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

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Version of record first published: 24 Sep 2006

To cite this article: Kevin Bartle, Neil Campbell, Warren L. Duffy, Stephen M. Kelly, Vicki Minter, Mary O'Neill & Rachel P. Tuffin (2001): Nematic Thiophenes for STN-LCDS and Flexoelectric LCDS, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 364:1, 881-888

To link to this article: http://dx.doi.org/10.1080/10587250108025061

Mol. Cryst. and Liq. Cryst., 2001, Vol. 364, pp. 881-888
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Nematic Thiophenes for STN-LCDS and Flexoelectric LCDS

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We report anew class of liquid crystals incorporating a 2,5-disubstituted thiophene ring and one or two conjugated *trans*-carbon-carbon double bonds in the terminal chain for use as components of nematic mixtures for TN-LCDs and STN-LCDs. The combination of these molecular elements contribute towards generating a high birefringence, a high nematic clearing point as well as a low viscosity for these materials. Several of these compounds exhibit a melting point below room temperature. This is the first time a room temperature nematic phase has been reported for phenyl thiophene derivatives. The new thiophene compounds can be used to induce a high birefringence in nematic mixtures for LCDs with short response times.

Keywords: nematics; thiophenes; high birefringence

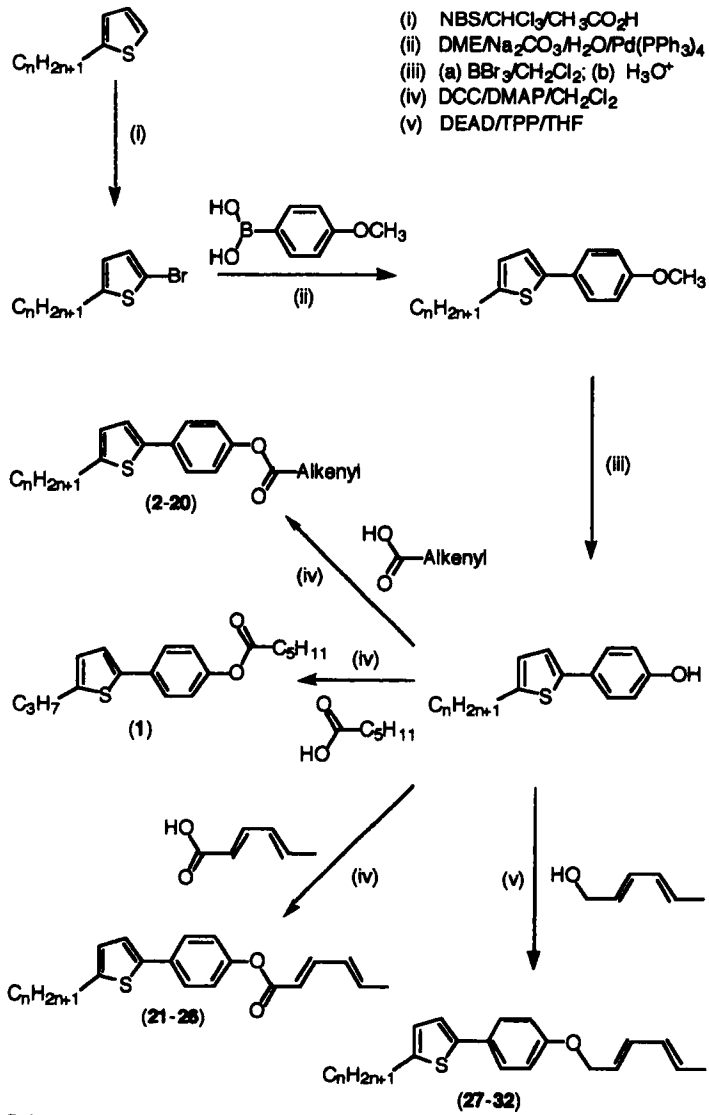
INTRODUCTION

Most commercially available instruments with a liquid crystal display (LCD) utilise the Twisted Nematic (TN)-LCD[1,2] or Super Twisted Nematic (STN)-LCD[3-6] with active matrix addressing or multiplex addressing.[6,7] These types of electro-optical device use nematic liquid crystals to produce light, large-area, flat-panel displays with a high contrast ratio, grey-scale (full colour), fast response times and wide operating temperatures. These LCD types require nematic mixtures of positive dielectric anisotropy in order to operate at low voltage with short

response times. Furthermore, a low viscosity and appropriate values of the elastic constants (especially k_{11} and k_{33}) are required in order to further reduce the response times. A low melting point (T_m < -50 °C) and a high clearing point (T_{N-I} > 80 °C -120 °C) are also essential requirements for commercial applications. Nematic mixtures of high birefringence enable thin cells to be used, since the product of the birefringence and the cell gap (Δnd) is fixed for operation in the first or second transmission minimum. A high birefringence can also give rise to short switching times, since both the switch-on and switch-off times are directly proportional to the square of the cell gap. The nematic mixtures used in LCDs are comprised of a mixture of polar and apolar components to generate the appropriate combination of property values.[8] Liquid crystals incorporating the 2,5-disubstituted ring have already been prepared.[9-12] However, the non-coaxial nature of the substituents in the 2- and 5-positions usually requires a molecular structure with a minimum of three rings in order for these materials to be mesomorphic. This is due to the large angle between the bonds at the 2- and 5-positions. This reduces the effective length-to-breadth ratio and the anisotropy of polarisability. Most of these three-ring compounds exhibit smectic phases, especially the smectic C phase.[12] Two-ring thiophene derivatives with only one other ring in the molecular core, which exhibit an enantiotropic nematic phase, are not known to the authors. We have synthesised a new class of apolar compounds suitable for TN-LCDs and STN-LCDs, incorporating a 2,5-disubstituted thiophene ring and one or two *trans*-carbon-carbon double bonds. These compounds fulfil many of the specifications for use in LCDs. These materials were designed so that they would exhibit a low melting point, a high clearing point, a wide nematic phase , a high birefringence and a low viscosity. They have also been screened for use in the Zenithal Bistable Display (ZBD) using flexoelectric nematic liquid crystals.[13]

SYNTHESIS

The esters **1-26** and ethers **27-32** shown in the tables 1-6 were prepared from a range of 2-*n*-alkyl-5-(4-hydroxyphenyl)thiophenes, see reaction scheme 1. The 2-*n*-alkyl-5-(4-hydroxyphenyl)thiophenes were prepared by brominating commercially available 5-*n*-alkylthiophenes using NBS.[14] The resultant aryl bromides were reacted with 4-methoxyphenyl boronic acid in a Suzuki aryl-aryl cross coupling reaction.[15] The resultant 2-*n*-alkyl-5-(4-methoxyphenyl)thiophenes were dealkylated in the usual way[16] using borontribromide to yield the desired phenols. The esters **1-26** were prepared in the usual way[17] using the commercially available alkenoic acids, (*E*)-*n*-alk-2-enoic acids and (*E*,*E*)-hexa-2,4-dienioc acid. The corresponding ethers **27-32** were prepared from (*E*,*E*)-hexa-2,4-dien-1-ol and the appropriate 2-*n*-alkyl-5-(4-hydroxyphenyl)thiophenes in a Mitsunobu alkylation reaction.[18]

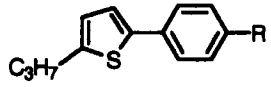


Scheme 1

RESULTS AND DISCUSSION

The structures and transition temperatures of 2-propyl-5-(4-[hexanoyloxy]phenyl)thiophene **1** and the analogous 2-propyl-5-(4-[hexenoyloxy]phenyl)thiophenes **2-5** are collated in Table 1. It is clear from the thermal data that only the 2-propyl-5-(4-[(*E*)-hex-2-enoyloxy]phenyl)thiophene **2** is mesomorphic. Indeed, this ester exhibits a nematic phase at room temperature as well as a high clearing point. The melting point is the lowest of the series. However, the other esters can be supercooled to room temperature without the appearance of a liquid crystalline phase. It was decided, therefore, to synthesise a series of homologues of ester **2** with a *trans*-carbon-carbon double bond in the 2-position of the terminal alkenoyloxy-chain. The liquid crystal transition temperatures for the 2-*n*-alkyl-5-(4-[(*E*)-hex-2-enoyloxy]phenyl)thiophenes **2** and **6-12** are listed in Table 2. The clearing point shows a clear odd-even effect. However, the clearing point is remarkably independent of chain length. In contrast there are wide differences in the melting points for individual homologues with no apparent trends. Only the propyl and ethyl homologues **2** and **7**, respectively, exhibit an enantiotropic nematic phase. The thermal data for 2-(4-[(*E*)-alk-2-enoyloxy]phenyl)-5-propylthiophenes **2** and **13-16** are collated in Table 3. These esters were prepared in order to establish the optimum length of the (*E*)-alk-2-enoyloxy chain having already determined that the combination of a propyl homologue with a (*E*)-hex-2-enoyloxy chain produced a nematic phase at room temperature. Three homologues **2**, **15** and **16** of the esters exhibit a melting point below room temperature and an enantiotropic nematic phase. The corresponding data for the 2-(4-[(*E*)-alk-2-enoyloxy]phenyl)-5-pentylthiophenes **9** and **17-20** are listed in Table 4. Only one homologue **20** possesses an enantiotropic nematic phase. However, its melting point is relatively high and the nematic temperature range is narrow. The presence of a conjugated *trans*-carbon-carbon double bond in the 2-position is clearly responsible, at least to a large extent, for the advantageous liquid crystalline transition temperatures of these esters. Therefore, it was decided to investigate the effect of the presence of two conjugated *trans*-carbon-carbon double bonds in similar compounds. The liquid crystal, transition temperatures for the (*E,E*)-2-*n*-alkyl-5-(4-[hexa-2,4-dienoyloxy]phenyl)thiophenes **21-26** are listed in Table 5. All of the esters prepared exhibit an enantiotropic nematic phase at elevated temperatures. It was also decided to prepare the analogous ethers **27-32** to the esters **21-26** in an attempt to produce similar materials, but with a lower viscosity. The thermal data for the corresponding 2-*n*-alkyl-5-(4-[(*E,E*)-hexa-2,4-dienyloxy]phenyl)thiophenes **27-32** are collated in Table 6. The first three homologues **27-29** of the series exhibit an enantiotropic nematic phase. However, a smectic A phase is observed from the second homologue **28** of the series. This transition temperature increases with chain length and the smectic A phase displaces the nematic phase from the hexyl homologue **30** onwards.

TABLE 1. Transition temperatures (°C) for the compounds below:



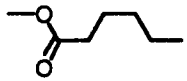
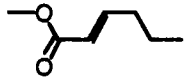
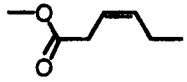
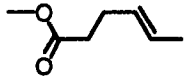
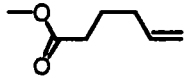
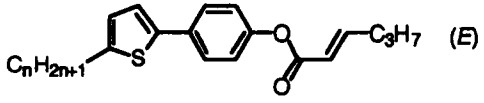
Compound	R		Cr		N		I
1			•	45		-	•
2		(E)	•	16	•	42	•
3		(Z)	•	38		-	•
4		(E)	•	44		-	•
5			•	40		-	•

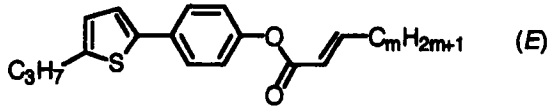
TABLE 2. Transition temperatures (°C) for the compounds below:



Compound	n	Cr		N		I
6	1	•	87		-	•
2	2	•	43	•	44	•
7	3	•	16	•	42	•
8	4	•	39	(•	37)	•
9	5	•	47	(•	46)	•
10	6	•	57	(•	42)	•
11	7	•	59	(•	49)	•
12	8	•	65	[•	47]	•

( ) Represents a monotropic transition temperature
[ ] Represents an extrapolated 'virtual' transition temperature

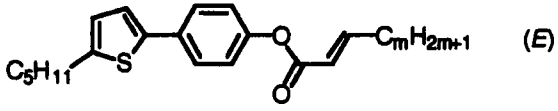
TABLE 3. Transition temperatures (°C) for compounds below:



Compound	n	Cr		N		I
13	1	•	37	•	47	•
14	2	•	32	(•	17)	•
2	3	•	16	•	42	•
15	4	•	17	•	29	•
16	5	•	21	•	42	•

( ) Represents a monotropic transition temperature

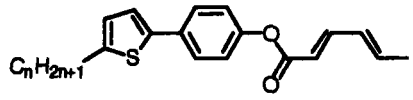
TABLE 4. Transition temperatures (°C) for compounds below:



Compound	n	Cr		N		I
17	1	•	66		-	•
18	2	•	64		-	•
9	3	•	47	(•	46)	•
19	4	•	37	(•	36)	•
20	5	•	44	•	49	•

( ) Represents a monotropic transition temperature

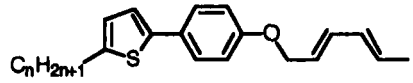
TABLE 5. Transition temperatures (°C) for the esters below:



(*E,E*)

Compound	n	Cr		N		I
21	3	•	75	•	136	•
22	4	•	80	•	122	•
23	5	•	75	•	125	•
24	6	•	79	•	116	•
25	7	•	86	•	117	•
26	8	•	82	•	111	•

TABLE 6. Transition temperatures (°C) for the ethers below:



(*E,E*)

Compound	n	Cr		SmA		N		I
27	3	•	85	•	-	•	98	•
28	4	•	81	•	92	•	96	•
29	5	•	98	(•	97)	•	100	•
30	6	•	95	•	99	•	-	•
31	7	•	95	•	101	•	-	•
32	8	•	86	•	100	•	-	•

( ) Represents a monotropic transition temperature

Physical data for some of the new materials have been measured for 10 % of the compound doped in the host nematic mixture DOP017. They indicate that even small concentrations of the new materials can increase the birefringence of the host nematic mixture significantly without increasing the response times or the clearing point of the resultant nematic mixture proportionately. The dienes esters **21-26** and ethers **27-32** give rise to especially large increases. The extrapolated birefringence for the new compounds at room temperature is high ($0.2 < \Delta n < 0.3$).

Provisional evaluation of the flexoelectric coefficients of these and other thiophenes suggest that a bent shape does not lead automatically to an increase in the flexoelectric coefficients of a polar host nematic mixture (E7) as expected. The value of e_b+e_s/K for compound **2** measured in the pure state at room temperature is lower (0.12 C N^{-1} m^{-1}) than that of E7 at the same temperature (0.76 C N^{-1} m^{-1}). However, the elastic constant value K may differ to some degree. The value extrapolated for compound **2** from mixtures with E7 agree well with that measured for the pure compound.

Acknowledgments
We gratefully acknowledge the EPSRC for support of an Advanced Fellowship (SMK) and postgraduate studentships (KB and GIT). DERA are also thanked for postgraduate studentships (WLD and NC).

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References

[1] M. Schadt, and W. Helfrich, *Appl. Phys. Lett.*, **18**, 127 (1971).

[2] M. Schadt, *Annu. Rev. Mater. Sci.*, **27**, 305 (1997).

[3] T. J. Scheffer and J. Nehring, *Appl. Phys. Lett.*, **45**, 1021 (1984).

[4] C. M. Waters, E. P. Raynes and V. Brimmel, Proc. SID '84, **25**, 261 (1984).

[5] N. Kando, T. Nakagomi and S. Hasagawa, *German Pat. Appl.*, DE 3403259 (1985).

[6] T. J. Scheffer and J. Nehring, *Annu. Rev. Mater. Sci.*, **27**, 555 (1997).

[7] W. E. Howard, *Proc. SID '86*, 313 (1986).

[8] G. W. Gray and S. M. Kelly, *J. Mater. Chem.*, **9**, 2037 (1999).

[9] H. Schubert, I. Sagildinov and J.V. Svetkin, *Z. Chem.*, **15**, 223 (1975).

[10] J. W. Brown, D. J. Byron, D. J. Harwood, R. C. Wilson and A. R. Tajbaksh, *Mol. Cryst. Liq. Cryst.*, **173**, 1667 (1989).

[11] G. Kossmehl and F. D. Hoppe, *Liq. Cryst.*, **15**, 383 (1993).

[12] A. J. Seed, K. J. Toyne and J. W. Goodby, *J. Mater. Chem.*, **5**, 653 (1995).

[13] G. P. Bryan-Brown, C. V. Brown, J. C. Jones, E. L. Wood, I. C. Sage, P. Brett and J. Rudin, *Proc. SID '97 Digest*, 37 (1997).

[14] V. Ramanathan and R. Levine *J. Org. Chem.*, **27**, 121 (1962).

[15] A. Suzuki, *Pure Appl. Chem.*, **66**, 213 (1994).

[16] J. F. McOmie, M. L. Watts and D. E. West, *Tetrahedron*, **24**, 2289 (1968).

[17] O. Mitsunobu, *Synthesis*, **1**(1981).

[18] B. Neises and W. Steglich, *Angew. Chem. Int. Ed. Engl.*, **17**, 522 (1978).