix (1:10 respectively). IR spectra were recorded using a Perkin-Elmer



Scheme 3. Reagents and conditions: (i) DCC, DMAP, CH₂Cl₂, (ii) CrO₃, H₂SO₄, H₂O, CH₃COCH₃.

Paragon 1000 Fourier transform-infrared (FTIR) spectrometer. ¹H NMR spectra were recorded using a JEOL Lambda 400 spectrometer and an internal standard of tetramethylsilane (TMS) was used. Aluminium backed TLC plates coated with silica gel (60 F254 Merck) were used to measure the progress of reactions. GC was carried out using a Chromopack CP3800 gas chromatograph equipped with a 10 m CP-SIL 5CB column. Purification of intermediates and final products was mainly accomplished by gravity column chromatography, using silica gel (40–63 microns, 60 Å) obtained from Fluorochem. The melting point and liquid crystal transition temperatures of the solids prepared were measured using a Linkam 350 hot stage and control unit in conjunction with a Nikon E400 polarizing microscope. The transition temperatures of all of the final products were confirmed using a Perkin-Elmer

DSC-7 and in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the reported value of the transition temperatures. Half-Cp-extrapolated was used to measure the value of the T_g . Thin layer chromatography (TLC), GC and elemental analysis, using a Fisons EA 1108 CHN, were employed to measure the purity of intermediates and final compounds.

The flexoelectric coefficients, e/k , are obtained from the field induced twist of a hybrid aligned nematic (HAN) cell of thickness d [42]. The nematic director is aligned homogeneously at one surface and homeotropically at the other surface, which produces a change of 90° in the director profile across the cell with a high degree of splay and bend distortion. This gives rise in turn to a flexoelectric field across the cell. A d.c. electric field, E , applied perpendicular to the splay–bend deformation, couples to the induced flexoelectric polarization resulting in a twist of the director in the plane perpendicular to the substrates. The twist angle ϕ , at the homeotropic surface, can be determined by the measurement of the degree of rotation of incident linearly polarized light. The flexoelectric coefficients are obtained by using the relationship $e/k = \pi\phi/Ed$. This method uses an in-plane electric field so that the results are not compromised by surface effects. Qinetiq provided test cells with an average cell gap of $50\ \mu\text{m}$. The flexoelectric coefficients were measured just below the nematic clearing point of the mixture ($0.98 \times T_{N-I}$ in K) to facilitate comparison at the same reduced temperature. The measurement error is 10% incorporating errors from both the gradient of ϕ versus E and the cell gap. A semiempirical hamiltonian (SEH) method, based on the Austin Model 1 function was utilized to calculate the dipole moment of the molecules [42]. The molecular conformations were minimized with respect to their energy using Cerius² Smart Minimizer. The molecular length a and breadth b , were measured using the resultant energy minimized structures.

2.3. Mesomorphic behaviour

The mesomorphic behaviour of the compounds collated in tables 1–5 were investigated between crossed polarizers using optical microscopy. Only the nematic phase (N), the smectic A phase (SmA) and the smectic C phase (SmC) were observed. Most of the compounds exhibit a nematic phase. Nematic droplets were observed on cooling from the isotropic liquid to form the schlieren texture with two- and four-point brushes characteristic of the nematic phase, along with optically extinct homeotropic areas. On cooling the sample further the texture often formed more optically extinct homeotropic areas, indicating that the phase is optically uniaxial. The birefringent and homeotropic areas flashed brightly on mechanical disturbance. This behaviour and the simultaneous presence of both the homeotropic and the schlieren textures, confirms that the mesophase observed is indeed a nematic phase. The SmA phase exhibited the focal-conic texture as well as optically extinct areas in the same sample. The simultaneous presence of these two textures is typical of the calamitic SmA phase or its chiral equivalent. The elliptical and hyperbolic lines of optical discontinuity characteristic of focal-conic defects were also observed. The focal conics develop dark bars across their backs on cooling into the SmC phase, and isotropic areas show a schlieren texture with only four-point brushes at this transition. The liquid crystal transition temperatures were confirmed by DSC, and good agreement ($\approx 1\text{--}2^\circ\text{C}$) with those determined by optical microscopy was obtained. The DSC values were determined twice in heating and cooling cycles on the same sample. The transition temperatures determined on separate samples of the same compounds were reproducible, and usually very little thermal degradation was observed even at relatively high temperatures. The baseline of the spectra was relatively flat, and sharp transition peaks were observed for each of the compounds studied.

Table 1. Transition temperatures ($^\circ\text{C}$) for the esters (**6** [37, 38], **11** [39], **16**, **18**).

Compound	R_1	R_2	R_3	Cr	SmA	N	I
6	H	$\text{C}_{10}\text{H}_{21}\text{O}$	H	• 97	•	222	• 224
11	$\text{C}_{10}\text{H}_{21}\text{O}$	$\text{C}_{10}\text{H}_{21}\text{O}$	H	• 131	•	143	—
16	$\text{C}_{10}\text{H}_{21}\text{O}$	H	$\text{C}_{10}\text{H}_{21}\text{O}$	• 84	—	—	•
18	$\text{C}_{10}\text{H}_{21}\text{O}$	$\text{C}_{10}\text{H}_{21}\text{O}$	$\text{C}_{10}\text{H}_{21}\text{O}$	• 83	—	—	•

3. Results and discussion

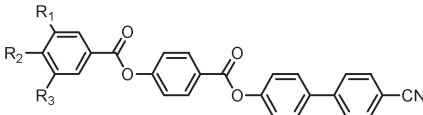
Several aromatic three-ring esters (**6**, **11**, **16**, **18**) incorporating either one, two or three decyloxy chains in position 3, 4 or 5 have been prepared, see table 1. The compound with one alkoxy chain in the 4-position (**6**), and consequently most linear geometry, exhibits a SmA and a N phase at high temperature [37, 38]. The presence of another alkoxy chain in the 3-position in compound (**11**) results in a depression of the clearing point and the complete suppression of the nematic phase [39]. The presence of an alkoxy chain in the 3- and 5-position, as in compounds (**16**, **18**), broadens the molecular shape dramatically resulting in the elimination of mesomorphic behaviour for these wedge-shaped compounds. Thus, it is evident from the thermal data collated in table 1 that broadening of this model system from a standard cigar to a wedge shape significantly decreases the tendency for mesophase formation.

The analogous aromatic four-ring di-esters to the compounds in table 1 have also been synthesized in an attempt to produce higher transition temperatures by increasing the molecular length, thereby increasing the length/breadth ratio, see table 2. The liquid crystal transition temperatures and mesophase temperature ranges of the four-ring di-esters (**22**, **25**, **28**, **31**) with an additional benzene ring are, as could have been expected, much higher than those of the corresponding mono-esters (**6**, **11**, **16**, **18**). This is due to the greater length/breadth ratio and the higher degree of molecular polarization and polarizability. However, only the compounds with either one or two adjacent alkoxy chains (**22** and **25**) exhibit mesomorphism, as is shown for the corresponding three ring compounds. This is probably due to steric effects. These materials should exhibit positive dielectric anisotropy due to the dipole moments associated with the ester and cyano groups directed along the molecular long axis. Therefore, an unusual feature of the thermal data given in table 2 is the SmC phase observed for the di-ester (**25**).

Compounds which exhibit the SmC phase are usually of low positive or negative dielectric anisotropy, often with dipole moments at the extremities of the molecular core and perpendicular to the molecular long axis [43].

The first five homologues (**68–72**) of the esters listed in table 3 are solely nematogens with a high clearing point. The next homologue, compound (**73**), has a monotropic SmC phase. Homologues with longer alkoxy chains exhibit higher smectic transition temperatures and the temperature range of their nematic phase is greatly reduced, up to compound (**79**) where the nematic phase is only present over a range of 1°C. The presence of a SmC phase is unexpected due to the large dipole moment associated with these molecules, i.e. they are of positive dielectric anisotropy. However, the large dipole moment is calculated to make an angle of 45° with the molecular axes and so has a large transverse component, which may contribute to the formation of a SmC phase. The wedge shape of these molecules will also pack efficiently into a tilted layer structure. The other significant feature of the thermal data collected in table 3 is the presence of an enantiotropic N phase for all of the homologues prepared. Figures 2 and 3 show possible conformations of compounds (**69** and **72**) produced by molecular modelling. As expected, the phenyl rings in the biphenyl moiety are not co-planar. Both compound (**69**) and compound (**72**) appear to adopt a wedge-shaped molecular conformation with a rod-like molecular core and an alkoxybenzoyloxy moiety as a large lateral substituent ($n=2$ and 5). This implies that space filling and not the length of the two alkoxy chains determines the molecular shape. This is a reasonable explanation considering the occurrence of microphase separation of the aliphatic chains and the aromatic cores. The presence of the alkoxybenzoyloxy moiety as a large lateral substituent in the compound (**77**) collated in table 3 results in a much lower clearing point compared with that of the analogous non-laterally-substituted

Table 2. Transition temperatures (°C) for the esters (**22**, **25**, **28**, **31**).



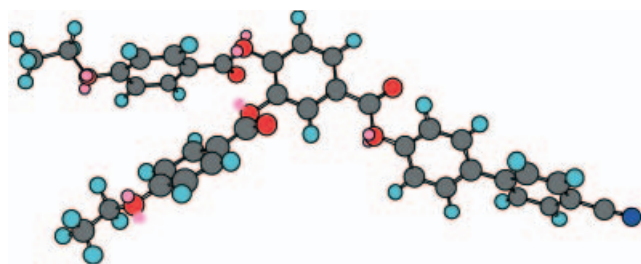
Compound	R_1	R_2	R_3	Cr	SmC	SmA	I
22	H	C ₁₀ H ₂₁ O	H	• 119	—	•	>300
25	C ₁₀ H ₂₁ O	C ₁₀ H ₂₁ O	H	• 140	• 183	—	•
28	C ₁₀ H ₂₁ O	H	C ₁₀ H ₂₁ O	• 131	—	—	•
31	C ₁₀ H ₂₁ O	C ₁₀ H ₂₁ O	C ₁₀ H ₂₁ O	• 118	—	—	•

Table 3. Transition temperatures ($^{\circ}\text{C}$) of the esters (**68–79**).

Compound	n	Cr	SmC	SmA	N	I
68	1	•	165	—	—	•
69	2	•	151	—	—	•
70	3	•	119	—	—	•
71	4	•	112	—	—	•
72	5	•	119	—	—	•
73	6	•	111	(• 103)	—	•
74	7	•	103	• 108	• 155	• 195
75	8	•	98	• 117	• 163	• 190
76	9	•	88	• 135	• 177	• 188
77	10	•	80	• 147	• 179	• 187
78	11	•	84	• 152	• 182	• 188
79	12	•	85	• 158	• 185	• 186

analogue (**22**) shown in table 2. A N phase is also induced for the compound (**77**) by the presence of the lateral substituent, as well as a lower transition temperature on heating the SmA phase, as expected. The melting point and nematic clearing of the various homologues (**68–79**) generally decrease as chain length increases, as would be expected, due to the increasing ratio of the flexible alkoxy chains.

In an attempt to obtain a wedge-shaped material with an enantiotropic nematic phase the compounds (**77** and **81**) were synthesized, see tables 3 and 4. Although the cyanophenyl ester with four phenyl rings (**81**) exhibits only a monotropic SmA phase [41] the cyanobiphenyl ester with five rings (**77**) exhibits a SmA, SmC and N phases at much higher transition temperatures. Compound (**77**) possesses exactly the order of mesophases (N, SmA, SmC) necessary for good alignment in a liquid crystal display device using smectic liquid crystals.

Figure 2. Molecular model representing compound (**69**).

In order to investigate the dependence of the transition temperatures on the presence of the two oxygen atoms next to the aromatic core, compound (**85**) was synthesized, with a methylene group (CH_2) in place of the oxygen atom present in compound (**71**). As can be seen from table 5, the presence of a pentyl chain rather than a butoxy chain induces an additional SmA phase as well as the N phase present for the butoxy homologue. The clearing point of the material is slightly lower than that of the butoxy homologue, as expected, due to the reduced degree of molecular polarizability.

Since it is thought, but not known, that materials that have either wedge- or banana-shaped geometry are needed to bring about flexoelectricity, compound (**89**) was synthesized. This represents a transition from the largely wedge-shaped materials to more banana-shaped ones. The lack of a side chain in the *para*-position suppresses any mesomorphic behaviour and compound (**89**) simply melts at 141°C to form the isotropic liquid.

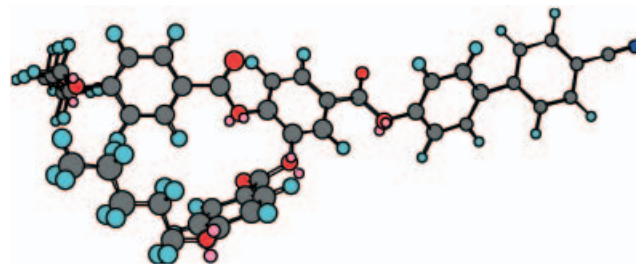
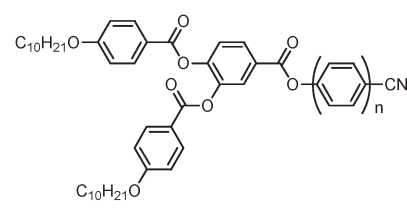
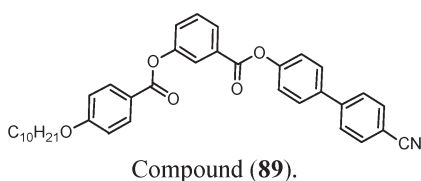
Figure 3. Molecular model representing compound (**72**).

Table 4. Transition temperatures (°C) of compounds (**77** and **81** [41]).


Compound	<i>n</i>	Cr	SmC	SmA	N	I	
81	1	•	106	—	(•	100)	•
77	2	•	80	•	147	•	179

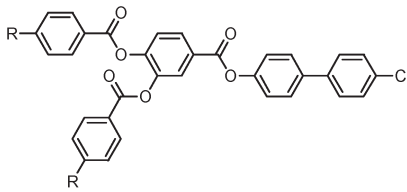
No monotropic phases could be observed on cooling before recrystallization occurred.



4. Physical properties

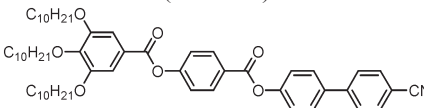
The flexoelectric coefficients of several of the compounds (**31**, **70**, **73**, **77** and **81**) as a dopant (3.4 mol wt%) in E7 are listed in table 6 [42]. No real trend can be observed for $(e_{11}+e_{33})/k$ for these compounds. The values for the flexoelectric coefficients are equivalent within experimental error for the mixtures containing compounds (**70**) and (**81**) despite the length-to-breadth ratio of these two compounds being quite different due to (**70**) being a biphenyl ester ($m=2$) and (**81**) a phenyl ester ($m=1$). There is a large increase in $(e_{11}+e_{33})/k$

between the mixtures containing compounds (**70**) and (**73**), which possess different chain lengths. The value for the mixture containing compound (**77**) is lower than that of the mixture containing compound (**73**). This suggests that the molecular organization is much more complex, taking into account the fact that the molecular packing of substituted benzonitriles in the nematic phase is characterized by antiparallel order and molecular interdigitation [44]. It is possible that antiparallel alignment of the polar end groups may lead to a quadrupolar charge distribution and, as a consequence, to a significant quadrupolar contribution to the flexoelectric effect [45]. However, compound (**77**) possesses long, flexible decyloxy chains, which may adopt any number of conformations, especially at high temperatures close to the clearing point. The dipole moment is seen to increase (5.6–6.2 D) as the chain length of the esters (**70**, **73**, **77**) increases. However, this trend is not reflected in the values of $(e_{11}+e_{33})/k$. The compounds (**31**, **70**, **73**, **77**, **81**) exhibit a very large net dipole moment with large lateral and longitudinal components, i.e. the dipole moment points at an angle of around 45° to the molecular long axis.

Table 5. Transition temperatures (°C) of compounds (**71** and **85**).


Compound	<i>R</i>	Cr	SmA	N	I
85	C ₅ H ₁₁	•	114	•	141
71	C ₄ H ₉ O	•	112	—	•

Table 6. Flexoelectric coefficients for various wedge-shaped compounds.

	Compound used as dopant	$e_{11}-e_{33}/k/\text{CN}^{-1}\text{m}^{-1}$
31	(100% E7) 	0.93 1.0
70	$n=3, m=2$	1.4
73	$n=6, m=2$	2.5
77	$n=10, m=2$	1.7
81	$n=10, m=1$	1.4

It is possible that the lack of a well defined analysis from this small group of compounds is a result of the direction of the molecular dipole. However, these values depend on many parameters, such as the length-to-breadth ratio, the magnitude and direction of the molecular dipole moment, and the conformation of the molecules and the complex interaction of the dopant with the host. The large flexoelectric effect associated with the nematic mixture E7 can be attributed to the molecular dimers known to be present in the N phase of liquid crystals with a terminal cyano group (-CN) and the large dipole moment associated the cyano group (4 D) [44]. The addition of the dopant may change the balance of the dimers and monomers making up E7. The observed results collated in table 6 may well be a combination of changes in the host and a large flexoelectric effect attributable to the dopant, i.e. a combination of dipolar and quadrupolar effects. This interpretation is consistent with previous findings using a swallow-tailed compound with a wedge shape, but without a terminal cyano group to induce a degree of molecular dimerization, where the effect on the flexoelectric coefficients was found to be small [3, 4]. Furthermore the host nematic compound for these experiments was 4-butyl-4'-methoxyazoxybenzene (BMAOB), which is an almost apolar host without a pronounced degree of molecular interdigitation and dimerization [3, 4]. Therefore, an exact interpretation of these results is difficult and requires a more detailed study. However, these initial results demonstrate clearly that relatively large increases in the magnitude of the flexoelectric coefficients of the guest-host mixture can be obtained by adding low concentrations of suitable wedge-shaped dopants with a large dipole moment.

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