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Nematic 2,5-disubstituted thiophenes†

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A large number of new liquid crystals incorporating the 2,5-disubstituted thiophene ring have been prepared and their mesomorphic behaviour studied in order to systematically investigate the correlation between the molecular structure and mesomorphism of thiophene derivatives with different shapes, polarisability and polarity. As a consequence of these investigations we have prepared a new class of liquid crystals incorporating a 2,5-disubstituted thiophene ring and a conjugated *trans*-carbon–carbon double bond in the terminal chain. These novel thiophene derivatives are the first liquid crystals incorporating a 2,5-disubstituted thiophene ring to exhibit a nematic phase at room temperature. This enables the flexoelectric coefficients of a bent-shaped molecule to be measured directly and at room temperature for the first time to the authors' knowledge. Many of these new thiophenes exhibit a high birefringence and a high nematic clearing point and are of potential use as components of nematic mixtures in LCDs.

The 2,5-disubstituted thiophene ring is a potentially useful element of the molecular structure of new nematic liquid crystals due to a number of factors:[1–10] it is aromatic and rigid in nature; the electron-rich sulfur atom in the thiophene ring results in a dipole moment perpendicular to the long molecular axis of the molecule, *i.e.*, apolar derivatives are potentially of negative dielectric anisotropy; the non-collinear nature of the 2,5-disubstituted thiophene ring and the lower symmetry generally result in a low melting point for thiophene derivatives.[11–34] This is due to the large angle between the thiophene ring and the bonds to the substituents at the 2- and 5-positions, see Table 1 and Fig. 1. However, this molecular geometry has been found not to be conducive to mesophase formation in general and nematic phase formation in particular. This finding is illustrated by the liquid crystalline transition temperatures, collated in Table 1, for a series of diesters differing only in the nature of the central ring X, including one or two thiophene rings.[13,22] The collinear nature of the bonds of the biphenyl central unit to the carboxy substituents in the four-ring ester **1** results in a large length-to-breadth ratio of the molecular structure containing four collinear aromatic rings. The rod-like molecular shape of the diester **1** also results in a high anisotropy of polarisability of the delocalised π-electrons in the four conjugated 1,4-disubstituted phenylene rings. The efficiency of packing of long, thin calamitic molecules also increases as the length-to-breadth ratio increases. The presence of strong local dipoles associated with the carboxy linking groups conjugated with the phenyl rings may also contribute to the high clearing point of these esters. The parallel, but not quite collinear, bonds of the corresponding bithiophene **2** give rise to a much lower clearing point than that of the biphenyl **1**. This is most likely due to the broadening of the molecular rotation volume caused by the shape of the two thiophene rings. This results in a lower effective length-to-breadth ratio for the bithiophene **2**. That the lower clearing point is due to shape rather than the presence of heteroatoms in the aromatic ring is shown by the fact that the clearing point of the phenyl diester **3** and the nitrogen heterocycles **4** and **5** are similar. The bonds to the substituents of these three six-membered aromatic rings are both parallel and collinear. The 2,5-disubstituted-thiophene derivative **6** with two non-collinear and non-parallel bonds to the substituents exhibits a clearing point about 100 °C lower than that of any of the diesters **3–5**. The clearing point of the 2,4-disubstituted thiophene **7** is even lower still due to a lower length-to-breadth ratio. The furan **8** possesses the lowest clearing point due to the even greater non-linear bond angle. Therefore, the thiophene ring has generally not been regarded as a standard molecular building block for liquid crystalline components of nematic mixtures for LCDs. However, in spite of this, a significant number of liquid crystals incorporating the 2,5-disubstituted thiophene ring and two other rings have been prepared.[5,11–34] Only a small number of thiophene derivatives with two-rings in the molecular core have been reported as exhibiting a nematic phase, *e.g.*, the 2-*n*-alkyl-5-(4-cyanophenyl)-thiophenes exhibit a monotropic nematic phase just above room temperature.[23,24] A diverse range of two-ring thiophenes with a thioether function joining the flexible terminal aliphatic chain to the rigid aromatic core have also been prepared.[28] Unfortunately, the melting point and clearing point of these materials are relatively high due, at least in part, to the high degree of anisotropy of polarisability contributed to by the thioether function. Against this background it was decided to synthesise a wide and diverse range of compounds incorporating the 2,5-disubstituted thiophene ring in an attempt to establish the exact combination of structural elements of a two-ring thiophene required to generate a low-melting, wide-range enantiotropic nematic phase of low viscosity and high birefringence of potential use for LCDs.[34]

Synthesis

The known 2-pentylthiophene-5-carboxylic acid, prepared by a literature method,[35] was esterified in the usual way[36] using DCC/DMAP (1,3-dicyclohexylcarbodiimide/4-dimethylamino-pyridine) with a range of alcohols and phenols to yield the

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†Electronic supplementary information (ESI) available: extensive synthetic information. See http://www.rsc.org/suppdata/jm/b2/b202073b/

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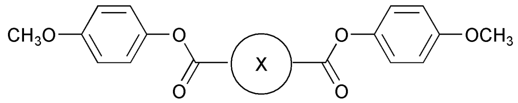
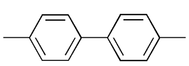
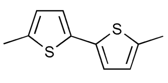
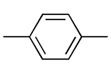
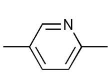
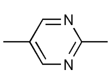
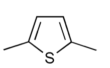
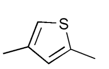
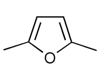
Table 1 Transition temperatures (°C) and the angle of deviation (ϕ) from linearity of the bonds connecting the carboxy substituents to the central ring X of the diesters **1–8**[3,12]



	X	Cr		SmA		N		I	ϕ/°	
1		●	193	●	231	●	>400	●	0	= collinear = parallel
2		●	246	●	–	●	283	●	0	≠ collinear = parallel
3		●	209	●	–	●	285	●	0	= collinear = parallel
4		●	173	●	–	●	255	●	0	= collinear = parallel
5		●	203	●	–	●	250	●	0	= collinear = parallel
6		●	164	●	–	●	166	●	32	≠ collinear ≠ parallel
7		●	185	●	–	●	[86][a]	●	40	≠ collinear ≠ parallel
8		●	163	●	–	●	[62]	●	53	≠ collinear

[a] [ ] Represents a virtual transition temperature.

esters **9–16** and **21–42**. The 4-*n*-alkylphenols, 4-*n*-alkoxyphenols, 4-cyanophenol, 1-hydroxy-4-pentylbicyclo[2.2.2]octane were commercially available. The 4-*n*-alkyl-4′-hydroxybiphenyls,[37] 4-(*trans*-4-*n*-alkylcyclohexyl)phenol,[38] 4-(4-pentylbicyclo[2.2.2]-octyl)phenol,[39] *trans*,*trans*-4-*n*-alkyl-4′-hydroxybicyclohexanes,[40] 4-*n*-alkyl-4′-hydroxytolanes,[41] various halogenated 4-hydroxybiphenyls[42] were prepared by literature methods or were supplied by E. Merck. The 4-(5-*n*-alkylthien-2-yl)phenols required to prepare the esters **9–13**, **17–19**, **71–76** and **83–102** and ethers **103–109** were prepared starting from 2-*n*-alkylthiophenes. These were brominated using NBS (*N*-bromosuccinimide) in a chloroform–acetic acid mixture[43] to yield 2-*n*-alkyl-5-bromothiophenes. A Suzuki palladium-catalysed aryl–aryl cross-coupling reaction[44,45] with 4-methoxyphenylboronic acid gave the 2-(4-methoxyphenyl)-5-*n*-alkylthiophenes.[29] Subsequent demethylation with boron tribromide[46] yielded the 4-(5-*n*-alkylthien-2-yl)phenols. The 4-(5-heptylthien-2-yl)phenol was prepared by a modified procedure. A Suzuki aryl–aryl cross-coupling reaction using 4-methoxyphenylboronic acid and 2-iodothiophene yielded 2-(4-methoxyphenyl)thiophene, which was alkylated using BuLi/TMEDA (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine) at −40 °C and 1-bromoheptane to

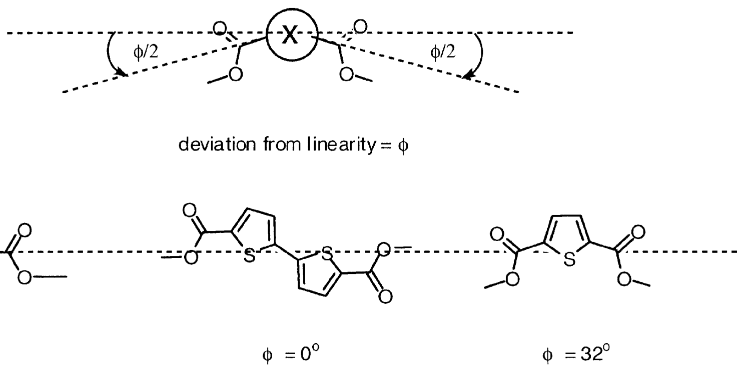


Fig. 1 Schematic representation of the deviation of the angle between the central ring X of the diesters **1–8** and the bonds to the carboxy group from 180°.

yield 2-heptyl-5-(4-methoxyphenyl)thiophene.[29] Cleavage of the methoxy group[45] yielded 2-heptyl-5-(4-hydroxyphenyl)-thiophene. The 2-cyano-5-(4-hydroxyphenyl)thiophene required for the esters **77–82**, was prepared by coupling of 2-bromo-thiophene-5-carbonitrile with 4-methoxyphenylboronic acid to give 2-(4-methoxyphenyl)thiophene-5-carbonitrile followed by removal of the methyl group to give 2-(4-hydroxyphenyl)-thiophene-5-carbonitrile. The benzoate **20** was prepared analogously using 4-pentylbenzoic acid and 4-hydroxy-4′-pentylbiphenyl.[37] The bis-2,5-(4-pentylphenyl)thiophene **43** was synthesised from 2,5-dibromothiophene and 4-pentylphenyl-boronic acid in an aryl–aryl cross-coupling reaction.[44,45] The tolane **44** was prepared by a palladium-catalysed alkynylation of 1,4-dibromobenzene with commercially available 2-pentyl-5-propynylthiophene. The 2,5-bis[(4-*n*-alkylphenyl)-ethynyl]thiophenes **45–49** and 2,5-bis[(4-*n*-alkoxyphenyl)ethynyl]thiophenes **50–54** were prepared by a palladium-catalysed cross-coupling reaction of 2,5-dibromothiophene and the appropriate (4-*n*-alkylphenyl)acetylenes and (4-*n*-alkoxyphenyl)-acetylenes. The two-ring acetylene derivative **55** was prepared analogously. The esters **56–68** were also prepared *via* a palladium-catalysed cross-coupling reaction[44,45] using 4-methoxyphenylboronic acid and 2,5-dibromothiophene to produce 2,5-bis(4-methoxyphenyl)thiophene followed by the removal of the methoxy group using boron tribromide[46] and esterification[36] with DCC and DMAP of the resultant diphenol with appropriate acids. Alkylation of 2,5-bis(4-hydroxyphenyl)thiophene in a Mitsunobu reaction[47] yielded the ethers **69** and **70**. The esters **110** and **111** were prepared by esterification of 4-cyano-4′-hydroxybiphenyl and 4-hydroxy-4′-pentylbiphenyl with (*E*,*E*)-2,4-hexadien-1-carboxylic acid.[36]

Results and discussion

1. Phase characterisation by thermal optical microscopy

The thermotropic mesophases observed for the compounds shown in Tables 2–11 were investigated between crossed polarisers using optical microscopy. Only the nematic phase, the smectic A phase (SmA) and the smectic C phase (SmC) were observed. The nematic phase was found above the smectic phase, if present, as expected, *e.g.*, see Tables 3–5 and 10. Where an enantiotropic nematic phase was formed on melting a bright, colourful and fluid Schlieren texture with 2-point and 4-point brushes was observed. A shimmering yellow, very mobile texture with broad disclination lines was observed just below the clearing point of the nematic phase. Nematic droplets were always apparent on cooling the sample of nematic material from the isotropic liquid formed above the clearing point. These droplets then coalesced quickly to reform the nematic Schlieren texture. Optically extinct homeotropic areas were also often observed. Where an enantiotropic or a monotropic nematic phase could not be observed directly an extrapolated value was determined in some cases, *e.g.*, see Table 2–9. An ideal, linear relationship between the clearing-point and the mixture composition was assumed across the phase diagram for mixtures of different composition of the test material in the commercial nematic mixture E7. Therefore, linear extrapolation of the transition temperature line to 100% of the test material gave the value of the virtual, extrapolated nematic clearing point. The extrapolation was made over as narrow a composition range as possible in order to be certain that no significant curvature of the line occurs. The focal conic (fan) texture was formed on cooling from either the nematic phase or the isotropic liquid in those compounds, *e.g.*, the ethers **105–109**, see Table 10, which exhibit a smectic A phase. Optically extinct homeotropic areas were also observed in the same samples. These areas were optically extinct when viewed between crossed polarisers, which indicates that the phase is optically uniaxial. This optical behaviour, *i.e.*, simultaneous presence of both homeotropic and focal-conic textures, indicates that the mesophase observed is a calamitic smectic A phase. The elliptical and hyperbolic lines of optical discontinuity typical of focal-conic defects were also noted. These textures classify the mesophase as being smectic A with a layered structure, where the long axes of the molecules are on average orthogonal to the layer planes and the in-plane and out-of-plane positional ordering of the molecules is short range. The optical texture of the ester **22** develop dark bars across the backs of the focal conics on cooling from the smectic A phase, see Table 3. At the same time the homeotropic areas developed a grey Schlieren texture with only four-point brushes. This behaviour is typical of the smectic C phase.

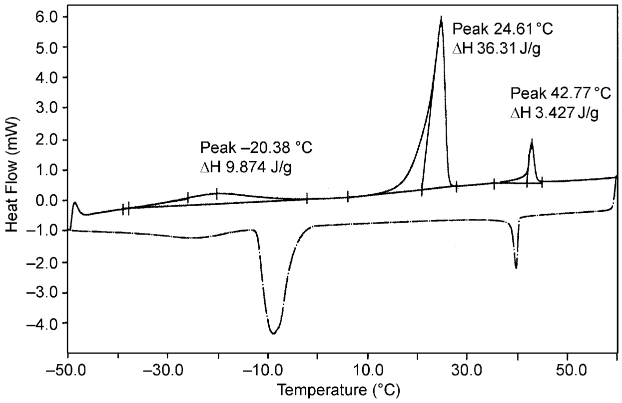


Fig. 2 Differential scanning thermogram as a function of temperature for the first heating and cooling cycle for the ester **93** (scan rate 10 °C min^{-1}).

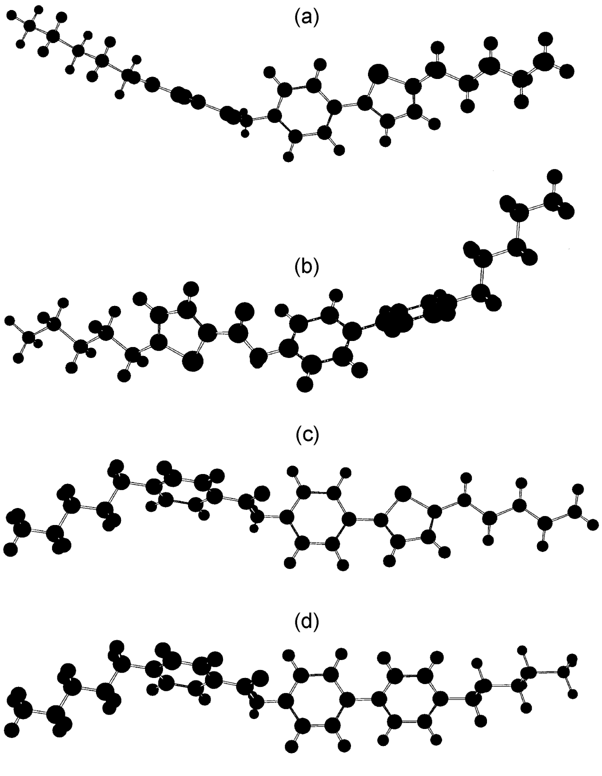
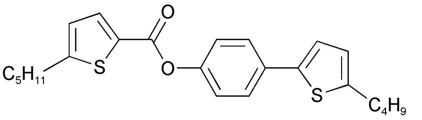
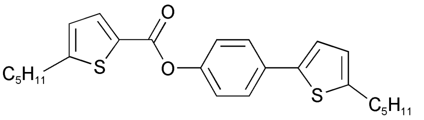
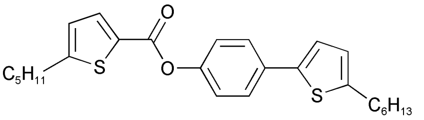
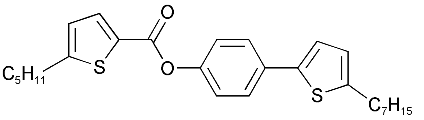
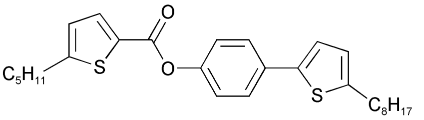
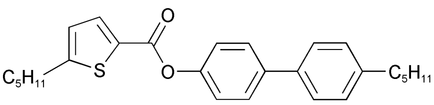
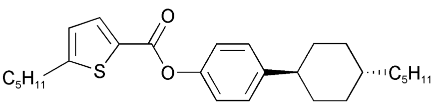
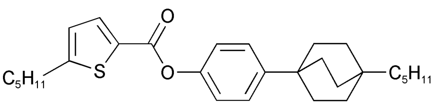
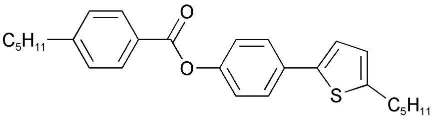
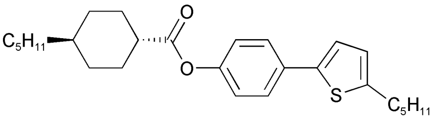
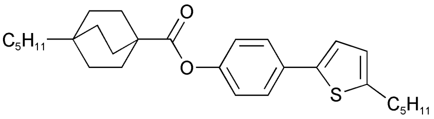
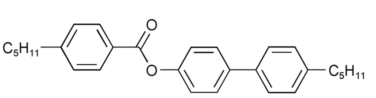


Fig. 3 (a) The energy minimised structure of compound **10** with two thiophene rings and one phenyl ring. (b) The energy minimised structure of compound **14** with one thiophene rings and two phenyl rings. (c) The energy minimised structure of compound **17** with one thiophene ring and two phenyl rings. (d) The energy minimised structure of compound **20** with no thiophene rings and three phenyl rings.

Table 2 Transition temperatures (°C) of various esters incorporating the 2,5-disubstituted thiophene ring **9–19** as well as the benzoate ester **20**

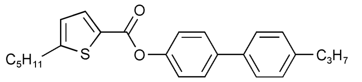
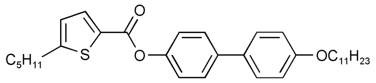
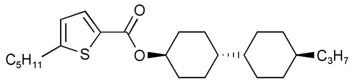
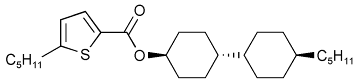
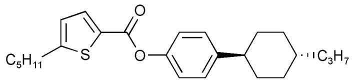
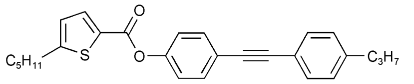
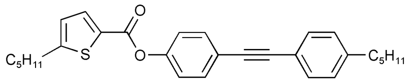
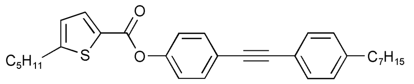
	Molecular structure	Cr		N		I
9		●	79	●	(72)[a]	●
10		●	87	●	(78)	●
11		●	88	●	(76)	●
12		●	89	●	(78)	●
13		●	91	●	(90)	●
14		●	97	●	122	●
15		●	94	●	123	●
16		●	131	●	169	●
17		●	118	●	135	●
18		●	113	●	154	●
19		●	97	●	180	●
20		●	97	●	172	●

[a] ( ) Represents a monotropic transition temperature.

2. Phase characterisation by differential scanning calorimetry

A typical thermogram obtained by differential scanning calorimetry of the liquid crystal transitions of the thiophene derivatives listed in the Tables 2–11 is shown in Fig. 2 for the ester **93**. The enthalpy of transition between the nematic phase and the isotropic liquid is relatively small (3.4 J g^{-1}), as

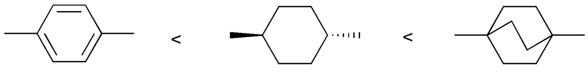
Table 3 Transition temperatures (°C) of a number of diverse 5-pentylthiophenyl-2-carboxylates **21–28**

	Molecular structure	Cr		SmC		N		I
21		●	86		–	●	125	●
22		●	88	●	119	●	135	●
23		●	57		–	●	133	●
24		●	100		–	●	137	●
25		●	110		–	●	127	●
26		●	84		–	●	150	●
27		●	74		–	●	130	●
28		●	77		–	●	129	●

expected. In comparison the enthalpy of fusion (36.3 J g^{-1}) is much higher. The enthalpy of transition of other thiophene derivatives from the lamellar smectic A and smectic C phases to either the relatively disordered nematic phase or the isotropic liquid is intermediate between these two values. The enthalpy of transition between the smectic A and the smectic C phase is small, as expected, as the change from an orthogonal to a tilted orientation within a lamellar arrangement is small. These values were determined twice on heating and cooling cycles on the same sample. However, the values obtained on separate samples of the same compounds were reproducible and very little thermal degradation was observed. The base line of the spectra is relatively flat and sharp transition peaks are observed. The values for the transition temperatures agree well ($\approx$1–2 °C) with those values determined by DSC.

3. Mesomorphism

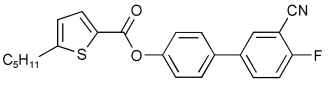
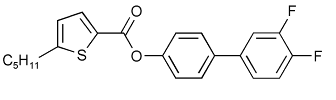
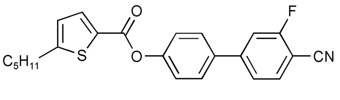
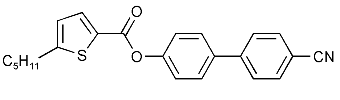
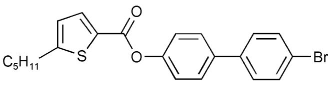
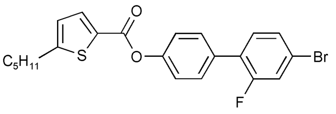
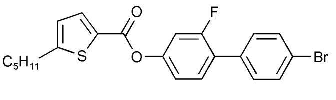
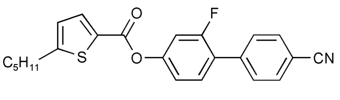
The esters **9–13** collated in Table 2 containing two thiophene-rings and an additional six-membered ring possess a non-linear molecular shape, see Fig. 3a and exhibit a monotropic nematic phase. The relatively low length-to-breadth ratio is responsible for the low clearing points and melting points, which are relatively independent of the length of the alkyl side chain. These and the other compounds collated in Table 2 allow a comparison to be made between a bent-shaped material **10** and the more linear materials **14–16** with only one thiophene ring and two six-membered rings in the molecular core, see Fig. 3b. The more linear shape of **14–16** compared to that of **10** results in the formation of an enantiotropic, rather than a monotropic, nematic phase. As the end ring changes from a phenyl- to a cyclohexyl- to a bicyclo[2,2,2]octyl-ring, the clearing point of each ester increases, but the melting point decreases. This pattern in the transition temperatures is seen again for the esters **17–19**, where the other thiophene ring of **10** is replaced by a 1,4-disubstituted phenyl-, cyclohexyl- or a bicyclo[2,2,2]octyl-ring, see Fig. 3c. Thus, the order of increasing clearing point of the nematic phase for both series is as shown below, which is consistent with previous results.[48]



The effect of the presence of a 2,5-disubstituted thiophene ring on the clearing point is demonstrated by comparing the clearing point of ester **10** with two 2,5-disubstituted thiophene rings with that of 4-pentylphenyl 4′-pentylbiphenyl-4-carboxylate **20** with phenyl rings in their place.[37] The clearing point of **20** is almost 100 °C higher. This is clearly attributable to the non-linear shape of the thiophene ring and the lower length-to-breadth ratio of the molecules compared to the more linear structure of the phenyl ester **20**, see Fig. 3d. The anisotropy of polarisability of the phenyl ester **20** will also be higher than that of the compounds **14** and **17**.

Each compound shown in Table 3 exhibits an enantiotropic nematic phase. The propyl biphenyl ester **21** has a marginally higher clearing point than that of the pentyl homologue **14**, see Table 2. However the undecyloxy homologue **22** has a higher clearing point than those of both alkyl homologues **14** and **21** and also exhibits a smectic C phase. This is due to the presence of the oxygen atom and the long alkoxy chain.[49] The

Table 4 Transition temperatures (°C) of various substituted biphenyl 5-pentylthiophenyl-2-carboxylates **29–36**

	Molecular structures	Cr		SmC		N		I
29		●	57		–		–	●
30		●	56		–	●	75	●
31		●	77			●	150	●
32		●	84		–	●	190	●
33		●	121	●	132	●	150	●
34		●	113		–		–	●
35		●	98		–	●	(95)[a]	●
36		●	90		–	●	153	●

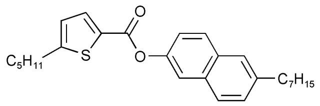
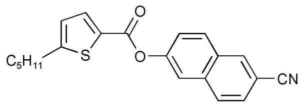
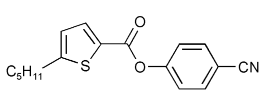
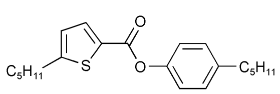
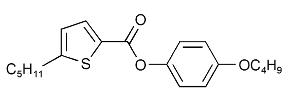
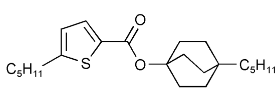
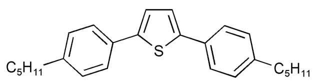
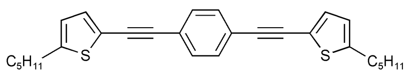
[a]( ) Represents a monotropic transition temperature.

propyl bicyclohexyl ester **23** has a higher clearing point than that of the propyl biphenyl ester **21** and exhibits a lower melting point and, therefore, a greater temperature range of the nematic phase. The clearing point of the pentyl bicyclohexane ester **24** is also higher than that of the pentyl biphenyl ester **14**. However, the melting points of the pentyl esters are very similar, unlike those of the propyl homologues, which leads to both compounds **14** and **24** having a similar nematic phase temperature range. The pentyl bicyclohexyl ester **24** exhibits a higher melting and clearing point than those of the analogous propyl bicyclohexyl ester **23**.

Comparison of the transition temperatures of the esters **21**, **23** and **25**, shown in Table 3, reveal that the replacement of a 1,4-disubstituted ring by a *trans*-1,4-disubstituted cyclohexane ring results in a step-wise increase in the clearing point of the nematic phase. Compounds **26–28** incorporate a carbon–carbon triple bond as a central linkage between the two phenyl rings in the molecular core. This results in a higher length-to-breadth ratio than that of the compounds **14** and **21** without a central linkage. This results in a higher clearing point for the tolanes **26** and **27** compared to that of the analogous biphenyls **14** and **21**. The melting point is also lower, which results in broader nematic temperature ranges for the two tolanes. Therefore the temperature range of the nematic phase decreases with increasing chain length.

Compound **29** shown in Table 4 possesses a bulky cyano group in the 3 position next to a small fluorine atom in the 4 position of the lateral phenyl ring. The presence of a cyano group in a lateral position results in the absence of any mesomorphic behaviour due to steric effects increasing the intermolecular separation and, therefore, decreasing the forces of attraction, and also due to the absence of dimerisation resulting in a low effective length-to-breadth ratio. The presence of two fluoro substituents in the 3 and 4 positions of compound **30** induce a low melting point and clearing point and a narrow nematic range. This is consistent with the smaller fluorine atom having a much smaller steric effect compared to that of the cyano group. The presence of a highly polarisable cyano group with a large permanent dipole moment in compound **31** as opposed to a fluorine atom in compound **30** in the terminal position results in a compound with higher melting point and a much higher clearing point than that of the difluoro compound **30**. This is due to the molecular dimerisation and a higher degree of molecular polarisation. The substitution of the fluorine atom of the 3 position in compound **31** by the slightly smaller hydrogen atom, to yield **32** results in a slightly higher melting point than compound **31**. However, the clearing point is significantly higher as expected due to the absence of a lateral substituent. The presence of a bromine atom in the terminal position in compound **33** rather than a terminal cyano group in material **32** results in a much lower clearing point and a much higher melting point. This is due to

Table 5 Transition temperatures (°C) of the two-ring 5-pentylthiophenyl-2-carboxylates **37–42** and the three-ring thiophene derivatives **43** and **44**

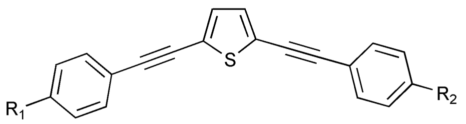
	Molecular structure	Cr		SmC		N		I
37		●	49	–		●	(42)[a]	●
38		●	93	–		●	(87)	●
39		●	<25	–		–		●
40		●	<25	–		–		●
41		●	<25	–		–		●
42		●	52	–		–		●
43		●	140	●	141	●	146	●
44		●	111	–		–		●

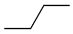
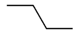
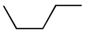
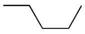
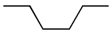
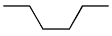
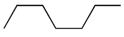
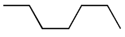
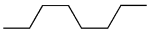
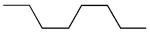
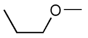
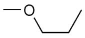
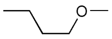
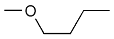
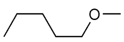
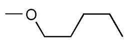
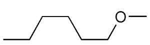
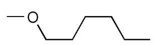
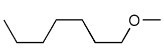
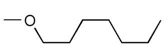
[a]( ) Represents a monotropic transition temperature.

the lower dipole moment of the bromine atom. The presence of a smectic C phase has also been induced.[50] The laterally fluoro-substituted bromo compound **34** is not mesomorphic. The presence of a fluorine atom next to the carbon–carbon single bond between the two phenyl rings in compound **34** could have a much greater influence on the mesomorphic behaviour of these compounds than the presence of the same substituent next to the terminal substituent due to a greater degree of twisting of the adjacent phenyl ring out of the plane of the substituted phenyl ring. In compounds **35** and **36** a lateral substituent is positioned on the central phenyl ring of the rigid core. Compound **36** exhibits a lower clearing point and a slightly higher melting point than those of the non-laterally substituted nitrile **32**. However, when comparing the effect of a fluorine atom in the same position on one or other of the phenyl rings for compounds **31** and **36**, respectively, it can be seen that there is very little dependence of the clearing point on the position of the lateral substituent. Both compounds exhibit an enantiotropic nematic phase. When considering compounds **33–35**, with a terminal bromine atom, the presence of a lateral fluorine atom in the other phenyl ring in compound **35** gives rise to a much lower clearing point than that of the analogous bromo-substituted compound **33** without a fluorine atom in a lateral position. Furthermore, the nematic phase is monotropic. Compound **35** has a lower melting point than that of compound **34** with a fluorine atom in the other ring in a position *meta* to the bromine atom.

Based on the interpretation of the thermal data listed in Tables 2-4, especially the very high clearing point of the 4-cyanophenyl substituted ester **32** in Table 4, various thiophene derivatives with effectively two-and-a-half rings **37**, **38** or two-rings **39–42** were synthesised, see Table 5, in an attempt to produce materials with a nematic phase closer to room temperature. Compounds **37** and **38** incorporate a naphthalene ring and exhibit a monotropic nematic phase. Compound **37** with a terminal heptyl chain possesses a much lower clearing point than that of compound **38** with the polar cyano group. The naphthalene ester **37** exhibits a much lower clearing point than that of the analogous tolane **28**, see Table 3, with two phenyl rings joined by a carbon–carbon triple bond in place of the naphthyl ring, due to the lower length-to-breadth ratio and anisotropy of polarisability of **37** due to the presence of the broad naphthalene ring. The two-ring compounds **39–42** containing a 1,4-disubstituted phenyl ring are liquids at room temperature, and, while compound **42** with a bicyclo[2.2.2]-octane ring is crystalline at room temperature, none of these esters is mesomorphic. The non-linear and non-planar conformation of the esters **39–41** is responsible for the absence of an observable nematic phase for these two-ring aromatic compounds. While the two-ring phenyl ester **40** is a liquid at room temperature, the corresponding biphenyl ester **14** with an additional 1,4-disubstituted phenyl ring exhibits an enantiotropic nematic phase and a high clearing point. This is clearly due to a more linear and planar molecular shape

Table 6 Transition temperatures (°C) for the 2,5-bis[(4-*n*-alkylphenyl)ethynyl]thiophenes **45–49** and the 2,5-bis[(4-*n*-alkoxyphenyl)ethynyl]thiophenes **50–54**



	R$_1$	R$_2$	Cr		N		I
45			●	88	●	112	●
46			●	72	●	81	●
47			●	59	●	94	●
48			●	51	●	69	●
49			●	42	●	83	●
50			●	136	●	174	●
51			●	95	●	168	●
52			●	87	●	139	●
53			●	81	●	137	●
54			●	79	●	126	●

with a much greater length-to-breadth ratio, and anisotropy of polarisability, see Fig. 3b. This interpretation appears to be further confirmed by the fact that the tolane **27**, with a larger length-to-breadth ratio than that of the biphenyl ester **14** due to the presence of an additional carbon–carbon triple bond as a central linkage in the molecular core, exhibits a higher nematic clearing point than that of the biphenyl **14**.

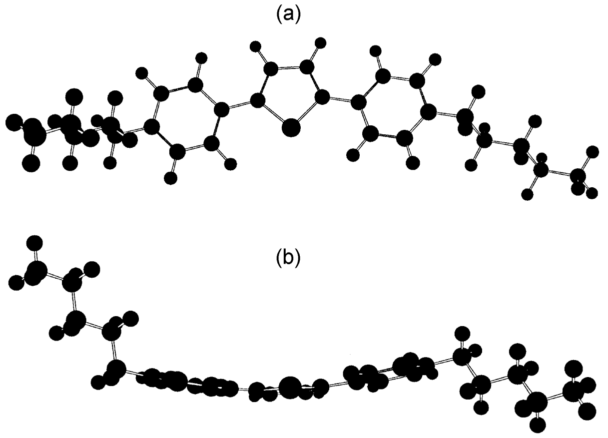
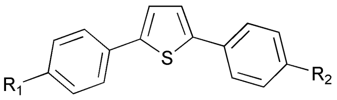
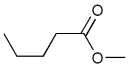
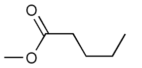
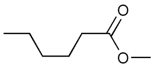
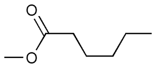
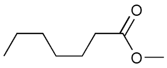
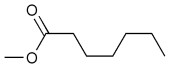
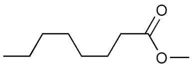
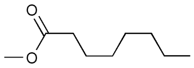
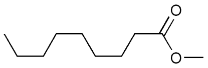
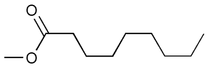
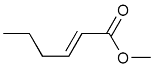
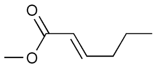
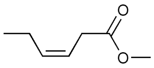
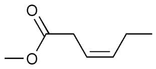
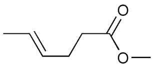
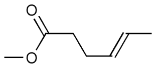
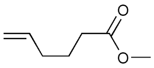
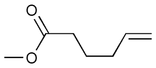
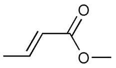
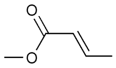
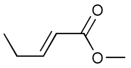
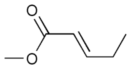
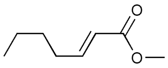
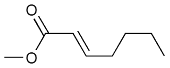
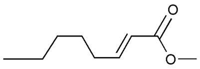
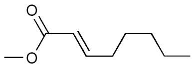
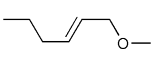
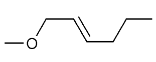
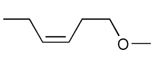
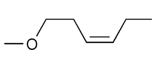


Fig. 4 (a) The energy minimised structure of compound **43** in the *x*–*y* plane viewed along the *z* axis. (b) The energy minimised structure of compound **43** in the *x*–*z* plane viewed along the *y* axis.

The thermal data for compounds **43** and **44**, shown in Table 5, show that a thiophene ring in the centre of the molecular core is more conducive to the induction of a nematic phase. The three aromatic rings making up the central core of compound **43** all lie in the same plane, see Fig. 4a and 4b. This may be due to the interaction between the electron rich sulfur atom and the hydrogen atoms *ortho* to the bonds between the thiophene ring and the two phenyl rings (estimated distance 2.7 Å). The bond angle of 148° between the two bonds to the substituent phenyl groups brings the electron rich thiophene atom and the hydrogen atoms on the phenyl rings *ortho* to the bonds close to each other. A dipolar attraction between them would result in a stabilisation of a planar structure for the molecular core. This may result in a relatively small intermolecular distance between adjacent molecules and in a resultant stabilisation of mesophase behaviour. The non-linear character of two 2,5-disubstituted thiophene rings in **44** cancels itself out to some degree, since the bonds to the two terminal pentyl chains are parallel, if not collinear, assuming a transoid diposition of the thiophene rings as appears likely, see Fig. 5a and 5b, *cf*., compound **2** in Table 1. The thiophene ring and the terminal alkyl chains are also in the same plane. However, the tolane **44** is not mesomorphic, whereas the diphenyl thiophene **2** exhibits polymorphism at high temperatures. The two thiophene rings in the tolane **44** are almost orthogonal to the central phenyl ring, which is decoupled from them by the carbon–carbon triple bonds. Therefore, it is the twisted

Table 7 Transition temperatures (°C) of the 2,5-bis(4-alkanoyloxyphenyl)thiophenes **56–60**, the 2,5-bis[4-(alkenoyloxy)phenyl]thiophenes **61–68** and the 2,5-bis[4-(hexenyloxy)phenyl]thiophenes **69** and **70**



	R_1	R_2	Cr		N		I
56			●	202	●	212	●
57			●	198	●	201	●
58			●	188	●	199	●
59			●	185	●	189	●
60			●	181	●	185	●
61			●	129	●	233	●
62			●	184		–	●
63			●	190	●	210	●
64			●	194		–	●
65			●	148	●	<250	●
66			●	140	●	240	●
67			●	109	●	157	●
68			●	130	●	212	●
69			●	162		–	●
70			●	187		–	●

molecular core of the tolane **44**, which is responsible for the absence of an observable liquid crystalline phase.

The tolanes **45–54** with a thiophene ring in the centre of the molecular core and two carbon–carbon triple bonds were prepared in order to generate a low melting point due to the non-planar structure of these materials, see Table 6. The melting and clearing point of both series decreases systematically with increasing chain length. This is due to the greater flexibility of longer alkyl chains, which increases the proportion of non-linear conformations of the terminal aliphatic chain and the consequent dilution of the attractive van der Waals forces between the aromatic cores. The melting and clearing points of the alkoxy substituted tolanes **50–54** are higher than those of

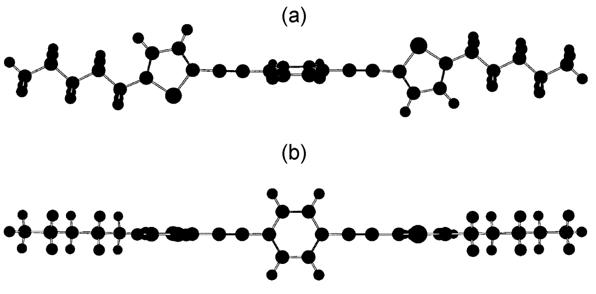
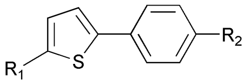
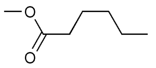
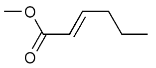
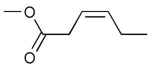
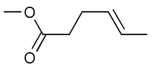
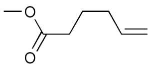
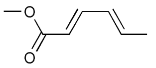
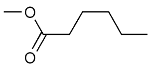
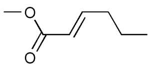
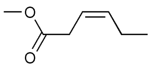
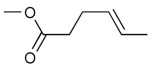
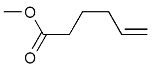
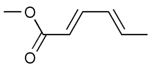


Fig. 5 (a) The energy minimised structure of compound **44** in the x–y plane viewed along the z axis. (b) The energy minimised structure of compound **44** in the x–z plane viewed along the y axis.

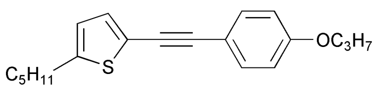
Table 8 Transition temperatures (°C) for the 2-(4-[hexanoyloxy]phenyl)-5-propylthiophene **71** and the 2-(4-[hexenoyloxy]phenyl)-5-propylthiophenes **72-75**, (4-[(*E*,*E*)-hexa-2,4-dienoyloxy]phenyl)-5-pentylthiophene **76**, 2-cyano-5-(4-[hexanoyloxy]phenyl)thiophene **77**, 2-cyano-5-(4-[hexenoyloxy]phenyl)thiophenes **78-81** and 2-cyano-5-(4-[(*E*,*E*)-hexa-2,4-dienoyloxy]phenyl)thiophene **82**



	R$_1$	R$_2$	Cr		N		I
71	C_3H_7		●	45		–	●
72	C_3H_7	 (*E*)	●	16	●	42	●
73	C_3H_7	 (*Z*)	●	38		–	●
74	C_3H_7	 (*E*)	●	44		–	●
75	C_3H_7		●	40		–	●
76	C_5H_{11}	 (*E*,*E*)	●	76	●	125	●
77	CN		●	77		–	●
78	CN	 (*E*)	●	83	●	(82)[a]	●
79	CN	 (*Z*)	●	53		–	●
80	CN	 (*E*)	●	74	●	(39)	●
81	CN		●	70		–	●
82	CN	 (*E*,*E*)	●	168	●	188	●

[a]( ) Represents a monotropic transition temperature.

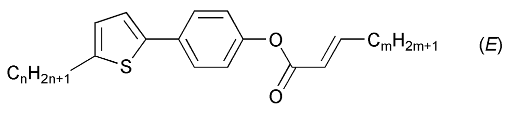
the corresponding alkyl-substituted homologues **45–49** in each case. This is due to the increased van der Waals forces due to the presence of the two oxygen atoms in conjugation with the aromatic core and the increase in effective size of the rigid molecular core compared to that of the corresponding alkyl-substituted materials with a methylene group in place of the oxygen atoms. An analogous two-ring material **55** was not mesomorphic. This may well be due to a non-planar structure, since both aromatic rings are relatively free to rotate around the carbon–carbon triple bond, *cf.* Fig. 5a and 5b.



Compound **55**; Cr-I = 43 °C

It is known that an ester group as a linkage between the central core and the terminal substituent, rather than between rings in the core of the molecule, can lead to the formation of a nematic phase of low viscosity.[51,52] The presence of a carbon–carbon double bond in such a terminal chain is also known to be conducive to mesophase formation.[51,52] Therefore, a series of 2,5-bis(4-*n*-alkanoyloxyphenyl)thiophenes **56–60** and related 2,5-bis[4-(alkenoyloxy)phenyl]thiophenes **61–68** were prepared, see Table 7. The melting and clearing points of the alkanoyloxy esters **56–60** decrease with increasing chain length as expected. This can be attributed to the flexibility of the alkyl chain and its apolar nature. The van der Waals forces between the relatively rigid aromatic cores are reduced by the presence of the aliphatic chains. The presence of a *trans*-carbon–carbon double bond located in the 2 or 4 position in the hexenoyloxy chain induces an enantiotropic nematic phase at higher temperatures for compounds **61** and **63**. Whereas the presence of a *cis*-carbon–carbon double bond in the 3 position (**62**) or

Table 9 Transition temperatures (°C) for the 2-*n*-alkyl-5-(4-[(*E*)-alk-2-enyloxy]phenyl)thiophenes **72** and **83–97**



	n	*m*	Cr		N		I
83	1	3	●	87		–	●
84	2	3	●	43		44	●
72	3	3	●	16	●	42	●
85	4	3	●	39	●	(37)[a]	●
86	5	3	●	47	●	(46)	●
87	6	3	●	57	●	(42)	●
88	7	3	●	59	●	(49)	●
89	8	3	●	65	●	[47][b]	●
90	3	1	●	37	●	47	●
91	3	2	●	32	●	(17)	●
92	3	4	●	17	●	29	●
93	3	5	●	21	●	42	●
94	5	1	●	66		–	●
95	5	2	●	64		–	●
96	5	4	●	37	●	(36)	●
97	5	5	●	44	●	49	●

[a]( ) Represents a monotropic transition temperature. [b][ ] Represents a virtual transition temperature.

a double bond in the 5 position (**64**) does not give rise to any mesomorphic behaviour. The clearing point of the (*E*)-hexen-2-yloxy ester **61** with an additional *trans*-carbon–carbon double bond in both terminal chains is somewhat higher than that of the corresponding hexanoyloxy ester **57** with two terminal aliphatic chains.[51–55] It may be due in part to the added rigidity of the (*E*)-2-alkenyl chain and a lower number of non-linear conformations of the chain. However, it may also be due to the presence of a planar molecular core, if it is assumed that a degree of hydrogen bonding exists between the *ortho*-hydrogen atom on the phenyl rings and the carbonyl function of the carboxy group. The carbon–carbon double bond is in the plane of the carboxy group due to delocalisation effects and conjugation between the π-electrons in both moieties. This will give rise to an almost planar structure for this molecule. The lower clearing point of the ethers **69** and **70** than those of the corresponding esters **61** and **62** could, thus, be explained by the absence of the carbonyl groups and the associated stabilisation of planarity. The melting point of the (*E*)-2-alkenyl-substituted esters **61** and **65–68** is much lower than that of the corresponding alkyl esters **56–60**, which is unusual. The nematic clearing point of the (*E*)-2-alkenoyloxy-substituted esters **61** and **65–68** is also much higher than that of the corresponding alkyl esters **56–60**. The combination of these two factors leads to a wide nematic phase for the (*E*)-2-alkenoyloxy-substituted esters **61** and **65–68**. Once again as the chain length of the alkenyl esters increases, the materials become less rod-like and more flexible, and consequently, the clearing point decreases. The very high clearing point of the nematic phase of some of these alkenoyloxy-substituted esters containing a thiophene ring suggested that equivalent two-ring esters could also exhibit a nematic above room temperature.

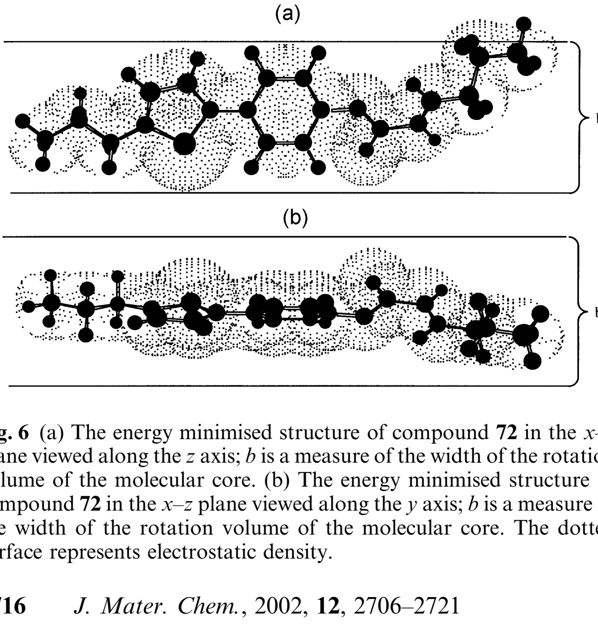


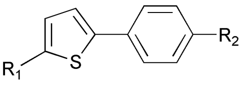
Fig. 6 (a) The energy minimised structure of compound **72** in the *x–y* plane viewed along the *z* axis; *b* is a measure of the width of the rotation volume of the molecular core. (b) The energy minimised structure of compound **72** in the *x–z* plane viewed along the *y* axis; *b* is a measure of the width of the rotation volume of the molecular core. The dotted surface represents electrostatic density.

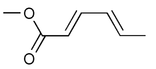
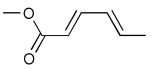
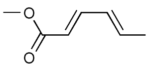
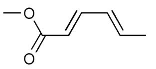
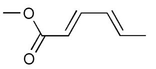
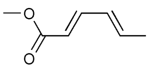
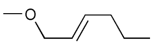
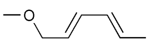
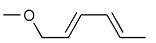
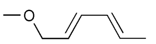
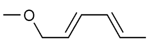
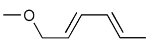
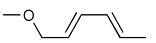
Only compound **72** of the compounds **71–75** collated in Table 8 is mesomorphic and exhibits a nematic phase at room temperature as well as a relatively high clearing point. It is clear from Fig. 6a and 6b that the phenyl ring in the molecular core is in the same plane as the thiophene ring. However, the carbon–carbon double bond and the carboxy group are also in this same plane. Therefore, compound **72** is a very flat, planar molecule with nearly all of the carbon and oxygen atoms making up the molecular skeleton in the same plane. Thus, the intermolecular distance between adjacent molecules of the ester **72** will be relatively small. The last two units of the alkenoyloxy chain project out of the rotation volume of the molecular core. The associated steric effect may be responsible for the relatively low melting point below room temperature as the symmetry is lowered. The transition temperatures for the corresponding esters **77–82** with a cyano group in place of the alkyl group exhibit a greater tendency to form a nematic phase at higher temperatures due to the high dipole moment and high anisotropy of polarisability induced by the presence of the cyano group. Furthermore, a degree of dimer formation, with a longer length-to-breadth ratio, could be expected. The melting point and clearing point of the cyano-substituted ester **78** is much higher than those of the propyl-substituted ester **72**. The high nematic clearing point of the alkenoate **78**, with a *trans*-carbon–carbon double bond in position 2, could be a result of the increased conjugation between the double bond and the carboxyl moiety. However, the isomeric alkenoate **80** with a *trans*-carbon–carbon double bond in position 4 also exhibits a monotropic nematic phase, although at a lower temperature. Therefore, conjugation alone cannot explain this situation. However, the presence of a conjugated *trans*-carbon–carbon double bond in the 2 position is responsible, at least to a large extent, for the advantageous liquid crystalline transition temperatures of these esters. This is confirmed by the very high clearing point of the nematic phase of the diene ester **82** with two *trans*-carbon–carbon double bonds in the terminal chain in positions 2 and 4.

The liquid crystal transition temperatures for the 2-*n*-alkyl-5-(4-[(*E*)-hex-2-enoyloxy]phenyl)thiophenes **72** and **83–89** are listed in Table 9. The clearing point shows a clear odd–even effect. There are wide differences in the melting points for individual homologues with no identifiable trend. Only the propyl homologue **72** exhibits an enantiotropic nematic phase at room temperature. The homologues **90–93** were prepared in order to establish the optimum length of the (*E*)-alk-2-enoyloxy chain having already determined that the combination of a propyl homologue with a (*E*)-hex-2-enoyloxy chain produced a nematic phase at room temperature, *cf.* compound **72**. Two further homologues **92** and **93** exhibit a melting point below room temperature as well as an enantiotropic nematic phase. Only one homologue **97** of the pentyl homologues **86** and **94–97** possesses an enantiotropic nematic phase. However, its melting point is relatively high and the nematic temperature range is narrow.

It was also decided to prepare the (*E*,*E*)-2-*n*-alkyl-5-(4-[hexa-2,4-dienoyloxy]phenyl)thiophenes **98–102**, the 2-(4-[(*E*)-hex-2-enyloxy]phenyl)-5-propylthiophene **103** and the 2-*n*-alkyl-5-(4-[(*E*,*E*)-hexa-2,4-dienyloxy]phenyl)thiophenes

Table 10 Transition temperatures (°C) for the 2-*n*-alkyl-5-(4-[(*E*,*E*)-hexa-2,4-dienoyloxy]phenyl)thiophenes **76** and **98–102**, 2-(4-[(*E*)-hex-2-enyloxy]phenyl)-5-pentylthiophene **103** and the 2-*n*-alkyl-5-(4-[(*E*,*E*)-hexa-2,4-dienyloxy]phenyl)thiophenes **104–109**

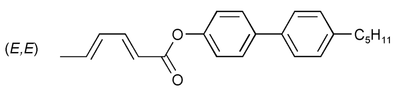
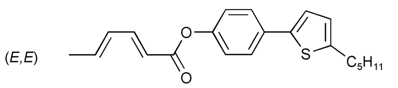
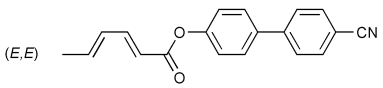
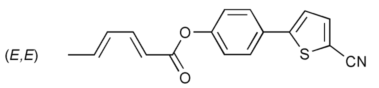


	R_1	R_2	Cr		SmA		N		I
98	C_3H_7	 (*E*,*E*)	●	75		–	●	136	●
99	C_4H_9	 (*E*,*E*)	●	80		–	●	122	●
76	C_5H_{11}	 (*E*,*E*)	●	75		–	●	125	●
100	C_6H_{13}	 (*E*,*E*)	●	79		–	●	116	●
101	C_7H_{15}	 (*E*,*E*)	●	86		–	●	117	●
102	C_8H_{17}	 (*E*,*E*)	●	82		–	●	111	●
103	C_3H_7	 (*E*)	●	82		–		–	●
104	C_3H_7	 (*E*,*E*)	●	85		–	●	98	●
105	C_4H_9	 (*E*,*E*)	●	81	●	92	●	96	●
106	C_5H_{11}	 (*E*,*E*)	●	98	●	(97)[a]	●	100	●
107	C_6H_{13}	 (*E*,*E*)	●	95	●	99		–	●
108	C_7H_{15}	 (*E*,*E*)	●	95	●	101		–	●
109	C_8H_{17}	 (*E*,*E*)	●	86	●	100		–	●

[a]( ) Represents a monotropic transition temperature.

104–109 shown in Table 10 in an attempt to produce materials with a nematic phase with a low viscosity, a high clearing point and a high birefringence.[56] All of the diene esters **98–102** prepared exhibit an enantiotropic nematic phase at elevated temperatures. The thermal data for the diene esters **98–102** shows that the added greater degree of anisotropy of the polarisability and polarisation attributable to the cyano-group compared to an alkyl terminal substituent leads to a higher nematic clearing point. The dienoate ester **98** with two *trans*-double bonds in positions 2 and 4 exhibits a higher clearing point than the corresponding alkenyl esters **72** and **74** with a single carbon–carbon double bond in either position 2 or 4 of the terminal chain, see Table 8. The 2-(4-[(*E*)-hex-2-enyloxy]phenyl)-5-propylthiophene **103** does not exhibit an observable liquid crystalline phase due to the high melting point. However, the first three homologues of the 2-*n*-alkyl-5-(4-[(*E*,*E*)-hexa-2,4-dienyloxy]phenyl)thiophenes **104–106** with an additional carbon–carbon double bond in position 4 of the terminal chain attached to the phenyl group exhibit an enantiotropic nematic phase. However, a smectic A phase is observed from the second homologue **105** of the series. The temperature for the smectic A to nematic transition increases

Table 11 Transition temperatures for the (*E*,*E*)-hexa-2,4-dienoyloxy-substituted compounds **76**, **82**, **110** and **111**

	Structure	Cr		N		I
110		●	86	●	168	●
76		●	76	●	125	●
111		●	160	●	227	●
82		●	168	●	188	●

with chain length and the smectic A phase displaces the nematic phase from the hexyl homologue **106** onwards.

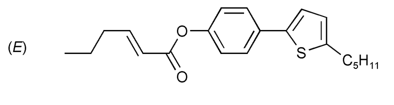
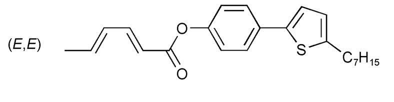
The liquid crystalline transition temperatures of the esters **76**, **82**, **110** and **111** collated in Table 11 demonstrate once again that the non collinear angle between the bonds connecting the thiophene ring to the rest of the molecule, *e.g.*, in the esters **76** and **82**, leads to a lower clearing point than that of the analogous phenyl esters, *e.g.*, **110** and **111**, with collinear bonds.

4. Physical properties

Several representative examples of the new compounds have been evaluated for potential use in nematic mixtures for TN-LCDs, STN-LCDs and LCDs based on flexoelectricity. A fixed amount (10 wt%) of two representative examples of the two-ring thiophenes **82** and **101** was dissolved in a standard nematic mixture (DOP017) and the physical properties of the two resultant mixtures assessed and compared to those of DOP-017 the host mixture, see Table 12. The presence of 10 wt% of the thiophene ester **82** with a *trans*-carbon–carbon double bond in the terminal chain leads to a small increase in the refractive indices and the birefringence of the host mixture. However, the clearing point of the doped mixture is substantially higher (+6 °C) than that of the host mixture. However, the values for the birefringence and clearing point of a nematic mixture containing the diene ester **101** with two *trans*-carbon–carbon bonds in the terminal chain are much higher than those of the first two mixtures. However, the response times, t_{on} and t_{off} (10–90% transmission) of TN-nematic cells containing the doped mixtures addressed under identical conditions are also greater than those of the host mixture. This may be explained, at least in part, by the lower dielectric anisotropy of the mixtures at a higher reduced temperature containing the apolar thiophene derivatives with a diople moment caused by the polarisable sulfur atom across the long molecular axis. However, the longer t_{off} time, which is independent of the dielectric anisotropy, does suggest a higher induced value for the viscosity, although t_{on} is increased (*ca.* 50%) more than t_{off} (*ca.* 25%). These initial results suggest that some of these new thiophene derivatives may be of use as components of nematic mixtures of negative dielectric anisotropy, *e.g.*, for VAN-LCDs, rather than positive dielectric anisotropy, in order to increase the birefringence and clearing point of the nematic phase.

Provisional evaluation of the flexoelectric coefficients of these and other liquid crystals with an unusual shape suggest that a bent shape does not lead automatically to an increase in the flexoelectric coefficients of a polar host nematic mixture (E7) as generally postulated.[57] The value of the bend and splay flexoelectric coefficients $e_b + e_s/K$ for ester **72** measured in the pure state at room temperature is lower (0.12 C N^{-1} m^{-1}) than that of E7 at the same temperature (0.76 C N^{-1} m^{-1}). However, the elastic constant value K of the doped mixtures may differ to some degree to that of the host mixture, E7. The value of $e_b + e_s/K$ extrapolated for compound **72** from mixtures with E7 agree well with that measured for the pure compound. However, the value measured for a mixture of the nematic mixture E7 doped with 10 wt% of the three-ring thiophene **43**, see Table 5, is almost double (1.44 C N^{-1} m^{-1}). This is a large effect for a 10 wt% concentration of the thiophene **43**. These results are still being evaluated and will be reported in detail elsewhere.[57] However, they do demonstrate the possible use of

Table 12 Transition temperatures, refractive indices and birefringence measured at 25 °C for the nematic host mixture DOP-017 and mixtures containing 10 wt% of the dopants **82** and **101**

	Structure	n_e	n_o	Δn	T_{N-I}
DOP-017	Host nematic mixture	1.580	1.485	0.094	45.2
+10 wt% **82**		1.587	1.489	0.099	51.4
+10 wt% **101**		1.600	1.490	0.110	59.0

some thiophene derivatives as dopants to increase the flexoelectric coefficients of nematic host mixtures for use in LCDs based on flexoelectricity.[58] A large value for the flexoelectric coefficients could lead to short response times for LCDs based on the flexoelectricity of nematic mixtures, such as ZBD.[58] A patent application has been submitted based on these preliminary results.[59]

Conclusions

The combination of molecular elements required to induce an enantiotropic phase at room temperature for an organic compound incorporating a 2,5-disubstituted thiophene ring has been identified. This is the first time a room temperature nematic phase has been reported for thiophene derivatives. The combination of these molecular elements also contribute towards generating a high birefringence, a high nematic clearing point as well as a relatively low viscosity for these materials. The new thiophene compounds can be used to induce a high birefringence in nematic mixtures for LCDs. The compounds synthesised may be potentially useful components of nematic mixtures of negative, rather than positive, dielectric anisotropy for use in LCDs, such as VAN-LCDs, or LCDs based on flexoelectric effects, such as ZBD.

Experimental

Techniques

The structures of intermediates and final products were confirmed by proton (^{1}H) nuclear magnetic resonance (NMR) spectroscopy (JEOL JMN-GX270 FT nuclear resonance spectrometer), infrared (IR) spectroscopy (Perkin-Elmer 783 infrared spectrophotometer) and mass spectrometry (MS) (Finnegan MAT 1020 automated GC/MS). Reaction progress and product purity was checked using a CHROMPACK CP 9001 capillary gas chromatograph fitted with a 10 m CP-SIL 5CB (0.12 μm, 0.25 mm) capillary column. All of the final products were more than 99.5% pure by GLC. Transition temperatures were determined using an Olympus BH-2 polarising light microscope together with a Mettler FP52 heating stage and a Mettler FP5 temperature control unit. The analysis of transition temperatures and enthalpies was carried out by a Perkin-Elmer DSC7-PC differential scanning calorimeter. Molecular modelling was carried out using ChemDraw Ultra 6, CambridgeSoft, USA, and MM1 energy minimisation. Simulations using either the TITAN (a proprietary Merck program) or Cerius 2[60] molecular modelling packages gave essentially the same results. The disposition of the thiophene and phenyl rings in the compounds **10**, **14**, **17**, **20**, **43**, **44** and **72** shown in Fig. 3–5, was chosen in each case to give the most linear structure. This is based upon the assumption that the preferred molecular conformation will be that giving rise to the highest length-to-breadth ratio and greatest anisotropy of polarisability consistent with current understanding of the nematic phase of thermotropic, calamitc liquid crystals. However, there is a high degree of free rotation about the inter-annular bonds and, as a consequence, a distribution of molecular conformations will be present. The out-of-plane nature of the rings in Fig. 3a–d and 5a, 5b are clearly a consequence of this. Therefore, an assumption of a cisoid or transoid disposition is irrelevant. The chemical bonds in the compounds shown in Fig. 4a, 4b define the molecular geometry of the aromatic core and, therefore, no assumptions need to be made. The terminal aliphatic chains are assumed to adopt an all-*trans*, antiperiplanar conformation.

Synthesis

A short reaction pathway to a typical liquid crystalline phenylthiophene derivative **72** is described below in order to illustrate the spectral data obtained for the final compounds **9–111** and the reaction intermediates leading to them. Extensive synthetic information is included in the Electronic Supplementary Information.†

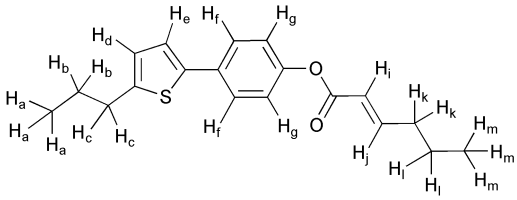
2-Bromo-5-propylthiophene. A solution of 2-propylthiophene (6.00 g, 0.0476 mol) and NBS (8.47 g, 0.0476 mol) in a 1 : 1 mixture of chloroform/acetic acid (50 cm^3) was stirred and heated under reflux for 30 min. Water (100 cm^3) and ether (100 cm^3) were added to the cooled solution. The organic layer was separated off and washed with 10% sodium hydroxide solution (1 × 100 cm^3) then brine (2 × 50 cm^3) and dried ($MgSO_4$). After filtration, the filtrate was concentrated under reduced pressure. The crude product was purified by distillation under reduced pressure to yield 8.82 g (89.9%) of the desired product. Boiling point. /°C: 98 @ 20 mmHg. ^{1}H NMR ($CDCl_3$) δ_H: 0.96 (t, J = 7.6, 3H), 1.65 (sext, J = 7.6, 2H), 2.71 (td, J = 7.6, J = 1.0, 2H), 6.52 (dt, J = 1.0, J = 3.7, 1H), 6.83 (d, J = 3.7, 1H). IR ν_{max}/cm^{-1}: 2967, 2935, 2875, 1448, 1047, 963, 789. MS *m*/*z*: 206, 204 (M^+), 177, 175, 96. GLC 98.3%.

2-(4-Methoxyphenyl)-5-propylthiophene. Tetrakis(triphenylphosphine)palladium(0) (2.31 g, 0.0020 mol) was added to a stirred solution of 2-bromo-5-propylthiophene (8.86 g, 0.0430 mol) and 4-methoxyphenylene boronic acid (7.90 g, 0.0520 mol) in a mixture of 20% sodium carbonate solution (50 cm^3) and 1,4-dioxane (100 cm^3). The reaction mixture was heated under reflux for 5 h. The cooled reaction mixture was diluted with ether (200 cm^3) and water (200 cm^3). The aqueous layer was washed with ether (2 × 50 cm^3) and the combined organic extracts were washed with a 10% HCl solution (1 × 100 cm^3) then with brine (2 × 100 cm^3) and dried ($MgSO_4$). After filtration, the solvent was removed under reduced pressure and the residue purified by column chromatography on silica gel using a 1 : 1 hexane/dichloromethane mixture as the eluent followed by recrystallisation from hexane to yield 5.80 g (58.1%) of the desired product. Melting point /°C: 41–42. ^{1}H NMR ($CDCl_3$) δ_H: 1.00 (t, J = 7.6, 3H), 1.72 (sext, J = 7.6, 2H), 2.78 (td, J = 7.6, J = 1.0, 2H), 3.82 (s, 3H), 6.71 (dt, J = 1.0, J = 3.7, 1H), 6.89 (d, J = 9.0, 2H), 7.00 (d, J = 3.7, 1H), 7.48 (d, J = 9.0, 2H). IR ν_{max}/cm^{-1}: 2961, 2874, 1551, 1469, 1290, 1255, 1181, 1034, 829, 793. MS *m*/*z*: 232 (M^+), 203, 188. GLC 99.8%.

4-(5-Propylthien-2-yl)phenol

A 1.0 M solution of boron tribromide in dichloromethane (50.0 cm^3, 0.0500 mol) was added dropwise to a cooled (0 °C) stirred solution of 2-(4-methoxyphenyl)-5-propylthiophene (5.80 g, 0.0250 mol) in dichloromethane (100 cm^3). The reaction mixture was stirred at room temperature overnight, , then poured onto an ice/water mixture (200 g) and stirred (30 min). The organic layer was separated and washed with brine (2 × 100 cm^3) and then dried ($MgSO_4$). The product was purified by column chromatography on silica gel using dichloromethane as the eluent, followed by recrystallisation from ethanol to yield 4.55 g (83.5%) of the desired product. The product was used without further purification. Melting point. /°C: 92–94. ^{1}H NMR ($CDCl_3$) δ_H: 0.99 (t, J = 7.6, 3H), 1.71 (sext, J = 7.6, 2H), 2.78 (td, J = 7.6, J = 1.0, 2H), 4.85 (s, 1H), 6.71 (dt, J = 1.0, J = 3.7, 1H), 6.81 (d, J = 9.0, 2H), 6.99 (d, J = 3.7, 1H), 7.43 (d, J = 9.0, 2H). IR ν_{max}/cm^{-1}: 3354, 2961, 2872, 1606, 1515, 1444, 1381, 1258, 1108, 952, 829, 795. MS *m*/*z*: 218 (M^+), 203, 189. GLC 99.7%.

4-(5-Propylthien-2-yl)phenyl (*E*)-hex-2-enoate 72.



A solution of *N*,*N*′-dicyclohexylcarbodiimide (0.47 g, 0.0023 mol) in dichloromethane (20 cm^3) was added to a solution of (*E*)-hex-2-enoic acid (0.26 g, 0.0023 mol), 4-(2-propylthiophen-5-yl)phenol (0.50 g, 0.0023 mol) and DMAP (0.11 g, 0.0009 mol) in dichloromethane (10 cm^3), at room temperature. The reaction mixture was stirred overnight, filtered, evaporated down under reduced pressure and then purified by column chromatography on silica gel using a 1 : 1 hexane/dichloromethane mixture as the eluent and recrystallisation from ethanol to yield 0.15 g (20.8%) of the desired product, see Tables 8 and 9 for the transition temperatures of this ester. ^{1}H NMR (CDCl$_3$) δ_H: 0.98 (t, J_{ab} = 7.6, 3H), 1.00 (t, J_{ml} = 7.6, 3H), 1.55 (sext, J_{ba} = 7.6, J_{bc} = 7.6, 2H), 1.73 (sext, J_{lk} = 7.3, J_{lm} = 7.6, 2H), 2.27 (dt, J_{kl} = 7.3, J_{kj} = 1.7, 2H), 2.79 (td, J_{cb} = 7.6, J_{cd} = 1.0, 2H), 6.02 (dt, J_{ji} = 15.9, J_{jk} = 1.7, 1H), 6.73 (dt, J_{dc} = 1.0, J_{de} = 3.4, 1H), 7.07 (d, J_{ed} = 3.4, 1H), 7.10 (d, J_{fg} = 9.0, 2H), 7.18 (d, J_{ij} = 15.8, 1H), 7.55 (d, J_{gf} = 9.0, 2H). IR ν_{max}/cm^{-1}: 2967, 2935, 2876, 1742, 1654, 1511, 1208, 1154, 1116, 979, 800. MS *m*/*z*: 314 (M$^+$), 218 (C$_{13}$H$_{14}$OS$^+$), 189 (C$_9$H$_{12}$OS$^+$), 97 (C$_6$H$_9$O$^+$). GLC 99.9%.

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