ARTICLE

Synthesis, mesomorphic behaviour and optical anisotropy of some novel materials for nematic mixtures of high birefringence[†]

Michael Hird,^{*a*} Kenneth J. Toyne,^{*a*} John W. Goodby,^{*a*} George W. Gray,^{*a*} Victoria Minter,^{*b*} Rachel P. Tuffin^{*b*} and Damien G. McDonnell^{*c*}

^aThe Department of Chemistry, University of Hull, Hull, UK HU6 7RX ^bQinetiQ Limited, St Andrews Road, Malvern, UK WR14 3PS ^cDefence Diversification Agency, Ively Road, Farnborough, UK GU14 0LX

Received 14th January 2004, Accepted 23rd March 2004 First published as an Advance Article on the web 28th April 2004

Structural moieties including core units (such as phenyl, naphthyl and thiophenyl), linking groups (such as ethynyl), terminal substituents (such as cyano, isothiocyanato and fluoro), and lateral fluoro substituents have been incorporated into novel materials designed to confer a high birefringence on nematic mixtures. The materials have all been prepared through convergent syntheses involving palladium-catalysed cross-coupling reactions of arylboronic acids. The materials were examined for their mesomorphic behaviour as neat materials and as mixtures; some materials were found to have extremely high nematic phase stability, and others were non-mesogenic. The materials were evaluated in nematic host mixtures for their optical anisotropy, and they were all found to show promisingly high values.

Introduction

The work reported here is part of a long, on-going programme on the synthesis and evaluation of nematic liquid crystals of high optical anisotropy.^{1–8} Nematic liquid crystal mixtures are of considerable commercial importance in display device applications; such mixtures contain many components in an attempt to optimise a range of properties, such as mesomorphic behaviour, viscosity, elastic constants, dielectric anisotropy and optical anisotropy.⁹ Components that confer a high optical anisotropy are particularly useful for supertwisted nematic displays, which enables the use of thinner cells and hence lower threshold voltages and enhanced transmission of light, and in polymer dispersed liquid crystal (PDLC) applications to provide a greater contrast between the two switched states. Additionally, nematic mixtures of very high optical anisotropy are essential for fast, third-order, non-linear switching using the optical Kerr effect;^{10,11} this particular application has been the basis behind a long term programme of synthesis and evaluation of materials of high optical anisotropy reported here and in several previous publications.^{1–8} More recently, nematic liquid crystals of high optical anisotropy have been recognised as having great technological importance in telecommunications devices, particularly those operating at 1550 nm.^{12,13}

In order to achieve a high optical anisotropy in a mesogenic material, structural units must be introduced into the molecules such that the E-ray is retarded and the O-ray is allowed to travel freely. The polarisable π -electrons of aromatic systems in conjugation are very effective in retarding the progress of the E-ray through the system, particularly where that conjugation is compact as in a naphthalene core unit, for example. Conjugated linking groups such as ethenyl and ethynyl further retard the progress of the E-ray and hence increase the birefringence. Terminal groups in liquid crystalline materials are often long flexible alkyl or alkoxy chains which serve to facilitate a low melting point; however, such units do nothing to retard the E-ray and so for high optical anisotropy one

† Electronic supplementary information (ESI) available: experimental procedures for all compounds not already given in this paper. See http://www.rsc.org/suppdata/jm/b4/b400630e/

conjugated, compact terminal group such as a cyano (–CN) or an isothiocyanato (–NCS) is more appropriate. The isothiocyanato group has been shown to be particularly effective in generating a high optical anisotropy due to the extended π -system spread over three atoms.^{3,8,14}

Accordingly, many of the structural architectures in the work reported here include terphenyl and naphthalene core units, with ethynyl linkages and cyano and isothiocyanato terminal units. Unfortunately, it has been found that those structural units that generate a high birefringence also generate a high melting point. Hence, other materials have been targeted that have only a biphenyl core unit without an ethynyl linkage; of course these compounds will not generate especially high birefringence, but should have lower melting points and be useful components in mixtures. Lateral fluoro substituents have been included in some of the materials reported here in an attempt to generate low melting points, despite the fact that such substitution causes additional inter-annular twisting of the aromatic rings and hence reduces the longitudinal polarisability resulting in a lower optical anisotropy. Thus the work reported here represents a broadening of the range of materials available for use in nematic mixtures of high birefringence, and an attempt to further rationalise, and increase the understanding of, the structural units that best generate the appropriate compromise of properties.

Discussion of synthetic methods

As mentioned above, a large variety of materials for applications in nematic mixtures of high birefringence form the basis of this publication. However, in all cases the synthesis of the final materials was greatly facilitated by the use of palladiumcatalysed cross-coupling reactions,^{15–21} indeed in the synthesis of some materials their use is virtually essential. Schemes 1–6 show the synthesis of several isothiocyanato-substituted materials, Schemes 7–10 show the synthesis of several cyanosubstituted materials, and Scheme 11 shows the synthesis of a few fluoro-substituted materials.

Despite the development of palladium-catalysed crosscoupling reactions to high levels, their exceptional versatility and their extremely wide tolerance to a whole range of









44

6a ... (i) Pent-1-yne, n-BuLi, THF; (ii) ZnCl₂, THF; (iii) **39**, Pd(PPh₃)₄.

 C_3H_7

42

- 6b ... (i) n-BuLi, THF; (ii) (MeO)₃B, THF; (iii) 10% HCI.
- 6c ... Pd(PPh₃)₄, DME, Na₂CO₃, H₂O.

NCS

6d ... H₂, Pd/C, THF, EtOH.

6e ... Thiophosgene, CHCl₃, CaCO₃.

Scheme 6

NO₂



Scheme 9

functional groups, those couplings involving isothiocyanato substituents fail.³ The use of thiophosgene and chloroform in aqueous calcium carbonate on an aromatic amine is a very useful and efficient method of introducing the isothiocyanato group,^{3,22} and this method was used to good effect in this research (Schemes 1–6). Note that extra care was taken in the handling of the aryl amines because of their suspected carcinogenic nature. Suzuki cross-coupling reactions^{15,18,20,21} involving arylboronic acids (*e.g.* compound **1**) and aryl halides (*e.g.* compound **3**) are invaluable in generating multiaryl

compounds (*e.g.* compound **4**), and this methodology was used to generate nitro-substituted materials (Schemes 1, 3, 5 and 6).

The appropriate nitro group (e.g. in compound 4) was then reduced to the amine function (e.g. in compound 6) which was then converted into the isothiocyanato group (e.g. in compound 8) as described above. Attempts to shorten the synthesis by coupling arylboronic acids (e.g. compound 1) to a 4-halogenoaniline (e.g. compound 11) instead of 1-bromo-4nitrobenzene (3) were met with substantial deamination,²³ hence the longer route via the nitro compound was much more



Scheme 11

efficient. The corresponding alkynylzinc chloride couplings^{1,2,16,20} involving terminal alkynes (*e.g.* compound **10**) and 4-iodoaniline (**11**), as shown in Schemes 2 and 4, caused no problems in generating the amino-substituted intermediates (*e.g.* compound **12**), which were converted into the desired terminal isothiocyanato-substituted materials (*e.g.* compound **13**) using the method described above.

Scheme 5, in particular, shows the lengthy syntheses required to generate highly-substituted aromatic intermediates of the desired substitution pattern, essential when lateral substituents are required. The introduction of the alkyl chain (*e.g.* for compound **37**) involved the coupling of an alkynylzinc reagent with the appropriate aryl iodide (*e.g.* compound **24**) and subsequent hydrogenation of the triple bond (*e.g.* compound **26**) to generate the required alkyl chain (*e.g.* compound **33**). An identical strategy for the introduction of the alkyl chain was used for the thiophene materials (Scheme 6).

The greater availability of phenols when compared with aryl bromides make the triflate leaving group very important in palladium-catalysed cross-coupling reactions.^{1,2,17,20} Triflate **45**, used in previous work, was easily prepared from the appropriate phenol, and serves as an excellent leaving group material in palladium-catalysed cross-coupling reactions to generate substituted phenyl naphthalenes **47–50** and **52** (Scheme 7) and naphthylthiophene **53** (Scheme 8). Compound **53** was hydrogenated to generate the saturated alkyl analogue (compound **54**).

The triflate coupling was used again in Scheme 9 since compound 55 is readily available and is easily converted into the appropriate triflate derivative as for compound 45. A simple palladium-catalysed cross-coupling reaction with boronic acid 32 generated the substituted terphenyl 57. Scheme 10 shows the efficient use of palladium-catalysed cross-coupling reactions involving diffuorophenylboronic acid 31 and thiophenylboronic acid 41 with 4-bromobenzonitrile (58) to give two-ring products 59 and 60 respectively. Hydrogenation of the alkyne unit in compound 60 generated the saturated alkyl analogue 61.

The synthesis of the terminal fluoro- and trifluoromethylphenylnaphthalenes are shown in Scheme 11. Again the efficiency and versatility of palladium-catalysed cross-coupling reactions is demonstrated through the coupling of the various fluoro-substituted bromobenzenes (62–64, 68 and 69) with the naphthylboronic acid (1) to generate final products 65–67, 70 and 71 respectively.

Discussion of results

The melting points, mesophase morphology, transition temperatures and optical anisotropy values for the reported novel compounds and some known materials for comparison are shown in Tables 1–6. of **Table 3** Transition temperatures (°C) and optical anisotropies of terphenyls and biphenyls with terminal cyano and isothiocyanato groups, and some lateral substituents

Com	pound	Physical properties	
No.	Structure	Transition temperatures	Δn
17	C5H11-	C 94.0 E 248.0 S _A 257.5 N 262.0 I	_
80 ²⁶		C 130.0 N 239.0 I	0.28
57	C ₅ H ₁₁ -CH ₃ -CN	C 58.5 N 113.0 I	0.25
81 ³	C ₅ H ₁₁ -	C 53.5 E 74.5 [N 43] I	0.41
82 ²⁷	C ₅ H ₁₁ -CN	C 24.5 N 35.5 I	0.25
37		C 44.5 [N 13] I	0.38
38		C 51.5 [N –24]	0.38
59		C 54.5 [N -11] I	0.22

Table 4	Transition	temperatures	(°C) :	and o	ptical	anis	otropie	s of
phenylthi	iophenes ar	id naphthylthi	ophene	es witl	h term	ninal	cyano	and
isothiocy	anato group	os						

Compound		Physical properties		
No.	Structure	Transition temperatures	Δn	
44	C5H11	C 72.5 [N 26] I	0.44	
61	C5H11 SCN	C 39.5 (N 16.0) I	0.37	
53	C3H7	C 104.0 (N 87.0) I	0.48	
54	C ₅ H ₁₁ S CN	C 72.5 N 92.0 I	0.40	
83 ²	с ₃ H ₇ -=-{>-{>{>	C 113.0 N 193.0 I	0.41	
84 ²	C5H11-CN	C 68.0 N 130.0 I	0.30	

Table 1	Transition	tem	peratures	(°C)	and	optical	anisotr	opies	o
phenylna	phthalenes	with	terminal	cyano	and	isothioc	yanato	group	s

Compounds		Physical properties		
No.	Structure	Transition temperatures	Δn	
8	C4H9O-	C 123.5 B 125.0 N 177.0 I	0.44	
9		C 55.0 E 93.0 S _A 104.0 N 140.5 I	0.43	
72 ⁸	C4H9S-	C 98.1 N 125.7 I	0.44	
73 ²	C4H9O-CN	C 125.0 N 159.0 I	0.33	
74 ²	C ₅ H ₁₁ -CN	C 84.0 N 126.5 I	0.30	
75 ⁸	C4H9S-CN	C 92.0 N 107.0 I	0.36	

Melting points, transition temperatures and mesophase morphology

Simple isothiocyanatobiphenyls tend to have rather high melting points and exhibit ordered smectic phases (*e.g.* E and B), whereas the corresponding cyanobiphenyls tend to be nematogens and hence are more suitable for commercial applications. However, such a lack of a nematic phase does not prevent use as an additive that confers a high optical anisotropy to nematic mixtures. Additionally, alternative structural units can be employed that do enable the nematic

Table 2 Transition temperatures ($^{\circ}$ C) and optical anisotropies ofphenyl-naphthylethynes and diphenylethynes with terminal cyano andisothiocyanato groups

Con	npound	Physical properties		
No.	Structure	Transition temperatures	Δn	
13		C 123.0 (S _A 117.0) N 190.5 I	0.63	
76 ⁸		C 91.5 N 136.7 I	0.54	
77 ²	C ₄ H ₉ O-	C 111.5 N 186.0 I	0.42	
78 ⁸	C4H9S-	C 87.0 N 131.8 I	0.46	
20	C5H11-	C 91.5 (B 85.5) [N 85] I	0.44	
79 ⁷	C4H9S-	C 84.8 B 85.4 [N 65] I	0.50	

Compound		Physical properties		
No.	Structure	Transition temperatures	Δn	
47		C 71.5 N 95.5 I	0.30	
48		C 94.5 [N 44] I	0.30	
49		C 84.0 (N 79.5) I	0.33	
50		C 78.0 [N 27] I	0.25	
52	C4H9O-CN	C 64.5 N 129.5 I	0.33	
85 ²	C4H9O-CN	C 98.5 N 167.5 I	0.33	

phase to be generated by terminal isothiocyanato-substituted materials. For example, some cyclohexylphenylisothiocyanates reported by Dabrowski and co-workers are nematogens with low melting points; however, these are of low optical anisotropy.^{24,25} The use of a longer core unit (*e.g.* compound **17** as seen in Table 3) markedly enhances the liquid crystal phase stability, and allows the generation of a nematic phase, albeit over a short temperature range. The use of a broadened

Table 6Transition temperatures ($^{\circ}$ C) and optical anisotropies of
phenylnaphthalenes with fluoro substituents

Compound		Physical properties			
No.	Structure	Transition temperatures	Δn		
65	C4H9O	C 128.5 [N 112] I	0.27		
66	C ₄ H ₉ O	C 81.5 [N 42] I	0.27		
67	C ₄ H ₉ O	C 72.0 (N 63.0) I	0.25		
70		C 177.5 [N 95] I	0.31		
71	C ₄ H ₉ O-CF ₃	C 73.5 S _A 105.5 [N 55] I	0.29		

naphthyl unit reduces the smectic phase stability by much more than the nematic phase stability to generate materials (e.g. compounds 8 and 9, Table 1) with broad nematic ranges. The use of the butylsulfanyl terminal chain (compound 72) completely eliminates all smectic phases, and leaves a nematic phase of lower phase stability than for the butoxy analogue (compound 8), and more surprisingly, the pentyl analogue (compound 9). However, the disadvantage of a large sulfur unit so close to the core would be expected to far outweigh any advantages of polarisability, and in fact such a trend in liquid crystal phase stability has been reported previously⁸ in the corresponding three, terminal cyano-substituted materials (compounds 73-75, Table 1). A respective comparison of the nematogenic terminal cyano-substituted compounds (73–75)^{2,8} shows them to have significantly lower nematic phase stability than the terminal isothiocyanato-substituted compounds (8, 9 and 72), again supported by previous results.

The introduction of a linear ethynyl linking group (compound 13, Table 2) serves to reduce the order of the smectic phase and the phase stability, so in comparison with compound 8, a crystal B phase has been replaced by a smectic A phase at lower phase stability. However, the nematic phase stability for compound 13 is much higher due to the enhanced molecular length and conjugation. The butylsulfanyl analogue (compound 76)⁸ shows a much lower melting point and no smectic phases, but does have a reduced nematic phase stability in comparison with the butoxy analogue (compound 13); a similar trend to that seen for the phenylnaphthalenes discussed above. The terminal cyano analogues (compounds 77 and 78)^{2,8} are both nematogens, and as was seen for the terminal isothiocyanato compounds (13 and 76) the sulfur unit in the terminal chain causes a significant reduction in melting point and a large reduction in nematic phase stability. Overall, the cyanosubstituted materials (77 and 78) both have lower melting points and lower nematic phase stability than the analogous terminal isothiocyanato compounds (13 and 76); again a similar trend to that seen for the phenylnaphthalenes discussed above. Compound 20 is a simple diphenylethyne core with a terminal isothiocyanato group, and despite the hydrocarbon terminal chain shows a very high melting point for a two-ring compound. Compound 20 shows a monotropic crystal B phase, but no nematic phase; however, an extrapolated value of 85 °C was recorded for the nematic phase stability. In comparison, the butylsulfanyl analogue (compound 79)⁷ melts at a slightly lower temperature, and surprisingly in view of the previous comparison between compounds 9 and 72, the crystal B phase stability is identical; however, the extrapolated nematic phase stability of 65 °C is lower, as expected.

The very high length to breadth ratio and strong longitudinal polarisability of terphenyl 17 brings extremely high liquid crystal phase stability (Table 3). The phase morphology is in keeping with the phenylnaphthalene analogue (compound 9), although in terms of transition temperatures the more linear terphenyl (compound 17) supports the smectic phase more than the nematic phase which leaves a rather short nematic temperature range. The terphenyl core structure shows up the vast difference that the isothiocyanato group makes to mesophase morphology in comparison to the well-known cyanoterphenyl system (compound $\hat{80}$)²⁶ which is nematogenic over a very wide temperature range to very high phase stability. A lateral methyl group was introduced into the cyanoterphenyl structure (compound 57) with the strong expectation of a large reduction in melting point, and of course a massive reduction in nematic phase stability. As can be seen from Table 3, the nematic phase stability has been reduced by 126 °C and the melting point reduced by just 71.5 °C to leave a much narrower nematic temperature range in comparison with the parent system (compound 80). Moving on to the smaller biphenyl systems shown in Table 3, it is apparent that despite three-ring systems being

Published on 28 April 2004. Downloaded by University of Hong Kong Libraries on 23/07/2013 09:36:49.

capable of generating massively high liquid crystal phase stability, the two-ring systems have low liquid crystal phase stability, although of course the pentylcyanobiphenyl (compound 82)²⁷ shows a useful room-temperature nematic phase. The terminal isothiocyanato biphenyl compound $(81)^3$ has a higher nematic phase stability (43 °C) than the analogous cyanobiphenyl (compound 82), although this value is an extrapolated value. The lateral fluoro substituent in isothiocvanato compound 37 has generated the desired result of a much lower melting point than the parent system (compound 81). Hence compound 37 should be a most useful component of nematic mixtures, despite a much lower virtual nematic phase stability in comparison to compound 81. The use of two lateral fluoro substituents fixed across the long molecular axis (compounds 38 and 59) proved to be unsuccessful in generating further reductions in the melting point. The location of the additional polar fluoro substituent in the outer-edge position has enhanced the melting point, yet the additional molecular breadth has considerably reduced the nematic phase stability.

Table 4 shows a series of thiophene materials, and despite the bent molecular structure of the 2,5-disubstituted thiophene core, the liquid crystal phase stability of the four materials is reasonably high. Unfortunately, the two-ring terminal isothiocyanato material (compound 44) has a high melting point, and even though the nematic phase stability was measured by extrapolation, it is surprisingly high (26 °C). Despite a lower nematic phase stability for the terminal cyano-substituted analogue (compound 61), the melting point is reasonably low (39.5 °C) and this allows a monotropic nematic phase to be exhibited at 16 °C. The 2,6-disubstituted naphthyl compound (54) has an enantiotropic nematic phase over a temperature range of 20 °C to a phase stability of 92 °C. In comparison with the linear phenylnaphthalene compound (84)², the bend from the thiophene unit (compound 54) has reduced the nematic phase stability by 38 °C, compared with a reduction of just 19.5 °C seen for the smaller systems (compare compound 61 and compound 82). It would seem that the bend is exaggerated in the larger systems causing a greater depression in clearing temperature. The use of an ethynyl terminal chain (compounds 53 and 83) usually has the effect of increasing the nematic phase stability, and this is seen for linear systems in the comparison of compound 83 with compound 84 (a significant 63 °C increase in clearing point caused by the ethynyl chain).² However, in the case of the bent molecular core in compounds 53 and 54, the clearing temperature is actually lower for the ethynyl compound (53) by a few °C compared with the alkyl compound (54). In this latter comparison the rigidity of the tolane exaggerates the molecular bend and hence reduces the nematic phase stability by much more than the increased polarisability is able to cause an increase.

Phenylnaphthalenes with a terminal cyano substituent have already been targeted by us as important materials of high optical anisotropy. In an attempt to reduce melting points, lateral substituents (e.g. fluoro and methyl) have been introduced into the phenyl ring. As can be seen from the transition temperatures shown in Table 5, the results are somewhat mixed. The introduction of the lateral fluoro substituent in the terminal alkyl material (compound 47) has actually caused a slight increase in melting point (compare with compound 84), accompanied by a significant reduction in nematic phase stability. On the other hand, the lateral fluoro substituent introduced into the terminal alkoxy material (compound 52) has caused a useful reduction of 34 °C in melting point; however, the reduction in nematic phase stability is also quite significant (compare with compound 85).² The use of two fluoro substituents generates quite a high melting point in compounds 48 and 49, and as expected the compound with the two fluoro substituents fixed either side of the core (48) has a much lower nematic phase stability (measured by

extrapolation) than where the two fluoro substituents are fixed on the same side of the molecule (compound **49**). The lateral methyl group is much larger than the lateral fluoro substituent and hence the nematic phase stability (measured by extrapolation) is much lower for compound **50** than for either compound **47** or compound **84**, and the melting point is also higher than for both the comparison compounds.

The efficiency of a terminal fluoro substituent to generate liquid crystal phases is known to be relatively poor; however, the terminal fluoro substituent is useful in giving a low resistivity in comparison with the terminal cyano group. Phenylnaphthalenes with a terminal fluoro substituent were prepared as materials of high birefringence yet, high resistivity. The melting point of the parent system (compound 2) is very high, and hence no liquid crystal phase is seen; however, the extrapolated nematic phase stability is very high (112 °C). A lateral fluoro substituent was introduced (compounds 66 and 67) to reduce the melting point with great success; however, the nematic phase stability was, of course, also reduced. The largest reduction in nematic phase stability came from the compound with the outer-edge lateral fluoro substituent (66), which is surprising because the inter-annular twisting caused by the inner core fluoro substituent of compound 67 would normally reduce the nematic phase stability most significantly. Perhaps the only explanation why compound 67 has a higher nematic phase stability than compound 66 is that the lateral fluoro substituent is more shielded by the broad naphthalene core in compound 67.

Optical anisotropy

Many examples of our previous work show that the optical anisotropy is significantly increased when a terminal alkyl chain is replaced by an alkoxy chain, and further increases can occur when an alkylsulfanyl chain is used. However, the comparison of compounds 8, 9 and 72 (Table 1) shows remarkably similar optical anisotropy values (0.43 to 0.44). It is most likely that this similarity is because the phenylnaphthalene core in conjunction with a terminal isothiocyanato confers such a high optical anisotropy that the influence of the terminal chain is minimal, and also there is the influence of the higher order parameter of those compounds with a smectic tendency to account for. The optical anisotropy values shown by the terminal cyano-substituted analogues (compounds 73-75) represent a more expected trend. It is noticeable that the terminal isothiocyanato moiety certainly confers a vastly higher optical anisotropy to compounds than the terminal cyano group (compare compound 9 with compound 74), a trend consistent with our previous work.^{3,7,8}

Much of our previous work has shown that the introduction of an ethynyl linking group significantly enhances optical anisotropy; 1,2,7 however, the massive value measured for compound 13 is much higher than expected in comparison with compound 8 (Table 2). In fact, compound 13 has a much higher optical anisotropy than the alkylsulfanyl analogue (compound 76), which is rather unusual. However, the higher order parameter generated by compound 13 because of the smectic tendency (not a feature of the alkylsulfanyl compound) is most likely responsible for the remarkably high optical anisotropy value. The comparison of the terminal cyanosubstituted materials (compounds 77 and 78) is more usual since there is no smectic tendency of either material. Just as for the directly-linked materials shown in Table 1, the ethynyllinked materials show a much higher optical anisotropy when substituted with a terminal isothiocyanato group than with a terminal cyano unit. The ethynyl linking group does not enhance the optical anisotropy too significantly for the simple two-ring material with a terminal isothiocyanato group and a simple alkyl chain. The value of 0.44 for compound 20 is not significantly higher than for compound 81. Compound 79

(alkylsulfanyl terminal chain) has a much higher optical anisotropy value than for compound 20 (alkyl terminal chain) and this comparison can be seen as fair because both compounds have a similar smectic tendency.

A terphenyl would be expected to have a high optical anisotropy because of the three aromatic rings in conjugation; however, the rather symmetrical, rigid structure makes solubility rather difficult in the host material, and so meaningful measurement was impossible. The known cyano terphenyl (compound 80) has a surprisingly low optical anisotropy (0.28), particularly since the biphenyl analogue (compound 82) produces a value of 0.25, and as already reported, the terminal isothiocyanato biphenyl (compound 81) has a significantly higher optical anisotropy (0.41). The introduction of a lateral methyl group (compound 57) further reduces optical anisotropy, but not significantly so (0.25). The effect of lateral fluoro substituents on optical anisotropy in biphenyl units (compounds 37, 38 and 59) was investigated, and, surprisingly, the value is not significantly lower than for the parent systems (81 and 82).

Thiophene liquid crystals have been shown in our previous work to confer a particularly high optical anisotropy.⁵ The effect of a thiophene in a phenylisothiocyanate (compound 44) on optical anisotropy is not so significant, but an increase is recorded compared with biphenyl 81, probably another example of the isothiocyanato moiety being so dominant that other structural changes have minimal effect on optical anisotropy. In the case of the cyanophenylthiophene material (compound 61) the optical anisotropy is significantly higher when compared with the cyanobiphenyl analogue (compound 82). The significant effect of the thiophene unit on optical anisotropy is further exemplified in the naphthalene systems, and the already high optical anisotropy value (0.41) for the ethynylphenylnaphthalene (compound 83) is increased to 0.48 in the thiophene analogue (compound 53). Such an increase is not massive, but the ethynyl unit is rather dominating the optical anisotropy. In the case of the alkylphenylnaphthalene (compound 84) the rather moderate optical anisotropy value of 0.30 is markedly increased by the introduction of a thiophene moiety in compound 54 to 0.40, a rather similar trend to that discussed above for the cyanophenyl unit (compounds 82 and 61).

Lateral fluoro substituents in the phenylnaphthalene systems (Table 5) have very little effect on the optical anisotropy (compare compounds 47 and 48 with the parent system 84, and compound 52 with parent system 85), rather similar in trend to the influence of lateral fluoro substituents in biphenyl systems discussed above. Surprisingly, the difluorophenylnaphthalene with the two fluoro substituents fixed on the same side of the molecule (compound 49) has a higher optical anisotropy (0.33) than the parent system or other fluoro-substituted analogues (compounds 84, 47 and 48), which all generate values of 0.30. Outer-edge fluoro substituents are known to promote smectic character, and so perhaps the high optical anisotropy value of compound 49 is due to the enhanced order parameter caused by the smectic character. The lateral methyl group is, as expected, more destructive of optical anisotropy than the lateral fluoro substituent, and such a reduction to 0.25 is consistent with results discussed above.

In contrast with terminal cyano groups, terminal fluoro substituents are useful at generating a positive dielectric anisotropy when a high resistivity is required. Accordingly, it would be useful to have a range of such materials that were also of high birefringence, hence compounds **65–67** with terminal fluoro substituents and compounds **70** and **71** with terminal trifluoromethyl groups (see Table 6). The terminal cyano group is well-recognised for generating high birefringence due to the high concentration of π -electrons; in contrast the terminal fluoro substituent would be expected to be rather poor.

However, the phenylnaphthalene core unit does aid high birefringence, and hence the birefringence of compound 65 (0.27) is not too much lower than that of the cyano-substituted analogue 73 (0.33). The birefringence of 0.27 is maintained when a lateral fluoro substituent at the outer edge of the core is employed (compound 66), but where the lateral fluoro substituent is in the inner core position (compound 67) then the increased inter-annular twisting causes a slight reduction in birefringence (0.25). The terminal trifluoromethyl group is known to enhance the smectic A character of materials, which will increase the order parameter and hence a higher than expected birefringence will result. Compound 70 exemplifies this reasoning with a birefringence of 0.31, which is remarkably similar to the terminal cyano-substituted analogue (73), despite the lack of π -electrons in the terminal group. The usual slight reduction in birefringence is seen when an inner core lateral fluoro substituent is introduced (compound 71); however, the value is still maintained higher than expected due to the smectic A character as discussed above.

The values of optical anisotropy of the novel materials and the referenced known materials reported here are wholly comparable as they have been measured in an identical manner. Unfortunately, a lack of published optical anisotropy values from other groups, and the fact that such values would be inconsistent with those of the materials reported here, prevents further meaningful comparison. However, a recent publication does provide optical anisotropy values of some isothiocyanato materials, but as mixtures and not as individual compounds.¹⁴

Summary

A rather diverse, but structurally comparable, range of materials has been prepared with 2,6-naphthyl and 1,4phenyl core units, single bond and ethynyl linking groups with alkyl, alkoxy, alkynyl, cyano, isothiocyanato, fluoro and trifluoromethyl terminal moieties, and lateral fluoro and methyl substituents. All such units chosen and their specific combinations give rise to a wealth of structure–property relationship information in respect of melting points, transition temperatures, mesophase morphology and optical anisotropy.

The 2,6-naphthyl core unit is an excellent core unit for conferring acceptable mesomorphic properties and a reasonably high optical anisotropy. The isothiocyanato terminal group is particularly useful for conferring a high optical anisotropy. The ethynyl linking group enhances optical anisotropy enormously, particularly where it links two aromatic core units rather than linking an alkyl chain to the aromatic core. Extremely high optical anisotropy (0.63) is seen for compound **13** with an alkoxy-naphthyl-phenyl-ethynylisothiocyanato construction.

Experimental

Confirmation of the structures of intermediates and products was obtained by ¹H and ¹³C NMR spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). Elemental analysis (Fisons EA1108 CHN) data were obtained for each final compound prepared (8, 9, 13, 17, 20, 37, 38, 44, 47–50, 52–54, 57, 59, 61, 65–67, 70, 71).

The progress of reactions was frequently monitored using a Chrompack 9001 capillary gas chromatograph fitted with a CP-SIL 5 CB 10 m \times 0.25 mm, 0.12 µm column (Cat. No. 7700).

Transition temperatures were measured using a Mettler FP5 hot-stage and control unit in conjunction with an Olympus BH2 polarising microscope and these were confirmed using differential scanning calorimetry (Perkin-Elmer DSC-7 and IBM data station). Where final compounds did not exhibit a nematic phase, virtual $T_{\rm N-I}$ values were determined from four binary mixtures (5–30% m/m) in E7 (a nematic host mixture with a $T_{\rm N-I}$ value of 60 °C). The $T_{\rm N-I}$ values obtained for the mixtures were extrapolated to 100% of the compound being examined using a linear regression computer program to give the line of best fit, and are accurate to ± 5 °C, assuming ideal mixing behaviour.

The purities of intermediates were checked by GLC analysis (see above) and the purity of each final compound (8, 9, 13, 17, 20, 37, 38, 44, 47–50, 52–54, 57, 59, 61, 65–67, 70, 71) was checked by HPLC analysis (Merck-Hitachi with Merck RP 18 column, Cat. No. 16 051) and were found to be >99.5% pure in each case.

The optical anisotropies of the compounds were measured using an Abbé refractometer (model 60/HR) at 589 nm (D₁ sodium line) connected to a Haake thermostatically controlled heating/cooling unit containing silicon fluid which was kindly supplied by our collaborators at DERA (Malvern), now QinetiQ. Three mixtures of each compound were formulated (5-25% m/m, depending on solubility) in I eutectic (a nematic host mixture with a $T_{\rm N-I}$ value of 104 °C). The refractive indices (n_e and n_o) of each mixture were measured between 5 and 65 °C at 10 °C intervals, and for each measurement a period of 20 min was allowed for the temperature of the prisms to stabilise. The optical anisotropy (Δn) values ($n_e - n_o$) were plotted against temperature and gave a straight line, which in all cases passed through the individual values. The value for the optical anisotropy at a reduced temperature of 0.7815 of the $T_{\rm N-I}$ value of each mixture was extrapolated to 100% of the compound. The reduced temperature value was used to give consistency to the results by taking into account the variation of the optical anisotropy with the T_{N-I} value, and hence allowing a fair comparison of the effect of various structural units on optical anisotropy between different compounds. The reduced temperature value corresponds to a temperature of 21.6 °C for the I eutectic host mixture which has a T_{N-I} value of 104 °C, and has been used by us in our extensive previous work, $^{7,\dot{8}}$ and by our collaborators at DERA (Malvern), now QinetiQ, for many years. However, in some cases the reduced temperature at which the measurements are quoted are rather low, and optical anisotropy values are always higher at lower temperatures.

Compounds 1,² 2,² 10,² 14,²⁸ 18,² 30,²⁹ 45,² 46¹⁸ and 51²⁹ were prepared according to a previous publications. Tetrakis-(triphenylphosphine)palladium(0) was prepared according to the literature procedure.³⁰ Compounds 3, 11, 21, 23, 39, 55, 58, 62–64, 68 and 69 are all commercially-available. The nematic host mixtures (E7 and I-eutectic) were kindly supplied by our collaborators at Merck Chemicals Limited.

Experimental procedures for all compounds except those referenced above are given as ESI.[†] Experimental procedures for all final products (8, 9, 13, 17, 20, 37, 38, 44, 47–50, 52–54, 57, 59, 61, 65–67, 70, 71) are also provided below, as are those of compounds 4 and 6 for essential reference.

Note that extra care was taken in the handling of the aryl amines because of their suspected carcinogenic nature.

2-Butoxy-6-(4-nitrophenyl)naphthalene (4)

A solution of compound 1 (3.22 g, 0.013 mol) in DME (30 ml) was added dropwise to a stirred, refluxing mixture of compound 3 (2.20 g, 0.011 mol), tetrakis(triphenylphosphine)-palladium($_0$) (0.40 g, 0.35 mmol), sodium carbonate (5 g) in DME (20 ml) and water (50 ml) under nitrogen. The mixture was heated under reflux for 16 h (GLC and TLC analyses revealed a complete reaction) and poured into water. The product was extracted into diethyl ether (×2) and the combined ethereal extracts were washed with brine, and dried (MgSO₄). The solvent was removed *in vacuo* and the crude

product was purified by column chromatography (silica gel/ hexane–dichloromethane, 2:1) to give a pale yellow solid which was recrystallised from ethanol to give colourless crystals.

Yield 3.13 g (89%); transitions (°C): C 106.0 N 119.5 I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 7.16 (1H, d), 7.21 (1H, dd), 7.70 (1H, dd), 7.81 (1H, d), 7.83 (1H, d), 7.84 (2H, d), 8.01 (1H, d), 8.32 (2H, d); IR (KBr) ν_{max} (cm⁻¹): 2960, 2940, 2860, 1630, 1595, 1520, 1395, 1345, 1205, 850, 755; MS *m*/*z* 321 (M⁺), 265, 219, 289.

2-(4-Aminophenyl)-6-butoxynaphthalene (6)

A stirred mixture of compound 4 (2.82 g, 8.79 mmol) and 5% palladium on carbon (1.50 g) in THF (135 ml) and ethanol (10 ml) was hydrogenated for 24 h (GLC and TLC analyses revealed a complete reaction), and the mixture was filtered and poured into water. The product was extracted into diethyl ether (\times 2) and the combined ethereal extracts were washed with water and dried (MgSO₄). The solvent was removed *in vacuo* to yield an off-white solid which was used without further purification.

Yield 2.21 g (86%); mp 141–142 °C; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 3.70 (2H, s), 4.05 (2H, t), 6.79 (2H, d), 7.14 (2H, d), 7.52 (2H, d), 7.65 (1H, d), 7.75 (2H, d), 7.88 (1H, d); IR (KBr) ν_{max} (cm⁻¹): 3560, 3390, 2960, 2940, 2860, 1620, 1605, 1520, 1505, 1390, 1275, 1250, 1205, 1175, 1125, 890, 860, 840, 820; MS *m/z* 291 (M⁺), 235.

2-Butoxy-6-(4-isothiocyanatophenyl)naphthalene (8)

A solution of compound **6** (2.05 g, 7.04 mmol) in chloroform (50 ml) was added to a stirred, cooled (0 °C) mixture of water (10 ml), calcium carbonate (1.10 g, 0.011 mol), chloroform (5 ml) and thiophosgene (1.00 g, 8.70 mmol). The stirred mixture was heated at 35 °C for 1.5 h and then poured into water. The aqueous layer was washed with dichloromethane and the combined organic extracts were washed with 1% aqueous hydrochloric acid and dried (MgSO₄). The solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/dichloromethane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (1:1) to yield colourless crystals.

Yield 2.05 g (87%); transitions (°C): C 123.5 B 125.0 N 177.0 I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 7.14 (1H, d), 7.18 (1H, dd), 7.32 (2H, d), 7.63 (1H, dd), 7.68 (2H, d), 7.77 (1H, d), 7.79 (1H, d), 7.93 (1H, d); IR (KBr) ν_{max} (cm⁻¹): 2960, 2940, 2860, 2050, 1625, 1605, 1605, 1500, 1395, 1280, 1255, 1210, 1175, 860, 840, 805; MS *m*/*z* 333 (M⁺), 277. Calc. for C₂₁H₁₉NOS: C, 75.64; H, 5.74; N, 4.20. Found: C, 75.57; H, 5.70; N, 4.20%.

2-(4-Isothiocyanatophenyl)-6-pentylnaphthalene (9)

Quantities: compound 7 (0.66 g, 2.28 mmol), thiophosgene (0.35 g, 3.04 mmol), calcium carbonate (0.38 g, 3.80 mmol). The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.36 g (48%); transitions (°C): C 55.0 E 93.0 S_A 104.0 N 140.5 I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.70 (2H, quint), 2.80 (2H, t), 7.32 (2H, d), 7.37 (1H, dd), 7.62 (1H, d), 7.65 (1H, dd), 7.69 (2H, d), 7.81 (1H, d), 7.85 (1H, d), 7.97 (1H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2100, 1500, 890, 840, 820; MS *m*/*z* 331 (M⁺), 274. Calc. for C₂₂H₂₁NS: C, 79.72; H, 6.39; N, 4.23. Found: C, 79.70; H, 6.36; N, 4.21%.

1-(6-Butoxynaphth-2-yl)-2-(4-isothiocyanatophenyl)ethyne (13)

Quantities: compound 12 (1.89 g, 6.00 mmol), thiophosgene (0.89 g, 7.74 mmol), calcium carbonate (0.95 g, 9.50 mmol). The experimental procedure was as described for the preparation of compound 8. The crude product was purified by column chromatography (silica gel/dichloromethane) to give an off-white solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.68 g (78%); transitions (°C): C 123.0 (S_A 117.0) N 190.5 I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.50 (2H, sext), 1.80 (2H, quint), 4.10 (2H, t), 7.10 (1H, d), 7.16 (1H, dd), 7.20 (2H, d), 7.51 (1H, dd), 7.53 (2H, d), 7.67 (1H, d), 7.71 (1H, d), 7.96 (1H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2120, 2060, 1620, 1600, 1590, 1510, 1390, 1260, 1215, 1175, 1135, 980, 940, 860, 840, 820; MS *m*/*z* 357 (M⁺), 301. Calc. for C₂₃H₁₉NOS: C, 77.28; H, 5.36; N, 3.92. Found: C, 77.22; H, 5.36; N, 3.87%.

4-Isothiocyanato-4"-pentylterphenyl (17)

Quantities: compound 16 (2.72 g, 8.63 mmol), thiophosgene (1.23 g, 0.011 mol), calcium carbonate (1.35 g, 0.014 mol). The experimental procedure was as described for the preparation of compound 8. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a colourless solid which was recrystallised from ethanol–ethyl acetate (1:2) to yield colourless crystals.

Yield 2.52 g (82%); transitions (°C): C 94.0 E 248.0 S_A 257.5 N 262.0 I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 7.27 (2H, d), 7.31 (2H, d), 7.55 (2H, d), 7.61 (4H, 2 × d), 7.68 (2H, d); IR (KBr) ν_{max} (cm⁻¹): 2960, 2940, 2860, 2020, 1490, 1400, 1005, 940, 810; MS *m*/*z* 357 (M⁺), 300. Calc. for C₂₄H₂₃NS: C, 80.63; H, 6.48; N, 3.92. Found: C, 80.59; H, 6.48; N, 3.90%.

1-(4-Isothiocyanatophenyl)-2-(4-pentylphenyl)ethyne (20)

Quantities: compound **19** (2.38 g, 9.05 mmol), thiophosgene (1.31 g, 0.011 mol), calcium carbonate (1.45 g, 0.015 mol). The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give an off-white solid which was recrystallised from ethanol to yield colourless crystals.

Yield 2.23 g (81%); transitions (°C): C 91.5 (B 85.5) [N 65] I; ¹H NMR (CDCl₃): δ 0.95 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 7.18 (2H, d), 7.22 (2H, d), 7.45 (2H, d), 7.51 (2H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2180, 2110, 1510, 1030, 840; MS *m/z* 305 (M⁺), 247. Calc. for C₂₀H₁₉NS: C, 78.65; H, 6.27; N, 4.59. Found: C, 78.60; H, 6.25; N, 4.55%.

2-Fluoro-4'-isothiocyanato-4-pentylbiphenyl (37)

Quantities: compound 35 (2.11 g, 8.21 mmol), thiophosgene (1.17 g, 0.010 mol), calcium carbonate (1.28 g, 0.013 mol). The experimental procedure was as described for the preparation of compound 8. The crude product was purified by column chromatography (silica gel/dichloromethane) to give an off-white solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.36 g (55%); transitions (°C): C 44.5 [N 13] I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 6.97 (1H, ddd), 7.03 (1H, dd), 7.28 (3H, m), 7.52 (2H, dd); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2120, 1490, 1410, 1130, 1110, 1010, 935, 880, 850, 810, 740, 580; MS *m/z* 299 (M⁺), 242. Calc. for C₁₈H₁₈FNS: C, 72.21; H, 6.06; N, 4.68. Found: C, 72.18; H, 6.02; N, 4.64%.

2,5-Difluoro-4'-isothiocyanato-4-pentylbiphenyl (38)

Quantities: compound 36 (1.47 g, 5.35 mmol), thiophosgene (0.78 g, 6.78 mmol), calcium carbonate (0.87 g, 8.70 mmol).

The experimental procedure was as described for the preparation of compound **8**. The crude product was purified by column chromatography (silica gel/dichloromethane) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.80 g (47%); transitions (°C): C 51.5 [N -24] I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 6.98 (1H, dd), 7.06 (1H, dd), 7.29 (2H, d), 7.51 (2H, dd); IR (KBr) ν_{max} (cm⁻¹): 2960, 2940, 2860, 2120, 1490, 1400, 1170, 935, 890, 840, 810; MS *m*/*z* 317 (M⁺), 260. Calc. for C₁₈H₁₇F₂NS: C, 68.11; H, 5.40; N, 4.41. Found: C, 68.04; H, 5.38; N, 4.35%.

2-(4-Isothiocyanatophenyl)-5-pentylthiophene (44)

Quantities: compound 43 (1.98 g, 8.08 mmol), thiophosgene (1.16 g, 0.010 mol), calcium carbonate (1.26 g, 0.0126 mol). The experimental procedure was as described for the preparation of compound 8. The crude product was purified by column chromatography (silica gel/dichloromethane) to give an off-white solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.63 g (70%); transitions (°C): C 72.5 [N 26] I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.40 (4H, m), 1.70 (2H, quint), 2.80 (2H, t), 6.75 (1H, d), 7.15 (1H, d), 7.19 (2H, d), 7.55 (2H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2040, 1505, 945, 835, 800; MS *m*/*z* 287 (M⁺), 230. Calc. for C₁₆H₁₇NS₂: C, 66.85; H, 5.96; N, 4.87. Found: C, 66.83; H, 5.95; N, 4.85%.

2-Cyano-6-(2-fluoro-4-pentylphenyl)naphthalene (47)

Quantities: compound 45 (1.26 g, 4.19 mmol), compound 30 (1.06 g, 5.05 mmol). The experimental procedure was as described for the preparation of compound 4, except that lithium chloride (0.55 g, 0.013 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane-dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.08 g (81%); transitions (°C): C 71.5 N 95.5 I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 7.04 (1H, ddd), 7.09 (1H, dd), 7.45 (1H, dd), 7.62 (1H, dd), 7.81 (1H, ddd), 7.94 (2H, d), 8.04 (1H, d), 8.24 (1H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2240, 1630, 1430, 1275, 1125, 895, 820; MS *m/z* 317 (M⁺), 273, 260. Calc. for C₂₂H₂₀FN: C, 83.25; H, 6.35; N, 4.41. Found: C, 83.25; H, 6.30; N, 4.40%.

2-Cyano-6-(2,5-difluoro-4-pentylphenyl)naphthalene (48)

Quantities: compound 45 (1.35 g, 4.49 mmol), compound 31 (1.18 g, 5.18 mmol). The experimental procedure was as described for the preparation of compound 4, except that lithium chloride (0.60 g, 0.014 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to give colourless crystals.

Yield 1.20 g (80%); transitions (°C): C 94.5 [N 44] I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 7.04 (1H, dd), 7.20 (1H, dd), 7.62 (1H, dd), 7.78 (1H, ddd), 7.96 (2H, d), 8.04 (1H, d), 8.25 (1H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2240, 1510, 1500, 1480, 1420, 1170, 910, 885, 825; MS *m*/*z* 335 (M⁺), 278. Calc. for C₂₂H₁₉F₂N: C, 78.78; H, 5.71; N, 4.18. Found: C, 78.75; H, 5.70; N, 4.13%.

2-Cyano-6-(2,3-difluoro-4-pentylphenyl)naphthalene (49)

Quantities: compound 45 (1.80 g, 5.98 mmol), compound 46 (1.75 g, 7.68 mmol). The experimental procedure was as described for the preparation of compound 4, except that

lithium chloride (0.80 g, 0.019 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to give colourless crystals.

Yield 1.37 g (68%); transitions (°C): C 84.0 (N 79.5) I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.40 (4H, m), 1.70 (2H, quint), 2.70 (2H, t), 7.06 (1H, ddd), 7.22 (1H, ddd), 7.97 (2H, m), 8.05 (1H, d), 8.26 (1H, d); IR (KBr) ν_{max} (cm⁻¹): 2960, 2940, 2240, 1460, 1275, 1090, 900, 875, 825, 805; MS *m*/*z* 335 (M⁺), 278. Calc. for C₂₂H₁₉F₂N: C, 78.78; H, 5.71; N, 4.18. Found: C, 78.73; H, 5.68; N, 4.16.

2-Cyano-6-(2-methyl-4-pentylphenyl)naphthalene (50)

Quantities: compound 45 (1.80 g, 5.98 mmol), compound 32 (1.48 g, 7.18 mmol). The experimental procedure was as described for the preparation of compound 4, except that lithium chloride (0.80 g, 0.019 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.53 g (82%); transitions (°C): C 78.0 [N 27] I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 7.11 (1H, dd), 7.13 (1H, d), 7.22 (1H, d), 7.60 (1H, dd), 7.64 (1H, dd), 7.81 (1H, d), 7.92 (2H, 2 × d), 8.26 (1H, d); IR (KBr) ν_{max} (cm⁻¹): 2960, 2940, 2860, 2230, 1630, 1475, 915, 900, 825, 480; MS *m*/*z* 313 (M⁺), 256, 140. Calc. for C₂₃H₂₃N: C, 88.13; H, 7.40; N, 4.47. Found: C, 88.10; H, 7.36; N, 4.45%.

2-(4-Butoxy-2-fluorophenyl)-6-cyanonaphthalene (52)

Quantities: compound 45 (2.30 g, 7.4 mmol), compound 51 (1.95 g, 9.20 mmol). The experimental procedure was as described for the preparation of compound 4, except that lithium chloride (1.00 g, 0.024 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 1:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.90 g (78%); transitions (°C): C 64.5 N 129.5 I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.50 (2H, quint), 1.85 (2H, quint), 4.00 (2H, t), 6.76 (1H, ddd), 6.82 (1H, dd), 7.45 (1H, dd), 7.61 (1H, dd), 7.78 (1H, ddd), 7.93 (2H, d), 8.00 (1H, d), 8.24 (1H, d); IR (KCl) v_{max} (cm⁻¹): 2960, 2940, 2860, 2240, 1630, 1520, 1495, 1475, 1315, 1290, 1165, 1130, 1040, 900, 840; MS *m*/*z* 319 (M⁺), 262. Calc. for C₂₁H₁₈FNO: C, 78.98; H, 5.68; N, 4.39. Found: C, 78.96; H, 5.68; N, 4.35%.

2-(6-Cyanonaphth-2-yl)-5-pent-1-ynylthiophene (53)

Quantities: compound **45** (2.00 g, 6.64 mmol), compound **41** (1.55 g, 7.99 mmol). The experimental procedure was as described for the preparation of compound **4**, except that lithium chloride (0.85 g, 0.020 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a pale yellow solid which was recrystallised from ethanol to yield very pale yellow crystals.

Yield 1.55 g (78%); transitions (°C): C 104.0 (N 87.0) I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.60 (2H, sext), 2.45 (2H, t), 7.11 (1H, d), 7.31 (1H, d), 7.58 (1H, dd), 7.77 (1H, dd), 7.85 (1H, d), 7.88 (1H, d), 7.96 (1H, d), 8.14 (1H, d); IR (KB) ν_{max} (cm⁻¹): 2990, 2960, 2880, 2220, 1620, 1600, 1495, 1445, 1165, 890, 800; MS *m*/*z* 301 (M⁺), 286, 272. C₂₀H₁₅NS: C, 79.70; H, 5.02; N, 4.65. Found: C, 79.66; H, 4.98; N, 4.62%.

2-(6-Cyanonaphth-2-yl)-5-pentylthiophene (54)

Quantities: compound **53** (0.70 g, 2.32 mmol), 10% palladium on carbon (0.30 g). The experimental procedure was as described for the preparation of compound **6**, except that the hydrogenation time was 6 h. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.50 g (71%); transitions (°C): C 72.5 N 92.0 I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.37 (4H, m), 1.70 (2H, quint), 2.83 (2H, t), 6.80 (1H, d), 7.30 (1H, d), 7.56 (1H, dd), 7.80 (1H, dd), 7.82 (1H, d), 7.84 (1H, d), 7.97 (1H, d), 8.15 (1H, d); IR (KBr) ν_{max} (cm⁻¹): 2990, 2960, 2880, 2220, 1620, 1600, 1495, 1445, 1165, 890, 800; MS *m*/*z* 305 (M⁺), 248. C₂₀H₁₉NS: C, 78.65; H, 6.27; N, 4.59. Found: C, 78.65; H, 6.26; N,4.57%.

2-Methyl-4-pentyl-4"-cyano-1,1':4',1"-terphenyl (57)

Quantities: compound **56** (1.93 g, 5.90 mmol), compound **32** (1.46 g, 7.09 mmol). The experimental procedure was as described for the preparation of compound **4**, except that lithium chloride (0.75 g, 0.018 mol) was added with the reagents. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.10 g (55%); transitions (°C): C 58.5 N 113.0 I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.37 (4H, m), 1.68 (2H, quint), 2.31 (3H, s), 2.63 (2H, t), 7.10 (1H, dd), 7.13 (1H, d), 7.19 (1H, d), 7.45 (2H, d), 7.64 (2H, d), 7.75 (4H, 2 × d); IR (KBr) ν_{max} (cm⁻¹): 2990, 2960, 2880, 2225, 1605, 1490, 1110, 1010, 825; MS *m*/z 339 (M⁺), 282.

4'-Cyano-2,5-difluoro-4-pentylbiphenyl (59)

Quantities: compound **58** (0.96 g, 5.27 mmol), compound **31** (1.38 g, 6.05 mmol). The experimental procedure was as described for the preparation of compound **4**. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.95 g (63%); transitions (°C): C 54.5 [N -11] I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.65 (2H, t), 7.01 (1H, dd), 7.09 (1H, dd), 7.63 (2H, dd), 7.73 (2H, d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2240, 1615, 1495, 1400, 1175, 900, 840, 820, 750, 560; MS *m*/*z* 285 (M⁺), 228.

2-(4-Cyanophenyl)-5-pentylthiophene (61)

Quantities: compound **58** (1.45 g, 7.97 mmol), compound **41** (1.85 g, 9.54 mmol). The experimental procedure was as described for the preparation of compound **4**. The crude product was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) and hydrogenated in THF (80 ml) and ethanol (20 ml) in the presence of 5% palladium-on-charcoal (0.30 g) catalyst at room temperature and atmospheric pressure. The catalyst was filtered off and the solvent was removed *in vacuo* and the residue was purified by column chromatography (silica gel/hexane–dichloromethane, 2:1) to give a colourless oil which was distilled [Kugelrohr, 150 °C (maximum) at 0.5 mmHg] to yield a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.45 g (71%); transitions (°C): C 39.5 (N 16.0) I; ¹H NMR (CDCl₃): δ 0.90 (3H, t), 1.35 (4H, m), 1.65 (2H, quint), 2.80 (2H, t), 6.79 (1H, d), 7.24 (1H, d), 7.61 (4H, 2 × d); IR (KBr) v_{max} (cm⁻¹): 2960, 2940, 2860, 2240, 1605, 1510, 1470, 1410, 1270, 1215, 1180, 1125, 950, 840, 805, 740, 555, 520; MS *m*/*z* 255 (M⁺), 198.

2-Butoxy-6-(4-fluorophenyl)naphthalene (65)

Quantities: compound 62 (1.35 g, 7.71 mmol), compound 1 (2.45 g, 0.01 mol). The experimental procedure was as described for the preparation of compound 4. The crude product was purified by column chromatography (silica gel/ hexane-dichloromethane, 3:1) to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 1.80 g (79%); transitions (°C): C 128.5 [N 112] I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 7.11-7.20 (4H, m), 7.61-7.67 (3H, m), 7.77 (2H, m), 7.90 (1H, d); IR (KCl) v_{max} (cm⁻¹): 2960, 2940, 2860, 1630, 1610, 1520, 1505, 1470, 1390, 1250, 1205, 1175, 840, 810; MS m/z 294 (M⁺), 238. Calc. for C₂₀H₁₉FO: C, 81.60; H, 6.51. Found: C, 81.56; H, 6.48%.

2-Butoxy-6-(3,4-difluorophenyl)naphthalene (66)

Quantities: compound 63 (1.30 g, 6.74 mmol), compound 1 (2.14 g, 8.77 mmol). The experimental procedure was as described for the preparation of compound 4. The crude product was purified by column chromatography (silica gel/ hexane-dichloromethane, 6:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.46 g (69%); transitions (°C): C 81.5 [N 42] I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 7.13-7.23 (3H, m), 7.40 (1H, m), 7.49 (1H, m), 7.60 (1H, dd), 7.78 (2H, 2 × d), 7.89 (1H, d); IR (KCl) v_{max} (cm⁻¹): 2960, 2940, 2860, 1630, 1600, 1530, 1500, 1390, 1310 1275, 1215, 1175, 1215, 1175, 1120, 875, 860, 830, 805, 780; MS m/z 312 (M⁺), 256. Calc. for C₂₀H₁₈F₂O: C, 76.90; H, 5.81. Found: C, 76.88; H, 5.78%.

2-Butoxy-6-(2,4-difluorophenyl)naphthalene (67)

Quantities: compound 64 (1.37 g, 7.10 mmol), compound 1 (2.27 g, 9.30 mmol). The experimental procedure was as described for the preparation of compound 4. The crude product was purified by column chromatography (silica gel/ hexane-dichloromethane, 3:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.40 g (63%); transitions (°C): C 72.0 (N 63.0) I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 6.90-7.00 (2H, m), 7.15 (1H, d), 7.18 (1H,dd), 7.49 (1H, m), 7.57 (1H, ddd), 7.77 (2H, 2 \times d), 7.87 (1H, d); IR (KCl) v_{max} (cm⁻¹): 2960, 2940, 2860, 1620, 1610, 1595, 1510, 1500, 1390, 1260, 1205, 1175, 1145, 1100, 1070, 900, 855, 805; MS m/z 312 (M⁺), 256. Calc. for C₂₀H₁₈F₂O: C, 76.90; H, 5.81. Found: C, 76.90; H, 5.80%.

2-Butoxy-6-[4-(trifluoromethyl)phenyl]naphthalene (70)

Quantities: compound 68 (1.46 g, 6.49 mmol), compound 1 (2.10 g, 8.60 mmol). The experimental procedure was as described for the preparation of compound 4. The crude product was purified by column chromatography (silica gel/ hexane-dichloromethane, 5:1) to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 1.72 g (77%); transitions (°C): C 177.5 [N 95] I; 1 H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 7.16 (1H, d), 7.19 (1H, dd), 7.67 (1H, dd), 7.71 (2H, d), 7.79 (2H, d), 7.81 (2H, d), 7.97 (1H, d); IR (KCl) v_{max} (cm^{-1}) : 2960, 2940, 2860, 1620, 1605, 1395, 1335, 1280, 1255, 1210 1130, 1115, 1075, 1015, 845, 820, 805; MS m/z 344 (M⁺) 288, 259. Calc. for C₂₁H₁₉F₃O: C, 73.24; H, 5.56. Found: C, 73.20; H, 5.53%.

2-Butoxy-6-[2-fluoro-4-(trifluoromethyl)phenyl]naphthalene (71)

Quantities: compound 69 (1.48 g, 6.09 mmol), compound 1 (1.93 g, 7.91 mmol). The experimental procedure was as described for the preparation of compound 4. The crude product was purified by column chromatography (silica gel/ hexane-dichloromethane, 6:1) to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.51 g (68%); transitions (°C): C 73.5 SA 105.5 [N 55] I; ¹H NMR (CDCl₃): δ 1.00 (3H, t), 1.55 (2H, sext), 1.85 (2H, quint), 4.10 (2H, t), 7.16 (1H, d), 7.20 (1H, dd), 7.45 (1H, dd), 7.51 (1H, dd), 7.61 (1H, ddd), 7.66 (1H, dd), 7.79 (1H, d), 7.81 (1H, d), 7.97 (1H, d); IR (KCl) v_{max} (cm⁻¹): 2960, 2940, 2860, 1620, 1605, 1430, 1340, 1240, 1195, 1160, 1130, 1120, 1070, 940, 885, 865, 835; MS m/z 362 (M⁺), 306. Calc. for C₂₁H₁₈F₄O: C, 69.41; H, 5.27. Found: C, 69.40; H, 5.25%.

References

- M. Hird, K. J. Toyne and G. W. Gray, *Liq. Cryst.*, 1993, **14**, 741. M. Hird, K. J. Toyne, G. W. Gray, S. E. Day and
- 2 D. G. McDonnell, Liq. Cryst., 1993, 15, 123.
- 3 M. Hird, A. J. Seed, K. J. Toyne, J. W. Goodby, G. W. Gray and D. G. McDonnell, J. Mater. Chem., 1993, 3, 851.
- A. J. Seed, K. J. Toyne and J. W. Goodby, J. Mater. Chem., 1995, 5. 2201.
- 5 A. J. Seed, K. J. Toyne and J. W. Goodby, J. Mater. Chem., 1995, 5, 653.
- A. J. Seed, K. J. Toyne, J. W. Goodby and D. G. McDonnell, *J. Mater. Chem.*, 1995, **5**, 1. G. J. Cross, A. J. Seed, K. J. Toyne, J. W. Goodby, M. Hird and
- 7 M. C. Artal, J. Mater. Chem., 2000, 10, 1555. A. J. Seed, K. J. Toyne, J. W. Goodby and M. Hird, J. Mater.
- 8 Chem., 2000, 10, 2069.
- S. M. Kelly, Flat Panel Displays: Advanced Organic Materials, Royal Society of Chemistry, Cambridge, UK, 2000.
- 10 L. Domash, P. Levin, J. Ahn, J. Kumar and S. Tripathy, in Lowerdimensional Systems and Molecular Electronics, R. M. Metzger, P. Day and G. C. Papavassiliou, ed., Plenum Press, New York, 1991, pp. 579.
- 11 P. N. Pasad, in Lower-dimensional Systems and Molecular Electronics, R. M. Metzger, P. Day and G. C. Papavassiliou, ed., Plenum Press, New York, 1991, pp. 563.
- A. d'Alessandro and R. Asquini, Mol. Cryst. Liq. Cryst., 2003, 12 398, 207.
- L. Petti, P. Mormile, G. Righini, L. Sirleto and G. Abbate, Mol. 13 Cryst. Liq. Cryst., 2001, 360, 131.
- 14 A. Spadlo, R. Dabrowski, M. Filipowicz, Z. Stolarz, S. Gauza, C. Fan and S. T. Wu, Liq. Cryst., 2003, 30, 191.
- 15 N. Miyaura, T. Yanagi and A. Suzuki, Synth. Commun., 1981, 11, 513.
- A. O. King, E. Negishi, F. J. Villani and A. Silveira, J. Org. Chem., 16 1978, 43, 358.
- A. M. Echavarren and J. K. Stille, J. Am. Chem. Soc., 1987, 109, 17 5478
- G. W. Gray, M. Hird, D. Lacey and K. J. Toyne, J. Chem. Soc., 18 Perkin Trans. 2, 1989, 2041.
- E. Negishi, A. O. King and N. Okukado, J. Org. Chem., 1977, 42, 19 1821
- M. Hird, G. W. Gray and K. J. Toyne, Mol. Cryst. Liq. Cryst., 20 1991, 206, 187.
- N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457. 21
- 22 R. Dabrowski, J. Dziaduszek and T. Szczucinski, Mol. Cryst. Liq. Cryst., 1985, 124, 241.
- M. Hird, A. J. Seed and K. J. Toyne, Synlett., 1999, 438. 23
- 24 R. Dabrowski, J. Dziaduszek and T. Szczucinski, Mol. Cryst. Liq. Cryst., 1984, 102, 155.
- J. W. Baran, Z. Raszewski, R. Dabrowski, J. Kedzierski and 25 J. Rutkowska, Mol. Cryst. Liq. Cryst., 1985, 123, 237.
- 26 G. W. Gray, K. J. Harrison and J. A. Nash, J. Chem. Soc., Chem. Commun., 1974, 431.
- 27 G. W. Gray, K. J. Harrison and J. A. Nash, Electron. Lett., 1973, 9, 130.
- 28 G. W. Gray, M. Hird and K. J. Toyne, Mol. Cryst. Liq. Cryst., 1991, 195, 221
- 29 G. W. Gray, M. Hird and K. J. Toyne, Mol. Cryst. Liq. Cryst., 1991. 204. 43.
- D. R. Coulson, Inorg. Synth., 1972, 13, 121. 30