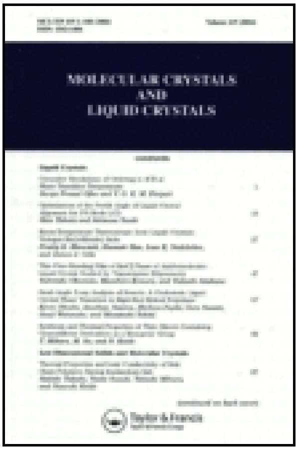

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Mesomorphic Transition Temperatures for the Homologous Series of 4-n-Alkyl-4′-Cyanotolanes and Other Related Compounds

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Mesomorphic Transition Temperatures for the Homologous Series of 4-*n*-Alkyl-4′-Cyanotolanes and Other Related Compounds†

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The C_1 to C_{12} homologues of the series of 4-*n*-alkyl-4′-cyanotolanes have been synthesised and their transition temperatures measured. The C_6, C_7, C_9, and C_{11} homologues produced enantiotropic nematic phases. Virtual nematic to isotropic liquid (N–I) transition temperatures were determined for the C_1 and C_2 derivatives; all the other homologues produced monotropic mesophases. The overall shapes of the N–I transition curves for the odd and even homologues are unusual. Smectic properties were not observed until after the C_{10} homologue‡. The N–I transition temperatures for the 4′-octyl and 4′-heptyloxy derivatives of 4-cyanostilbene were higher (~30°C) than those of the corresponding tolane derivatives. However the stilbene derivatives were highly unstable. The isomeric compounds 4-cyano-4′-(4″-octylphenyl)tolane and 4-(4″-cyanophenyl)-4′-octyltolane were found to exhibit smectic A and nematic phases, while the bromo-substituted precursors of these compounds exhibited smectic E, B, and A phases.

INTRODUCTION

The 4-*n*-alkyl-4′-cyanobiphenyls[1] have been found to be very useful liquid crystalline materials. Quite apart from their technological applications, their stability and low melting points have greatly eased the problems associated with the measurement of spectroscopic and other physical data for nematic and smectic A liquid crystal phases. In particular, the linear nature of the molecules and the presence of a cyano group make the compounds suitable for Raman spectroscopic studies of aligned mesophases. An

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† Presented at the Sixth International Liquid Crystal Conference, Kent State University, Kent, Ohio, U.S.A., August 1976.

‡ See note added in proof at end of this paper.

attempt to find another homologous series of low melting liquid crystalline materials similar in molecular geometry to the 4-*n*-alkyl-4′-cyanobiphenyls led to the synthesis of the 4-*n*-alkyl-4′-cyanotolanes.

The synthetic route used to prepare the 4-*n*-alkyl-4′-cyanotolanes could be readily adapted to the synthesis of a number of related compounds. These include 4-cyano-4′-*n*-heptyloxytolane, the 4′-*n*-octyl and -*n*-heptyloxy derivatives of 4-cyanostilbene, the isomeric compounds 4-cyano-4′-(4″-*n*-octylphenyl)tolane and 4-(4″-cyanophenyl)4′-*n*-octyltolane, and the bromo-substituted precursors of these two isomeric compounds.

The stabilities of the above compounds and the relative thermal stabilities of their mesophases are discussed and compared with the respective stabilities for the corresponding derivatives of 4-cyanobiphenyl.

RESULTS AND DISCUSSION

The 4-*n*-alkyl-4′-cyanotolanes were prepared by the synthetic route illustrated in the Scheme. The melting points, mesomorphic transition temperatures, and enthalpies of fusion for the members of this homologous series and for two related compounds are given in Table I.

SCHEME

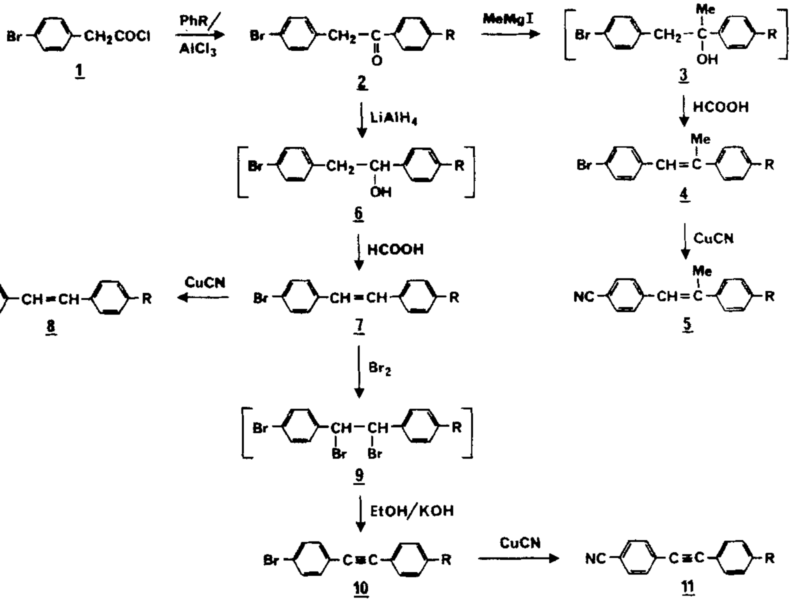
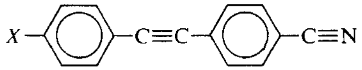
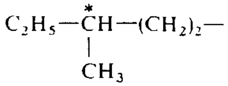


TABLE I

Thermodynamic data for the compounds



Substituent *X*	Transition temperatures (°C) C–N or I	 S_A–N	 N–I	Enthalpy of fusion (kcal mol^{-1})
CH_3	160		[65]ᵃ	6.5
C_2H_5	110		[62]ᵃ	6.2
n-C_3H_7	87		[78]	7.2
n-C_4H_9	84		[57]	5.9
n-C_5H_{11}	79.5		[70.5]	6.9
n-C_6H_{13}	57.5		57.9	9.0
n-C_7H_{15}	59		67.5	5.5
n-C_8H_{17}	63.5		[60]	8.1
n-C_9H_{19}	60		66.5	8.4
n-$C_{10}H_{21}$	65.5		[63.6]	8.5
n-$C_{11}H_{23}$	64	[61.4]	66.7	13.6
n-$C_{12}H_{25}$	72	[64.7]	[66]	12.6
 $C_2H_5{-}\overset{*}{C}H(CH_3){-}(CH_2)_2{-}$	81		[28]ᵃ	5.9
n-$C_7H_{15}O$	81		93.5	8.3

C = crystal; N = nematic; S_A = smectic A; I = isotropic liquid
[ ] = a monotropic transition
ᵃ Virtual N–I or Ch–I transition temperatures

A plot of the transition temperatures for the *n*-alkyl compounds against *n*, the number of carbon atoms in the alkyl chain, is shown in Figure 1. The enantiotropic nematic to isotropic liquid (N–I) transition temperatures of the C_6, C_7, C_9, and C_{11} homologues, the monotropic N–I transition temperatures of the C_3, C_4, C_5, C_8, C_{10}, and C_{12} homologues, and the monotropic nematic to smectic A (N – S_A) transition temperatures of the C_{11} and C_{12} homologues were all determined directly by optical microscopy. The N–I transition temperatures for the C_1 and C_2 homologues are virtual N–I transition temperatures obtained from the extrapolations in the plots shown in Figures 2 and 3. The smectic phases of the C_{11} and C_{12} homologues were shown to be smectic A phases by miscibility studies using the known smectic A phase of 4-cyano-4′-*n*-octyloxybiphenyl.

The melting points of the 4-*n*-alkyl-4′-cyanotolanes first of all fall sharply as the homologous series is ascended, producing a minimum at the C_6 homologue. Then there is a tendency for the melting points to alternate and give an average gradual increase for the remaining homologues. A number

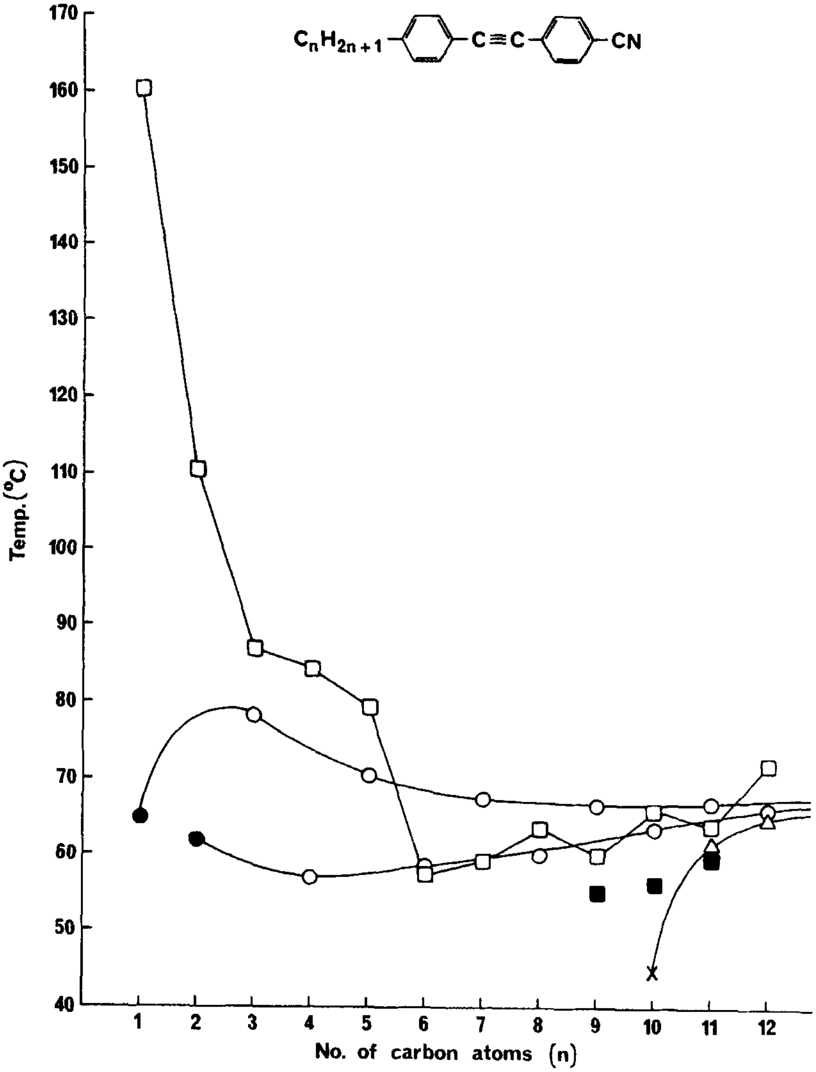


FIGURE 1 The transition temperatures for the homologous series of 4-*n*-alkyl-4′-cyanotolanes: □ melting point (C–N or I); ■ melting point of a second crystal form; ○ N–I transition temperature; ● virtual N–I transition temperature; △ S_A–N transition temperature; X temperature at which nematic phase solidifies.

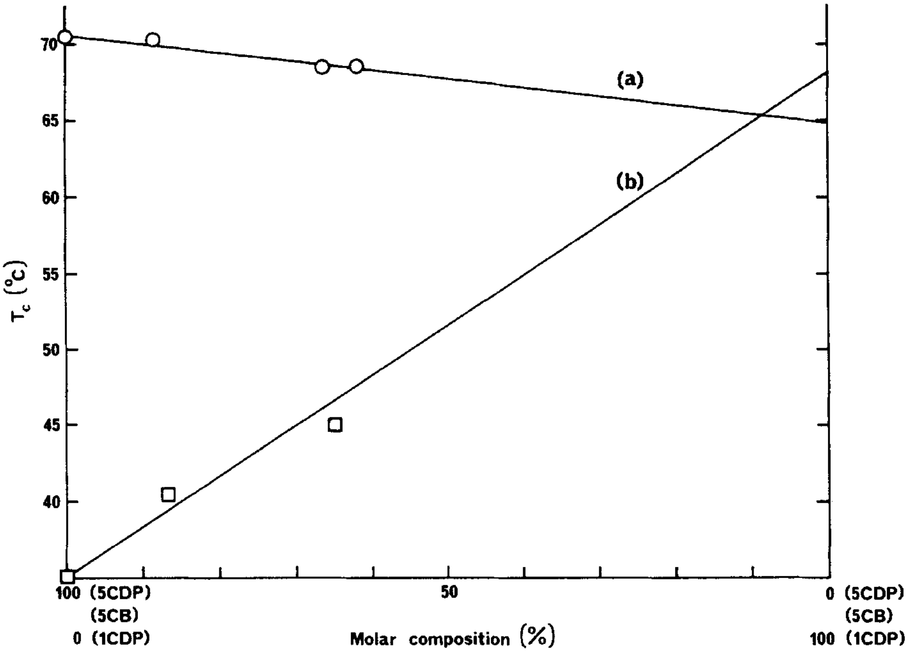


FIGURE 2 N-I Transition temperatures, T_c, of binary mixtures of (a) 4-cyano-4′-methyltolane (1 CDP) and 4-cyano-4′-pentyltolane (5 CDP); and (b) 1 CDP and 4-cyano-4′-pentylbiphenyl (5 CB)—see Table I.

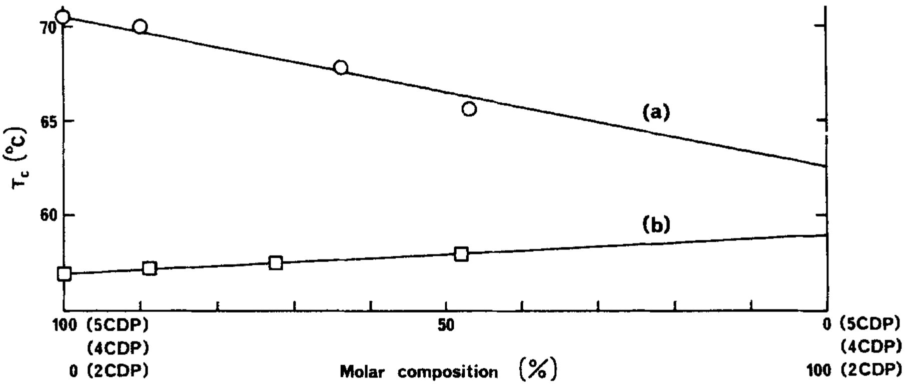


FIGURE 3 N-I Transition temperatures, T_c, of binary mixtures of (a) 4-cyano-4′-ethyltolane (2 CDP) and 4-cyano-4′-pentyltolane (5 CDP); and (b) 2 CDP and 4-cyano-4′-butyltolane (4 CDP)—see Table I.

of interesting polymorphic transitions were observed for the compounds; the observations are summarised below.

When the nematic melt of 4-cyano-4′-*n*-nonyltolane solidifies and the solid is reheated, melting occurs at 55°C, but the stable solid phase (m.p. 60°C) is then seen to grow as needles in the nematic phase.

When a sample of 4-cyano-4′-*n*-decyltolane is crystallised from ethanol, it appears to produce two solid forms which melt at 63°C and 65.5°C. Crystallisation from the nematic phase produces a third crystal form which has a crystal–nematic (C–N) transition temperature of 56.6°C. However, the other two crystal forms then grow as plates (m.p. 63.5°C) and fine needles (m.p. 65.5°C) in this nematic phase.

When the smectic phase of 4-cyano-4′-*n*-undecyltolane is allowed to crystallise at 56°C, a second solid phase is produced, which melts at 59°C to give a smectic A (S_A) phase. However, the S_A phase then rapidly solidifies to give the stable solid form (m.p. 64°C).

The overall shapes of the N–I transition curves shown in Figure 1 are unusual and once again it would seem that the present theories on the variation of N–I transition temperatures with chain length are not able to explain the observed variations, as is the case for the 4-*n*-alkyl-4′-cyanobiphenyls.[2] If the methyl and ethyl homologues are omitted from Figure 1, then the N–I curves are no longer unusual, with the odd homologues lying on an initially falling and finally a gently rising N–I curve, the even homologues lying on a rising N–I curve, and a gradual decrease in the alternation of the N–I transition temperature occurring as the series is ascended. However, the inclusion of the methyl homologue produces a maximum (at C_3) in the N–I curve for the odd homologues, and the inclusion of the ethyl homologue produces a minimum (at C_4) in the N–I curve for the even homologues. The values of the virtual N–I transition temperatures for 4-cyano-4′-methyltolane (1 CDP) and 4-cyano-4′-ethyltolane (2 CDP) are not of course considered to be very accurate, because of the unavoidably long extrapolations required in Figures 2 and 3 respectively, even though the error indicated by the two pairs of measurements seems to be only ±2°C. However, Figure 2 indicated clearly that 1 CDP has a lower N–I transition temperature than 4-cyano-4′-*n*-pentyltolane (5 CDP), and so it follows that 1 CDP has a lower N–I transition temperature than 4-cyano-4′-*n*-propyltolane (3 CDP). Similarly, Figure 3 indicates that 2 CDP has a higher N–I transition temperature than 4-*n*-butyl-4′-cyanotolane (4 CDP). The general shapes shown in Figure 1 for the two transition curves therefore seem to be real.

As expected, the longer and more polarisable 4-*n*-alkyl-4′-cyanotolanes have higher N–I transition temperatures than the corresponding 4-*n*-alkyl-4′-cyanobiphenyls. The rise in the N–I transition temperature on passing from 1 CDP to 3 CDP and the subsequent fall in the N–I transition temperatures on passing from 3 CDP to 5 CDP to 4-cyano-4'-heptyltolane (7 CDP) indicate that the molecules are in some way behaving differently from the molecules of 4-*n*-alkyl-4'-cyanobiphenyls whose N–I transition curve for the odd homologues has a minimum at C_3.[2] It appears that in the nematic phase, the longer and more polarisable core part of the molecule of the 4-cyanotolane is able to force the *n*-propyl chain of 3 CDP into the planar all-*trans* conformation (which is the most favourable conformation to produce a stable nematic phase) much more readily than is possible with the shorter and less polarisable molecular core in the case of 4-cyano-4'-*n*-propylbiphenyl.

The higher N–I transition temperatures resulting from the presence of the acetylenic link will also give rise to increases in the thermal energies of the alkyl chains. It is possible that this increase in thermal energy is large enough to cause a greater amount of disorder in the relatively longer alkyl chains of 5 CDP and 7 CDP compared with that in the relatively short alkyl chain of 3 CDP, so producing a falling N–I curve. However, the gradient of the N–I curve for the odd homologues of the 4-*n*-alkyl-4'-cyanotolanes soon levels off and may even show an upward trend for the homologues above C_9.

The shape of the N–I curve for the even homologues of the 4-*n*-alkyl-4'-cyanotolanes is however very similar to the corresponding N–I curve for the even homologues of the 4-*n*-alkyl-4'-cyanobiphenyls[2] and presumably a similar explanation of this shape can be proposed.

Probably the most interesting feature of the mesomorphic properties of the 4-*n*-alkyl-4'-cyanotolanes is the absence of any smectic properties for the homologues below C_{11}, despite the fact that the nematic phases of these homologues can be cooled below the smectic A to nematic (S_A–N) transition temperatures of the corresponding 4-*n*-alkyl-4'-cyanobiphenyls. A comparison of the variations in the thermal stabilities of the S_A phases with *n* (the number of carbons in the alkyl chain) for the series of 4-*n*-alkyl-4'-cyanotolanes and 4-*n*-alkyl-4'-cyanobiphenyls is shown in Figure 4.

The central, acetylenic link appears to favour the formation of the nematic phase, but to inhibit the formation of a S_A phase when the alkyl chain is not too long. However, once the formation of the S_A phase does occur (as in the case of 4-cyano-4'-undecyltolane, 11 CDP), then the acetylenic link increases the thermal stability of the S_A phase relative to that of the corresponding 4'-substituted 4-cyanobiphenyl—see Figure 4. It is thought that the unusual smectic properties of the homologous series of 4-*n*-alkyl-4'-cyanotolanes may be due to the repulsive nature of the lateral interactions between triple bonds, an effect which may be strong enough to inhibit the formation of smectic layers for homologues below C_{11}. However, once these repulsive forces are outweighed by the increasing attractive interactions involving

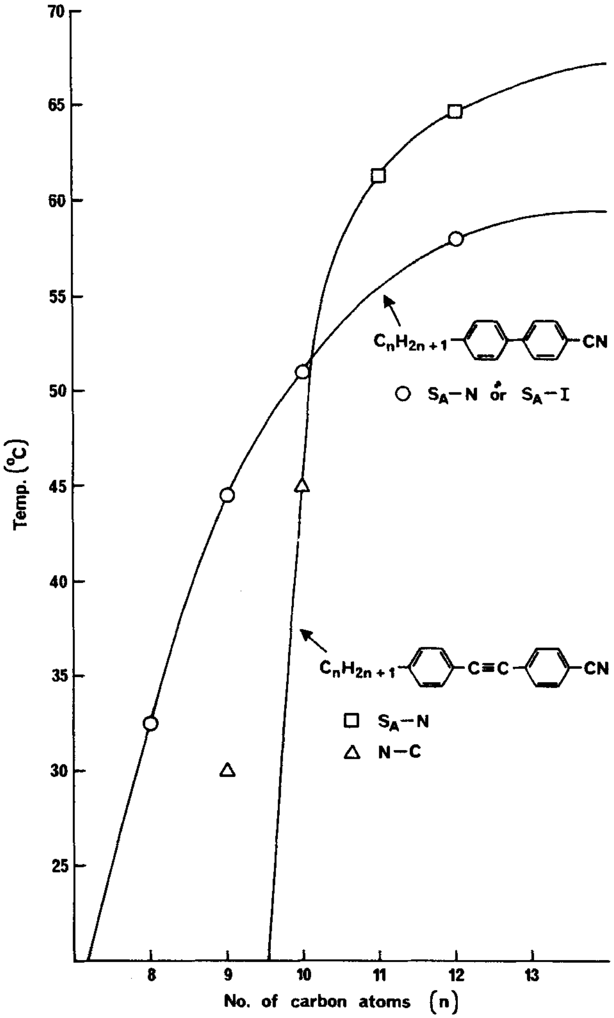


FIGURE 4 A comparison of the trends in the thermal stabilities of the smectic A phases of 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkyl-4′-cyanotolanes with increasing alkyl chain length (*n*).

longer alkyl chains, then the core part of the molecular structure of a 4-cyanotolane may contribute, through its greater length and rigidity by constraining the alkyl chains in a more ordered state, thereby forming a S_A phase of higher thermal stability than that which can be formed by the 4-*n*-alkyl-4′-cyanobiphenyls with their shorter core structures.

The molecules in the S_A phase of 4-cyano-4′-*n*-octylbiphenyl have been shown by X-ray studies[3] to form interdigitated bilayers (the layer spacing is about 1.4 molecular lengths). It is hoped that a similar study of the S_A phase of 11 CDP will reveal the presence or absence of a bilayer structure.

The melting points and compositions of eutectic mixtures of 4-*n*-alkyl-4′-cyanotolanes were calculated by the method described by Hulme *et al.*[4] A comparison of the observed and predicted melting points of the mixtures is given in Table II and indicates that the 4-*n*-alkyl-4′-cyanotolanes do not exhibit ideal behaviour. Moreover, the sharpness of the melting points of the "non-eutectic" mixtures may indicate that mixtures of 4-*n*-alkyl-4′-cyanotolanes form solid solutions over a fairly wide range of compositions.

The study of the homologous series of 4-*n*-alkyl-4′-cyanotolanes had produced some interesting results; it was therefore decided to extend this investigation to other 4′-substituted derivatives of 4-cyanotolane and to include some corresponding derivatives of 4-cyanostilbene.

TABLE II

A comparison of the observed and predicted melting points of mixtures of 4-*n*-alkyl-4′-cyanotolanes

Components	Composition (mole %)	Type of mixture	Predicted C–N (°C)	Observed C–N (°C)
7 CDP 9 CDP	58 42	Predicted eutectic	38	45–48.8
7 CDP 9 CDP	70 30	Predicted eutectic + excess of 7 CDP	—	45.6–47
5 CDP 6 CDP 7 CDP 9 CDP	16.5 22.4 38.6 22.5	Predicted eutectic	25	41.8–42.4
5 CDP 6 CDP 7 CDP 9 CDP	13.2 37.9 30.9 18.0	Predicted eutectic + excess of 6 CDP	—	41.5–43.0

The potentially cholesteric liquid crystalline material (+)-4-cyano-4′-(3″-methylpentyl)tolane (3M5 CDP) was prepared by the method described in the Scheme by starting with (+)-3-methylpentylbenzene. The presence of the methyl group in the middle of the pentyl chain of 5 CDP produced a negligible change in the melting point, but a very large decrease in the N–I transition temperature. It was not possible to observe a direct cholesteric to isotropic liquid (Ch–I) transition, but binary mixtures of 3M5 CDP and 4-cyano-4′-*n*-pentylbiphenyl (5 CB) were used to obtain a virtual Ch–I transition temperature for 3M5 CDP, as shown in Figure 5. A 10% w : w solution of 3M5 CDP in 5CB produced a cholesteric phase with a pitch length of 4 μm. This pitch length is comparable with that[5] of a 10% solution

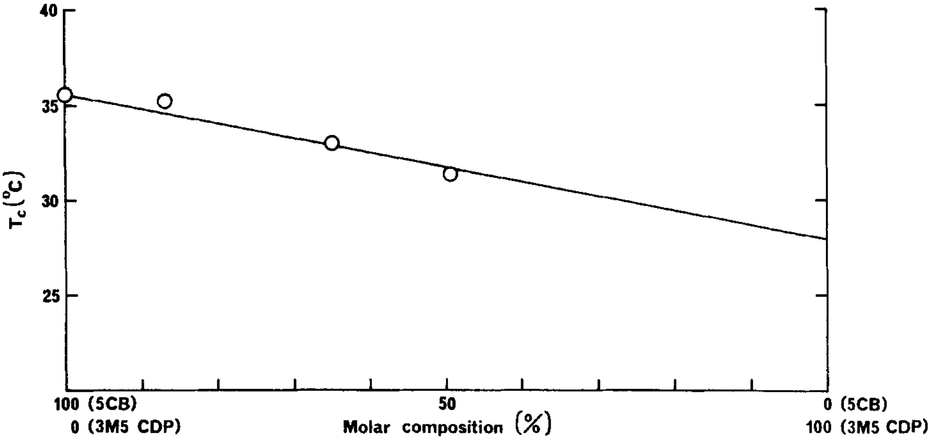


FIGURE 5 Ch–I Transition temperatures, T_c, of binary mixtures of (+)-4-cyano-4′-(3″-methylpentyl)tolane (3M5 CDP) and 4-cyano-4′-*n*-pentylbiphenyl (5CB)—see Table I.

4-cyano-4′-(3″-methylpentyl)biphenyl in E_3.† The specific rotation $[\alpha]_D^{20}$ of a 10% w : v solution of 3M5 CDP in chloroform was +15.2°.

A sample of 4-cyano-4′-*n*-heptyloxytolane (7 OCDP) was prepared by the route illustrated in the Scheme by starting with 4-*n*-heptyloxybenzene (i.e., R = $C_7H_{15}O$—). 7 OCDP exhibits a very complex series of solid–solid and solid–liquid–solid phase transitions; it is hoped to characterise these transitions in the near future. As expected, the heptyloxy compound has a higher (33.5°C) N–I transition temperature than the corresponding octyl derivative; however, the melting point of the stable crystal form of 7 OCDP is only 18°C higher than that of 4-cyano-4′-octyltolane (8 CDP)—see Table I. If this behaviour is general, then the 4-*n*-alkoxy-4′-cyanotolanes may be more useful materials for technological and research purposes than the 4-*n*-alkyl-4′-cyanotolanes. The synthesis of the homologous series of 4-*n*-alkoxy-4′-cyanotolanes is therefore being completed to permit comparisons with the 4-*n*-alkyl derivatives and with the corresponding 4-*n*-alkoxy-4′-cyanobiphenyls.

The two isomeric tolane derivatives that are analogous to 4-cyano-4″-*n*-octyl-*p*-terphenyl (8 CT) were also prepared. 4-Cyano-4′-(4″-*n*-octylphenyl) tolane (COPT) was prepared by the route illustrated in the Scheme by using 4-*n*-octylbiphenyl (i.e., R = —C_6H_4—C_8H_{17}). 4-(4″-Cyanophenyl)-4′-*n*-octyltolane (CPOT) was prepared by the route shown in the Scheme by

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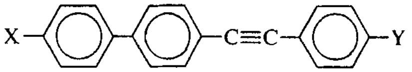
† E_3 is a eutectic mixture of 4-*n*-alkyl-4′-cyanobiphenyls and 4-*n*-alkoxy-4′-cyanobiphenyls available from BDH Limited, Poole, Dorset, England.

starting with 4-(4′-bromobiphenylyl)acetyl chloride instead of 4-bromophenylacetyl chloride. It is difficult to obtain accurate values for the transition temperatures for these isomers and their bromo-substituted precursors because of thermal decomposition. However, the values that were obtained are given in Table III. Satisfactory values for the transition temperatures of the bromo-stilbene precursors to COPT and CPOT could not be obtained because of the rapid rate of decomposition of these compounds at the required temperatures (~250°). The smectic phases listed in Table III have so far been characterised only by optical microscopy.

TABLE III

Transition temperatures for the compounds



Substituents X	Substituents Y	Abbreviation used in text	Transition temperatures (°C) C–S_A or S_E	S_E–S_B	S_B–S_A	S_A–N or I	N–I
n-C_8H_{17}	Br	BOPT	207	211	221	225	
n-C_8H_{17}	CN	COPT	139			164	228
Br	*n*-C_8H_{17}	BPOT	215	219	223	232	
CN	*n*-C_8H_{17}	CPOT	153			210	245

C = Crystal; S = smectic; N = nematic; I = isotropic liquid.

The higher transition temperatures of CPOT compared with COPT are probably due to stronger conjugative interactions (greater anisotropy of molecular polarisability) for the former compound. The S_A phases of both compounds could not be supercooled below the melting points of the compounds; in fact, the C–S_A phase transition appeared to be reversible at the same temperature on cooling, and it is possible that crystallisation is actually initiated by the formation of a second smectic phase. The terphenyl analogue of CPOT and COPT, i.e., 8 CT has the transition temperatures (°C)

$$\mathrm{C} \xrightarrow{127} S_E \xrightleftharpoons{128} S_B \xrightleftharpoons{133} S_A \xrightleftharpoons{197} \mathrm{N} \xrightleftharpoons{216} \mathrm{I} \qquad \text{Ref. 1}$$

The lower N–I transition temperature of 8 CT is easily related to its lower anisotropy of polarisability compared with that of the two tolanes, but the effect of this structural change on the smectic A properties is apparently less straightforward.

The thermal stabilities of the S_A phases increase in the order COPT < 8 CT < CPOT. It would appear that relative to the group, —C_6H_4—CN the —C≡C—C_6H_4—CN group reduces the thermal stability of the S_A

phase, as in the case of the 4-*n*-alkyl-4′-cyanotolanes. On the other hand, the $—C{\equiv}C—C_6H_4—C_6H_4—CN$ group appears to increase the thermal stability of the S_A phase.

It is planned to make a study of the transition temperatures of binary mixtures of CPOT and 8 CT, and COPT and 8 CT, since this may provide virtual values for the S_E–S_B and S_B–S_A transition temperatures for the isomeric tolane derivatives for comparison with those of 8 CT.

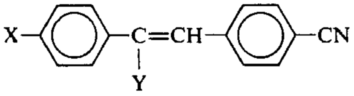
The mesomorphic properties of 4-bromo-4′-(4″-*n*-octylphenyl)tolane (BOPT) and 4-(4″-bromophenyl)4′-*n*-octyltolane (BPOT) compared with those of the corresponding cyanotolanes, i.e., COPT and CPOT respectively, are consistent with the observed fact that a cyano group is always much higher in the nematic thermal stability order for terminal substituents than is a bromo group. Furthermore, the cyano group always lies lower than a bromo substituent in the smectic A thermal stability order for terminal substituents and can sometimes lie even lower than hydrogen in this order. The analogous terphenyl derivative, 4-bromo-4″-*n*-octyl-*p*-terphenyl (8 BT) does not exhibit any mesomorphic properties, but melts at 238°C. Once again a study of the transition temperatures of binary mixtures of the analogous terphenyl (8 BT) and tolane derivatives (BPOT and BOPT) should provide interesting results.

Samples of 4-cyano-4′-*n*-octylstilbene (8 CS) and 4-cyano-4′-*n*-heptyloxystilbene (7 OCS) were prepared by the method illustrated in the Scheme (compound **8**, R = C_8H_{17} and OC_7H_{15}, respectively). A comparison of the mesomorphic properties of 8 CS and 7 OCS with those of the corresponding tolanes shows that the stilbene derivatives are lower melting and produce the more thermally stable smectic A and nematic phases—see Tables I and IV. The observation concerning nematic thermal stability disagrees with the classical view that more linear molecules will give rise to higher N–I transition temperatures. It is of course possible that the stilbenes do have higher anisotropies of molecular polarisability than the corresponding tolanes, despite the difference in molecular shape. No information about this is available, although the dielectric permittivities of 4-cyano-4′-*n*-heptyloxytolane and 4-cyano-4′-*n*-heptyloxystilbene have been measured and the results are given for reference in Table V. If this is not the case, one can only speculate that bent molecules such as stilbenes can give rise to more thermally stable nematic phases because neighbouring molecules can become to some extent interlocked and so require more thermal energy for their conversion into the disordered state of the isotropic liquid.

The low melting points and high N–I transition temperatures of 8 CS and 7 OCS would appear to make these compounds and other members of the same homologous series suitable for both research and technological uses. However, the two named compounds were found to be unstable as solids

TABLE IV

Thermodynamic data for the compounds



Substituents		Transition temperatures (°C)			Enthalpies of fusion (kcal mol^{-1})
X	Y	C–S_A, N or I	S_A–N	N–I	
n-C_8H_{17}	H	49[a]	74.5	85	3.2
n-$C_7H_{15}O$	H	72[b]	83	125	9.3
n-C_8H_{17}	Me	39[c]		[37]	5.0
n-$C_7H_{15}O$	Me	72[d]		82	10.2

C = crystal; S_A = smectic A; N = nematic; I = isotropic liquid.

[ ] = a monotropic transition

[a] This compound has an unstable solid phase which melts at 28°C, and then crystallises to produce the stable crystal form, m.p. 49°C.

[b] This compound possesses two unstable crystal forms which melt at 67 and 69°C.

[c] When the nematic phase of this compound crystallises two unstable crystal forms are produced which melt at 18 and 34°C.

[d] When the nematic phase of this compound is allowed to solidify, an unstable solid phase is obtained which undergoes an exothermic solid–solid phase transition to the stable crystal form at 40°C.

TABLE V

Dielectric permittivities (ε) of 4-cyano-4′-*n*-heptyloxystilbene (7 OCS) and 4-cyano-4′-*n*-heptyloxytolane (7 OCDP)

Compound	Temperature (°C)	Dielectric permittivities		
		$\varepsilon_{\parallel}$	$\varepsilon_{\perp}$	ε_a
7 OCS	84.5	16.9	5.8	11.1
	87	16.9	5.9	11.0
7 OCDP	79.5	13.2	5.9	7.3
	82.5	12.9	6.1	6.8
	84.5	12.6	6.2	6.4

at room temperature and highly unstable as isotropic liquids. Thin films of the solid phase of 8 CS and 7 OCS mounted between a glass microscope slide and cover slip were exposed to ordinary conditions of atmosphere and light for 24 hours. The N–I transition temperatures of the compounds were lowered by 3°C and 1°C, respectively. A similar test involving 4-cyano-4′-*n*-octyltolane produced a drop in the N–I transition temperature of 2°C after one month. The high photochemical stabilities of 4-*n*-alkyl-4′-cyanobiphenyls have already been reported.[1]

The rapid lowering of the N–I transition temperatures of 8 CS and 7 OCS with time is probably due to the formation of the non-mesomorphic *cis* isomer.[6] The rate of *cis-trans* isomerism is possibly enhanced by the presence of the cyano group, which will withdraw electrons from the CH=CH bond, so reducing its bond order and therefore the energy barrier to the rotation necessary for isomerism. It was decided to test this possibility by preparing the following compounds; 4-cyano-4′-*n*-octyl-α′-methylstilbene (8 CMS, compound **5** in the Scheme with R = n-C_8H_{17}) and 4-cyano-4′-*n*-heptyloxy-α′-methylstilbene (7 OCMS, compound **5** in the Scheme with R = n-$C_7H_{15}O$). In these two compounds, the α′-methyl group should force the benzene ring containing the cyano group out of the plane of the sp^2 hybridised —CH=CH— system by steric interaction with the ring-hydrogen in the 2-position. This steric intramolecular interaction will reduce the conjugation throughout the molecule and should increase the energy barrier to *cis–trans* isomerism. However, the stability of the stilbene derivatives was only slightly increased by the presence of the α′-methyl group. Moreover, the thermal stabilities of the nematic phases were decreased by approximately 45°C, and the melting points of the compounds were almost unchanged—see Table IV. After considering the above data it was concluded that the 4-*n*-alkyl- and 4-*n*-alkoxy-derivatives of 4′-cyanostilbene did not warrant further study.

On the other hand, the study of the 4-*n*-alkyl-4′-cyanotolanes and other related tolane derivatives has raised a number of interesting points and problems to which it is hoped that answers will be provided in the near future.

EXPERIMENTAL

Thermodynamic measurements

The transition temperatures given in Tables I–IV and Figures 1–5 were determined by optical microscopy (Nikon L–Ke polarising microscope) with the aid of a Mettler FP 52 heating stage and FP 5 control unit. Enthalpies of C–I, C–N, or C–S_A transitions were measured using a Stanton Redcroft model 671 low temperature differential thermal analyser. Indium was used as a calibration standard and the accuracy of the enthalpies is estimated as ±10%. The dielectric permittivities of 4-cyano-4′-*n*-heptyloxytolane and 4-cyano-4′-*n*-heptyloxystilbene were measured by Dr A. H. Price and Dr R. Moutran.

Preparation of materials

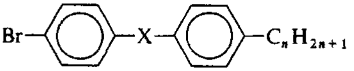
The materials reported in this paper were prepared by the methods illustrated in the Scheme or by syntheses adapted from these methods by changing the starting materials. The preparation of all the 4-*n*-alkyl-4′-cyanotolanes, **11**, is illustrated for the case of 4-cyano-4′-*n*-octyltolane. The melting points of the precursors to these compounds and to other related compounds are shown in Table VI. The purities of all the final products and of all those reaction intermediates which were isolated were carefully checked by thin layer chromatography and mass spectrometry. In addition, satisfactory elemental analysis results were obtained for all the materials, and structural checks were carried out wherever they were desirable using nuclear magnetic resonance spectroscopy and infrared spectroscopy.

(+)-4-Cyano-4′-(3″-methylpentyl)tolane was prepared by the synthetic route shown in the Scheme by starting with (+)-3-methylpentylbenzene.

TABLE VI

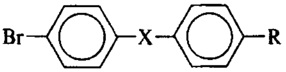
Melting points (°C) of compounds of the types

(1)



X \ *n*	1	2	3	4	5	6	7	8	9	10	11	12
$-CH_2-\underset{\underset{O}{\|}}{C}-$	129	145	141	125	126	105	115	110	109	97	107	105
$-CH{=}CH-$	211	182	154	151	137	147	146	144	143	137	138	135
$-C{\equiv}C-$	159	141	103	76	86	71	80	70	69	69	71	73

(2)



X \ R	$CH_3CH_2-\underset{\underset{CH_3}{\mid}}{\overset{*}{C}H}-CH_2-CH_2-$	$n\text{-}C_7H_{15}O-$	$n\text{-}C_8H_{17}-$
$-CH_2-\underset{\underset{O}{\|}}{C}-$	129[a]	109	110
$-CH{=}CH-$	141[b]	177	144
$-C{\equiv}C-$	79[c]	102	70
$-CH{=}\underset{\underset{CH_3}{\mid}}{C}-$	—	82	70

[a] $[\alpha]_D^{20} = +9.2°$
[b] $[\alpha]_D^{20} = +11.4°$
[c] $[\alpha]_D^{20} = +11.6°$
measured as 10% w:v solutions in chloroform.

This optically active alkylbenzene was prepared by Huang Minlon[1] reduction of the ketone obtained from the Friedel Crafts reaction between (+)-3-methylpentanoyl chloride and benzene.[7] (+)-3-Methylpentanoic acid was obtained as a gift from D. G. McDonnell[8] of this laboratory.

4-Cyano-4'-*n*-heptyloxytolane (**11**, R = *n*-$C_7H_{15}O$) was prepared by the synthetic route described in the Scheme by starting with *n*-heptyloxybenzene which was prepared in the usual manner.[9] The Friedel Crafts reaction between 4-bromophenylacetyl chloride and *n*-heptyloxybenzene was carried out using petroleum ether (b.p. 40–60°C), since the use of this solvent greatly reduced the formation of tarry side-products.

Samples of the 4'-*n*-octyl and 4'-*n*-heptyloxy derivatives of 4-cyanostilbene (**8**, R = *n*-C_8H_{17} and *n*-$C_7H_{15}O$, respectively) and 4-cyano-α'-methylstilbene (**5**) were prepared by the synthetic routes shown in the Scheme. The cyanation of **7** was carried out by the method used for the cyanation of 4-bromo-4'-*n*-octyltolane (**10**, R = *n*-C_8H_{17}). The preparation of **3** (R = *n*-C_8H_{17} and *n*-$C_7H_{15}O$) was achieved by the method reported by Young *et al.*[10] The dehydration of **3** and the cyanation of **4** were carried out by the methods used to prepare 4-bromo-4'-*n*-octylstilbene and 4-cyano-4'-*n*-octyltolane, respectively.

4-Cyano-4'-(4''-*n*-octylphenyl)tolane (**11**, R = —C_6H_4—C_8H_{17}-*n*) was prepared by the methods described for the preparation of 4-cyano-4'-*n*-octyltolane by starting with 4-*n*-octylbiphenyl instead of *n*-octylbenzene, with the following exceptions. The ketone (**2**, R = —C_6H_4—C_8H_{17}-*n*) was dissolved in a 3 : 1 mixture of dry ether and dry tetrahydrofuran instead of dry ether alone, prior to reduction with lithium aluminium hydride. The bromination of the stilbene (**7**, R = —C_6H_4—C_8H_{17}-*n*) was carried out using chloroform instead of ether.

4-(4''-Cyanophenyl)-4'-*n*-octyltolane (CPOT, see Table IV) was prepared by the methods used to synthesise 4-cyano-4'-*n*-octyltolane with the adaptations described for the preparation of 4-cyano-4'-(4''-octylphenyl)tolane and by using 4-(4'-bromobiphenylyl)acetyl chloride instead of **1**. 4-(4'-Bromobiphenylyl)acetyl chloride was prepared by treating 4-(4'-bromobiphenylyl) acetic acid[11] with thionyl chloride—see synthesis of **1**.

4-Bromophenylacetyl chloride (**1**) A mixture of thionyl chloride (10 ml) and commercially available 4-bromophenylacetic acid (10 g, 0.047 mole) was heated under reflux for 1 hour. The reaction mixture was allowed to cool and the excess of thionyl chloride was removed by rotary evaporation. The residue was used without purification in the Friedel Crafts reaction.

4-n-Octyl-α-(4'-bromophenyl)acetophenone (**2**, R = *n*-C_8H_{17}) To commercially available *n*-octylbenzene (10.6 g, 0.056 mole) and anhydrous aluminium trichloride (7.0 g, 0.052 mole) dissolved in dry nitrobenzene (40 ml), 4-bromophenylacetyl chloride was added dropwise; the temperature of the reaction mixture was maintained below 15°C during the addition. The reaction mixture was stirred overnight at room temperature and then poured onto a mixture of ice (60 g), water (12 ml), and concentrated hydrochloric acid (24 ml). The resultant mixture was stirred for 30 min and the nitrobenzene layer was separated off, chloroform being added to effect a more efficient separation. The organic layer was washed with water. The chloroform and nitrobenzene were then removed by steam distillation. The solid residue was extracted into benzene; the extract was dried (anhydrous sodium sulphate) and then decolourised with animal charcoal. The benzene was removed by rotary evaporation; crystallisation of the crude product from ethanol followed by vacuum desiccation gave 11 g (57 % from the acid) of pure material, m.p. 109–111°C (Found: C, 68.1; H, 7.1; Br, 20.9 %. $C_{22}H_{27}BrO$ requires C, 68.2; H, 7.0; Br, 20.7 %).

4-Bromo-4'-n-octylstilbene (**7**, R = n-C_8H_{17}) A solution of the ketone (**2**, R = n-C_8H_{17}) (7.5 g, 0.018 mole) in dry ether (240 ml) was added dropwise over a period of 20 min to a stirred mixture of lithium aluminium hydride (0.6 g, 0.016 mole) in dry ether (60 ml). The reaction mixture was stirred and heated under reflux for 3 hours. The excess of reducing agent was destroyed by the careful addition of water (20 ml), followed by concentrated hydrochloric acid (12 ml). The ethereal layer was washed with water (3 × 200 ml), dried (anhydrous sodium sulphate), and then evaporated to dryness. The alcohol (**6**, R = n-C_8H_{17}) so obtained was not purified, but was immediately treated with 98 % formic acid (100 ml). This mixture (it is not necessary for all the alcohol to dissolve in the formic acid) was heated under reflux for 1 hour. The reaction mixture was allowed to cool and then added to water (200 ml). The crude product was obtained by filtration, washed well with water, and then boiled in ethanol (50 ml). On cooling, the product was isolated by filtration and then dried in a vacuum desiccator. This procedure gave 5.5 g (82 % from the ketone) of pure material, m.p. 144°C (Found: C, 71.3; H, 7.5; Br, 21.8 %. $C_{22}H_{27}Br$ requires C, 71.2; H, 7.3; Br, 21.6 %). In the preparation of some other 4-*n*-alkyl-4'-bromostilbenes it was necessary to use a 3 : 1, v:v mixture of ether and tetrahydrofuran in order to dissolve the ketone **2** in a suitable volume of solvent.

4-Bromo-4'-n-octyltolane (**10**, R = n-C_8H_{17}) Bromine (3.3 g, 0.021 mole) was added to a solution of 4-bromo-4'-*n*-octylstilbene (3.7 g, 0.01 mole) in ether (200 ml). This solution was stirred for 2 hours. The excess of bromine was destroyed by the addition of an aqueous solution of sodium metabisulphite. The ethereal layer was washed with water (3 × 100 ml), dried (anhydrous sodium sulphate), and then evaporated to dryness. The unpurified stilbene dibromide (**9**, R = n-C_8H_{17}) so obtained was then added to a hot solution of potassium hydroxide (9 g) in absolute ethanol (15 ml).[12] The reaction mixture was stirred and heated in an oil bath at 140–150°C for 24 hours. The reaction mixture was allowed to cool and then water (50 ml) was added. The organic product was extracted into ether (2 × 50 ml). The ethereal solution was washed with water (2 × 50 ml), dried (anhydrous sodium sulphate), and then evaporated to dryness. The residue was crystallised from ethanol and the required product, 1.3 g (35 %), m.p. 69–71°C obtained after vacuum desiccation (Found: C, 71.3; H, 6.8; Br, 20.5 %. $C_{22}H_{25}Br$ requires C, 71.5; H, 6.8; Br, 21.7 %). In the preparation of some other 4-n-alkyl-4′-bromotolanes, it was necessary to use chloroform instead of ether in order to dissolve the stilbene **7** in a reasonable volume of solvent.

4-Cyano-4′-n-octyltolane (**11**, R = n-C_8H_{17}) Cuprous cyanide (0.8 g, 9 mmole) was added to a solution of 4-bromo-4′-n-octyltolane (1.3 g, 3.5 mmole) in N-methyl-2-pyrrolidone (4 ml). This mixture was stirred and heated in an oil bath at 200°C for 2 hours. The cooled reaction mixture was poured into a solution of ferric chloride (2.2 g) in water (33 ml) and concentrated hydrochloric acid (2 ml) and heated at 50–60°C for 15 min. The organic product was extracted into ether (3 × 60 ml). The ethereal solution was washed with water (3 × 50 ml), dried (anhydrous sodium sulphate), treated with animal charcoal, and then evaporated to dryness. The residue was crystallised from ethanol, further purified by column chromatography on silica gel with a 3 : 2 mixture of chloroform and petroleum ether (b.p. 40–60°C) as eluant, and then finally recrystallised from ethanol, followed by vacuum desiccation. This procedure gave 0.4 g (36 %) of the required product—see Table I—(Found: C, 87.8; H, 8.0; N, 4.5 %. $C_{23}H_{25}N$ requires C, 87.6; H, 7.9; N, 4.4 %). The final step in the purification of the low melting compounds 4-cyano-4′-n-octylstilbene and 4-cyano-4′-n-octyl-α′-methylstilbene was vacuum distillation.

4-n-Heptyloxy-α-(4′-bromophenyl)acetophenone (**2**, R = n-$C_7H_{15}O$) To a mixture of a sample of n-heptyloxybenzene[9] (b.p. 137–9°C/15 mm, 20 g, 0.104 mole) and anhydrous aluminium trichloride (14.0 g, 0.104 mole) in petroleum ether (b.p. 40–60°C, 200 ml) stirred in an ice bath, was added 4-bromophenylacetyl chloride (obtained from 20 g, 0.094 mole of the acid, see above) over a period of 45 min. During the addition the temperature of the reaction mixture was kept at 5–10°C. The reaction mixture was then stirred for 3½ hours at 10–15°C and then poured onto a mixture of ice (120 g), water (24 ml), concentrated hydrochloric acid (48 ml), and chloroform (200 ml). The resultant mixture was stirred for 30 min; the organic layer was then separated off, washed with water (2 × 100 ml), dried (anhydrous sodium sulphate), and then evaporated to dryness. The residue was crystallised three times from ethanol and dried in a vacuum desiccator. This procedure gave 16.0 g (44%) of pure material, m.p. 108–110°C (Found: C, 64.6; H, 6.4; Br, 20.4%. $C_{21}H_{25}BrO_2$ requires C, 64.8; H, 6.4; Br, 20.6%).

Note added in proof

Since this paper was presented, it has been found that the C_{10} homologue, i.e., 4-cyano-4′-decyltolane exhibits a monotropic S_A–N phase transition at 50.5°C; this new fact does not affect the arguments presented in this paper. However, in the light of this new information, it is worth noting that smectic properties are first observed for the C_8 homologue in the series of 4-*n*-alkyl-4′-cyanobiphenyls and for the C_{10} homologue in the series of the 4-*n*-alkyl-4′-cyanotolanes. In the latter series the rigid, linear molecular core is two carbon atoms longer than the molecular core of the 4-*n*-alkyl-4′-cyanobiphenyls. This may indicate that for smectic phases to *originate* in both these series it is necessary for the alkyl chains and molecular cores to be of approximately equal lengths.

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