Nematic tolanes and acetylenes

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The first liquid crystals incorporating a non-conjugated carbon–carbon triple bond in the terminal chain to exhibit a nematic phase above the melting point are reported. A variety of compounds incorporating a carbon–carbon triple bond in the terminal chain or between two phenyl rings have been synthesised as part of an investigation of the effects of the shape, conformation and rigidity of the terminal chains of liquid crystals on their mesophase behaviour. A series of related tolanes incorporating an alkenyloxy chain with an additional carbon–carbon double bond or a simple alkoxy chain as a terminal substituent also were prepared for comparison purposes.

It became clear very early on in liquid crystal research that at least one of the terminal substituents attached to the molecular core had to be a flexible aliphatic chain in order to dilute the central organic core and thereby induce a relatively low melting point, or at least a melting point low enough for a liquid crys-talline phase to be observed.¹⁻¹⁰ The dispersion forces between the molecular cores of many liquid crystals, especially those containing two or more aromatic rings, would lead to high melting points in the absence of at least one terminal aliphatic substituent. It is for this reason that most early synthetic liquid crystals possessed two terminal alkyl or alkoxy chains.¹⁻¹⁰ Most mesomorphic compounds incorporating two short terminal aliphatic chains usually exhibit a nematic phase. However, most liquid crystalline materials with long terminal chains, e.g. 7–12 methylene units, often exhibit a smectic phase, sometimes in addition to a nematic phase, especially in the absence of lateral substituents. The viscosity of the nematic phase also increases as a homologous series is ascended. Therefore, in order to promote the formation of a nematic phase-rather than a smectic phase—with a low viscosity, short alkyl chains are often incorporated into liquid crystals designed for LCDs based on the nematic phase.

The presence of a carbon-carbon double bond in a terminal chain has been shown to strongly influence the mesomorphism of particular compounds and their physical properties. It was found that the presence of a trans carbon-carbon double bond separated from the molecular core by an odd number of carbon atoms in the terminal alkenyl chain exhibit a high nematic clearing point.^{11–15} The corresponding compounds containing the cis isomers of the same chains, i.e. with the carbon-carbon double bond in the same position, but with the opposite configuration, exhibit very low (usually extrapolated) nematic clearing points. This big difference in clearing points may be attributed to the non-linear conformation of an alkenyl chain containing a cis carbon-carbon double bond in these positions. It is has been postulated that either a linear or zig-zag fully extended conformation of the terminal aliphatic chain promotes nematic phase formation by maintaining the rod-like shape of the molecule or, more exactly, of its rotation volume. This results in a high length-to-breadth ratio, a high anisotropy of molecular polarisability and a small intermolecular distance between parallel molecules, which leads to an optimum balance between attractive dispersion forces and steric and electronic repulsive forces. The high clearing point of some alkenyl compounds is consistent with this interpretation in that the greater rigidity of the alkenyl chain results in fewer non-linear

conformations. A higher degree of molecular polarisability due to the π -electrons in the carbon–carbon bond may also contribute to a higher clearing point.^{11–15}

The influence of a carbon-carbon triple bond located in the terminal chain on the mesomorphic behaviour of liquid crystals has been studied to a much lesser degree.^{16–18} In most reported cases, the triple bond is attached directly to the molecular core. Conjugated triple bonds give rise to high transition temperatures due to a combination of a high length-to-breadth ratio and a high degree of anisotropy of polarisability due to the extended conjugation.^{16–18} Unfortunately, the thermal and UV stability of conjugated acetylenes has been found to be insufficient to permit their use in LCDs. Non-conjugated triple bonds attached to the core of a molecule also usually give rise to high melting points and low clearing points.16-18 In contrast to alkenyl-substituted liquid crystals, there are almost no references¹⁸ to liquid crystals with a carbon-carbon triple bond located within the terminal chain itself, *i.e.* not attached directly to the molecular core. A series of model compounds has now been synthesised to extend these studies. Tolanes^{19,20} have been chosen as model compounds due to their high tendency for nematic phase formation, absence of polymorphism, ease of synthesis and almost rigid, linear molecular structure with very little conformational deviation. A propyl chain was chosen as a fixed terminal substituent to minimise the effect of the conformation of this chain as another variable parameter. The only dipole moment is associated with the oxygen atom. Moreover, the oxygen atom is conjugated with the aromatic ring and contributes to the high clearing points of the nematic phases often observed for tolanes. There are no functional groups or atoms with a strong permanent dipole, such as a cyano group, and, therefore, no interdigitation of neighbouring molecules is expected. Thus, it was hoped that the tolanes chosen would represent a simple system for the study of the effects, especially conformational effects, of the presence of a carbon-carbon triple bond in the terminal chain of a compound on its mesomorphic behaviour.

Results and discussion

Synthesis

The 4-*n*-alkyl-4'-hydroxytolanes were prepared by Sonogashira cross-coupling of commercially available (4-*n*-alkylphenyl)-acetylenes and 4-iodophenol using a palladium catalyst.²¹ The ethers 1–14 were prepared *via* Williamson ether alkylation of

	n	т	Cr		Ν		Ι	Ref.
1	3	1	•	61	•	66	•	20
2	3	2	•	89	•	96	•	20
3	3	3	•	83	•	$(75)^{a}$	•	20
4	3	4	•	73	•	84	•	
5	3	5	•	57	•	70	•	20
6	3	6	•	56	•	76	•	
7	3	7	•	48	•	70.5	•	19
8	5	1	•	47	•	58	•	20
9	5	2	•	62	•	89	•	20
10	5	3	•	55	•	72	•	20
11	5	4	•	64	•	79	•	20
12	5	5	•	51	•	70	•	19,20
13	5	6	•	48	•	77	•	,
14	5	7	•	45	•	74	•	

the resultant 4-*n*-alkyl-4'-hydroxytolanes with commercially available 1-bromoalkanes. The Mitsonubu alkylation reaction²² was used to prepare the respective alkenyloxy tolanes **15–18** and hexa-2,4-dienyloxytolane **19** from the corresponding alcohols. The alkynyloxy tolanes **20–37** were prepared by Williamson ether alkylation of the 4-*n*-alkyl-4'-hydroxytolanes and the appropriate tosylates produced in the normal way

Table 2 Transition temperatures (°C) for the alkenyl ethers (15–18), diene ether (19) and the acetylenes $(20{-}28)$

C₃H₇-

		–OR	Cr		Ν		
5	(<i>E</i>)	-OCH ₂ CH=CHC ₃ H ₇	٠	77	•	84	
6	(Z)	-OC ₂ H ₄ CH=CHC ₂ H ₅	٠	50	٠	$(49)^{a}$	
7	(E)	-OC ₃ H ₆ CH=CHCH ₃	٠	76	٠	86	
8	(Z)	-OC ₄ H ₈ CH=CH ₂	٠	49	٠	61	
9	(E,E)	-OCH ₂ CH=CHCH=CHCH ₃	٠	92	٠	141	
0		–OCH ₂ C≡CCH ₃	•	97			
1		$-OCH_2C \equiv CC_3H_7$	٠	60			
2		$-OCH_2C \equiv CC_4H_9$	٠	52			
3		$-OCH_2C \equiv CC_5H_{11}$	•	42			
4		–OC ₂ H ₄ C≡CH	•	76	٠	$(47)^{a}$	
5		$-OC_2H_4C \equiv CCH_3$	•	72		_	
6		$-OC_2H_4C \equiv CC_2H_5$	•	56			
7		-OC ₃ H ₆ C=CH	•	56	•	57	
8		–OC₄H ₈ C≡CH	•	64	٠	$(59)^{a}$	

Table 3 Transition temperatures (°C) for the tolanes (29-37)

from the commercially available acetylenic alcohols and 4-methylbenzenesulfonyl chloride.

Phase characterisation by thermal optical microscopy

The thermotropic mesophases observed for the compounds shown in Tables 1-3 were investigated between crossed polarisers using optical microscopy. The only phase observed was the nematic phase. Nematic droplets were observed on cooling from the isotropic liquid to form the Schlieren texture with two and four-point brushes characteristic of the nematic phase, along with optically extinct homeotropic areas. As the sample was cooled further, the texture often formed more optically extinct homeotropic areas, which indicates that the phase is optically uniaxial. The birefringent and homeotropic areas flashed brightly on mechanical disturbance. This behaviour and the simultaneous presence of both the homeotropic and the Schlieren texture confirms that the mesophase observed is indeed a nematic phase. The compounds prepared with a carbon-carbon triple bond within the terminal chain did not exhibit an observable nematic phase despite substantial supercooling below the melting point for most homologues.

Phase characterisation by differential scanning calorimetry

The values for the transition temperatures were confirmed by differential scanning calorimetry (DSC). Good agreement ($\sim 1-2$ °C) with the values determined by optical microscopy were obtained. A typical thermogram obtained by DSC of the liquid crystal transitions of the mesomorphic tolanes and



	–OR	Cr		Ν		Ι
29	-OCH ₂ C=CCH ₃	•	100			•
30	$-OCH_2C \equiv CC_3H_7$	•	59			•
31	-OCH2C=CC4H9	•	39		_	•
32	-OCH2C=CC5H11	•	46		_	•
33	–OC ₂ H ₄ C≡CH	•	67	•	$(64)^{a}$	•
34	$-OC_2H_4C \equiv CCH_3$	•	72		_	•
35	$-OC_2H_4C \equiv CC_2H_5$	•	56			•
36	–OC ₃ H ₆ C≡CH	•	56	•	57	•
37	–OC ₄ H ₈ C≡CH	•	64	•	$(60)^{a}$	•
^a Monotrop	ic transition temperature.					



Fig. 1 Differential scanning thermogram as a function of temperature for the first heating and cooling cycle for the tolane 15 (scan rate $10 \,^{\circ}\text{C min}^{-1}$).

acetylenes listed in Tables 1-3 is shown in Fig. 1 for the tolane 15. The enthalpy of transition between the nematic phase and the isotropic liquid is relatively small (3.8 J g^{-1}), as expected. In comparison, the enthalpy of fusion (91.2 J g^{-1}) of the transition from the crystalline state to form the nematic phase is much higher. These values were determined twice on heating and cooling cycles on the same sample. The values obtained on separate samples of the same compounds were reproducible and very little thermal degradation was observed. The baseline of the spectrum is relatively flat and sharp transition peaks are observed. Both transitions are first order as expected. A degree of supercooling below the melting point is observed on the cooling cycle. The energy of crystallisation is much lower than that of melting, which suggests the formation of a different crystal form on cooling. This is confirmed by the appearance of an exothermic peak at 35 °C due to a crystal-crystal transition, and the same peak on the second heating cycle as on the first.

Mesomorphism

The thermal data for two short homologous series of 4-n-alkyl-4'-alkoxytolanes (1–14) are collated in Table 1 and plotted against the number of carbon atoms (m) in the terminal alkoxy chain in Fig. 2 and 3. All the homologues of the 4-n-alkoxy-4'-propyltolanes (1–7) exhibit a nematic phase, although the nematic phase for compound 3 is monotropic, *i.e.* formed on cooling below the melting point. An odd–even effect is observed for the nematic clearing point, as expected (Fig. 2); see below.



Fig. 2 Plot of the transition temperatures of the 4-n-alkoxy-4'-propyltolanes (1–7) against the number of the carbon atoms (m) in the alkoxy chain.



Fig. 3 Plot of the transition temperatures of the 4-n-alkoxy-4'-pentyltolanes (8–14) against the number of the carbon atoms (m) in the alkoxy chain.

The melting point decreases with increasing chain length due to a higher degree of flexibility of the terminal chain and a higher number of non-linear conformations. The van der Waals forces of attraction between the aromatic cores are also diluted by longer chains. The same trends in the transition temperatures are observed for the corresponding 4-*n*-alkoxy-4'-pentyltolanes (8–14) as for compounds 1–7 (see Fig. 3), although all the homologues 8–14 exhibit an enantiotropic nematic phase. The melting point (av. 53 °C) and the clearing point (av. 74 °C) of the pentyl homologues 8–14 are lower on average than those (av. 67 and 77 °C, respectively) of the propyl homologues 1–7. However, the difference in the average melting points is greater than that in the average clearing points and so the temperature range for the nematic phase is broader for the pentyl homologues.

The chemical bonds in compound 4, shown in Fig. 4, define the molecular geometry of the aromatic core and, therefore, no assumptions about the shape of the core need to be made: the 1,4-disubstituted phenyl rings and the conjugated carbon– carbon triple bond situated between the phenyl rings of the tolanes automatically generate a linear structure. However, there is a high degree of free rotation about the interannular bonds and, as a consequence, the phenyl rings adopt an out-of-plane, orthogonal arrangement to each other. It is reasonable to assume that the terminal propyl chain will adopt an all-*trans*, antiperiplanar (zig-zag) conformation, as any other conformation would be strongly non-linear and include eclipsed



Fig. 4 The energy-minimised structure of compound **4** with an all-*trans*, antiperiplanar conformation of the hexyloxy chain (a) in the x-y plane viewed along the z axis and (b) in the x-z plane viewed along the y axis.

carbon-hydrogen bonds involving the second and third carbon atoms in the chain. This assumption would not have to be valid for longer alkyl chains. Therefore, the only real degree of molecular flexibility is located in the second terminal (alkoxy) chain. An all-trans conformation of the terminal hexyloxy chain of the ether 4 is shown in Fig. 4(a) and (b) (from different perspectives) and a corresponding alternating cis-trans conformation is shown in Fig. 5(a) and (b). Molecular modelling packages only really find the lowest energy conformation of an alkyl chain as submitted, i.e. fully-extended or linear. Fig. 4 shows the fully-extended terminal hexyloxy chain to be planar and Fig. 5 shows an out-of-plane bond between the second and third carbon atoms in the alternating linear (cis-trans) conformation of the hexyloxy chain. However, the latter conformation would still give rise to a more symmetrical rotation volume and a higher length-to-breadth ratio, plus a greater degree of molecular polarisability (see also Table 4, where these two extreme conformations of the terminal hexyloxy chain are shown schematically). On this basis, the assumption of an extended all-trans conformation appears unreasonable, although it has been used to explain the alternation in the clearing point of homologous series, such as that shown in Fig. 2 and $3.^{2-4,23-25}$ It was postulated that the alternation is due to alternating effects on the anisotropy of polarisablity on ascending a homologous series as the polarisability increases on passing from an odd number of carbon atoms in an alkoxy chain to an even number.^{23–25} The axial polarisability is increased about twice as much as the polarisability in an orthogonal direction on passing from an even to an odd alkoxy chain. As a consequence, the anisotropy of molecular polarisability is greater for homologues with even alkoxy chains, e.g. ethoxy or butoxy, and the plot of the clearing points lies above that of the corresponding homologues with an odd alkoxy chain, e.g. propoxy and pentoxy (see Fig. 2 and 3). However, this simple rationale does not explain the more complex plots of clearing point against chain length observed for many different classes of liquid crystals.¹⁻¹⁰ Therefore, it seems reasonable to assume that a combination of these two extreme conformations, as well intermediate conformations, is most probably present in the nematic phase. This can be attributed to thermal fluctations and molecular rotation with a statistical preference for an alternating *cis-trans* conformation, probably due to space filling and entropy requirements, in spite of the partially or fully eclipsed, anticlinic carbon-carbon bonds present in this conformation. However, it is also highly likely that some of the population of chains will also be in extended the all-trans conformation; see below.

The position and configuration of the *trans* and *cis* carbon– carbon double bonds of the alkenyloxy-substituted tolanes **15–18** were chosen on the basis of previous studies^{11–15} to give rise to the highest clearing point for a nematic phase. A clear alternation in the clearing point is seen on ascending the series.



Fig. 5 The energy-minimised structure of compound 4 with an alternating *trans–cis* conformation of the hexyloxy chain (a) in the x-y plane viewed along the z axis and (b) in the x-z plane viewed along the y axis.

The trans double bond in 15 and 17 leads to higher clearing points than that of the hexyloxy tolane 4, without a double bond in the chain; the double bonds in cis and terminal positions in 16 and 18, respectively, give rise to a lower clearing point. This may be explained by assuming an all-trans, antiperiplanar conformation of the terminal chain (see Table 4). The shape of the chains in 16 and 18 distorts the ideal rotation volume, whereas the conformation of the chains in 15 and 17 remains within it. The added rigidity of these alkenyloxy chains compared to that of the hexyloxy-substituted tolane 4 will also contribute to a higher clearing point. A higher degree of polarisability due to the presence of the sp²-hybridised π -bonds may also contribute. This interpretation seems to be confirmed by the very high clearing point of the nematic phase formed by the (E,E)-hexa-2,4-dienyloxy-substituted tolane 19 with two conjugated trans carbon-carbon double bonds in the terminal chain. If the terminal chain of the tolanes 15-19 were to adopt the corresponding alternating cis-trans conformation, shown in Table 4, then a higher clearing point than that of the analogous hexyloxy-substituted tolane 4 would be expected for all of them: the shape of the chain is identical, but the chain would adopt fewer non-linear conformations due to the added rigidity caused by the carbon-carbon double bond and the anisotropy of molecular polarisability should be higher due to the π -electrons in the double bond. This is seen not to be the case.

The situation is even more complex for the analogous tolanes 20-28, with carbon-carbon triple bonds in their terminal chains (see Table 2). Only the tolanes 24, 27 and 28, with carbon-carbon triple bonds in terminal positions, exhibit an observable nematic phase. This can be explained if the same assumption of an all-trans, antiperiplanar conformation of the terminal chain is made for compounds 20-28, incorporating a triple bond, as that made for the analogous materials 15-19, incorporating a double bond. The shape of the terminal chain of 20-23, 25 and 26, with a triple bond contained within the chain, does not fit completely within the rotation volume of this chain conformation (see Table 4 for 21 and 26). This is consistent with the non-mesomorphic nature of these materials. However, the chain of 21 would fit within the rotation volume of an alternating (cis-trans) conformation of the chain and, consequently, a high clearing point would be expected. This is clearly not so. The chain of 26 fits within neither rotation volume and this compound is not mesomorphic. However, the triple bonds in terminal positions of 24, 27 and 28 only extends to a small degree from either of these ideal shapes. Therefore, a lower clearing point would be expected for these tolanes compared to that of the hexyloxy-substituted tolane 4 and, indeed, this is observed to be the case for all the acetylenes studied with a carbon-carbon triple bond in the terminal positions of the chains. The same trends are observed for the corresponding pentyl homologues 29-37, with carbon-carbon triple bonds in their terminal chains (see Table 3), i.e. only 33, 36 and 37, with triple bonds in terminal positions, exhibit an observable nematic phase. Therefore, the correlation between the position of the carbon-carbon triple bond in the terminal chain and the observed liquid crystalline behaviour described above may be generally valid. In this case, only acetylenes with the triple bond in a terminal position will show a pronounced tendency for mesophase formation. However, the clearing point will be at least marginally lower than that of an analogous compound with a saturated ethyl group (C_2H_5) in place of the acetylene moiety. Any other position of the triple bond in the chain, not immediately adjacent to or conjugated with the molecular core, will lead to very low clearing points or to the complete absence of any observable mesomorphic behaviour.

Physical properties

Several representative examples of the new compounds have been evaluated as potential components of nematic mixtures

Table 4 Two	possible	notations	that model	the	conformation	of t	he t	terminal	chain	(incorporating	six	carbon	atoms)	of t	the 4	4-substituted-4
propyltolanes	s (4, 15–19	9, 21, 26 a	nd 28)													

		C ₃ H ₇ -						
			$T_{\rm N-I}$ predictio	n				
	All-trans conformation	Alternating <i>cis-trans</i> conformation	All-trans	cis-trans	$T_{\rm N-I}/^{\circ}{\rm C}$			
6			Parity	Parity	76			
15		-0	Higher	Higher	84			
16			Lower	Higher	49			
17		o	Higher	Higher	86			
19		o	Highest	Highest	141			
21			Low	Higher	< 60			
26		o	Lowest	Lowest	< 56			
28		o	Lower	Lower	59			

for use in LCDs. A fixed amount (10 wt%) of the acetylene **28** was dissolved in a standard nematic mixture (ZLI 3086) from E. Merck. The presence of 10 wt% of **28**, with a carbon–carbon triple bond in the terminal position of the flexible aliphatic chain, leads to a corresponding increase ($\sim 10\%$) in the

refractive indices and the birefringence of the host mixture. However, the clearing point of the doped mixture is the same as that of the host mixture. The birefringence of this guest-host mixture is plotted against temperature in Fig. 6. The plot shows a non-linear dependence of the birefringence on temperature,



Fig. 6 Plot against temperature of the birefringence of compound 28 (10%) in a host nematic mixture.

which reflects the usual increase in the order parameter below the clearing point with decreasing temperature. A similar increase in the birefringence of this host mixture was obtained using equivalent amounts of the corresponding alkenyl derivatives, e.g. 17. Initial investigations of the photochemical stability of 28 (Heraeus Instruments Suntest CPS+) indicated that such compounds with non-conjugated carbon-carbon triple bond in the terminal chain could be sufficiently stable for use in LCDs. This is consistent with the absorption spectrum of this kind of compound, cf. the UV/vis spectrum of a solution of the corresponding pentyl homologue 37 (10 wt%) in ethanol (Fig. 7). There is no absorption above 330 nm, which is below the cut-off frequency of a standard LCD with glass substrates and polarisers. These initial results suggest that liquid crystals with a carbon-carbon triple bond in a terminal position of the flexible aliphatic chain may be of potential use as components of nematic mixtures of LCDs. However, further tests, including switching studies of nematic mixtures and more stringent stability tests, are required to confirm these findings.

Conclusions

The results of this study appear to be consistent with the empirical interpretation of Gray^{2–4} of the nematic state, which presupposes that molecules responsible for the formation of the nematic phase are dynamic entities, which must consist of a fairly rigid molecular core and at least one terminal chain in an all-*trans*, antiperiplanar conformation, with a subtle balance between flexibility and rigidity. The carbon–carbon double bond in a limited number of positions and configurations in the terminal chain consistent with this conformation seems to embody this compromise. The carbon–carbon triple bond does not. Perhaps a degree of fluidity of the chain is necessary to satisfy a requirement for space filling between molecules. The



simple presumption that a high length-to-breadth ratio and degree of molecular polarisability, due to a long, thin rotation volume around the molecular long axis, automatically gives rise to a higher clearing point for the nematic phase does not appear to be valid. This is clearly the case for these simple tolanes with alkoxy, alkenyloxy and acetylene terminal chains, where dipole-dipole interactions due to non-conjugated heteroatoms, which are known to lead to low clearing points^{8–10}, or other strong dipole–dipole or dipole-induced interactions, are absent.

Experimental

Techniques

The structures of intermediates and final products were confirmed by ¹H NMR (JOEL JMN-GX270 FT) and IR (Perkin Elmer 783) spectroscopy, and mass spectrometry (MS; Finnegan MAT 1020 automated GC/MS). Reaction progress and product purity wer 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 using a Perkin-Elmer DSC7-PC differential scanning calorimeter. Molecular modelling was carried out using ChemDraw Ultra 626 and MM1 energy minimisation. Simulations using the Cerius 2²⁷ molecular modelling packages gave essentially the same results.

Synthesis

A short reaction pathway to several typical liquid crystalline tolanes (4, 15–20) is described below in order to illustrate the spectral data obtained for the final compounds in Tables 1-3 and the reaction intermediates leading to them.

4-Hydroxy-4'-propyltolane. 4-Propylphenylacetylene (5.00 g, 34.72 mmol) was added dropwise at room temperature to a mixture of 4-iodophenol (7.28 g, 33.67 mmol), Pd(PPh₃)₂Cl₂ (0.46 g, 0.66 mmol), copper iodide (0.25 g, 1.32 mmol), triethylamine (5.00 g, 49.60 mmol) and tetrahydrofuran (40 cm³). The mixture was stirred for 24 h at room temperature, then filtered and the filtrate evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 1:1 (v/v) mixture of light petroleum (b.p. 40-60 °C) and dichloromethane as eluent, and recrystallised from hexane to yield the desired phenol (4.42 g, 57%). Purity 96.2% (GLC). ¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.94 (t, 3H), 1.65 (sext, 2H), 2.59 (t, 2H), 4.96 (s, 1H), 6.81 (dt, J = 8 Hz, 2H), 7.14 (dt, J = 8 Hz, 2H)2H), 7.41 (dt, J = 2 Hz, 2H), 7.44 (dt, J = 2 Hz, 2H). IR (KBr) $v_{\text{max}}/\text{cm}^{-1}$: 3500, 2960, 1600, 1520, 1450, 1250, 1100, 840. MS: *m*/*z* 236 (M⁺), 207, 178.

4-Hexyloxy-4'-propyltolane (6). A mixture of 1-bromohexane (0.19 g, 1.17 mmol), 4-hydroxy-4'-propyltolane (0.25 g, 1.06 mmol), potassium carbonate (0.58 g, 4.24 mmol) and butanone (40 cm³) was heated at 80 °C overnight. The cooled reaction mixture was filtered and the filtrate evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 95:5 (v/v) mixture of light petroleum (b.p. 40–60 °C) and ethyl acetate as eluent, and recrystallised from ethanol to yield the desired ether (0.18 g, 52%). Purity 99.7% (GLC). ¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.90 (t, 3H), 0.94 (t, 3H), 1.34 (m, 4H), 1.45 (sext, 2H), 1.64 (quint, 2H), 1.78 (quint, 2H), 2.59 (t, 2H), 3.96 (t, 2H), 6.86 (dt, J = 8 Hz, 2H), 7.14 (dt, J = 8 Hz, 2H), 7.42 (dt, J = 8 Hz, 2H), 7.45

(dt, J = 8 Hz, 2H). IR (KBr) v_{max}/cm^{-1} : 2930 (C–H stretch), 1604 (C=C stretch), 1515 (C=C stretch), 1248 (C–O stretch), 1077 (C–H in-plane def. 1,4-disub.), 840 (C–H out-of-plane def. 1,4-disub.). MS: m/z 320 (M⁺), 236, 207.

4-[(E)-2-Hexenyloxy]-4'-propyltolane (15). A solution of triphenylphosphine (0.61 g, 2.33 mmol), (E)-2-hexen-1-ol (0.23 g, 2.33 mmol), 4-hydroxy-4'-propyltolane (0.50 g, 2.12 mmol), diethyldiazodicarboxylate (0.40 g, 2.33 mmol) and tetrahydrofuran (40 cm³) was prepared at 0 °C. The reaction mixture was stirred at room temperature overnight. The solvent was removed under reduced pressure and the crude product was purified by column chromatography on silica gel using a 90:10 (v/v) mixture of light petroleum (b.p. 40-60 °C) and ethyl acetate as eluent. The crude product was recrystallised from ethanol to yield the desired ether (0.18 g, 26%). Purity 99.8% (GLC). ¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.91 (t, 3H), 0.94 (t, 3H), 1.45 (sext, 2H), 1.65 (sext, 2H), 2.07 (m, 2H), 2.59 (t, 2H), 4.49 (d, 2H), 5.71 (m, 1H), 5.87 (m, 1H), 6.87 (dt, J = 8 Hz, 2H), 7.14 (dt, J = 8 Hz, 2H), 7.41 (dt, J = 8 Hz, 2H), 7.44 (dt, J = 8 Hz, 2H). IR (KBr) v_{max}/v_{ma cm⁻¹: 2926 (C-H stretch), 1604 (C=C stretch), 1514 (C=C stretch), 1284 (C-H out-of-plane def. trans-C=C), 1239 (C-O stretch), 1175 (C-H in-plane def. 1,4-disub.), 1003 (C-H in-plane def. 1,4-disub.), 968 (C-H out-of-plane def. trans-C=C), 837 (C-H out-of-plane def. 1,4-disub.). MS: m/z 318 (M⁺), 236, 207.

4-[(Z)-3-Hexenyloxy]-4'-propyltolane (16). Synthesised as for 15, using (Z)-3-hexen-1-ol (0.23 g, 2.33 mmol). Yield 0.22 g, 33%. Purity 99.9% (GLC). ¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.94 (t, 3H), 0.99 (t, 3H), 1.64 (sext, 2H), 2.10 (m, 2H), 2.56 (m, 4H), 3.97 (t, 2H), 5.42 (m, 1H), 5.55 (m, 1H), 6.85 (dt, J = 8 Hz, 2H), 7.14 (dt, J = 8 Hz, 2H), 7.42 (dt, J = 8 Hz, 2H), 7.44 (dt, J = 8 Hz, 2H). IR (KBr) $v_{\rm max}/{\rm cm}^{-1}$: 2934 (C–H stretch), 1605 (C=C stretch), 1508 (C=C stretch), 1247 (C–O stretch), 1176 (C–H in-plane def. 1,4-disub.), 1029 (C–H in-plane def. 1,4-disub.), 835 (C–H out-of-plane def. 1,4-disub.). MS: m/z 318 (M⁺), 235, 206.

4-[(*E*)-**4-**Hexenyloxy]-**4**'-propyltolane (17). Synthesised as for 15, using (*E*)-4-hexen-1-ol (0.23 g, 2.33 mmol). Yield 0.28 g, 41%. Purity 99.8% (GLC). ¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.94 (t, 3H), 1.65 (m, 5H), 1.84 (m, 2H), 2.16 (m, 2H), 2.59 (t, 2H), 3.97 (t, 2H), 5.48 (m, 1H), 5.55 (m, 1H), 6.85 (dt, *J* = 8 Hz, 2H), 7.14 (dt, *J* = 8 Hz, 2H), 7.41 (dt, *J* = 8 Hz, 2H), 7.45 (dt, *J* = 8 Hz, 2H). IR (KBr) $\nu_{\rm max}/{\rm cm}^{-1}$: 2940 (C–H stretch), 1604 (C=C stretch), 1513 (C=C stretch), 1285 (C–H out-of-plane def. *trans*-C=C), 1249 (C–O stretch), 1119 (C–H in-plane def. 1,4-disub.), 1048 (C–H in-plane def. 1,4-disub.), 966 (C–H out-of-plane def. *trans*-C=C), 836 (C–H out-of-plane def. 1,4-disub.). MS: *m*/*z* 318 (M⁺), 236, 207.

4-(5-Hexenyloxy)-4'-propyltolane (18). Synthesised as for **15**, using 5-hexen-1-ol (0.23 g, 2.33 mmol). Yield 0.25 g, 37%. Purity 99.9% (GLC).¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.94 (t, 3H), 1.64 (m, 4H), 1.81 (m, 2H), 2.13 (m, 2H), 2.59 (t, 2H), 3.98 (t, 2H), 5.02 (m, 2H), 5.84 (m, 1H), 5.83 (dd J = 18, 1 Hz, 1H), 6.85 (dt, J = 8 Hz, 2H), 7.14 (dt, J = 8 Hz, 2H), 7.41 (dt, J = 8 Hz, 2H), 7.44 (dt, J = 8 Hz, 2H). IR (KBr) $v_{\rm max}/{\rm cm}^{-1}$: 2942 (C–H stretch), 1610 (C=C stretch), 1518 (C=C stretch), 1247 (C–O stretch), 1172 (C–H in-plane def. 1,4-disub.), 1021 (C–H in-plane def. 1,4-disub.), MS: m/z 318 (M⁺), 236, 207.

4-[(*E***,***E***)-2,4-Hexadienyloxy)]-4'-propyltolane (19).** Synthesised as for **15**, using (*E*,*E*)-2,4-hexadien-1-ol (0.23 g, 2.33 mmol). Yield 0.20 g, 30%. Purity 99.7% (GLC).¹H NMR (CDCl₃): $\delta_{\rm H}$ 0.94 (t, 3H), 1.64 (sext, 2H), 1.77 (d, 3H), 2.59 (t, 2H), 4.55 (d, 2H), 5.75 (m, 2H), 6.09 (m, 1H), 6.33 (m, 1H), 6.87 (dt, *J* = 8 Hz, 2H), 7.14 (dt, *J* = 8 Hz, 2H), 7.42 (dt, *J* = 8 Hz, 2H), 7.44 (dt, *J* = 8 Hz, 2H). IR (KBr) $\nu_{\rm max}/{\rm cm}^{-1}$: 2918 (C–H stretch), 1607

(C=C stretch), 1515 (C=C stretch), 1243 (C–O stretch), 1175 (C–H in-plane def. 1,4-disub.), 993 (C–H in-plane def. 1,4-disub.), 835 (C–H out-of-plane def. 1,4-disub.). MS: m/z 316 (M⁺), 236, 207.

2-Butynyl toluene 4-sulfonic acid ester. A solution of p-toluenesulfonyl chloride (3.48 g, 18.2 mmol) in pyridine (1.92 g, 24.3 mmol) and chloroform (40 cm³) was added dropwise to a solution of 2-butyn-1-ol (0.85 g, 12.1 mmol) in chloroform (40 cm³) at 0 °C. The reaction mixture was maintained at 0 °C overnight. After stirring for 1 h at room temperature, diethyl ether (20 cm³) and water (30 cm³) were then added. The organic layer was separated off and the aqueous layer extracted into dichloromethane. The combined organic layers were washed with water $(1 \times 100 \text{ cm}^3)$, dried (MgSO₄), filtered and the filtrate evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 90:10 (v/v) mixture of light petroleum (b.p. 40-60 °C) and ethyl acetate as eluent to yield a clear liquid (1.22 g, 45%), which was used without further purification. Purity 97.3% (GLC). ¹H NMR (CDCl₃): $\delta_{\rm H}$ 1.88 (t, 3H), 2.50 (s, 3H), 4.68 (quart, 2H), 7.43 (d, 2H), 7.82 (d, 2H). IR (KBr) v_{max}/cm^{-1} : 2930, 1600, 1320, 1270, 1130, 1050, 960, 810. MS: m/z 244 (M⁺), 155, 91.

4-(2-Butynyloxy)-4'-propyltolane (20). A mixture of 2-butynyl toluene 4-sulfonic acid ester (0.19 g, 1.17 mmol), 4-hydroxy-4'-propyltolane (0.25 g, 1.06 mmol), potassium carbonate (0.58 g, 4.24 mmol) and butanone (40 cm³) was heated at 80 °C overnight. The cooled reaction mixture was filtered and the filtrate evaporated down under reduced pressure. The crude product was purified by column chromatography on silica gel using a 95:5 (v/v) mixture of light petroleum (b.p. 40-60 °C) and ethyl acetate as eluent, and recrystallised from ethanol to yield the desired ether (0.17 g, 50%). Purity 99.8% (GLC). ¹H NMR $(CDCl_3): \delta_H 0.95 (t, 3H), 1.65 (sext, 2H), 1.88 (t, J = 2 Hz, 3H),$ 2.58 (t, 2H), 4.68 (quart, J = 2 Hz, 2H), 6.95 (dt, J = 8 Hz, 2H), 7.14 (dt, J = 8 Hz, 2H), 7.41 (dt, J = 8 Hz, 2H), 7.45 (dt, J = 8 Hz, 2H). IR (KBr) $v_{\text{max}}/\text{cm}^{-1}$: 2929 (C–H stretch), 1602 (C=C stretch), 1507 (C=C stretch), 1240 (C-O stretch), 1003 (C-H in-plane def. 1,4-disub.), 833 (C-H out-of-plane def. 1, 4-disub.). MS: m/z 288 (M⁺), 235, 206.

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