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Liquid Crystals

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To cite this Article Aziz, Nayar , Kelly, Stephen M. , Duffy, Warren and Goulding, Mark(2008) 'Banana-shaped dopants for flexoelectric nematic mixtures', *Liquid Crystals*, 35: 11, 1279 – 1292

To link to this Article: DOI: 10.1080/02678290802522114

URL: <http://dx.doi.org/10.1080/02678290802522114>

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Banana-shaped dopants for flexoelectric nematic mixtures

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(Received 8 January 2008; final form 28 September 2008)

The synthesis is reported of new *meta*-substituted quaterphenyls and several related dimers as dopants for nematic mixtures with flexoelectric properties. The number and nature of the terminal substituents is varied from apolar with a small dipole moment to polar with a strong dipole moment. The number of methylene units in the flexible aliphatic spacer between the polyfluorinated aromatic groups of the dimers is also varied. Dimers capable of banana-shaped conformers induce an increase in the flexoelectric coefficients of mixtures containing them and reduce the clearing point to a small extent.

Keywords: banana-shaped dopant; flexoelectric nematic; quarterphenyl; dimer

1. Introduction

It was postulated almost four decades ago that, if a molecule has a shape polarity as well as a permanent dipole moment, then a polarisation of the bulk phase would be induced by introducing deformations into the director field and that this spontaneous polarisation could be coupled to an applied electric field in a new kind of LCD (1). It was suggested that the molecules required to display this effect should be wedge-, pear- or banana-shaped molecules rather than the classic rod-like or lath-like shape of calamitic nematic liquid crystals (1–4). The flexoelectric polarisation, \mathbf{P} , in a nematic phase can be represented as:

$$\mathbf{P} = e_1 \mathbf{n}(\nabla \cdot \mathbf{n}) + e_3 \mathbf{n} \times (\nabla \times \mathbf{n}), \quad (1)$$

where e_1 and e_3 are the flexoelectric coefficients associated with the splay and bend deformations and \mathbf{n} is the nematic director (5). Figure 1 illustrates schematically the flexoelectric effect for a banana-shaped molecule. A curvature strain, e.g. a bend deformation, gives a preferred molecular orientation and induces a spontaneous polarisation because of the associated molecular dipole.

Several different types of fast LCDs with sub-millisecond switching utilising the flexoelectric effect in the chiral nematic (5–8) or the nematic phase have been developed (9–11). Some of these LCDs exhibit a range of advantageous properties compared to those of standard commercial LCDs, such as bistability, ultra-fast switching, high optical contrast and, in some cases, recovery from direct mechanical distortion. The lack of commercial nematic or chiral nematic mixtures specifically designed and optimised for the flexoelectric effect is one of the major constraints on the develop-

ment of bistable nematic displays. The flexoelectric effect was measured initially using 4-methylbenzylidene-4'-butylaniline (MBBA), which is a standard calamitic compound with a nematic phase at room temperature (12). Therefore, there is a requirement for new nematic liquid crystals with large flexoelectric coefficients to facilitate the commercialisation of this new class of ultra-fast LCDs. Unfortunately, there are only a limited number of nematic liquid crystals that have been specifically synthesised for use in bistable nematic LCDs based on the flexoelectric effects (13–21). There is still no real guide to the design and synthesis of new flexoelectric nematic materials for bistable nematic LCDs.

A range of theoretical models has been developed in attempts to correlate molecular structure to the flexoelectric effect (22–30). These theories have been improved steadily, since the initial discovery of flexoelectricity, and become much more reliable over time. However, they differ in the relative emphasis they place on the importance of shape anisotropy as well as dipolar and quadrupolar effects. Helfrich, for example, uses Meyer's dipolar model to establish theoretical expressions for the flexoelectric coefficients and found that for a banana-shaped molecule $e_3 \Theta (b/a)^{2/3} \mu$, where a is the molecular length, b the molecular breadth, Θ the molecular bend angle and μ the transverse dipole moment (22). Prost and Marcerou used a quadrupolar model to explain the flexoelectric effect (24). Osipov invoked a mean field theory and postulates that dipolar effects are only significant in banana-shaped molecules with a transverse dipole moment and suggested that $e_3 \Theta \mu$, but also that it is proportional to a (25). Other authors use density functional theories (27). Ferrarini and

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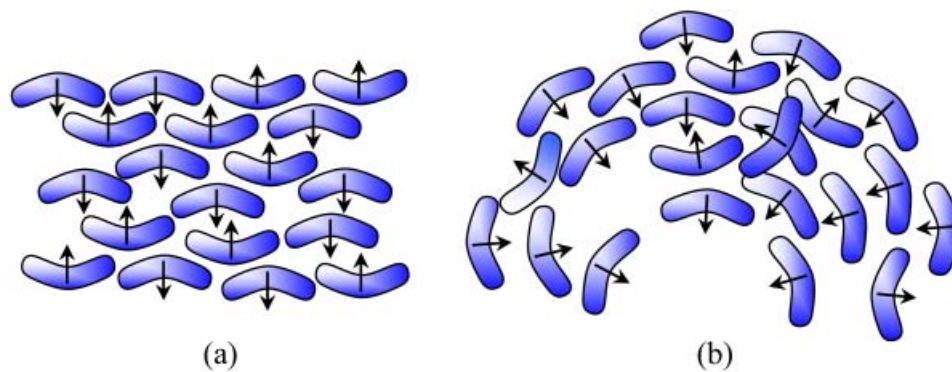


Figure 1. (a) Unstrained configuration for a nematic liquid crystal with polar banana shaped molecules; (b) Bend deformations couple to a non-zero polarisation.

colleagues use a combination of quantum mechanical calculations at a molecular level and molecular field and continuum elastic theories to relate the flexoelectric coefficients and molecular structure (29). A recent mean-field model appears to be successful in relating the dipolar and quadrupole contributions to the flexoelectric response to molecular structure (30). Therefore, a better understanding of the relationship between molecular structure of nematic liquid crystals and the flexoelectric coefficients would be scientifically interesting and possibly of significant commercial importance. Hence, the synthesis and evaluation of new materials to be used as dopants in flexoelectric mixtures could make a useful contribution to improving the degree of understanding of this property/structure relationship.

Initially, many different values of the flexoelectric coefficients for the same compound [mostly MBBA and 4-cyano-4'-pentylbiphenyl (5CB)] were reported. However, more reliable methods for measuring the flexoelectric coefficients have been developed in the meantime (30–39). For example, a domain wall method involving bulk torques has been used to measure the flexoelectric coefficients (3, 4, 31). A domain structure with a defined period is induced in a nematic phase by application of an electric field, which then allows e_1+e_3 to be calculated. A more common method involves applying an electric field across a hybrid aligned nematic (HAN) cell. This method has been used by many investigators to determine the magnitude of e_1+e_3 by measurement of the twist angle (32–37). For example, Sambles and co-workers used a fully-leaky guided mode optical waveguide method to study the flexoelectric effect of the nematic mixture E7 in HAN cells (36). Twisted nematic cells have been used recently in combination with analysis of conoscopic images to yield a value for e_1-e_3 of the nematic mixture E7 (38). Another new method developed to determine the flexoelectric coefficients is based on measuring the

electric current produced by periodic mechanical flexing of a nematic phase (39). However, the uniformly-lying helix (ULH) configuration is a relatively simple and reliable method for screening new compounds in chiral nematic mixtures for their efficacy in improving the flexoelectric response (6, 14–16). Therefore, we have chosen to use this method to evaluate the flexoelectric properties of nematic mixtures containing the new materials.

A large banana-shaped, bent-core compound consisting of five phenyl rings connected by four ester linking units has been reported to exhibit a giant flexoelectric effect due to its bent shape and large dipole moment (39). These recent findings confirm an earlier report of large flexoelectric effects obtained using a similar bent-core molecule consisting of five phenyl rings connected by a mixture of ester and imine linking groups as a dopant in a nematic mixture (18). The presence of a small amount (5 wt %) of the bent-core dopant was found to substantially increase (+30%) the flexoelectric ratio (e_1+e_3/K) of the host mixture (E7) as well as changing the sign of the combined flexoelectric coefficients. The so-called giant flexoelectric effect probably has an intermolecular origin, rather than an intramolecular one, and so its interpretation is complex. However, this type of bent-core compound is too large to be used in commercial flexoelectric nematic mixtures as it would induce a very large viscosity and slow response times in commercial LCDs based on the flexoelectric effect (5–11). Therefore, we now report the synthesis of a series of somewhat smaller bent-core molecules, but also with a banana-shape (see Figure 2), with four directly-linked phenyl rings, rather than five rings linked by carboxyl (ester) groups, to be used as dopants for nematic mixtures to increase their flexoelectric response. The *meta*-substituted quaterphenyl materials collated in Table 1 are rigid and consist of three phenyl rings in a linear configuration with *para*-substitution and a fourth phenyl ring

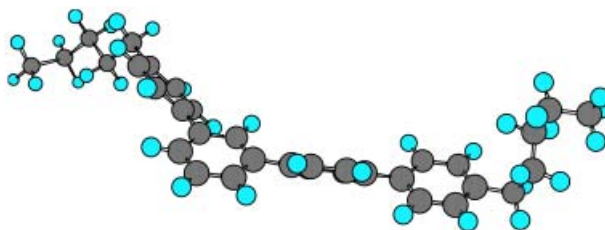


Figure 2. A model of the asymmetrical compound (9), as modelled using ChemDraw Pro 3D software.

Table 1. Chemical structures and melting points ($^{\circ}\text{C}$) of a series of quaterphenyls (9–17).

	Molecular structure	Cr	I
9		•	•
10		•	•
11		•	•
12		•	•
13		•	•
14		•	•
15		•	•
16		•	•
17		•	•

substituted in the *meta*-position giving rise to a bend in the molecular structure and two molecular axes. This substitution pattern allows the dielectric constants of this kind of compound to be varied, e.g. the dielectric constant perpendicular to the nematic director, ϵ_{\perp} , can be increased by incorporating fluoro- or cyano-substituents with a substantial dipole moment in a terminal, rather than a lateral, position in the molecular structure. The strongly nonlinear structure of these aromatic molecules means that they are biaxial with two effective length-to-width ratios. Both of the effective length-to-breadth ratios are relatively low and, consequently it is unlikely that liquid crystalline behaviour would be observed. However, these materials should enable some correlations between molecular structure and flexoelectric coefficients to be established.

Another approach to producing potential flexoelectric dopants with a banana shape consisting of four phenyl rings and incorporating a large dipole moment is to link two polyfluorinated biphenyl moieties together by an aliphatic spacer (13–17). Mixtures of such dimers exhibit a nematic phase with large flexoelectric coefficients (15–17). We report several dimers with odd or even spacers and three adjacent fluorine atoms on the terminal phenyl ring of the biphenyl core in an attempt to produce dopants with a large flexoelectric effect in host nematic mixtures. The dimers with an odd number of methylene units in the spacer are capable of exhibiting a banana shape and a large resultant dipole moment. However, recent results suggest that the presence of just one gauche conformation in the flexible spacer with an even number of methylene units between the aromatic groups can also result in a non-linear banana-shape and a large resultant flexoelectric polarisation (29). The presence of a low concentration (3–10 wt %) of a dopant has been shown to induce a flexoelectric effect up to six or seven times greater in magnitude than that of the host (18–21). Therefore, in order to facilitate comparisons between these results we chose to add a similar low concentration (8 wt %) of the new dopants to the host nematic mixture. A low concentration of the dopant may result in a modest increase in the viscosity of the resultant nematic guest host mixture and so give rise to short response times in

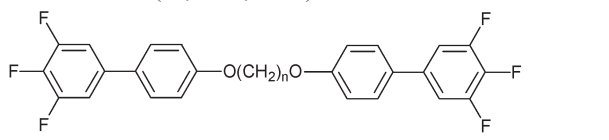
LCDs using them (5–11). The magnitude of the flexoelectric coefficients has also been shown to be dependent upon dopant concentration (21).

2. Experimental

Instrumentation

All commercially-available starting materials, reagents and solvents were used as supplied and were obtained from Aldrich, Strem Chem Inc, Acros or Lancaster Synthesis. All reactions were carried out using a dry nitrogen atmosphere and the temperatures were measured internally. Mass spectra were recorded using a gas chromatography/mass spectrometer (GC/MS)-QP5050A Shimadzu with electron impact (EI) at a source temperature of 200°C. The mass ion of the material is identified by M^+ . ^1H NMR spectra were recorded using a JEOL Lambda 400 spectrometer with an internal standard of tetramethylsilane (TMS). Purification of intermediates and final products was achieved by column chromatography, using silica gel (40–63 μm , 60 Å) obtained from Fluorochem, and recrystallisation from appropriate solvents. The melting point and other liquid crystal transition temperatures were measured using a Linkam 350 hot-stage and control unit in conjunction with a Nikon E400 polarising optical microscope. The melting points of the final products and the nematic clearing points of the guest–host nematic mixtures containing them as dopants were also determined using a Perkin-Elmer DSC-7 and in conjunction with a TAC 7/3 instrument controller, using the peak measurement for the value of the transition temperatures reported. The purity of the final quaterphenyl compounds was determined by elemental analysis using a Chromopack CP3800 gas chromatograph equipped with a 10m CP-SIL 5CB column. AM1 calculations were carried out with ChemDraw pro 3D MOPAC 2000. The physical property data given in Tables 2 and 3 were measured

Table 2. Chemical structure and melting points for a series of the dimers (32; $n=7, 9-12$).



n	Cr	I
7	•	104
9	•	69
10	•	112
11	•	67
12	•	101

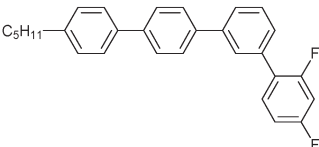
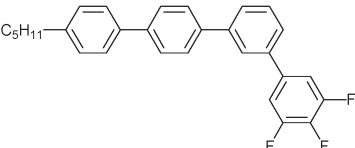
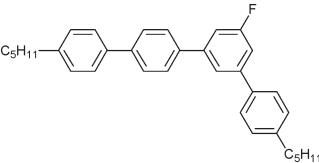
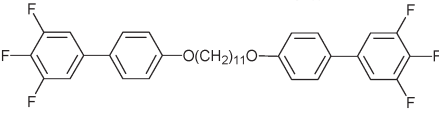
on instruments at Merck using standard techniques. The dielectric permittivity and elastic constant measurements were carried out using MLC-6437-000 as the host nematic mixture containing 8 wt % of the test materials as dopants. The flexoelectric measurements were then determined using the same mixtures with the addition of a small amount (1.8 wt %) of a standard chiral dopant A to the mixtures in order to produce a chiral nematic phase essential for measurement of flexoelectric coefficients using the UHL method (5–7). MLC-6437-000 is a multi-component nematic mixture from E. Merck. It is comprised mainly of polyfluorinated liquid crystals and is of positive dielectric anisotropy.

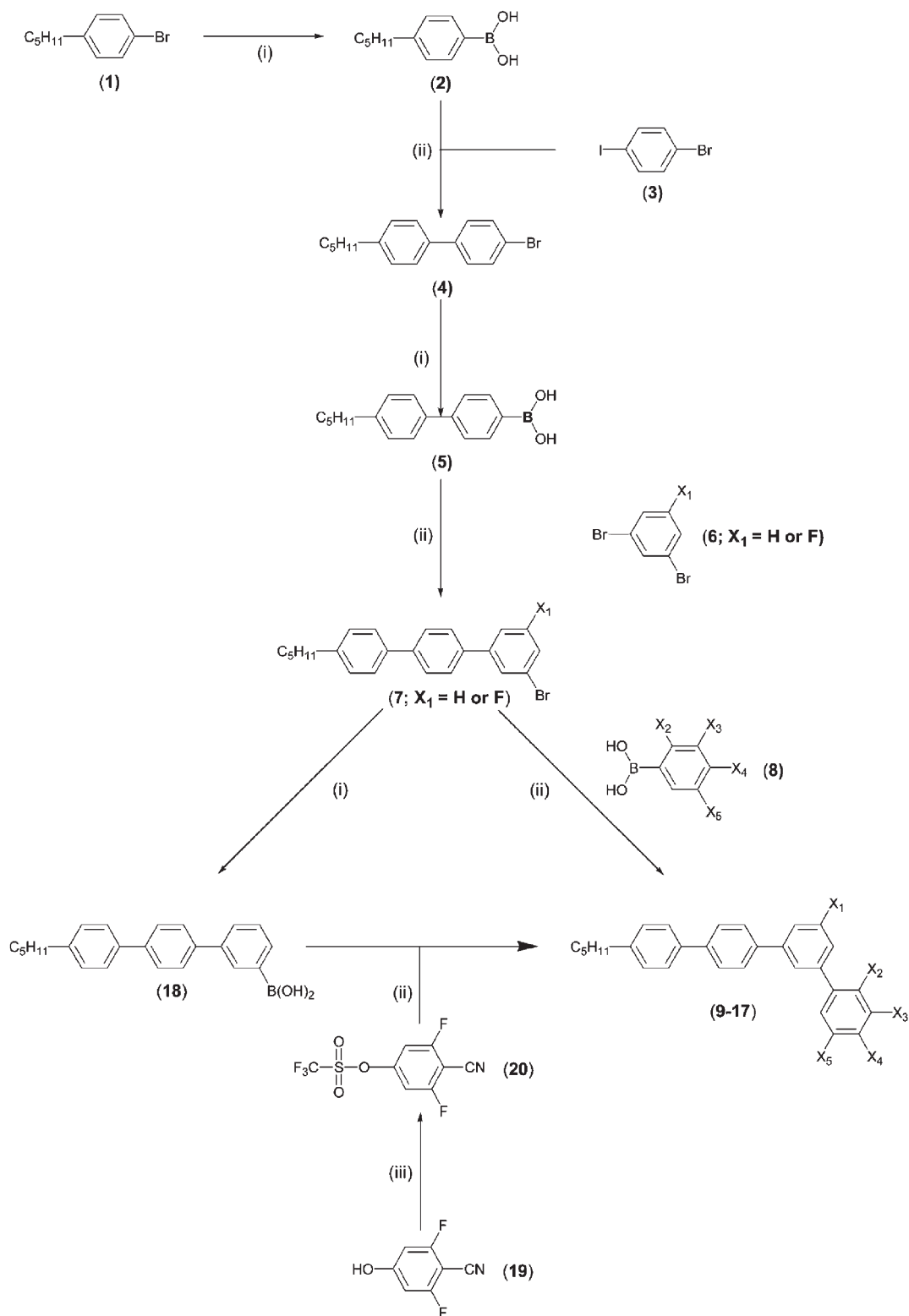
Synthesis

The series of substituted quaterphenyls (9–17) shown in Table 1 were synthesised using the procedures shown in Scheme 1. Commercially available 1-bromo-4-pentylbenzene (1) was converted into the corresponding phenyl boronic acid (2) using a standard procedure (40) and then reacted in a Suzuki aryl–aryl coupling reaction with 1-bromo-4-fluorobenzene (3) to form 4-bromo-4'-pentylbiphenyl (4) (41, 42), which was converted into the boronic acid (5) as usual (40). The 3-bromo-substituted terphenyls (7; $X_1=\text{H}$ or F) were synthesised by coupling the aryl boronic acid (5) with either 1,3-dibromobenzene (6; $X_1=\text{H}$) or 1,3-dibromo-5-fluorobenzene (6; $X_1=\text{F}$) (41, 42). A Suzuki aryl–aryl coupling reaction between the 3-bromo-substituted terphenyls (7; $X_1=\text{H}$ or F) and a number of substituted phenylboronic acids (8; $X_{2-5}=\text{H}$, F, CN or C_5H_{11}) yielded the desired final products (9–17). The bromo-terphenyl (7; $X_1=\text{H}$) was converted into the corresponding phenyl boronic acid (18) using the standard procedure (40). The final product (11) was synthesised by coupling the aryl boronic acid (18) with the triflate (20) produced from the corresponding phenol (19) in a standard way (43).

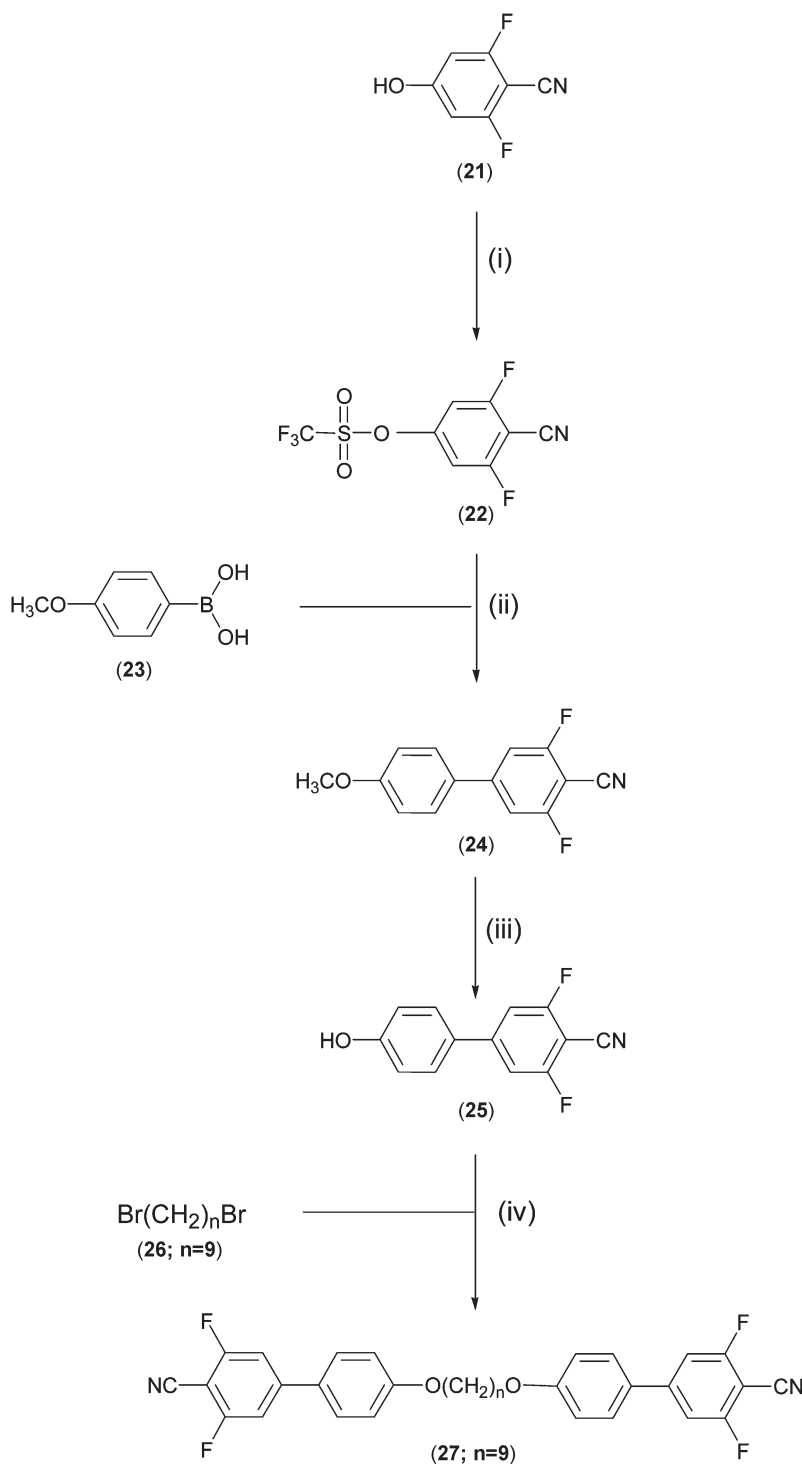
The 4-cyano-3,5-difluoro-substituted dimer (27; $n=9$) was synthesised as usual by the reaction of the 4-cyano-3,5-difluoro-4'-hydroxybiphenyl (25) and commercially-available α,ω -dibromoalkanes (26; $n=9$) utilising the Williamson ether synthesis shown in Scheme 2 (44). The triflate (22) was reacted in Suzuki aryl–aryl coupling reaction with the 4-methoxyphenylboronic acid (23) to synthesise 4-cyano-3,5-difluoro-4'-methoxybiphenyl (24) (41, 42). The aryl ether (24) was dealkylated using boron tribromide (45) at 0°C to produce the phenol (25), which was reacted in a Williamson alkylation reaction with 1,9-dibromononane (26; $n=9$) to produce the 4-cyano-3,5-difluoro-substituted dimer (27; $n=9$).

Table 3. Molecular structures, dielectric constants (ϵ_{\parallel} and ϵ_{\perp}), dielectric anisotropy ($\Delta\epsilon$), splay and bend elastic constants (k_1 and k_3), flexoelectric ratio (\bar{e}/κ), average flexoelectric coefficient (\bar{e}) and nematic clearing point (T_{N-I}) of the guest–host nematic mixtures incorporating 8 wt % of the quaterphenyls (**12–14**) and the dimer (**32**; $n=11$). The corresponding values for the host nematic mixture MLC6437-000 are given for comparison purposes.

Compound	ϵ_{\parallel}	ϵ_{\perp}	$\Delta\epsilon$	$k_1/10^{-12}\text{N}$	$k_3/10^{-12}\text{N}$	$\bar{e}/\kappa/\text{C m}^{-1}\text{N}^{-1}$	$\bar{e}/10^{-12}\text{C m}^{-1}$	$T_{N-I}/^{\circ}\text{C}$
MLC6437-000	25.55	7.45	18.1	8.33	10.33	0.34	3.2	67
	24.73	6.78	17.9	8.33	7.71	0.27	2.14	59
	24.04	7.04	17.0	8.31	8.57	0.31	2.64	60
	26.24	7.01	19.2	8.08	6.86	0.27	1.99	58
	24.24	6.93	17.3	8.47	8.46	0.39	3.31	65



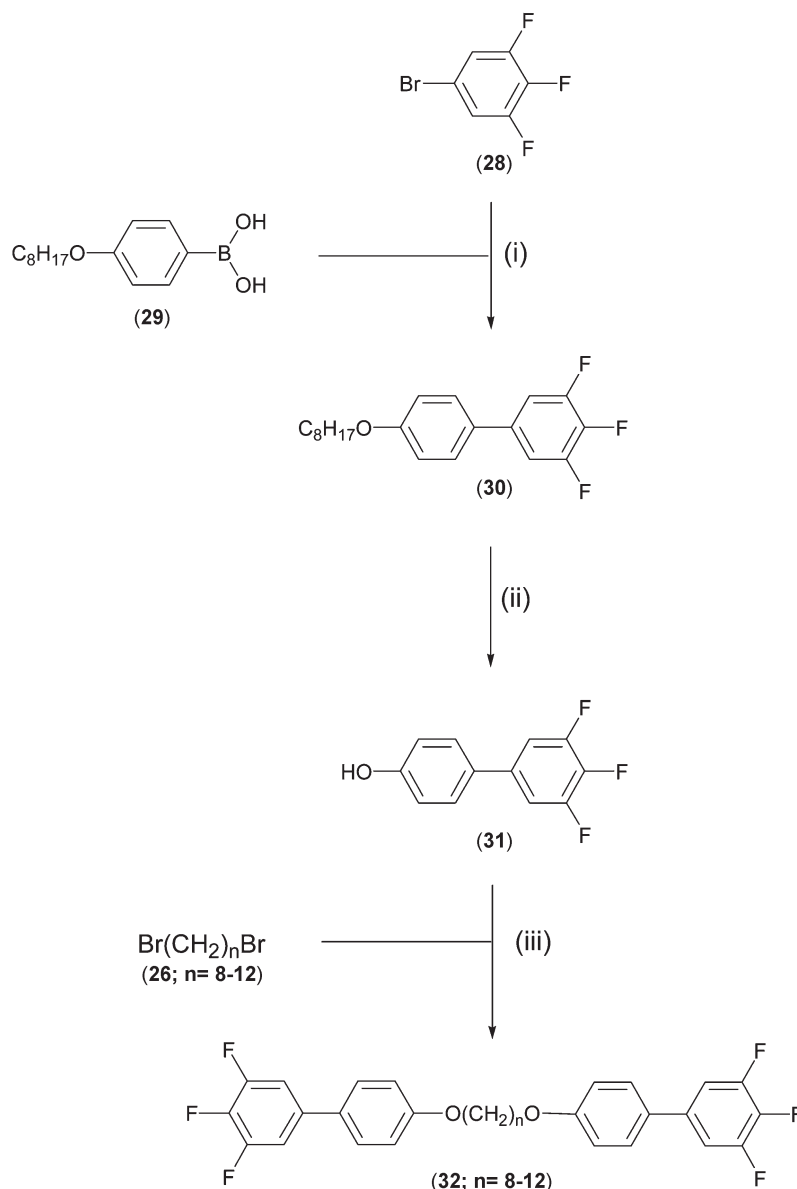
Scheme 1. Synthesis of substituted quaterphenyls (9–17). Reagents and conditions: (i) (a) *n*-butyllithium, THF, (−78°C), (b) $\text{B}(\text{OCH}_3)_3$, (c) HCl (aq); (ii) $(\text{PPh}_3)_4$, 2M Na_2CO_3 (aq), 1,2-dimethoxyethane (reflux); (iii) (a) trifluoromethanesulfonic acid anhydride, DCM, (b) 2,6-lutidine (0°C), (c) H_2O .



Scheme 2. Synthesis of the 4-cyano-3,5-difluoro-substituted dimer (**27**, $n=9$). Reagents and conditions: (i) (a) trifluoromethanesulfonic acid anhydride, DCM, (b) 2,6-lutidine (0°C), (c) H_2O ; (ii) (a) $\text{Pd}(\text{PPh}_3)_4$, 2M Na_2CO_3 (aq), 1,2-dimethoxyethane (reflux); (iii) (a) BBr_3 , CHCl_3 (0°C), (b) H_2O ; (iv) K_2CO_3 , butanone (reflux).

The 3,4,5-trifluoro-substituted dimers (**32**; $n=8-12$) were prepared in a similar fashion, as shown in Scheme 3. The 1-bromo-3,4,5-trifluorobenzene (**28**) was reacted in Suzuki aryl-aryl coupling reaction with

the 4-octyloxyphenylboronic acid (**29**) to synthesise 4-octyloxy-3',4',5'-trifluorobiphenyl (**30**) (*41*, *42*). The aryl ether (**30**) was dealkylated using boron tribromide (**45**) to produce 4-hydroxy-3',4',5'-trifluorobiphenyl



Scheme 3. Synthesis of the 3,4,5-trifluoro-substituted dimers (**32**, $n=8-12$). Reagents and conditions: (i) (a) trifluoromethanesulfonic acid anhydride, DCM, (b) 2,6-lutidine (0°C), (c) H_2O ; (ii) (a) $\text{Pd}(\text{PPh}_3)_4$, 2M Na_2CO_3 (aq), 1,2-dimethoxyethane (reflux); (iii) (a) BBr_3 , CHCl_3 (0°C), (b) H_2O ; (iv) K_2CO_3 , butanone (reflux).

(31), which was reacted in a Williamson alkylation reaction with α,ω -dibromoalkanes (**26**; $n=8-12$) to produce the dimers (**32**; $n=8-12$).

3''-Bromo-4-pentyl-[1,1',4',1'']-terphenyl (7; $X_1=H$).

Tetrakis(triphenylphosphine)palladium(0) (1.96 g, 1.69 mmol) and 4-pentylbiphenyl-4'-yl boronic acid (**5**) (5.00 g, 18.70 mmol) were added to 1,3-dibromobenzene (**6**; $X_1=H$) (4.00 g, 16.95 mmol), aqueous 2M sodium carbonate solution (20 cm^3), water and 1,2-dimethoxy ethane (70 cm^3). The mixture was heated under reflux overnight. The solution was allowed to

cool to room temperature and then poured into water. The organic phase was then extracted into diethyl ether ($3 \times 100\text{ cm}^3$) and the combined extracts were then washed with brine ($3 \times 100\text{ cm}^3$) and dried over MgSO_4 . The solvent was removed on a rotary evaporator and the residue purified by column chromatography using hexane and ethyl acetate (80:20) as the eluent and recrystallisation from ethanol to yield a white solid. Yield: 2.26 g, 36%; m.p. 117°C . ^1H NMR (CDCl_3): δ 0.90 (t, 3H, $J=7.00\text{ Hz}$), 1.34 (sext, 2H), 1.36 (quint, 2H), 1.65 (quint, 2H), 2.65 (t, 2H, $J=7.86\text{ Hz}$), 7.27 (d, 2H, $J=8.12\text{ Hz}$), 7.33 (d, 2H, $J=7.88$), 7.48 (d, 1H,

$J=8.44$ Hz), 7.56 (d, 2H, $J=8.12$ Hz), 7.62 (d 2H, $J=8.44$ Hz), 7.65 (d, 2H, $J=8.72$ Hz), 7.78 (t, 1H, $J=1.82$ Hz). IR ($\nu_{\max}/\text{cm}^{-1}$): 2920, 2854, 2230, 1565, 1503, 1078, 836, 684. MS m/z : 380 (M^+), 321 (M100), 241. Elemental analysis: calculated, C 72.82, H 6.11; found, C 73.06, H 6.36%.

4,4'''-Dipentyl-[1,1';4',1'';3'',1''']-quaterphenyl (9).

Tetrakis(triphenylphosphine)palladium(0) (0.12 g, 0.11 mmol) and 4-pentylphenylboronic acid (**8**; $X_2=X_3=X_5=H$; $X_4=C_5H_{11}$) (0.24 g, 1.27 mmol) were added to 3''-bromo-4-pentyl-[1,1',4',1'']-terphenyl (**7**; $X_1=H$) (0.40 g, 1.10 mmol), aqueous 2M sodium carbonate solution (10 cm^3), water and 1,2-dimethoxy ethane (30 cm^3). The mixture was heated under reflux overnight. The solution was allowed to cool to room temperature and then poured into water. The organic phase was then extracted into diethyl ether (3 \times 50 cm^3) and the combined extracts were then washed with brine (3 \times 50 cm^3) and dried over MgSO_4 . The solvent was removed on a rotary evaporator and the residue purified by column chromatography using hexane as the eluent and recrystallisation from ethanol to yield a white solid. Yield: 0.27 g, 48%; m.p. 148°C. ^1H NMR (CDCl_3): δ 0.91 (t, 6H, $J=7.00$ Hz), 1.34 (sext, 4H), 1.36 (quint, 4H), 1.65 (quint, 4H), 2.65 (t, 4H, $J=7.30$ Hz), 7.29 (d, 4H, $J=8.30$ Hz), 7.53 (d, 2H, $J=7.66$ Hz), 7.59 (dd, 4H), 7.72 (d, 2H, $J=8.72$ Hz), 7.73 (d 2H, $J=8.68$ Hz), 7.51 (s, 1H), 7.87 (t, 1H, $J=1.68$ Hz). IR ($\nu_{\max}/\text{cm}^{-1}$): 2924, 2856, 1500, 1475, 1004, 696. MS m/z : 446 (M^+), 389 (M100), 332, 165. Elemental analysis: calculated, C 91.47, H 8.52; found, C 91.47, H 8.79%.

3''-Bromo-5''-fluoro-4-pentyl-[1,1',4',1'']-terphenyl (7; $X_1=F$).

Tetrakis(triphenylphosphine)palladium(0) (0.91 g, 0.79 mmol) and 4-pentylbiphenyl-4'-ylboronic acid (**5**) (2.53 g, 9.45 mmol) were added to 1,3-dibromo-5-fluorobenzene (**6**; $X_1=F$) (2.00 g, 7.88 mmol), aqueous 2M sodium carbonate solution (20 cm^3), water and 1,2-dimethoxy ethane (60 cm^3). The mixture was heated under reflux overnight. The solution was allowed to cool to room temperature and then poured into water. The organic phase was then extracted into diethyl ether (3 \times 50 cm^3) and the combined extracts were then washed with brine (3 \times 50 cm^3) and dried over MgSO_4 . The solvent was removed on a rotary evaporator and the residue purified by column chromatography using hexane as the eluent and recrystallisation from ethanol to yield a white solid. Yield: 1.40 g, 45%; m.p. 79°C. ^1H NMR (CDCl_3): δ 0.91 (t, 3H, $J=6.74$ Hz), 1.34 (sext, 2H), 1.35 (quint,

2H), 1.64 (quint, 2H), 2.64 (t, 2H, $J=7.60$ Hz), 7.20 (t, 1H, $J=2.24$ Hz), 7.24 (t, 1H, $J=2.24$ Hz), 7.28 (d, 2H, $J=8.12$ Hz), 7.55 (d, 2H, $J=8.12$ Hz), 7.58 (d 2H, $J=7.56$ Hz), 7.62 (s, 1H), 7.67 (d, 2H, $J=8.12$ Hz). IR ($\nu_{\max}/\text{cm}^{-1}$): 2928, 2855, 2230, 1618, 1564, 1488, 1263, 1106, 1121, 901, 883, 812, 745. MS m/z : 398 (M^+), 341 (M100). Elemental analysis: calculated, C 69.34, H 5.52; found, C 69.61, H 5.69%.

3''-Boronic acid-4-pentyl-[1,1',4',1'']-terphenyl (18).

A solution of *n*-butyllithium in hexane (1.26 cm^3 , 2.5M, 3.16 mmol) was added dropwise to a stirred solution of 3''-bromo-4-pentyl-[1,1',4',1'']-terphenyl (**7**; $X_1=H$) (1.00 g, 2.60 mmol) in THF (70 cm^3) at -78°C . Trimethyl borate (0.82 g, 7.91 mmol) was then added dropwise over a period of 30 min. The reaction mixture was stirred and allowed to warm to room temperature overnight. The reaction mixture was then stirred with 20% hydrochloric acid (100 cm^3) and then extracted with diethyl ether (2 \times 100 cm^3). The combined extracts were washed with water (2 \times 100 cm^3) and dried over MgSO_4 . The solvent was removed under reduced pressure to yield a white solid. Yield: 0.62 g, 69%; m.p. 117°C. The raw product was used in the next step without further purification.

4-Cyano-3,5-difluorobenzenesulfonic acid trifluoromethyl ester (22).

A solution of trifluoromethanesulfonic acid anhydride (8.736 g, 0.0309 mol) in dichloromethane (60 cm^3) was added dropwise to stirred mixture of 2,6-difluoro-4-hydroxybenzoxonitrile (**21**) (2 g, 0.0129 mol) and 2,6-lutidine (3.32 g, 0.030 mol) in dichloromethane (30 cm^3) at 0°C . The reaction mixture was allowed to warm to room temperature, stirred for five hours, added to water (200 cm^3) and the product extracted into dichloromethane (3 \times 50 cm^3). The combined organic layers were washed with 10% aqueous solution of sodium carbonate (2 \times 100 cm^3) and then dried over MgSO_4 . The solvent was removed on a rotary evaporator and the residue purified by column chromatography using hexane and dichloromethane (20:80) as the eluent. The product was used without further purification. Yield: 5.6 g, 86.4%; m.p. 40°C. ^1H NMR (CDCl_3): δ 7.90 (d, 2H). IR ($\nu_{\max}/\text{cm}^{-1}$): 1476, 1432, 1212, 1126, 954, 836, 801. MS m/z : 287 (M^+), 223 (M100), 138.

4-Cyano-3,5-difluoro-4'-methoxybiphenyl (24).

Tetrakis(triphenylphosphine)palladium(0) (2.01 g, 1.74 mmol) and 4-methoxyphenylboronic acid (**23**)

(3.18 g, 20.90 mmol) were added to a mixture of 4-cyano-3,5-difluorobenzene-sulfonic acid trifluoromethyl ester (**22**) (5 g, 17.42 mmol), aqueous 2M sodium carbonate solution (10 cm³), water and 1,2-dimethoxyethane (70 cm³). The resultant mixture was heated under reflux overnight, allowed to cool to room temperature and then poured into water. The organic phase was then extracted into diethyl ether (3 × 50 cm³) and the combined extracts were then washed with brine (3 × 50 cm³) and dried over MgSO₄. The solvent was removed on a rotary evaporator and the residue purified by column chromatography using hexane and ethyl acetate (80:20) as the eluent and recrystallisation from ethanol to yield a white solid. Yield: 2.30 g, 45%; m.p. 222°C. ¹H NMR (CDCl₃): δ 3.87 (s, 3H), 7.03 (d, 2H, *J*=8.16 Hz), 7.27 (d, 2H, *J*=10.00 Hz), 7.56 (d, 2H, *J*=9.00 Hz). IR (ν_{max}/cm⁻¹): 2943, 2233, 1630, 1604, 1562, 1439, 1178, 1025, 817, 588. MS *m/z*: 245 (M⁺), 230 (M100), 202, 176. Elemental analysis: calculated, C 68.57, H 3.67, N 5.71; found, C 68.81, H 3.64, N 5.72%.

4-Cyano-3,5-difluoro-4'-hydroxybiphenyl (**25**).

Boron tribromide (1M solution in chloroform, 2 cm³, 17.85 mmol) was added dropwise to stirred solution of 4-cyano-3,5-difluoro-4'-methoxybiphenyl (**24**) (1.75 g, 7.14 mmol) at 0°C. The temperature was allowed to rise to room temperature overnight and the solution added to ice water (200 cm³) with vigorous stirring. The product was extracted into diethyl ether (2 × 200 cm³), washed with aqueous sodium carbonate (2M, 150 cm³), dried over MgSO₄, evaporated down and the residue purified by column chromatography to yield a white solid. Yield: 1.43 g, 87%; m.p. 222°C. ¹H NMR (CDCl₃): δ 6.89 (d, 2H, *J*=8.68 Hz), 7.71 (d, 4H, *J*=8.68 Hz), 10.20 (s, 1H). IR (ν_{max}/cm⁻¹): 2928, 2855, 2230, 1618, 1564, 1488, 1263, 1106, 1121, 901, 883, 812, 745. MS *m/z*: 231 (M⁺), 202 (M100), 176. Elemental analysis: calculated, C 67.53, H 3.03, N 6.06; found, C 67.66, H 2.88, N 6.17%.

Bis(4-cyano-3,5-difluorobiphenyl-4'-oxy)nonane (**27**; *n*=9).

The 4-cyano-3,5-difluoro-4'-hydroxybiphenyl (**25**) (0.25 g, 1.08 mmol), 1,9-dibromononane (**26**; *n*=9) (0.12 g, 0.42 mmol) and potassium carbonate (0.52 g, 3.80 mmol) in butanone (15 cm³) was heated at 100°C for 3 h. Excess potassium carbonate was filtered off and precipitated product rinsed through with DCM (3 × 20 cm³). The solution was concentrated on to silica gel for purification by column chromatography using

hexane and ethyl acetate (90:10) as the eluent and recrystallisation from ethanol. Yield: 0.38 g, 33%; m.p. 67°C. ¹H NMR (CDCl₃): δ 1.35 (quint, 10H), 1.75 (quint, 4H), 3.94 (t, 4H, *J*=9.52 Hz), 6.92 (d, 4H, *J*=9.00 Hz), 7.14 (d, 4H, *J*=9.00 Hz), 7.44 (d, 4H, *J*=8.68 Hz). IR (ν_{max}/cm⁻¹): 2927, 2235, 1603, 1560, 1437, 1173, 1037, 619. MS *m/z*: 586 (M⁺), 231 (M100), 165, 143. Elemental analysis: calculated, C 71.67, H 5.11, N 4.77; found, C 71.83, H 5.26, N 4.73%.

4-Octyloxy-3',4',5'-trifluorobiphenyl (**30**).

Tetrakis(triphenylphosphine)palladium(0) (2.54 g, 2.20 mmol) and 4-octyloxyphenyl-boronic acid (**29**) (6.60 g, 26.43 mmol) were added to 1-bromo-3,4,5-trifluorobenzene (**28**) (4.67 g, 22.02 mmol), aqueous 2M sodium carbonate solution (20 cm³), water and 1,2-dimethoxyethane (70 cm³). The mixture was heated under reflux overnight. The solution was allowed to cool to room temperature and then poured into water. The organic phase was then extracted into diethyl ether (3 × 100 cm³) and the combined extracts were then washed with brine (3 × 100 cm³) and dried over MgSO₄. The solvent was removed on a rotary evaporator and the residue purified by column chromatography using hexane and ethyl acetate (80:20) as the eluent and recrystallisation from ethanol to yield a white solid. Yield: 7.28 g, 98%; m.p. 35°C. ¹H NMR (CDCl₃): δ 0.90 (t, 3H, *J*=6.72 Hz), 1.31 (quint, 8H), 1.47 (sext, 2H), 1.80 (quint, 2H), 3.98 (t, 2H, *J*=6.76 Hz), 6.96 (d, 2H, *J*=8.72 Hz), 7.14 (m, 2H), 7.42 (d, 2H, *J*=8.72 Hz). IR (ν_{max}/cm⁻¹): 2922, 2852, 1608, 1509, 1246, 1042, 855, 761. MS *m/z*: 336 (M⁺), 224 (M100). Elemental analysis: calculated, C 90.75, H 9.25; found, C 90.77, H 9.00%.

4-Hydroxy-3',4',5'-trifluorobiphenyl (**31**).

Boron tribromide (1M solution in chloroform, 4 cm³, 44.60 mmol) was added dropwise to stirred solution of 4-octyloxy-3',4',5'-trifluorobiphenyl (**30**) (6.00 g, 17.84 mmol) at 0°C. The temperature was allowed to rise to room temperature overnight and the solution added to ice water (200 cm³) with vigorous stirring. The product was extracted into diethyl ether (2 × 200 cm³), washed with aqueous sodium carbonate (2M, 150 cm³), dried over MgSO₄ and purified by column chromatography using hexane and ethyl acetate (80:20) as eluent to yield a white solid. Yield: 2.91 g, 73%; m.p. 237°C. ¹H NMR (CDCl₃): δ 4.90 (s, 1H), 6.91 (d, 2H, *J*=8.40 Hz), 7.12 (t, 2H, *J*=7.96 Hz), 7.38 (dd, 2H, *J*=8.44 Hz). IR (ν_{max}/cm⁻¹): 2928, 2855, 2230, 1618, 1564, 1488, 1263, 1106, 1121, 901, 883, 812, 745. MS *m/z*: 224 (M⁺), 195 (M100), 169. Elemental analysis: calculated, C 67.53, H 3.03; found, C 67.21, H 2.95%.

Bis(3,4,5'-trifluorobiphenyl-4'-oxy)heptane (**32**; $n=7$).

A mixture of 4-hydroxy-3',4',5'-trifluorobiphenyl (**31**) (0.38 g, 2.12 mmol), 1,7-dibromoheptane (**26**; $n=7$) (0.25 g, 0.97 mmol) and potassium carbonate (1.12 g, 8.50 mmol) in butanone (15 cm³) was heated at 100°C for 3 h. Excess potassium carbonate was filtered off and precipitated product rinsed through with DCM (3 × 20 cm³). The solution was concentrated on to silica gel for purification by column chromatography using silica gel and hexane ethyl acetate (90:10) as the eluent and recrystallisation from ethanol. Yield: 0.22 g, 42%; m.p. 104°C. ¹H NMR (CDCl₃): δ 1.50 (quint, 6H), 1.81 (quint, 4H), 4.00 (t, 4H, $J=6.44$ Hz), 6.96 (d, 4H, $J=9.00$ Hz), 7.18 (m, 4H), 7.44 (d, 4H, $J=8.72$ Hz). IR ($\nu_{\max}/\text{cm}^{-1}$): 2934, 2855, 1608, 1505, 1240, 809, 757, 629. MS m/z : 544(M⁺), 351(M100). Elemental analysis: calculated, C 68.38, H 4.77; found, C 68.61, H 4.72%.

Mesomorphic properties

The melting point of the quaterphenyls (**9–17**) and dimers (**32**; $n=7$, 9–12) recorded in Tables 1 and 2 and the nematic clearing point of the nematic mixtures containing them were determined using polarising optical microscopy (POM). A nematic (N) phase was observed for all of the guest–host mixtures containing the quaterphenyls (**9–17**) and dimers (**32**; $n=7$, **9–12**) as dopants. A Schlieren texture with 2-brush and 4-brush disclinations is seen for the nematic phase between crossed polarisers in an optical microscope. Small droplets are seen on cooling slowly from the isotropic phase, which then coalesce to form the Schlieren texture of the nematic phase with two and four point brushes. The nematic mixtures exhibit a significant biphasic region consisting of co-existing nematic and isotropic regions. The clearing point quoted (T_{N-I}) in Table 3 is that measured half-way between the onset of the biphasic region and the complete disappearance of the nematic phase. The quaterphenyls (**9–17**) and dimers (**32**; $n=7$, 9–12) did not exhibit any observable mesomorphism.

Physical properties

The flexoelastic ratio (\bar{e}/κ) was determined using a standard procedure in UHL cells (6, 7). The flexoelastic ratio and the splay and bend elastic constants (k_1 and k_3) collated in Tables 3 were measured just below the nematic clearing point ($0.9T_{N-I}$ in K) of the mixture. A chiral additive was employed as a second dopant (1.8 wt %) in the test nematic mixture made up of 8 wt % of each material to be tested dissolved in the host nematic mixture (MLC-6437-000). The presence of

such a small amount of the chiral dopant was assumed to have little effect on the elastic, dielectric and flexoelectric properties of the nematic mixture. The pitch length, P_0 , of the doped chiral nematic mixtures was measured using the Cano-wedge technique below the nematic clearing point ($0.9T_{N-I}$ in K) of the mixtures. The flexoelectric effect was observed in 4.35 to 5 μm spaced glass cells treated with rubbed polyimide for planar alignment. The samples were examined on a hot stage held on the rotating sample stage of a polarising microscope (Olympus BX 51). Transparent ITO electrodes on the inner walls of the cells made it possible to apply an electric field across the sample. The wave forms were generated using a Wave Tek Arbitrary Wave form Generator 75. The applied fields were either square-waves and could be varied in amplitude from zero to 15 V μm⁻¹. The flexoelectro-optical effect was best observed with the chiral nematic helix perpendicular to both the applied field and the viewing direction, that is, with the uniformly-lying helix (ULH) form of the focal conic texture in the plane of the cell. The optic axis of the test chiral nematic sample is also in the plane of the cell. This alignment was obtained by applying a low voltage across the cell, while unidirectionally shearing the cell. The shearing promotes the uniform alignment of the disordered focal conic texture with the helical axis and the optic axis in the plane of the cell. The rotation angles of the optic axis, ϕ , were evaluated by placing the sample between crossed polarisers and measuring the half angle between the two extinction positions. The relationship between $\tan \phi$ and E shows a linear response at low fields over the reduced temperature ranges in each case as expected. The rotation of optic axis through an angle, ϕ , induced by flexoelectric coupling (ϕ) is related to the natural helical pitch of the phase as in the equation below:

$$\tan \phi = \bar{e}P_0E/2\pi\kappa, \quad (2)$$

where $\bar{e}=(e_1+e_3)/2$ is the average flexoelectric coefficient, P_0 is the pitch of the chiral nematic phase, E is the applied electric field and $\kappa=(k_1+k_3)/2$ is the average elastic constant, where k_1 and k_3 are the splay and bend elastic constants, respectively. The measurement error for the flexoelastic ratio (\bar{e}/κ) is estimated as 5–10% incorporating errors from the gradient of $\tan \phi$ versus E .

3. Results and discussion

Transition temperatures

None of the quaterphenyls (**9–17**) shown in Table 1 exhibits any observable mesomorphism, despite substantial supercooling below the melting point. This is

perhaps to be expected taking into account the nonlinear, banana-shape of the quaterphenyls, as shown by Figure 2. There is significant interannular twisting ($\sim 35^\circ$) about the C–C bonds connecting the phenyl rings in the aromatic core of the quaterphenyls (9–17), as expected. The presence of the fluorine atom in quaterphenyls 14–17 in a lateral position results in a lower melting point (101°C, on average) than that (132°C, on average) of the corresponding non-fluorinated quaterphenyls (9–13) with a hydrogen atom in place of the fluorine atom (see Table 1). This is due to steric effects attributable to the presence of the fluorine atom in a lateral position, which increases the intermolecular distance and thereby reduces the intermolecular forces of attraction. It is interesting to note the difference in melting points (47°C) of the highly polar compounds (11) with a very large dipole attributable to the cyano group and that of compound 13 with a fluorine atom in place of the cyano group. The 4-cyano-3,5-difluoro-substituted dimer (27; $n=9$) shown in Scheme 2 is also not liquid crystalline, although the melting point is low (67°C). The data collated in Table 2 for the related dimers (32; $n=7, 9-12$), with a fluorine atom in place of the cyano group, show that these symmetrical compounds are also not mesomorphic. This is consistent with the data in Table 1 for related quaterphenyls with only fluoro- and cyano-substituents in a terminal as well as lateral positions. The melting points of the dimers (32; $n=7, 9-12$) show an odd–even effect, which is often observed for homologous series of dimers (46, 47). The homologues (32; $n=7, 9$ and 11) with an odd number of methylene units (CH_2) in the central spacer unit should have a bent molecular shape (46, 47). The homologues (32; $n=10$ and 12) with an even number of methylene units (CH_2) in the central spacer unit possess a linear conformation (assuming an all-trans, anti-periplanar conformation of the spacer). As there is often a direct correlation between the magnitude of the melting point and the effective length-to-breadth ratio of liquid crystals, the non-linear conformation of the homologues (32; $n=9$ and 11) may explain the lower value of their melting point compared to those of the homologues (32; $n=10$ and 12).

Physical properties

Unfortunately, although nine quaterphenyls (9–17, see Table 1) were synthesised only three homologues (12–14) were soluble enough in the host nematic mixture at the desired concentration (8 wt %) to enable the desired measurements to be made (see Table 3). This unfortunate solubility problem limits the scope for interpretation of the observed results and the usefulness of such materials as dopants in

flexoelectric nematic mixtures. However, the limited amount of data is still useful. The dipole moment due to the presence of fluoro-substituents in a lateral positions across the long axis two of the quaterphenyls (12 and 13) leads to slightly lower values of both dielectric constants (ϵ_{\parallel} and ϵ_{\perp}) and the dielectric anisotropy ($\Delta\epsilon$) of the doped nematic mixtures compared to those of the host nematic mixture MLC6437-000. The higher values for ϵ_{\parallel} and the dielectric anisotropy of the mixture containing the mono-fluorinated quaterphenyl (14) are surprising. The magnitude of the splay elastic constant (k_1) of the doped guest–host mixtures does not differ greatly from that of the host mixture MLC6437-000 and lay probably within the limits of experimental error. However, the values for the bend elastic constant (k_3) of the doped guest–host mixtures are significantly lower than that of the host nematic mixture. This is a large change with respect to such a low concentration of the dopants. It suggests that the one constant approximation for the elastic constants usually made during the calculation of the average flexoelectric coefficient may not be completely valid (5, 6).

The effects on the flexoelastic ratio (\bar{e}/κ), the average flexoelectric coefficient [$\bar{e}=(e_1+e_3)/2$] and the nematic clearing point (T_{N-I}) of the novel banana-shaped compounds as dopants at low concentration (8 wt %) in the commercial nematic mixture MLC6437-000 are also shown in Table 3. The presence of a small concentration (8 wt %) of the new banana-shaped quaterphenyls (12–14) leads to a significantly lower nematic clearing point (T_{N-I}) than that of the host mixture, although the reduction is very similar in each case (7–9°C). This suggests that the extrapolated values for the nematic clearing point of these dopants may be similar, are probably very low and certainly of the same order of magnitude. This is not surprising taking into account the non-linear shape and the high degree of inter-annular twist between the phenyl rings in the aromatic core of the quaterphenyls, as shown by Figure 2. The flexoelastic ratio (\bar{e}/κ) and the average flexoelectric coefficients (\bar{e}) of the doped nematic mixtures containing the three quaterphenyls (12–14) are all also lower than the corresponding values of the host nematic mixture at the same reduced temperature. This observation appears not to be consistent with the postulation that such molecules should be wedge-, pear- or banana-shaped molecules, rather than the classic rod-like or lath-like shape of calamitic nematic liquid crystals (1–4). However, it appears to be consistent with the recent finding that long, rigid-rod molecules are more suitable as dopants to increase the flexoelastic ratio and the flexoelectric coefficients of host nematic mixtures, which may be

attributable to significant quadrupolar effects associated with the effect of splay and bend deformations of molecular dimers (21). It is possible that the sign of the flexoelectric coefficients of the quaterphenyls is not the same as that of the host nematic mixture.

Dimer **32** ($n=11$) is the only one of the dimers (**32**; $n=7, 9-12$) shown in Table 2 soluble enough in the host nematic mixture at the desired concentration (8 wt %) to enable the desired measurements to be made (see Table 3). This is probably attributable to the length of the spacer group and the nonlinear conformation of this dimer with an odd number of methylene units ($n=11$) in the spacer (29). The presence of a small concentration (8 wt %) of the dimer (**32**; $n=11$) in the guest–host mixture leads to a slightly lower nematic clearing point than that of the host mixture. This suggests a higher value for the effective nematic clearing point of the dimer (**32**; $n=11$) than that of the quaterphenyls (**12–14**). The presence of three fluorine atoms in lateral and terminal positions results in a polar compound. However, the dielectric anisotropy of the host nematic mixture is lowered by addition of a small amount (8 wt %) of the dimer (**32**; $n=11$). This may be due to the bent shape of conformers of this molecule resulting in a negative value for $\Delta\epsilon$, which will lower the high positive value of the host mixture. The bent shape of some conformers of the dimer (**32**; $n=11$) should induce a large effective value of the dipole moment and length-to-breadth ratio and should increase the flexoelastic ratio ($\bar{\epsilon}/\kappa$) and the average flexoelectric coefficients (\bar{e}), since the dipole moment of compound (**32**; $n=11$) has large contributions from μ_{\parallel} and μ_{\perp} . This is indeed observed to be the case (see Table 3), although the increase is not very large. This behaviour is consistent with the relatively high flexoelectric coefficients determined for nematic mixtures consisting of related polyfluorinated dimers (15–17). The magnitude of the flexoelastic ratio ($\bar{\epsilon}/\kappa$) of the guest–host mixture containing the dimer (**32**; $n=11$) is comparable with that ($0.6 \text{ C m}^{-1} \text{ N}^{-1}$) found for the dimer 1,8-bis(4'-cyanobiphen-4'-yloxy)octane with an even spacer group (17). It is somewhat lower than that ($1.0 \text{ C m}^{-1} \text{ N}^{-1}$) for related symmetrical dimers of low positive $\Delta\epsilon$ with an odd spacer group (17). However, the average elastic constant (κ) of the guest–host mixture containing the dimer (**32**; $n=11$) is almost twice the value ($4.7 \times 10^{-12} \text{ N}$) found for related dimers with an odd spacer group (16), which would account for the much of the difference in the flexoelastic ratio ($\bar{\epsilon}/\kappa$). The dimer (**32**; $n=11$) exhibits a similar value for the splay elastic constant as the host mixture, but a lower value for the bend elastic constant, as seen for the quaterphenyls (**9**). The $\bar{\epsilon}/\kappa$ value is also similar to the value ($0.6 \text{ C m}^{-1} \text{ N}^{-1}$) found for similar mixtures (8 wt %) of an apolar symmetrical dimer with an odd

spacer group in E7 (20). These measurements are consistent with previous determination of the flexoelectric coefficients measured as chiral mixtures in ULH cells (17) at high concentration (94–98 wt %) and in nematic mixtures in HAN cells at low concentration (8 wt %) (20). They are also comparable to values ($\approx 0.5 \text{ C m}^{-1} \text{ N}^{-1}$) reported for some polar asymmetrical dimers with odd spacer groups (20).

4. Conclusion

Banana-shaped quaterphenyls consisting of three phenyl rings in a linear configuration with *para*-substitution with the fourth phenyl ring substituted in the *meta*-position have no observable liquid crystalline properties. The dielectric constant perpendicular to the nematic director, ϵ_{\perp} , can be increased by incorporating atoms with a substantial dipole moment in a terminal, rather than a lateral position in the molecular structure. The quaterphenyls prepared are not good dopants in flexoelectric nematic mixtures, in that they lead to a significant depression in the nematic clearing point, where they are soluble, and do not induce high values of the flexoelectric coefficients as predicted by standard theories for the flexoelectric effect. Dimers with banana-shaped conformers do induce an increase in the flexoelectric coefficients of mixtures containing them and reduce the clearing point only marginally.

Acknowledgements

We express our thanks to the Merck Chemicals Ltd for funding a PhD studentship (NA). We would also like to thank B. Worthington ($^1\text{H NMR}$) and K. Welham (MS) for spectroscopic measurements.

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