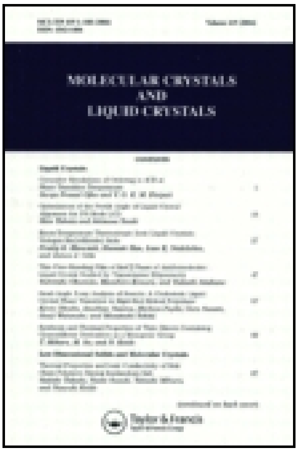

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The Synthesis and Transition Temperatures of Some Lateral Cyano-Substituted-1,1′:4′,1″-terphenyls

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The Synthesis and Transition Temperatures of Some Lateral Cyano-Substituted-1,1′:4′,1″-terphenyls

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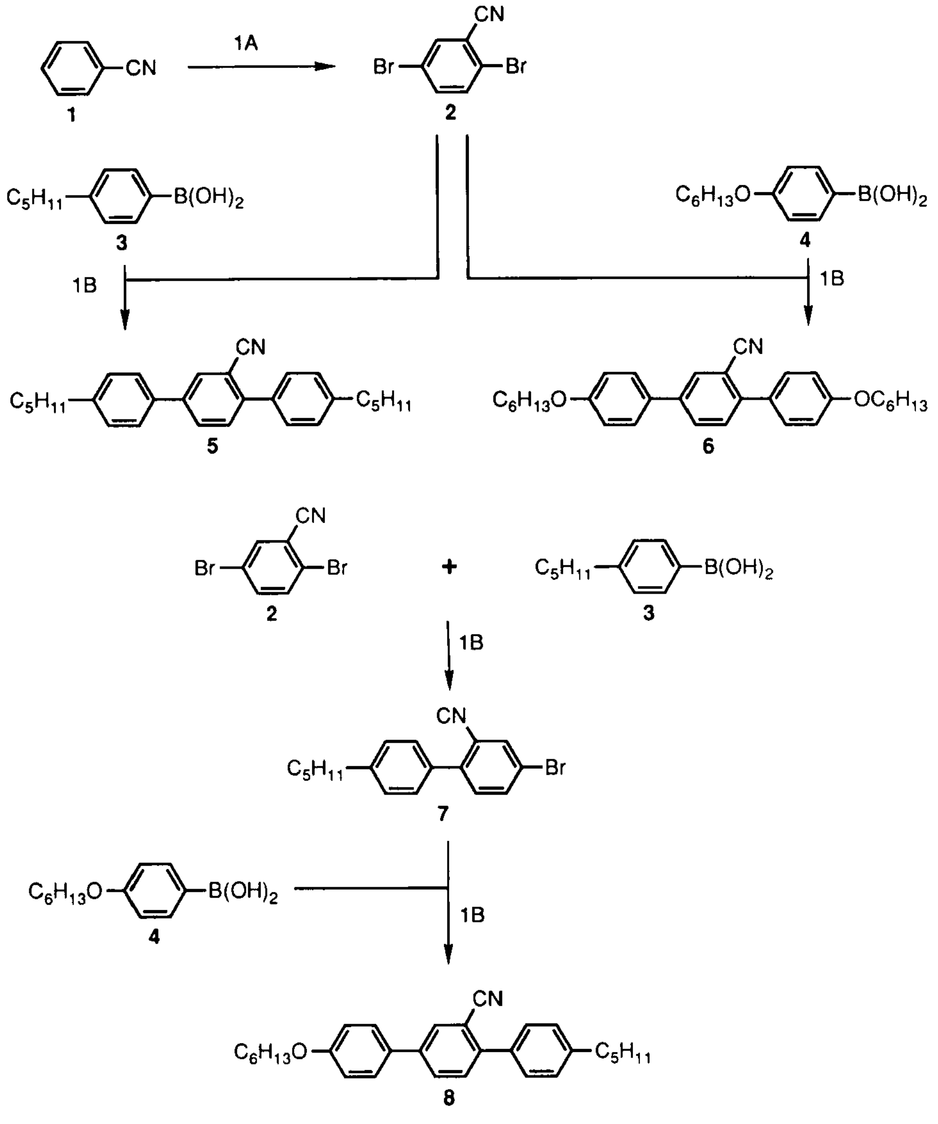
In recent years we have used palladium-catalysed cross-coupling procedures to prepare a large number of very interesting lateral mono- and di-fluoro-substituted terphenyls. Similar methodology has been applied in the synthesis of lateral cyano-substituted terphenyls to assess the extent to which the mesophases of such systems can tolerate the larger cyano group; the synthetic routes to these compounds are discussed in detail. The compounds with the lateral cyano-substituent in the centre ring have very low melting points and the liquid crystal phases exhibited (S_C, S_A and nematic) are dependent on the terminal substituents. The compounds with the cyano-substituent at the edge of the terphenyl core are still quite low melting and they have very wide S_A ranges.

Keywords: lateral cyano-substitution, 1,1′:4′,1″-terphenyls, palladium-catalysed cross-coupling

INTRODUCTION

Lateral groups necessary to bring about negative dielectric anisotropy are usually bulky and so lead to high viscosities and reduced mesophase thermal stabilities.[1–6] However, laterally monofluoro-substituted terphenyls[7–12] (slightly positive ($\Delta\varepsilon$) and laterally difluoro-substituted terphenyls ($\Delta\varepsilon$ values typically -2 to -4)[12–16] generally have high clearing points. It was anticipated that a lateral cyano-substituent, although larger than a lateral fluoro-substituent, would not depress the clearing point of terphenyl systems to an unacceptable level and such compounds may even retain a tendency to form the S_C phase. The magnitude of the negative dielectric anisotropy for such systems may be sufficient to counter their expected higher viscosity values when considered for use in ferroelectric (S_C^*) mixtures and in nematic materials for ECB applications. For these reasons compounds **5**, **6**, **8**, **15**–**17**, **24** and **25** were prepared to provide a series of compounds with the lateral cyano group at a variety of positions in alkyl/alkoxy terminally substituted terphenyls.

An important method for preparing terphenyls, as used in some of our previous work,[11–14] is to couple a biphenyl system with a phenyl system or to couple a phenyl system twice (two mol equivalents) in the same reaction with another phenyl system. The latter approach was used initially because the preparation of 2,5-dibromobenzonitrile (**2**) was described in the literature[17] and, in the first instance, was easier to make than a suitable biphenyl system. Compound **2** (see Scheme I) was prepared by a 'swamping-catalyst' method[17] (large excess of aluminium chloride) in the



1A ...... $AlCl_3$, Br_2.

1B ...... $Pd(PPh_3)_4$, benzene, EtOH, 2M-Na_2CO_3.

SCHEME I

absence of a solvent. The first bromination is directed by the nitrile group, as expected, to the 3-position, but the second bromination occurs *para* to the bromo-substituent (i.e., the orientation of the second substitution is dominated by the first bromo-substituent).

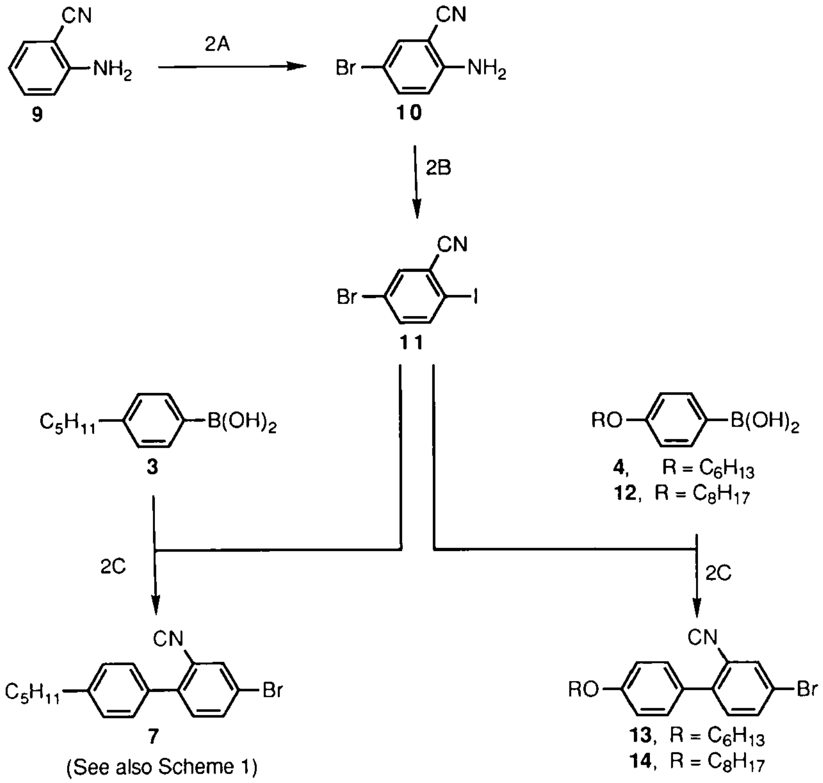
Compound **2** was then coupled by using the procedure we have previously described[11–14] to give terphenyls (compounds **5** and **6**) in excellent crude yields by using twice the normal amounts of the appropriate boronic acid and catalyst. The obvious limitation to this coupling method is that the terphenyl products can only have identical end-group substituents (compounds **5** and **6**).

The possibility that one bromo-substituent in compound **2** may be sufficiently more reactive towards coupling than the other was investigated with the prospect of providing a means to lateral cyano-substituted terphenyls with different end-group substituents. However, careful glc analysis of such a reaction revealed the formation of both possible biphenyl products and the terphenyl product from double coupling, along with unreacted starting material, and so indicated a low selectivity for reaction at the two bromo-substituted sites. Purification of the mixture by column chromatography gave two fractions; the first consisted of starting material and compound **7**, and the second fraction was a mixture of the isomer of compound **7** and the terphenyl. Removal of the starting material from the first fraction by Kugelrohr distillation gave enough pure material (compound **7**) to allow a second coupling (to compound **4**) and enabled the synthesis, in good yield, of the unsymmetrical terphenyl **8**.

A better way of synthesising the unsymmetrical terphenyls made use of compound **11** (see Scheme II) which was prepared by bromination of anthranilonitrile (2-aminobenzonitrile, compound **9**) with *N*-bromosuccinimide (to give a near quantitative yield of compound **10**) and subsequent diazotisation/iodination to give a very efficient preparation of compound **11**.

The selective coupling reactions of compound **11** with boronic acids **3**, **4** and **12** worked very well. The normal coupling conditions were used and the reaction was carefully monitored by glc and tlc analysis and the reaction was terminated when only a small amount of starting material remained (usually around 2 h). The crude material contained the desired product with small amounts of starting material and the terphenyl from double coupling, and none of the possible iodo-substituted biphenyl was detected. Careful purification by column chromatography then gave remarkably good yields of the desired biphenyl compounds **7**, **13** and **14**. [In the light of subsequent experience with these reactions we believe that a method offering total selectivity would be to couple 5-bromo-2-methoxybenzonitrile (compare with compounds **21** and **22**) with a phenylboronic acid. Demethylation of the biphenyl product, followed by the preparation of the triflate derivative[18] would enable another coupling,[19–21] with a different phenylboronic acid, at the triflate site to give the desired unsymmetrical terphenyl. This type of 'selective' coupling, although involving more steps, is a more specific process.]

At this stage it is appropriate to discuss the identification of compound **7**. When compound **7** was prepared by the first method (i.e. selective coupling to compound **2**) it was uncertain which possible isomer had been isolated. The appearance of both the ^{13}C and ^{1}H nmr spectra would be expected to be little different for either



2A ...... NBS, CH_2Cl_2.

2B ...... (i) $NaNO_2$, 36% HCl; (ii) KI.

2C ...... $Pd(PPh_3)_4$, benzene, EtOH, 2M-Na_2CO_3.

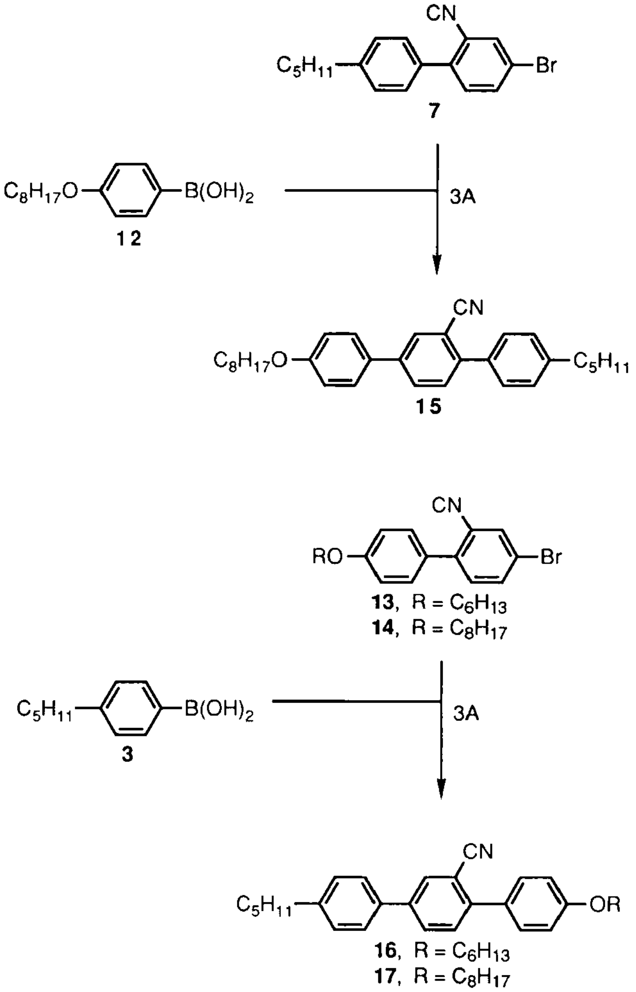
SCHEME II

isomer but, using substituent chemical shift values, the relative shifts for the two isomers were calculated and the correct structure of compound **7** was confirmed. This was, of course, verified by the unambiguous preparation of compound **7** by the second method.

The bromobiphenyl compounds prepared (**7**, **13** and **14**) were used in further coupling reactions to produce three more lateral cyano-substituted terphenyls (compounds **15**–**17**, see Scheme III).

Scheme IV shows the route to lateral cyano-substituted terphenyls with the cyano-substituent on the edge of the aromatic core *ortho* to a terminal alkoxy group. The preparation of the appropriate 2-alkoxy-5-bromobenzonitriles (**21** and **22**) by the bromination of compounds **19** and **20** occurred cleanly and efficiently (glc analysis did not reveal the presence of any mono-brominated product *ortho* to the alkoxy-substituent nor of any di-brominated material, despite the use of excess bromine).

The boronic acid species in the subsequent coupling reactions was chosen to be



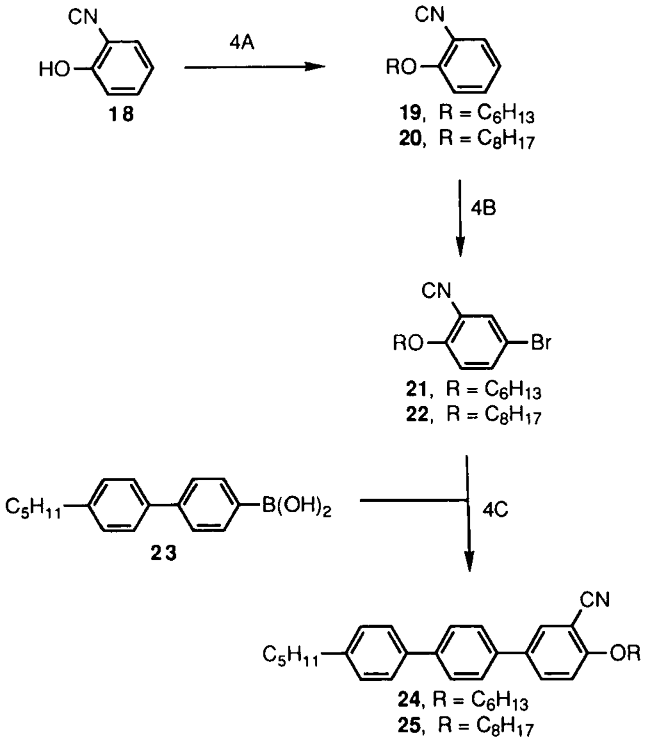
3A ...... $Pd(PPh_3)_4$, benzene, EtOH, 2M-Na_2CO_3

SCHEME III

the biphenyl unit (compound **23**) because the alternative boronic acids of compounds **21** and **22** would have been more difficult to make in the presence of the nitrile group.

DISCUSSION OF TRANSITION TEMPERATURES

Compounds **5**, **6**, **8** and **15–17** (see Table III) have the lateral cyano-substituent in the centre ring and their transition temperatures can be compared with the appropriate parent system (see Table I) to assess the effect of the cyano group on



4A ...... RBr, K_2CO_3, acetone.

4B ...... Br_2, $CHCl_3$.

4C ...... $Pd(PPh_3)_4$, benzene, EtOH, 2M-Na_2CO_3.

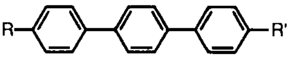
SCHEME IV

terphenyls and with the appropriate monofluoroterphenyl (see Table II) to assess the relative effects of a cyano- and a fluoro-substituent.

Compounds **5** and **6** have, in each case, identical chains at the terminal positions and although compound **6** is a dialkoxy-substituted compound (which we have not usually prepared because of their unacceptably high melting points) the melting point is low enough in this case for an S_C phase to be revealed (albeit monotropically). Compound **5**, being dialkyl-substituted, is low-melting (40.0°C), and the cyano-substituent has caused a depression in the melting point of 152.0°C compared to compound **26** and the additional depression in melting point over the monofluoroterphenyl (compound **29**) is 11.5°C. The alkyl-alkoxy-substituted compounds (**8**, mp 35.5°C and **16**, mp 48.5°C) compared with their parent system (compound **27**, mp 205.0°C),[11] show the melting point depressions caused by the lateral cyano-substituent to be 169.5 and 156.5°C respectively. Similarly, the octoxy homologues **15** and **17** have had their melting points reduced from 194.5°C (compound **28**)[11] by 161.0 and 159.5°C respectively. The very large depressions in melting points

TABLE I

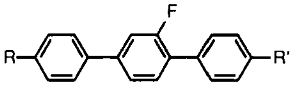
Transition temperatures (°C) for 4-alkoxy-4″-alkyl- and 4,4″-dialkylterphenyls (**26**,[22] **27**[11] and **28**[11])



Compound			Transition Temperatures (°C)			
No.	R	R'	K	S_B	S_A	I
26	C_5H_{11}	C_5H_{11}	* 192.0	-	* 213.0	*
27	C_5H_{11}	$C_6H_{13}O$	* 205.0	* 216.0	* 228.5	*
28	C_5H_{11}	$C_8H_{17}O$	* 194.5	* 211.0	* 221.5	*

TABLE II

Transition temperatures (°C) for 4- or 4″-alkoxy-4- or 4″-alkyl- and 4,4″-dialkyl-2′-fluoroterphenyls (**29**–**34**)[7–10]



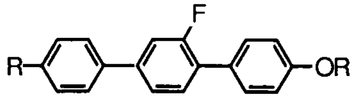
Compound			Transition Temperatures (°C)								
No.	R	R'	K	S_G	S_J	S_B	S_I	S_C	S_A	N	I
29	C_5H_{11}	C_5H_{11}	* 51.5	-	-	* 62.0	-	-	* 109.5	* 136.5	*
30	$C_6H_{13}O$	C_5H_{11}	* 70.0	* 78.0	-	* 92.0	* 93.0	* 118.0	* 155.0	* 166.5	*
31	$C_8H_{17}O$	C_5H_{11}	* 69.0	* 83.0	-	* 100.5	-	* 124.0	* 158.0	* 161.0	*
32	C_5H_{11}	$C_6H_{13}O$	* 62.5	-	(* 47.5	-	* 50.0)	* 113.5	-	* 162.5	*
33	C_5H_{11}	$C_8H_{17}O$	* 47.0	-	(* 40.0)	-	* 53.5	* 116.5	* 130.0	* 155.0	*
34	C_3H_7	C_9H_{19}	* 46.0	-	-	(* 35.0)	-	* 52.0	* 89.0	* 126.5	*

caused by the lateral cyano-substituent in the central ring of the terphenyl therefore lie within a relatively narrow range of 152.0 to 169.5°C and in all cases, except for compound **6**, compounds of very low melting point have been produced. When compounds **5**, **8** and **15**–**17** are compared with their appropriate fluoro-substituted compounds (**29**–**33** respectively) then melting points are seen to be lower for the cyano-substituted systems by 11.5, 34.5, 35.5, 14.0 and 12.0°C respectively.

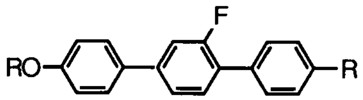
Compared to the fluoro-substituent, the protruding, linear cyano-substituent has a much greater effect on mesophase thermal stability than on melting points. Compound **5**, despite a low melting point, only exhibits monotropic mesophases, and the reduction in S_A phase thermal stability is 179.5°C (compound **26**,[22] $T_{S_A\text{-}I}$ at 213.0°C). Comparing compound **5** with its fluoro-substituted analogue (**29**), it is seen that the S_B phase has been totally eliminated and the S_A and N phases have been reduced by 76.0 and 98.5°C respectively. Note that the nematic phase has been reduced more than the smectic phase; this is presumably because the more dipolar cyano-substituent supports the smectic phase thermal stability more effectively than the fluoro-substituent (such dipole effects do not affect the nematic phase[23]).

An interesting feature revealed by compounds **8** and **15–17** is that when the cyano-substituent is pointing towards the alkoxy-substituent (compounds **16** and **17**) then S_C and N phases are exhibited; however, when it points towards the alkyl-substituent then the compounds (**8** and **15**) are purely S_A in character. For compounds **8** and **15** the S_A phase thermal stabilities of 97.5 and 103.0°C respectively are lower than the parent systems (compounds **27** and **28**)[11] by 131.0 and 118.5°C respectively. The additional reduction over the fluoro-substituent (compounds **30** and **31** respectively) are 57.5 and 55.0°C respectively. Compounds **16** and **17** cannot be compared directly with their parent systems which do not show S_C or N phases, but S_C/N phase thermal stabilities of 29.5/77.5 and 42.0/78.0°C for compounds **16** and **17** respectively represent reductions from the values for the fluoro-substituted analogues (compounds **32** and **33** respectively) of 84.0/85.0 and 74.5/77.0°C respectively.

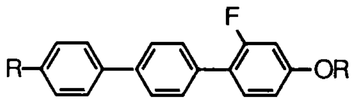
The effect of lateral mono-fluoro- and di-fluoro-substitution in terphenyls has recently been discussed in terms of a fluoro-substituent's ability to broaden the molecule and its ability to cause twisting about the inter-annular bond connecting two benzene rings to leave an alkoxy- or alkyl-substituted phenyl or biphenyl unit which may or may not carry a fluoro-substituent; a third effect for fluoro-substitution on an 'outer' edge was also discussed.[16] On this basis, for substitution patterns of type **I–IV**, smectic A character was seen when the fluoro-substituent was part of an untwisted, alkoxy-substituted biphenyl unit (eg, **II**), and the greatest S_C character was seen for compounds with untwisted, alkoxy-substituted biphenyl units (eg, **IV**); smectic C stabilities for compounds with untwisted, alkyl-substituted biphenyl units (eg, **I** and **III**) were similar. A comparable situation is seen for the cyano-substituted systems shown in Table III. In these cases, when the cyano-substituent is part of an untwisted, alkoxy-substituted biphenyl unit (ie, compounds **8** and **15**; comparable to **II**) the highest S_A character is produced, and when the cyano group is part of an untwisted, alkyl-substituted biphenyl unit (ie, compounds **16** and **17**; comparable to **I**) then S_C character is seen.



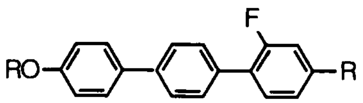
I



II



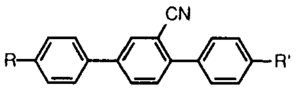
III



IV

TABLE III

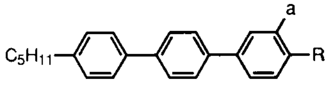
Transition temperatures (°C) for 4-alkoxy-2′-cyano-4″-pentyl-4″-alkoxy-2′-cyano-4-pentyl-, 2′-cyano-4,4″-dihexoxy- and 2′-cyano-4,4″-dipentylterphenyls (**5**, **6**, **8** and **15**–**17**)



Compound			Transition Temperatures (°C)								
No.	R	R'	K		S_C		S_A		N		I
5	C_5H_{11}	C_5H_{11}	*	40.0	-------------		(*	33.5	*	38.0)	*
6	$C_6H_{13}O$	$C_6H_{13}O$	*	101.5	(*	61.0)	*	110.0	*	114.0	*
8	$C_6H_{13}O$	C_5H_{11}	*	35.5	--------------		*	97.5	--------------		*
15	$C_8H_{17}O$	C_5H_{11}	*	33.5	--------------		*	103.0	--------------		*
16	C_5H_{11}	$C_6H_{13}O$	*	48.5	(*	29.5)	--------------		*	77.5	*
17	C_5H_{11}	$C_8H_{17}O$	*	35.0	*	42.0	--------------		*	78.0	*

TABLE IV

Transition temperatures (°C) for 4-alkoxy-3-cyano- or -3-fluoro-4″-pentylterphenyls (**24**, **25** and **35**[11], **36**[11])



Compound			Transition Temperatures (°C)									
No.	R	a	K		S_G		S_B		S_C		S_A		I
24	$C_6H_{13}O$	CN	*	62.0	------------		------------		------------		*	163.5	*
25	$C_8H_{17}O$	CN	*	62.0	------------		------------		------------		*	160.0	*
35	$C_6H_{13}O$	F	*		*	160.0	---------------		*	162.0	*	201.0	*
36	$C_8H_{17}O$	F	*		*	146.0	*	158.0	---------------		*	195.0	*

The effect of cyano- and comparable fluoro-substitution on an 'outer' edge of the terphenyl core is illustrated by the values in Table IV. Although the cyano-substituted compounds melt at a reasonable 62.0°C, corresponding to reductions in melting points of 143.0 and 132.5°C respectively, compared with the parent systems, they only show an S_A phase. The clearing points for compounds **24** and **25** are, however, only depressed by 65.0 and 61.5°C respectively; the reasons given for the similar effects seen with fluoro-substitution at the 'outer' edge are the competing effects of molecular broadening and the advantageous space-filling by a substituent *ortho* to a terminal group.[11–13,16] In comparison with the fluoro-substituted compounds (**35** and **36**)[11] the $T_{SA\text{-}I}$ values are further reduced by 37.5 and 35.0°C respectively, which is less than for the differences seen in the centre ring comparisons.

Promising results (see Table V) were obtained when small amounts (5–16 wt%) of compounds **5** were mixed with two monofluoroterphenyls (**33** and **34**). It can be seen that the ordered smectic phases are totally eliminated but the S_C, S_A and N phases are affected much less severely.

Overall, these lateral cyano-substituted terphenyls have remarkably low melting points and, although much reduced when compared with the fluoro-substituted analogues, their mesophase thermal stabilities are still reasonably high. The type of mesophase exhibited depends on the structure of the compound and the S_C phase is seen in certain compounds.

TABLE V

Transition temperatures (°C) for mixtures of compound **5** in host materials **33** and **34**

Composition	K	S_J	S_I	S_C	S_A	N	I
100% **33**	* 47.0	(* 40.0)	* 53.5	* 116.5	* 130.0	* 155.0	*
95% **33** 5% **5**	* 39.0 (18.0)	----------	----------	* 108.5	* 123.0	* 149.0	*
84% **33** 16% **5**	* 37.0 (8.0)	----------	----------	* 90.5	* 102.0	* 137.5	*

Composition	K	S_B	S_C	S_A	N	I
100% **34**	* 46.0	(* 35.0)	* 52.0	* 89.0	* 126.5	*
95% **34** 5% **5**	* 42.5 (3.0)	------------	* 48.0	* 80.0	* 122.0	*
85% **34** 15% **5**	* 36.0 (-2.0)	------------	* 39.0	* 60.5	* 113.0	*

Note: the figures given in brackets after the melting temperatures are the recrystallisation temperatures of the mixture.

EXPERIMENTAL

Confirmation of the structures of intermediates and products was obtained by ^{1}H nmr spectroscopy (JEOL JNM-GX270 spectrometer), infrared spectroscopy (Perkin-Elmer 457 grating spectrophotometer) and mass spectrometry (Finnigan-MAT 1020 GC/MS spectrometer). The progress of reactions was usually monitored using a Perkin-Elmer 8320 capillary gas chromatograph fitted with a 12 m QC2/BP1-1.0 SGE column. 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-2C and data station). The purity of each of the compounds in Tables III and IV was checked by glc analysis (see above) and by hplc analysis (Microsorb C18 80-215-C5 RP column) and all compounds were >99.9% pure.

The preparations of compounds **3**, **4**, **12** and **23** were described in Reference 11.

2,5-Dibromobenzonitrile (2)

Bromine (44.0 g, 0.275 mol) was added dropwise to a mixture of compound **1** (10.00 g, 0.097 mol) and aluminum chloride (42.0 g, 0.31 mol) at room temperature. The mixture was heated at 120°C for 7 h and poured into ice/water. The product was extracted into ether (twice), the combined ethereal extracts were washed with aqueous sodium thiosulphate and dried ($MgSO_4$). The solvent was removed *in vacuo* to give an off-white solid (glc analysis revealed the presence of three components) which was recrystallised from benzene to yield colourless crystals (pure by glc analysis).

Yield 12.15 g (48%); mp 144–145°C (lit.,[17] 144–145°C); ^1H nmr ($CDCl_3$) δ 7.55(1H, q), 7.60(1H, q), 7.80(1H, q); ir (KCl) ν_{max} 3090, 3060, 2240, 1460, 1380, 1270, 1200, 1090, 1040, 830 cm^{-1}; ms *m/z* 261 (M^+), 220, 197, 180, 168, 153.

2′-Cyano-4,4″-dipentylterphenyl (5)

Tetrakis(triphenylphosphine)palladium(0) (0.3749 g, 0.325 mmol), followed by a solution of compound **3** (2.88 g, 0.015 mol) in ethanol (35 ml), was added to a stirred solution of compound **2** (1.40 g, 5.36 mmol) in benzene (35 ml) and 2M-sodium carbonate (35 ml). The mixture was heated under reflux for 16 h (or until glc and/or tlc analysis revealed a complete reaction), cooled and ether and water were added. The separated aqueous extract was washed with ether, the combined organic extracts were washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* and the residue was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 2:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.13 g (53%); transitions (°C) K 40.0 (S_A 33.5 N 38.0) I; ^1H nmr ($CDCl_3$) δ 0.90(6H, t), 1.35(8H, m), 1.65(4H, quint), 2.65(4H, t), 7.29(2H, d), 7.31(2H, d), 7.52(4H, d), 7.56(1H, d), 7.83(1H, q), 7.95(1H, d); ir (KCl) ν_{max} 2950, 2920, 2850, 2210, 1600, 1480, 800 cm^{-1}; ms *m/z* 395(M^+), 338, 281.

2′-Cyano-4,4″-dihexoxyterphenyl (6)

Quantities: compound **2** (1.30 g, 4.98 mmol), compound **4** (3.33 g, 0.015 mol), tetrakis(triphenylphosphine)palladium(0) (0.3554 g, 0.308 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 2:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 0.87 g (38%); transitions (°C) K 101.5 (S_C 61.0) S_A 110.0 N 114.0 I; ^1H nmr ($CDCl_3$) δ 0.90(6H, t), 1.35(8H, m), 1.45(4H, quint), 1.80(4H, quint), 4.00(4H, t), 7.00(2H, d), 7.03(2H, d), 7.52(4H, 2xd), 7.55(1H, d), 7.80(1H, q), 7.90(1H, d); ir (KCl)ν_{max} 2950, 2860, 2220, 1610, 1530, 1490, 1480, 1290, 1250, 1180, 1030, 830 cm^{-1}; ms *m/z* 455(M^+), 384, 371, 287.

4-Bromo-2-cyano-4′-pentylbiphenyl (7)

Method 1

Quantities: compound **2** (1.80 g, 6.90 mmol), compound **3** (1.20 g, 6.25 mmol), tetrakis(triphenylphosphine)palladium(0) (0.4510 g, 0.390 mmol).

The experimental procedure was as described for the preparation of compound **5** except that the reaction mixture was carefully monitored by glc and tlc analysis and was heated under reflux for 2 h. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 3:1] to give two fractions: (a) two components; compound **2** and compound **7** (product), (b) two components; compound **5** and 4-bromo-3-cyano-4′-pentylbiphenyl. The product was purified by distillation (Kugelrohr at 0.1 mmHg) to yield a pale yellow liquid.

Yield 0.42 g (20%); ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(4H, m), 1.60(2H, quint), 2.60(2H, t), 7.30(2H, d), 7.35(1H, d), 7.45(2H, d), 7.70(1H, q), 7.85(1H, d); ir (film) ν_{max} 2980, 2960, 2860, 2250, 1490, 1475, 1390, 1275, 1195, 1100, 1015, 835, 845 cm^{-1}; ms *m/z* 329(M^+), 327(M^+), 272, 270, 190.

Method 2

Quantities: compound **11** (3.50 g, 0.011 mol), compound **3** (2.53 g, 0.013 mol), tetrakis(triphenylphosphine)palladium(0) (0.6421 g, 0.56 mmol).

The experimental procedure was as described in Method 1 except that the reaction mixture was heated under reflux for 3 h. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a pale-yellow liquid.

Yield 2.67 g (74%); spectroscopy values were identical to those for the compound obtained from method 1.

2′-Cyano-4″-hexoxy-4-pentylterphenyl (8)

Quantities: compound **7** (method 1) (0.34 g, 1.0 mmol), compound **4** (0.44 g, 1.98 mmol), tetrakis(triphenylphosphine)palladium(0) (0.1645 g, 0.14 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a colourless solid which was recrystallised from ethanol to give colourless crystals.

Yield 0.26 g (61%); transitions (°C) K 35.5 S_A 97.5 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.35(8H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 7.00(2H, d), 7.30(2H, d), 7.51(1H, d), 7.53(2H, d), 7.55(2H, d), 7.80(1H, q), 7.90(1H, d); ir (KCl) ν_{max} 2960, 2945, 2860, 2220, 1605, 1485, 1245, 835 cm^{-1}; ms *m/z* 425(M^+), 368, 341, 284.

2-Amino-5-bromobenzonitrile (10)

N-Bromosuccinimide (37.7 g, 0.21 mol) was added in small portions over 40 min to a stirred, cooled (−10 to 0°C) solution of compound **9** (25.00 g, 0.212 mol) in dry dichloromethane (150 ml) under dry nitrogen. The mixture was stirred at 0°C for 1.25 h (glc analysis revealed a complete reaction) and washed with a large amount of water. The aqueous layer was washed with dichloromethane and the combined organic phases were washed with water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give a red-purple solid.

Yield 39.0 g (94%); mp 92–94°C; ^{1}H nmr ($CDCl_3$) δ 4.50(2H, s), 6.65(1H, d), 7.40(1H, q), 7.50(1H, d); ir (KCl) ν_{max} 3450, 3360, 2220, 1635, 1560, 1490, 1305, 1155 cm^{-1}; ms *m/z* 198(M$^+$), 196(M$^+$), 116, 90.

5-Bromo-2-iodobenzonitrile (11)

A stirred mixture of compound **10** (25.00 g, 0.127 mol) and 36% hydrochloric acid (110 ml) was warmed gently to obtain a solution, then cooled to −5°C and a solution of sodium nitrite (10.50 g, 0.152 mol) in water (50 ml) was added dropwise whilst maintaining the temperature at −5°C. The mixture was stirred at 0°C for 0.5 h, cyclohexane (100 ml) was added and a solution of potassium iodide (43.5 g, 0.26 mol) in water (100 ml) was added dropwise at between 0 and 5°C. The mixture was stirred at room temperature for a few hours (overnight for convenience) and the product was extracted into ether (twice). The combined organic extracts were washed with sodium metabisulphite, 10% sodium hydroxide, water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give an off-white solid.

Yield 35.0 g (87%); mp 113–114°C; ^{1}H nmr ($CDCl_3$) δ 7.40(1H, q), 7.72(1H, d), 7.78(1H, d); ir (KCl) ν_{max} 3090, 3060, 2240, 1450, 1375, 1270, 1195, 1090, 1025, 825 cm^{-1}; ms *m/z* 309(M$^+$), 307(M$^+$), 179, 125.

4-Bromo-2-cyano-4′-hexoxybiphenyl (13)

Quantities: compound **11** (1.80 g, 5.84 mmol), compound **4** (1.56 g, 7.03 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3572 g, 0.31 mmol).

The experimental procedure was as described for the preparation of compound **7** except that the mixture was heated under reflux for 1.75 h. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a colourless solid.

Yield 1.72 g (82%); ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.35(4H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 7.00(2H, d), 7.35(1H, d), 7.45(2H, d), 7.70(1H, q), 7.85(1H, d); ir (KCl) ν_{max} 2955, 2945, 2880, 2240, 1620, 1525, 1480, 1265, 1185 cm^{-1}; ms *m/z* 359(M$^+$), 357(M$^+$), 275, 273, 245, 243.

4-Bromo-2-cyano-4′-octoxybiphenyl (14)

Quantities: compound **11** (2.50 g, 8.12 mmol), compound **12** (2.44 g, 9.76 mmol), tetrakis(triphenylphosphine)palladium(0) (0.4927 g, 0.43 mmol).

The experimental procedure was as described for the preparation of compound **7** except that the mixture was heated under reflux for 2 h. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a colourless solid.

Yield 2.50 g (80%); mp 41–43°C; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(8H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 7.00(2H, d), 7.35(1H, d), 7.45(2H, d), 7.70(1H, q), 7.85(1H, d); ir (KCl) ν_{max} 2960, 2950, 2860, 2240, 1615, 1625, 1475, 1265, 1250, 1185, 1055, 830 cm^{-1}; ms *m/z* 387(M$^+$), 385(M$^+$), 273, 271, 262, 260.

2′-Cyano-4″-octoxy-4-pentylterphenyl (15)

Quantities: compound **7** (1.30 g, 3.96 mmol), compound **12** (1.19 g, 4.76 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2655 g, 0.23 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give an off-white solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.18 g (66%); transitions (°C) K 33.5 S_A 103.0 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.30(12H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 7.00(2H, d), 7.30(2H, d), 7.51(1H, d), 7.53(2H, d), 7.54(2H, d), 7.75(1H, q), 7.90(1H, d); ir (KCl) ν_{max} 2980, 2960, 2880, 2250, 1620, 1500, 1260, 1200, 835 cm^{-1}; ms *m/z* 453(M$^+$), 396, 341, 283.

2′-Cyano-4-hexoxy-4″-pentylterphenyl (16)

Quantities: compound **13** (1.50 g, 4.19 mmol), compound **3** (1.05 g, 5.47 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3140 g, 0.27 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a pale yellow solid which was recrystallised (charcoal decolourisation) from ethanol to yield colourless crystals.

Yield 0.80 g (44%); transitions (°C) K 48.5 (S_C 29.5) N 77.5 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.35(8H, m), 1.45(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 7.00(2H, d), 7.30(2H, d), 7.51(1H, d), 7.54(4H, d), 7.80(1H, q), 7.95(1H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 2240, 1615, 1490, 1480, 1255, 1190, 830 cm^{-1}; ms *m/z* 425(M$^+$), 341, 284.

2′-Cyano-4-octoxy-4″-pentylterphenyl (17)

Quantities: compound **14** (1.48 g, 3.83 mmol), compound **3** (1.01 g, 5.26 mmol), tetrakis(triphenylphosphine)palladium(0) (0.2812 g, 0.34 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 1:1] to give a colourless solid which was recrystallised from ethanol to yield colourless crystals.

Yield 1.16 g (67%); transitions (°C) K 35.0 S_C 42.0 N 78.0 I; ^{1}H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.30(12H, m), 1.50(2H, quint), 1.65(2H, quint), 1.80(2H, quint), 2.65(2H, t), 4.00(2H, t), 7.00(2H, d), 7.30(2H, d), 7.51(1H, d), 7.54(4H, d), 7.80(1H, q), 7.95(1H, d); ir (KCl) ν_{max} 2960, 2940, 2860, 2230, 1610, 1490, 1475, 1255, 1185, 830 cm^{-1}; ms *m/z* 453(M$^+$), 396, 341, 284.

2-Hexoxybenzonitrile (19)

Quantities: compound **18** (8.10 g, 0.068 mol), 1-bromohexane (13.50 g, 0.082 mol), potassium carbonate (18.77 g, 0.136 mol).

The experimental procedure was as described in a previous publication.[13]

Yield 13.11 g (95%); bp 115–118°C at 0.1 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.85(3H, t), 1.30(4H, m), 1.45(2H, quint), 1.80(2H, quint), 4.05(2H, t), 6.95(2H, m), 7.50(2H, m); ir (film) ν_{max} 2980, 2960, 2880, 2250, 1610, 1595, 1505, 1465, 1300, 1270, 1175, 1120, 765 cm^{-1}; ms *m/z* 203(M$^+$), 160, 146, 132.

2-Octoxybenzonitrile (20)

Quantities: compound **18** (7.50 g, 0.063 mol), 1-bromo-octane (14.00 g, 0.127 mol), potassium carbonate (17.50 g, 0.127 mol).

The experimental procedure was as described for the preparation of compound **19**.

Yield 13.90 g (96%); bp 130–135°C at 0.05 mmHg; ^{1}H nmr ($CDCl_3$) δ 0.85(3H, t), 1.30(8H, m), 1.45(2H, quint), 1.80(2H, quint), 4.05(2H, t), 6.95(2H, m), 7.50(2H, m); ir (film) ν_{max} 2940, 2860, 2240, 1600, 1585, 1495, 1455, 1290, 1265, 1170, 1115, 760 cm^{-1}; ms *m/z* 231(M$^+$), 174, 160, 146, 125, 199.

5-Bromo-2-hexoxybenzonitrile (21)

Bromine (19.32 g, 0.121 mol) was added dropwise over 15 min to a stirred solution of compound **19** (12.25 g, 0.060 mol) in chloroform (30 ml) at room temperature. The stirred solution was heated under reflux for 42 h (glc analysis revealed a complete reaction, with only one product peak). The cooled solution was washed with aqueous sodium metabisulphite, water and dried ($MgSO_4$). The solvent was removed *in vacuo* to give an off-white solid.

Yield 16.10 g (95%); mp low, around 25°C; ^{1}H nmr ($CDCl_3$) δ 0.90(3H, t), 1.30(4H, m), 1.45(2H, quint), 1.85(2H, quint), 4.05(2H, t), 6.85(1H, d), 7.58(1H, q), 7.62(1H, d); ir (KCl) ν_{max} 2980, 2940, 2860, 2240, 1600, 1500, 1475, 1400, 1290, 1265, 1140, 1015, 820 cm^{-1}; ms *m/z* 283(M$^+$), 282, 281(M$^+$), 280, 199, 197.

5-Bromo-2-octoxybenzonitrile (22)

Quantities: compound **20** (13.50 g, 0.058 mol), bromine (18.70 g, 0.117 mol).

The experimental procedure was as described for the preparation of compound **21**.

Yield 17.50 g (97%); mp 36–37°C; ^{1}H nmr ($CDCl_3$) δ 0.85(3H, t), 1.25(8H, m), 1.45(2H, quint), 1.80(2H, quint), 4.00(2H, t), 6.85(1H, d), 7.58(1H, q), 7.62(1H, d); ir (KCl) ν_{max} 2980, 2940, 2860, 2250, 1600, 1500, 1480, 1400, 1295, 1265, 1140, 1000, 835 cm^{-1}; ms *m/z* 311(M$^+$), 309(M$^+$), 254, 252, 199, 197.

3-Cyano-4-hexoxy-4″-pentylterphenyl (24)

Quantities: compound **21** (1.55 g, 5.50 mmol), compound **23** (1.91 g, 7.13 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3910 g, 0.34 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 2:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 1.10 g (47%); transitions (°C) K 62.0 S_A 163.5 I; ^1H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.35(8H, m), 1.50(2H, quint), 1.65(2H, quint), 1.85(2H, quint), 2.65(2H, t), 4.10(2H, t), 7.03(1H, d), 7.27(2H, d), 7.54(2H, d), 7.57(2H, d), 7.66(2H, d), 7.76(1H, q), 7.81(1H, d); ir (KCl) ν_{max} 2960, 2940, 2880, 2240, 1610, 1495, 1290, 1125, 815 cm^{-1}; ms *m/z* 425(M^+), 368, 341, 284.

3-Cyano-4-octoxy-4″-pentylterphenyl (25)

Quantities: compound **22** (1.55 g, 5.00 mmol), compound **23** (1.75 g, 6.53 mmol), tetrakis(triphenylphosphine)palladium(0) (0.3794 g, 0.33 mmol).

The experimental procedure was as described for the preparation of compound **5**. The crude product was purified by column chromatography [silica gel/petroleum fraction (bp 40–60°C)-dichloromethane, 2:1] to give a colourless solid which was recrystallised from ethanol-ethyl acetate (2:1) to yield colourless crystals.

Yield 1.85 g (82%); transitions (°C) K 62.0 S_A 160.0 I; ^1H nmr ($CDCl_3$) δ 0.90(6H, 2xt), 1.30(12H, m), 1.50(2H, quint), 1.65(2H, quint), 1.85(2H, quint), 2.65(2H, t), 4.10(2H, t), 7.03(1H, d), 7.27(2H, d), 7.54(2H, d), 7.57(2H, d), 7.66(2H, d), 7.76(1H, q), 7.81(1H, d), ir (KCl) ν_{max} 2970, 2940, 2860, 2240, 1615, 1500, 1475, 1295, 1270, 1140, 815 cm^{-1}; ms *m/z* 453(M^+), 438, 425, 411, 396, 390, 284.

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