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Synthesis and Evaluation of Nematic 4-Alkenyloxy- and 4-Alkenoyloxy-4'-Cyanobiphenyls

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There is a direct correlation between the physical properties of a nematic mixture utilised in TN- and STN-LCDs and display optical performance. Since it is known that the presence of a carbon-carbon double bond in nematic liquid crystals can influence some physical properties of nematics advantageously[1,2], we have introduced a carbon-carbon double bond into the terminal chain of a variety of laterally and terminally substituted biphenyl derivatives. The position and configuration of the double bond has been varied systematically and the optimal combination for nematic phase formation and low melting point identified. Homologous series of 4-(*E*)-alk-2-enyloxy-4'-cyanobiphenyls (ethers) and 4-(*E*)-alk-2-enyloyloxy-4'-cyanobiphenyls (esters) have been synthesised. The esters exhibit higher nematic-to-isotropic transition temperatures and wider temperature ranges of the nematic phase than the corresponding ethers. Some initial correlations have been established between the transition temperatures, viscosity, elastic constants, dipole moments, birefringence, etc. and molecular structure.

Keywords: double bonds; TN and STN-LCDs

INTRODUCTION

The supertwisted liquid crystal display device[3-5] fulfils most of the requirements of portable devices, such as mobile phones, personal digital

assistants and laptop computers e.g. low manufacturing costs, high-information-content, good contrast and low power consumption. However, in order to optimise the performance of STN-LCDs there is a requirement for nematic liquid crystals with an improved spectrum of physical properties. Certain modifications of the molecular structure could provide these physical requirements and therefore allow for the fine-tuning of liquid crystal mixtures for such devices. In this work a carbon-carbon double bond has been introduced into the terminal chain of widely used 4-*n*-alkoxy-4'-cyanobiphenyls[6-8] in order to study their effect on the transition temperatures and other physical properties of relevance to STN displays. These compounds offer the advantages of being easy to prepare using short reaction pathways and relatively cheap, commercially available starting materials. The required alkenols and alkenoic acid are readily available with the desired position and configuration of the carbon-carbon double bond.

SYNTHESIS

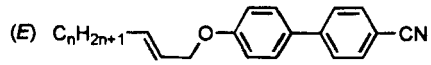
The 4-alkenyloxy- and 4-alkenoyloxy-4'-cyanobiphenyls reported in the tables were synthesised using standard procedures starting from commercially available 4-cyano-4'-hydroxybiphenyl and alkenols or alkenoic acids.

RESULTS AND DISCUSSION

4-Alkenyloxy-4'-cyanobiphenyls (ethers)

The effect on the transition temperatures of a *trans*-carbon-carbon double bond in the 2-position of a terminal chain is shown in table 1. For the compounds (**1**, **2** or **3**) with short chains, i.e. n = 1, 2 or 3, the presence of the double bond gives rise to higher melting points and higher nematic-to-isotropic clearing points when compared to the transition temperatures of the analogous materials without a carbon-carbon double bonds see table 2 (**6**, **7** or **8**). However for compounds (**4** and **5**) where n = 4 and 5, there is a significant reduction in the melting point without any reduction in the nematic-to-isotropic clearing point. This is unusual behaviour for compounds with a (*E*)-2 double bond in the terminal alkenyl chain.

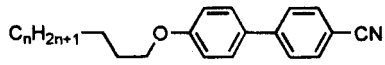
TABLE 1 The transition temperatures (°C) of the 4-[(*E*)-alk-2-enyloxy]-4'-cyanobiphenyls (**1** – **5**).



	n	Cr		SmA		N		I
1	1	•	100	——		•	104	•
2	2	•	89	——		•	(81)	•
3	3	•	74	——		•	82	•
4	4	•	39	——		•	74	•
5	5	•	42	•	45	•	80	•

For compounds where n = 5 (**5** and **10**) an enantiotropic smectic A phase is observed. However, the presence of a (*E*)-2 double bond in compound (**5**) lowers the SmA-N transition temperature, giving rise to an increase in the nematic phase temperature range, compared with the mesomorphic behaviour of the analogous 4-cyano-4'-octyloxybiphenyl (**10**).

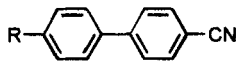
TABLE 2 The transition temperatures (°C) of the 4-alkoxy-4'-cyanobiphenyls (**6** – **10**).

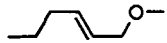
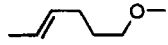
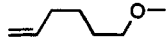


	n	Cr		SmA		N		I	Ref.
6	1	•	78	——		•	(76)	•	[7]
7	2	•	83	——		•	(68)	•	[8]
8	3	•	58	——		•	77	•	[7]
9	4	•	54	——		•	75	•	[7]
10	5	•	55	•	67	•	80	•	[6]

The transition temperatures collated in table 3 show the effect of the configuration and position of a carbon-carbon double bond in the terminal chain. For compounds (**3**) and (**12**) the *trans*-double bond is pointing across the long molecular axis, giving rise to high clearing points and narrow nematic phase ranges compared with those observed for the 4-cyano-4'-hexyloxybiphenyl (**8**) without a carbon-carbon double bond in the terminal chain. However, when the double bond is approximately parallel to the long molecular axis, i.e. for compounds (**11**) and (**13**), the melting points are significantly lower than those observed for the compounds (**3**, **8** and **12**). Thus, a clear odd-even effect is observed.

TABLE 3 The transition temperatures (°C) of the 4-alkoxy-4'-cyanobiphenyls (**8**) and the 4-alkenyloxy-4'-cyanobiphenyls (**3**, and **11** – **13**).



	R	Cr	N	I	Ref.
8		• 58	• 77	•	[7]
3	(*E*) 	• 74	• 82	•	—
11	(*Z*) 	• 46	• (30)	•	—
12	(*E*) 	• 74	• 81	•	—
13		• 33	• 51	•	—

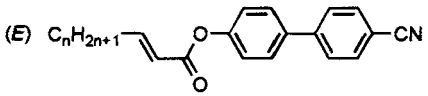
( ) represents a monotropic transition temperature

4-Alkenyloyloxy-4'-cyanobiphenyls (esters)

The transition temperatures recorded in tables 4 and 5 clearly show that the presence of a *trans*-carbon-carbon double bond in the 2-position of the alkenoyloxy chain results in a high clearing point and a broad nematic phase. For the esters (**14** – **18**) with a double bond in the 2-position the clearing point is much higher resulting in broader nematic phase ranges compared to those of the related esters (**19** – **23**) without a carbon-carbon double bond in the terminal chain. Similarly to the situation observed for the analogous ether (**4**)

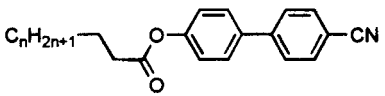
the melting point of the 4-cyano-4'-[(*E*)-hept-2-enoyloxy]biphenyl (**17**) when n = 4 is significantly lowered, when compared to that of the equivalent compound (**22**) without a double bond.

TABLE 4 The transition temperatures (°C) of the 4-[(*E*)-alk-2-enoyloxy]-4'-cyanobiphenyls (**14** – **18**).



	n	Cr		N		I
14	1	•	140	•	165	•
15	2	•	106	•	132	•
16	3	•	92	•	131	•
17	4	•	48	•	118	•
18	5	•	100	•	123	•

TABLE 5 The transition temperatures (°C) of the 4-alkanoyloxy-4'-cyanobiphenyls (**19** – **23**).



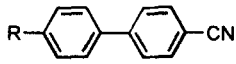
	n	Cr		N		I	Ref.
19	1	•	78	•	(75)	•	[9]
20	2	•	35	•	65	•	[10]
21	3	•	56	•	72	•	[11]
22	4	•	59	•	71	•	[11]
23	5	•	78	•	(75)	•	[11]

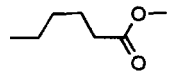
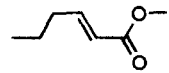
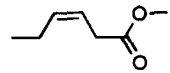
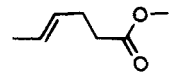
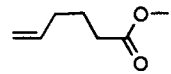
( ) represents a monotropic transition temperature

The thermal data collated in table 6 for the 4-cyano-4'-hexanoyloxybiphenyl (**21**) and the 4-cyano-4'-hexenoyloxybiphenyls (**16**, **24** – **26**) illustrate the

effect on the liquid crystal transition temperatures of a carbon-carbon double bond in various positions and conformations in the terminal chain. These were chosen to maintain a linear conformation of the chain. A clear odd-even effect for the clearing point is observed for the *trans*- and *cis*-substituted compounds. The values of the former are much higher than those of the latter. The very high clearing point and broad nematic range of 4-cyano-4'-[(*E*)-hex-2-enoyloxy]biphenyl (**16**) is notable. The clearing points of the other alkenoyloxy-substituted compounds (**24** – **26**) are either comparable or lower than that of the reference 4-cyano-4'-hexanoyloxybiphenyl (**21**).

TABLE 6 The transition temperatures (°C) of 4-cyano-4'-hexanoyloxybiphenyl (**21**) and the 4-cyano-4'-hexenoyloxybiphenyls (**16**, and **24** – **26**).



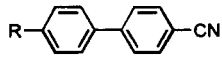
	R	Cr	N	I	Ref.
21		• 56	• 76	•	[11]
16	(E) 	• 92	• 131	•	—
24	(Z) 	• 61	• (27)	•	—
25	(E) 	• 97	• (74)	•	—
26		• 46	• (38)	•	—

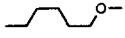
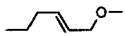
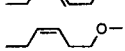
( ) represents a monotropic transition temperature

PHYSICAL PROPERTIES

The physical data collated in table 7 show the effect of an (*E*)-2 or (*Z*)-3 double bond in the terminal chain of the 4-alkenyloxy-4'-cyanobiphenyls on the viscosity (η) and birefringence (Δn). The birefringence of 4-cyano-4'-[(*E*)-hex-2-enyloxy]biphenyl (**3**) is higher than that of the 4-cyano-4'-hexyloxybiphenyl (**8**) with a comparable viscosity at room temperature. The birefringence of 4-cyano-4'-[(*Z*)-hex-3-enyloxy]biphenyl (**11**) is lower than that of the 4-cyano-4'-hexyloxybiphenyl (**8**) with a lower viscosity at room temperature. Therefore materials with double bonds can be used to optimise components of nematic liquid crystal mixtures for improved display performance.

TABLE 7 Viscosity (η) and birefringence (Δn) values for the of 4-cyano -4'-hexyloxy]biphenyl (**8**), 4-cyano-4'-[(*E*)-hex-2-enoyloxy]biphenyl (**3**) and the 4-cyano-4'-[(*Z*)-hex-3-enoyloxy]biphenyl (**11**).



	R	η30°C /CP†	Δn 30°C	η20°C /CP†	Δn 20°C	η0.8T_{N-I} /CP†	Δn0.8T_{N-I}
8		126*	0.211*	374*	0.221*	13218*	0.254*
3	(*E*) 	127**	0.235**	216**	0.253**	2934**	0.268**
11	(*Z*) 	96**	0.198**	189**	0.203**	4972**	0.228**

* 10 & 20 wt% in an apolar mixture
** 10 wt% in an apolar mixture
† error + or - 50%

CONCLUSION

From the results presented here we can conclude the following points:

- A (*E*)-2 double bond in conjugation with an ester group leads to higher nematic-to-isotropic transition temperatures and broader nematic ranges than those of similar ethers.
- In some instances the combination of chain length and (*E*)-2 double bond can lead to lower melting points and broader nematic temperature ranges than those of materials without a double bond in the terminal chain.
- The carbon-carbon double bond can be used to modulate the viscosity and birefringence of readily available components of nematic mixtures.
- These observations are consistent with the behaviour of related alkenyl-substituted cyclohexane liquid crystals[1].

Acknowledgements

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