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Laterally fluorinated tolanes of low melting point

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Tolanes having a terminal polar group and a lateral fluoro substituent are reported with the desirable features of high birefringence, wide nematic range and low melting point.

Dielectrically neutral tolanes are useful components of liquid crystal mixtures for use in electrooptic applications. They usually have relatively high birefringence, a low viscosity and modest melting points (see table 1). However, they are often of relatively low clearing point and in some instances it would be desirable if they added to the overall positive dielectric anisotropy of the liquid crystal mixture so that they could help to produce lower threshold voltage liquid crystal mixtures. To be able to do this the molecules must incorporate a polar terminal substituent. However, tolanes with such a terminal group usually have a high melting point which, due to reduced solubility, reduces their usefulness in liquid crystal mixture formulation. Thus their higher clearing point, high birefringence and positive dielectric anisotropy cannot be fully utilised. Some examples are given in table 1 where a comparison of polar ($Y = \mathrm{CN}$) and non-polar ($Y =$ alkyl or alkoxy) tolanes can be seen.

The higher than expected melting point of tolanes (or acetylenic compounds in general) may be due to their linear molecular structure which allows them to pack efficiently into a crystal lattice. Additionally, in tolanes with a polar, terminal substituent the effects of increased lateral attractions often leads to very high melting points. In this project the aim was to produce lower melting acetylenic compounds having a positive dielectric anisotropy. In the course of this work, tolanes containing a lateral substituent (in order to reduce the molecular symmetry) and the incorporation of a flexible portion within the molecule (to lessen the molecular rigidity) were evaluated.

The acetylenic linkage was introduced by coupling an appropriate aryl bromide or iodide (prepared by standard methods) to trimethylsilyl acetylene as previously described [10, 11]. Hydrolysis of the silyl protecting group, followed by a further coupling reaction with a second aryl group gave the diphenyl acetylene. The products from each stage of the synthesis were purified to >98 per cent purity and analysed by HPLC (Hewlett–Packard 1090 with diode array detector) or capillary gas chromatography (Perkin–Elmer 8500 with FID). The final products were purified by flash chromatography and crystallization to $>99{\cdot}5$ per cent purity. The identity of all the compounds was confirmed by ^{1}H NMR (Joel PMX 60 SI) and mass spectrometry

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Table 1. Physical data for some two ring tolanes illustrating the high melting point of the terminal cyano compounds.

Compound	*R*	*Y*	T_{CN}/°C	T_{NI}/°C	Δn	η/cSt	Ref.
1	C_5H_{11}	OCH_3	43	55	0·256	20	[1]
2	C_5H_{11}	C_6H_{13}	31	21	0·224	13	[2]
3	C_5H_{11}	CN	80	70	0·307	—	[3]
4	C_4H_9O	CN	108	111	—	—	[4]
5	$C_5H_{11}O$	CN	78	94	—	—	[4]

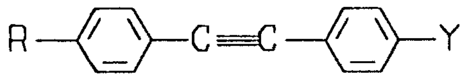

Figure 1.

(Nermag R10-10S quadrupole mass spectrometer). Phase types and transition temperatures were determined by a combination of hot stage (Mettler FP 5) optical microscopy and DSC analysis (Du Pont 1090). Physical measurements (viscosity, refractive index and dielectric anisotropy) were carried out on 10 per cent *w*/*w* solutions of the test compound in a low dielectric host (ZLI 4792) at 20°C. Extrapolated viscosities were measured by a capillary flow method and birefringences were measured using an Abbe refractometer with Na_D light. The dielectric anisotropy was measured using a capacitative method at 1 kHz.

The effects of lateral fluorination and the incorporation of an ethyl linkage can be conveniently subdivided into three sections, (i) two ring compounds (diphenyl acetylene), (ii) three ring compounds and (iii) three ring compounds also containing an ethyl linkage.

(i) *Two ring compounds.* Data on a range of these systems containing the polar terminal groups fluoro, chloro and trifluoromethoxy are given in table 2, and a comparison with the non-lateral fluoro compounds is also shown. In each case lateral fluorination (X or $Z = F$) has significantly reduced the melting point of the compounds and the liquid crystal clearing point (nematic to isotropic phase relative to the unsubstituted compound [X and $Z = H$]). The melting point depression can be rationalized if it is considered that the lateral fluorine atom disrupts the overall symmetry of the molecule thus leading to a less efficient molecular packing in the solid phase. It is well known [12] that broadening a molecule by lateral substituents leads to a lower nematic phase stability due to reduced intermolecular attractions.

Most of the nematic to isotropic transition temperatures, given in table 2, are extrapolated from mixtures of the guest tolane in a dielectrically neutral host (ZLI 3086); such values can only be regarded as a guide to the actual clearing temperature and a detailed analysis of these is not therefore worthwhile.

The chloro group can effectively extend the electronic conjugation of the molecule and its larger atomic size extends the length of the molecule compared to the smaller fluorine substituent. Thus the chloro terminal substituent leads to higher T_{NI} and birefringence values. However, the conjugated, two atom linear cyano terminal group (in compound **3**), leads to even higher values of T_{NI} and the birefringence.

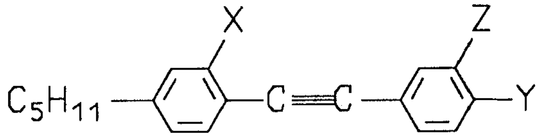

Figure 2.

Table 2. Comparative physical data for two ring tolanes with a polar terminal substituent with and without a lateral fluorine substituent.

Compound	X	Z	Y	T_{CI}/°C	T_{NI}/°C	Δn	η/cSt	Ref.
6	H	H	F	65	—	—	9	[5]
7	F	H	F	17	[−20]	0·20	10	
8	H	H	OCF_3	49	0	—	—	[6]
9	F	H	OCF_3	9	−8	0·19	7	
10	H	H	Cl	69	[37]	0·24	17	[7]
11	F	H	Cl	53	[6]	0·23	15	
12	H	F	Cl	50	[6]	0·21	22	[7]

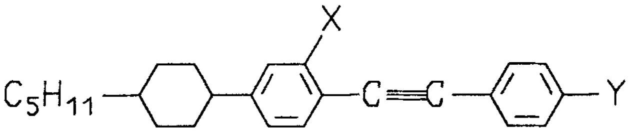

Figure 3.

Table 3. Comparative physical data for three ring acetylenes with a polar substituent with and without a lateral fluorine substituent.

Compound	X	Y	T_{CN}/°C	T_{NI}/°C	Δn	η/cSt	Ref.
13	H	F	94	192	0·23	24	[8]
14	F	F	78	163	0·23	33	

The available data on viscosity suggests that lateral fluorination has led to only a small increase in viscosity. Interestingly, the position of a lateral fluoro group appears to have an effect on the viscosity and birefringence (see compounds **11** and **12**).

(ii) *Three ring compounds.* Data on these materials are shown in table 3. In this case only fluorine was used as the terminal group. Lateral fluorination has lowered the melting point compared to the non-fluoro analogue; the same arguments as discussed earlier account for this feature. The clearing point has also been depressed by 29°C, similar to that in the two ring compounds (compounds **10** and **11**). In this case a significant increase in viscosity is observed. A totally aromatic system is exemplified by compound **15**. Even with lateral fluorination this material has a very high melting point and high smectic stability, but a very high birefringence is exhibited. The extensive electronic conjugation in the aromatic system leads to an increased molecular polarizability as evidenced by the high birefringence. However, this also results in an increase in intermolecular attractive forces leading to high melting points, and as in this case, an increased tendency for the molecules to form into layers as indicated by the high smectic stability.

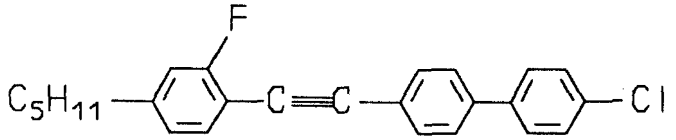

Figure 4.

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C–S_A 126°C: S_A–N 141°C: N–I 211°C

$\Delta n = 0{\cdot}38$: $\eta_{20} = 55$ cSt

(iii) *Three ring compounds with an ethyl linkage.* The effect of lateral monofluorination is illustrated by comparing compounds **16** and **17**; the lower melting point and T_{NI} of **17** can be explained, as discussed earlier, in terms of reduced intermolecular attractions caused by broadening of the molecule and disruption of the linear molecular structure which weakens the molecular packing in the solid phase. Further effects are also seen by introducting an ethyl linkage into the system. It is well-known [13] that an ethyl linkage lowers T_{NI} by virtue of it increasing the molecular flexibility which in turn leads to effective broadening of the molecule and reduction in the effect of intermolecular attractive forces. This is seen by comparing compounds **14** and **17**. Because neither the cyclohexyl ring in **14** or the ethyl linkage in **17** can extend the conjugation of the molecule (and only an ethyl linkage differentiates the molecules in molecular size) the birefringence of the compounds is very similar. The ethyl linked compound **17** has a lower viscosity than **14**, although this may be slightly anomalous due to the lower clearing point of **17** and, therefore, of the mixture which was used for the measurement. However, this feature is often seen in ethyl linked materials although the reasons for it are unclear. The dielectric anisotropy of compound **17** is +9; it therefore is a useful positive dielectric anisotropy compound and the low melting point,

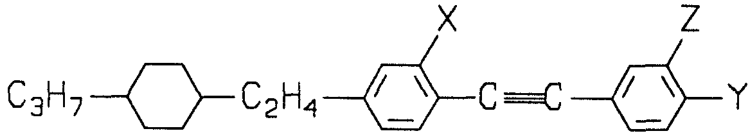

Figure 5.

Table 4. Physical data for a range of three ring acetylenes having a polar terminal group, an ethyl linkage and a lateral fluorine substituent.

Compound	*X*	*Z*	*Y*	T_{CN}/°C	T_{NI}/°C	Δn	η/cSt	Ref.
16	H	H	F	86	149	0·23	20	[9]
17	F	H	F	51	131	0·23	20	
18	F	F	F	46	105	0·21	19	
19	F	H	Cl	80	159	0·27	24	
20	F	H	OCF_3	57†	142	0·21	13	
21	H	F	F	85	125	—	—	[9]

† C–S_B 57°C, S_B–N 102°C.

high birefringence and low viscosity make this class of compound particularly interesting.

When the position of the lateral fluorine is changed such that it is ortho to the terminal fluoro group (compound **21**) the resultant compounds shows a lower clearing point and the melting point is similar to the non-fluoro compound **16**. Therefore, in both the two ring compounds and these materials it is shown that a lateral fluorine in the centre of the molecule (i.e. compound **17**) has a more beneficial effect on the melting point than if the fluoro group is ortho to the terminal group. This feature suggests that a lateral substituent in the centre of a molecule disrupts the crystal lattice most.

When two lateral fluorines are used a particularly interesting low melting point compound (**18**) is produced. The T_{NI} is also lowered by the additional lateral fluorine substituent. The terminal chloro compound (**19**) has the highest birefringence of this family, again this is due to increased conjugation in the molecule, but this has also led to a higher melting point and viscosity. The trifluoromethoxy compound (**20**) has a high smectic tendency, this is probably due to the dipole moment of the OCF_3 group lying across the molecule and thus encouraging layer formation and the formation of smectic phases.

The combination of a centrally positioned lateral fluoro substituent and an ethyl linkage is very effective in lowering the melting point of tolanes which otherwise tend to have high melting points.

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