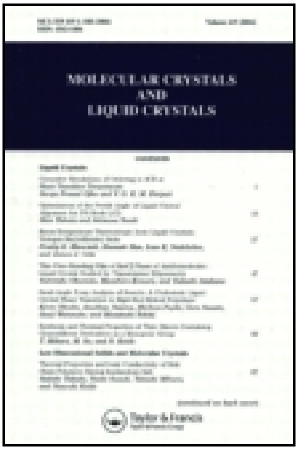


Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Novel Nematic Compounds Incorporating Two Conjugated Carbon-Carbon Double Bonds in the Terminal Chain

Warren L. Duffy [a], J. Clifford Jones [b], Stephen M. Kelly [a], Victoria Minter [b] & Rachel Tuffin [b]
[a] The Department of Chemistry, The University of Hull, Hull, HU6 7RX, UK
[b] The Defence Evaluation and Research Agency, St. Andrews Rd, Malvern, Worcs., WR14 3PS, UK

Version of record first published: 24 Sep 2006

To cite this article: Warren L. Duffy, J. Clifford Jones, Stephen M. Kelly, Victoria Minter & Rachel Tuffin (1999): Novel Nematic Compounds Incorporating Two Conjugated Carbon-Carbon Double Bonds in the Terminal Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 332:1, 91-99

To link to this article: http://dx.doi.org/10.1080/10587259908023748

Mol. Cryst. Liq. Cryst., 1999, Vol. 332, pp. 91-99
Reprints available directly from the publisher
Photocopying permitted by license only

Published by license under the
Gordon and Breach Science Publishers imprint.
Printed in Malaysia

Novel Nematic Compounds Incorporating Two Conjugated Carbon-Carbon Double Bonds in the Terminal Chain

WARREN L. DUFFY[a], J. CLIFFORD JONES[b], STEPHEN M. KELLY[a],
VICTORIA MINTER[b] and RACHEL TUFFIN[b]

[a]*The Department of Chemistry, The University of Hull, Hull, HU6 7RX, UK and* [b]*The Defence Evaluation and Research Agency, St. Andrews Rd, Malvern, Worcs., WR14 3PS, UK*

The position and configuration of a carbon-carbon double bond strongly influence the transition temperatures, elastic and dielectric constants, viscosity, birefringence, etc of nematic liquid crystals incorporating them. This behaviour can probably be attributed to conformational effects and anisotropic π electron density distribution and can be used to improve the optical performance of STN-LCDs. However, relatively few liquid crystals incorporating two carbon-carbon double bonds have been reported[1–3]. Therefore, we have synthesised a wide variety of new compounds incorporating two conjugated *trans*-carbon-carbon double bonds in the same terminal chain. The effects on their physical properties on the presence of two double bonds have been compared with those of the corresponding material either without a carbon-carbon double bond or with just one carbon-carbon double bond in the same position. Strong non-additive effects were found and of the dienes prepared exhibit high birefringence and nematic clearing points as well as being of surprisingly low viscosity.

Keywords: dienes; double bonds; TN and STN-LCDs

INTRODUCTION

After the invention of the Twisted Nematic Liquid Crystal Display (TN-LCD)[4] it was hoped that it would lead to the first flat panel display with both high-information content and low power consumption, and perhaps supersede the Cathode Ray Tube (CRT) for television applications. However, it later became apparent that this would not happen with the TN-LCD due to its poor contrast and long response times at high rates of multiplexability. To overcome these problems two technologies were developed after many years of research, the Thin Film Transistor LCD (TFT-LCD)[5] and Supertwisted Nematic LCD (STN-LCD)[6-8]. The TFT-LCD uses a different form of addressing called Active Matrix Addressing. This involves the addressing, *via* a transistor, of an individual electrode for each pixel. However, this technique although significantly superior in performance to the STN-LCD, is more power consuming and also more expensive due to a more complex manufacturing process and, in parts to poor manufacturing yields. The STN-LCD is basically very similar to the TN-LCD in construction and therefore, relatively cheap to manufacture. Increasing the twist angle from 90° to ~270° has allowed the STN display to be more multiplexable than the TN-LCD resulting in displays with significantly higher information content. In order to further improve this device and, in particular response times, the liquid crystal mixture itself can be further optimised. It has been shown that improved components of liquid crystal mixtures incorporate certain groups, such as unsaturated carbon-carbon bonds in well defined configurations and positions in order to meet particular physical requirements of the TN and STN devices[9,10].

In this work two *trans*-carbon-carbon double bonds have been incorporated into the terminal chain of known liquid crystal structures and their effect on the transition temperatures and physical properties such as viscosity (η) and optical anisotropy (Δn) studied.

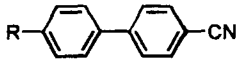
SYNTHESIS

The compounds reported in this work were synthesised using standard liquid crystal chemistry from known intermediates and commercially available starting materials. This will be reported in detail elsewhere.

RESULTS AND DISCUSSION

From the transition temperatures recorded in tables 1 and 2 it is evident that the presence of one *trans*-carbon-carbon double bond in the 2 or 4 position of the alkenyloxy chain results in marginally higher clearing points ($T_{N\text{-}I}$), but significantly higher melting points (Cr-N) than those of the reference 4-cyano-4'-hexyloxybiphenyl (**1**). The presence of two *trans*-carbon-carbon double bonds in the terminal chain of 4-cyano-4'-hexyloxybiphenyls leads to significant increases in the nematic-to-isotropic clearing point and nematic phase temperature range.

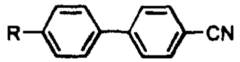
TABLE 1. The transition temperatures (°C) of the 4-cyano-4'-hexyloxybiphenyl (**1**), 4-cyano-4'-hexenyloxybiphenyl (**2** and **3**) and 4-cyano-4'-(*E*,*E*)-hexa-2,4-dienyloxybiphenyl (**4**).

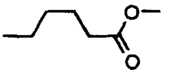
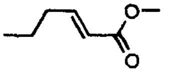
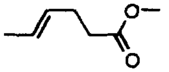
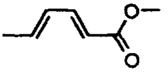


	R	Cr		N		I	Ref.
1		•	58	•	77	•	[11]
2	(*E*) 	•	74	•	82	•	—
3	(*E*) 	•	74	•	81	•	—
4	(*E*,*E*) 	•	125	•	152	•	—

The presence of one or two carbon-carbon double bonds has a greater effect on the transition temperatures of the esters (**5** – **8**), see table 2, than on those of the analogous ethers (**1** – **4**), see table 1. This can probably be attributed to the increase in conjugation and rigidity. It is clear from the thermal data collated in tables 1 and 2 that the dienes prepared (**4** and **8**) both exhibit strong non-additive effects compared to the materials with one double bond.

TABLE 2. The transition temperatures (°C) of the 4-cyano-4'-hexanoyloxybiphenyl (**5**) 4-cyano-4'-hexanoyloxybiphenyl (**6** and **7**) and 4-cyano-4'-(*E*,*E*)-hexa-2,4-dienyloyloxybiphenyl (**8**).

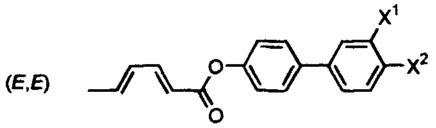


	R	Cr		N		I	Ref.
5		•	56	•	72	•	[12]
6	(*E*) 	•	92	•	131	•	—
7	(*E*) 	•	97	•	(74)	•	—
8	(*E*,*E*) 	•	160	•	227	•	—

( ) represents a monotropic transition temperature

The thermal data collated in tables 3 and 4, show the effects of lateral and terminal substituents and their associated dipole moments on the transition temperatures of 4-substituted-4'-(*E*,*E*)-hexa-2,4-dienoyloxybiphenyls (**8** - **16**). The use of a polar terminal substituent, i.e. a cyano group, can yield materials with broad nematic temperature ranges and high nematic-to-isotropic clearing points, as can be seen for compounds (**8**) and (**13**). The replacement of a terminal cyano substituent in compound (**8**) with the less polar fluoro substituent in compound (**11**) results in the lowering of the melting point and the nematic-to-isotropic transition temperature. However, there is no significant reduction in the nematic phase temperature range. Replacement of these polar substituents with an apolar alkyl chain (with five carbon atoms) to form compound (**10**) leads to a lower melting point and maintains a high clearing point and as a consequence, a broader nematic phase temperature range is observed. The presence of a lateral fluorine substituent in the compounds (**12** and **13**) leads to lower clearing points, but higher melting points than those of the comparable compounds (**8** and **11**, respectively) with hydrogen in place of fluorine. The effect of the bulky cyano group and low dipole moment of the fluorine atom in compound (**14**) prevents observable mesophase formation. The strong tendency for compounds containing two *trans*-carbon-carbon double bonds in conjugation with an ester moiety to form liquid crystal mesophases is clearly seen for compound (**9**) where monotropic smectic A and nematic phases are observed despite the absence of a terminal substituent. This does not occur for the analogous ether (**15**), see table 4.

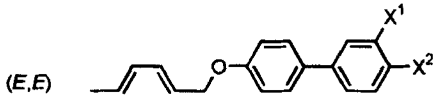
TABLE 3. The transition temperatures (°C) of variously substituted 4-(*E*,*E*)-hexadienoyloxybiphenyls (**8** – **14**).



	X^1	X^2	Cr		SmA		N		I
9	H	H	•	110	•	(84)	•	(92)	•
10	H	C_5H_{11}	•	86	—		•	168	•
11	H	F	•	96	—		•	158	•
8	H	CN	•	160	—		•	227	•
12	F	F	•	112	—		•	125	•
13	F	CN	•	183	—		•	201	•
14	CN	F	•	170	—		—		•

( ) represents a monotropic transition temperature

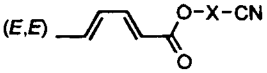
TABLE 4. The transition temperatures (°C) of 4-(*E*,*E*)-hexa-2,4-dienyloxybiphenyl (**15**), 4-(*E*,*E*)-hexa-2,4-dienyloxy-4'-pentylbiphenyl (**16**) and 4-cyano-4'-(*E*,*E*)-hexa-2,4-dienyloxybiphenyl (**4**)



	X^1	X^2	Cr		SmA		N		I
15	H	H	•	89	—		—		•
16	H	C_5H_{11}	•	119	•	136	—		•
4	H	CN	•	125	—		•	152	•

The liquid crystal transition temperatures collated for the compounds (**8**, **17** and **18**) in table 5 show that a minimum of a one-and-a-half fused naphthalene ring system is required for nematic phase formation, when a cyano group is present as a terminal substituent. The one-ring ester is not mesomorphic. However, when a phenyl ring is substituted with two hexa-2,4-dienoyloxy chains, as in compounds (**19** – **21**) nematic phase behaviour can be observed at elevated temperatures for the one-ring diester (**20**), see table 6. The presence of inverted carbonyl functions in compound (**20**) compared to compound (**19**) results in the absence of observable liquid crystalline properties. The diether (**21**) is also not mesomorphic.

TABLE 5. The transition temperatures (°C) of the 4-cyanophenyl, 2-cyanonaphthyl-6-yl and 4-cyanobiphenyl-4'-yl (*E,E*)-hexa-2,4-dienoates (**8**, **17** and **18**).



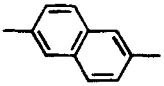
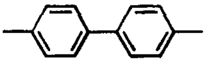
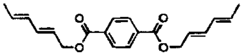
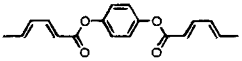
	X	Cr		N		I
17		●	111	———		●
18		●	116	●	141	●
8		●	160	●	227	●

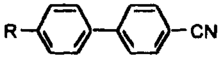
TABLE 6. The transition temperatures for the diesters (**19** and **20**) and diether (**21**).

	Structure	Cr		N		I
19		●	86	———		●
20		●	183	●	186	●
21		●	130	———		●

PHYSICAL PROPERTIES

The physical data collated in table 7 show the effect of (*E*)-2, (*Z*)-3 and (*E,E*)-2,4 double bonds in the terminal chain of the 4-alkenyloxy- and 4-alkadienyloxy-4'-cyanobiphenyls on the viscosity (η) and birefringence (Δn). The birefringence of 4-cyano-4'-[(*E*)-hex-2-enyloxy]biphenyl (**2**) is higher than that of the 4-cyano-4'-hexyloxybiphenyl (**1**) with a comparable viscosity at room temperature. The birefringence of 4-cyano-4'-[(*Z*)-hex-3-enyloxy]biphenyl (**3**) is lower than that of the 4-cyano-4'-hexyloxybiphenyl (**1**) with a lower viscosity at room temperature. The birefringence of 4-cyano-4'-[(*E*,*E*)-hex-2,4-dienyloxy]biphenyl (**4**) is higher than that of the 4-cyano-4'-hexyloxybiphenyl (**1**) 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 4-cyano-4'-hexyloxybiphenyl (**1**), 4-hexenyloxy-4'-cyanobiphenyl (**2** and **3**) and 4-[(*E*,*E*)-2,4-hexadienyloxy]-4'-cyanobiphenyl (**4**).
below.



	R	$\eta 30°C$ /CP[†]	Δn 30°C	$\eta 20°C$ /CP[†]	Δn 20°C	$\eta 0.8T_{N\text{-}I}$ /CP[†]	Δn $0.8T_{N\text{-}I}$
1		126[*]	0.211[*]	374[*]	0.221[*]	13218[*]	0.254[*]
2	(*E*) 	127[**]	0.235[**]	216[**]	0.253[**]	2934[**]	0.268[**]
3	(*Z*) 	96[**]	0.198[**]	189[**]	0.203[**]	4972[**]	0.228[**]
4	(*E*,*E*) 	26[‡]	0.328[‡]	57[‡]	0.333[‡]	202[‡]	0.298[‡]

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

CONCLUSION

In this work it has been shown that the presence of <u>one</u> or <u>two</u> carbon-carbon double bonds in the terminal chain can have a positive effect on a number of liquid crystal properties such as:

- strong tendency for nematic phase formation
- increasing the nematic-to-isotropic transition temperature
- broadening the nematic phase temperature range
- lower viscosity
- increased birefringence

Acknowledgements
We would like to thank the EPSRC for the funding of an Advanced Fellowship (S. M. K.) and to DERA for providing the physical data and also for the funding of a Research Studentship (W. L. D.).

References

[1] Y. Goto and Y. Ogawa, EPA 0 280 902, (1988).
[2] W. Maier and K. Markau, Z. *Phys. Chem. N. F.*, **28**, 190, (1961).
[3] S. M. Kelly, *Liq. Cryst.*, **20,** 493, (1996).
[4] M. Schadt and W. Helfrich, 532261, (1970).
[5] T. P. Brody, J. A. Asars and G. D. Dixon, *IEEE Trans. Electron Dev.*, **20**, 995, (1973).
[6] T. J. Scheffer and J. Nehring, *Appl. Phys. Let.*, **45,** 1021, (1984).
[7] H. Watanabe *et al.*, *Society for Information Displays,* 416, (1988).
[8] C. M. Waters and E. P. Raynes, *Displays,* **8,** 59, (1987).
[9] M. Petrzilka, *Mol. Crys. Liq. Crys.*, **131**, 109, (1985).
[10] M. Schadt, R. Buchecker and K. Müller, *Liq. Cryst.*, **5**, 293, (1989).
[11] G. W. Gray, K. J. Harrison and J. A. Nash, *Electron. Lett.,* **37,** 18, (1973).
[12] J. C. Dubois and A. Zann, *J. Phys. (Paris), Suppl.*, **37**, 35, (1976).