COMMUNICATION

www.rsc.org/materials

Journal of Materials

Chemistry

## Non-symmetric liquid crystal trimers. The first example of a triply-intercalated alternating smectic C phase<sup>†</sup>

Corrie T. Imrie,\*<sup>*a*</sup> Peter A. Henderson<sup>*a*</sup> and John M. Seddon<sup>*b*</sup>

 <sup>a</sup>Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen, UK. E-mail: c.t.imrie@abdn.ac.uk; Fax: 44 1224 272921; Tel: 44 1224 272943
<sup>b</sup>Imperial College of Science, Technology and Medicine, Exhibition Road, London, UK. E-mail: j.seddon@imperial.ac.uk; Fax: 44 207 594 5801; Tel: 44 207 594 5111

Received 22nd March 2004, Accepted 22nd June 2004 First published as an Advance Article on the web 12th July 2004

Non-symmetric liquid crystal trimers containing three different mesogenic units and two flexible spacers have been synthesised, and exhibit a new smectic modification, the triply-intercalated alternating smectic C phase.

A new class of truly multi-functional liquid crystals consisting of molecules containing differing mesogenic units connected via flexible spacers are attracting increasing interest.<sup>1</sup> The exciting potential exists to tailor the properties of these materials in a rational manner by changing the chemical nature of both the mesogenic units and the spacers while the covalent attachment of these differing liquid crystal units prevents their phase separation as might otherwise occur in simple physical mixtures. Yelamaggad et al., for example, reported recently the first example of a liquid crystal consisting of molecules containing four differing mesogenic units.<sup>2</sup> In order to effect control over the properties of these materials and realize this potential, however, it is not sufficient only to simply attach units together having the desired range of properties but we must also understand how these units self-organize in liquid crystal phases. Thus, here we report the thermal behavior of molecules containing three differing mesogenic units and two different alkyl spacers; their chemical structures and the acronyms used to refer to them are shown in Scheme 1. MeO6E.11CN and CN6E.11OMe contain both electron rich and electron deficient liquid crystal units as it is known that these exhibit specific electrostatic interactions which play an important role in the self-organization of a range of systems including binary mixtures,<sup>3,4</sup> liquid crystal dimers<sup>5</sup> and copolymers.<sup>6,7</sup> In order to understand the behavior of these



Scheme 1 Synthesis of non-symmetric trimers.

† Electronic supplementary information (ESI) available: characterization and thermal analysis of the trimers and their intermediates. See http://www.rsc.org/suppdata/jm/b4/b404319g/

**Table 1** Transition temperatures and entropy changes of the liquidcrystal trimers<sup>a</sup>

Trimer	Cr–N, *Cr–Sm/ °C (Δ <i>S</i> / <i>R</i> )	$Sm-N/^{\circ}C$ ( $\Delta S/R$ )	$N-I/^{\circ}C$ ( $\Delta S/R$ )
MeO6E.110Me	138 (18.6)		178 (0.92)
MeO6E.11CN	141 (21.8)	[122 (1.05)]	188 (0.93)
CN6E.110Me	*120 (16.4)	134 (1.60)	188 (0.99)
CN6E.11CN	122 (13.6)		191 (0.81)
<sup><i>a</i></sup> Cr: crystal; Sm: sitions are given in	smectic; N: nematic; 1 square brackets.	I: isotropic. Mon	otropic tran-

novel systems we also report the properties of the corresponding molecules containing two identical terminal liquid crystal units, see Scheme 1. The four target structures shown in Scheme 1 belong to the general class of liquid crystals termed non-symmetric liquid crystal trimers.<sup>1,8</sup> The synthetic route to obtain the trimers is shown in Scheme 1.

The transition temperatures and associated entropy changes, expressed as the dimensionless quantity  $\Delta S/R$ , for the four liquid crystal trimers are listed in Table 1. All four materials exhibit an enantiotropic nematic phase, which was identified on



Fig. 1 Textures of CN6E.110Me at 133  $^{\circ}$ C showing (a) focal conic fans and (b) regions of fans in co-existence with a Schlieren texture exhibiting both two- and four-point brush disclinations.



Fig. 2 X-Ray diffraction pattern of the smectic phase of CN6E.110Me.

DOI: 10.1039/b404319g

2486



Fig. 3 Molecular shapes of (a) CN6E.11OMe and (b) CN6E.10OMe.

the basis of the characteristic Schlieren optical texture containing two- and four-point singularities observed when viewed under the polarized light microscope; this texture also flashed when subjected to mechanical stress. The values of the entropy changes are consistent with this assignment.

On cooling the nematic phases exhibited by MeO6E.11CN and CN6E.11OMe under the polarized light microscope a welldefined focal conic fan texture is developed, see Fig. 1(a), which on shearing gives a Schlieren texture. On cooling a homeotropically aligned nematic sample, a texture consisting of regions of well-defined focal conic fans and Schlieren texture containing both two- and four-point brush disclinations was obtained, see Fig. 1(b). A Schlieren texture containing both types of point singularity would normally be thought of to imply a nematic phase but such an assignment is in conflict with the presence of focal conic defects which indicate a layered structure. This texture is characteristic, however, of a particular modification of the smectic C phase in which the sense of the tilt angle alternates between adjacent layers such that the global tilt angle is zero.

The X-ray diffraction pattern of the smectic mesophase exhibited by CN6E.11OMe contains a single peak in the low angle region implying a layered structure with a sinusoidal density wave along the layer normal, and a broad peak in the wide angle region centered at a spacing of  $4.38 \pm 0.05$  Å, indicating a liquid-like arrangement of the molecules within the layers, see Fig. 2. The layer spacing *d* is 19.0  $\pm$  0.2 Å, which is close to one-third that of the estimated all-*trans* molecular length, *l*, of the most extended conformation of 60.4 Å. The layer spacing has only a small temperature dependence, and has the same value on heating and on cooling. The monotropic nature of the smectic phase shown by MeO6E.11CN precluded its study using X-ray diffraction. The molecular arrangement within the smectic phase will be discussed later.

The observation of smectic behavior for MeO6E.11CN and CN6E.11OMe but not for MeO6E.11OMe and CN6E.11CN is not simply a consequence of lower melting points for the former and, in fact, of the four trimers MeO6E.11CN exhibits the highest melting point. Indeed, it is important to note that the nematic phases of both MeO6E.11OMe and CN6E.11CN can be supercooled to temperatures lower than the smecticnematic transition temperatures observed for the other two trimers. This strongly suggests that interactions involving the unlike terminal mesogenic units play an important role in the formation of the smectic phase. To test this suggestion, the phase behavior of an equimolar mixture of MeO6E.11OMe and CN6E.11CN was determined and this did indeed show an induced smectic phase in addition to a nematic phase. Unfortunately, the monotropic nature of this smectic phase precluded its study using X-ray diffraction. Replacing the undecyl spacer in MeO6E.11CN and CN6E.11OMe by either a



**Fig. 4** Schematic representation of the local molecular order within a triply-intercalated alternating smectic C structure of CN6E.110Me.

decyl or dodecyl spacer gives solely nematic materials.9 The nematic phases of these compounds can also be supercooled to temperatures lower than the smectic-nematic transition temperatures seen for MeO6E.11CN and CN6E.11OMe. Thus, the formation of the smectic phase is strongly dependent on the length and parity of the flexible spacer. Given that the principal difference between the trimers on varying spacer length is their average molecular shape, it seems reasonable to assume that shape also play an important role in smectic phase formation. Specifically, MeO6E.11CN and CN6E.11OMe have stretched S-shaped structures in which all three mesogenic units are inclined with respect to each other, whereas the corresponding decyl or dodecyl compounds have hockey-stick-like shapes in which two mesogenic units are coparallel while the third is inclined to the other two, see Fig. 3. It appears that only the S-shaped molecules exhibit this phase.

Fig. 4 shows a highly schematic representation of the local molecular arrangement within an alternating smectic C phase for which d/l is approximately 0.33. Within this structure the S-shaped molecules can pack efficiently and a microphase separation occurs to give two types of domains, one consisting of alkyl chains and the other of mesogenic units. Each layer of the mesogenic units contains an equal number of the three different moieties which is both entropically favorable and also maximizes the favorable electrostatic interactions between the electron deficient cyano-substituted units and the electron rich central and methoxy-substituted groups. The alternation in the sense of the tilt angle requires a correlation of the mesogenic groups on passing through the phase and this is provided by a combination of the specific interaction between the electron rich and electron deficient units and the flexible spacers providing the oligomeric nature of the system.

There are few examples of smectic liquid crystal trimers in the literature<sup>10–18</sup> and the only layer spacings reported for these imply monoloayer arrangements.<sup>10,16,17</sup> One of these had an alternating tilt angle between the layers and was termed as anticlinic, <sup>16</sup> which may be a more appropriate term than alternating SmC. A liquid crystal tetramer consisting of molecules containing four mesogenic units and three flexible spacers has been reported which shows an orthogonal smectic phase for which *dll* was approximately 0.25,<sup>19</sup> while for non-symmetric liquid crystal dimers intercalated phases are characterized by values of *dll* of approximately 0.5.<sup>5,8</sup> Thus, the triply-intercalated arrangement reported here is a new smectic modification but is strongly reminiscent of phases seen in semi-flexible main chain liquid crystal polymers.<sup>20</sup> Further studies are now required to establish the molecular features required for its formation.

## Acknowledgements

We would like to thank Mr Nick Brooks for his help with the X-ray measurements.

## References

- C. T. Imrie and P. A. Henderson, Curr. Opin. Colloid Interface Sci., 2002, 7, 298.
- 2 C. V. Yelamaggad, S. Anitha Nagamani, U. S. Hiremath, D. S. Shankar Rao and S. Krishna Prasad, *Liq. Cryst.*, 2002, 29(2), 231.
- 3 K. Praefcke and D. Singer, 'Charge-transfer systems', in *Handbook of Liquid Crystals*, D. Demus, J. W. Goodby, G. W. Gray,

H. W. Spiess and V. Vill, ed., Wiley-VCH, Weinheim, 1998, vol. 2B, pp. 945-967.

- M. M. Naoum, R. I. Nessim, G. R. Saad and T. Y. Labeeb, Liq. 4 Cryst., 2002, 29(7), 929.
- C. T. Imrie, Struct. Bonding, 1999, 95, 149. 5
- A. A. Craig and C. T. Imrie, Polymer, 1997, 38(19), 4951. 6
- C. T. Imrie, *Trends Polym. Sci.*, 1995, **3**, 22. C. T. Imrie and G. R. Luckhurst, 'Liquid Crystal Dimers and 8 Oligomers', in *Handbook of Liquid Crystals*, D. Demus, J. W. Goodby, G. W. Gray, H. W. Spiess and V. Vill, ed., Wiley-VCH, Weinheim, 1998, vol. 2B, pp. 801–833. P. A. Henderson and C. T. Imrie, *Liq. Cryst.*, 2004, submitted.
- 9
- R. Centore, A. Roviello and A. Sirigu, Mol. Cryst. Liq. Cryst., 10 1990, 182B, 233.
- B.-Q. Chen, A. Kameyama and T. Nishikubo, Macromolecules, 11 1999, **32**, 6485.

- 12 T. Ikeda, T. Miyamoto, S. Kurihara, M. Tsukada and S. Tazuke, Mol. Cryst. Liq. Cryst., 1990, 182B, 357.
- C. T. Imrie and G. R. Luckhurst, J. Mater. Chem., 1998, 8(6), 13 1339.
- 14 G. R. Luckhurst, Macromol. Symp., 1995, 96, 1.
- 15 A. T. M. Marcelis, A. Koudijs and E. J. R. Sudhölter, Liq. Cryst., 1995, 18(6), 851.
- 16 I. Nishiyama, J. Yamamoto, J. W. Goodby and H. Yokoyama, J. Mater. Chem., 2003, 13, 2429.
- A. C. Sentman and D. L. Gin, Adv. Mater., 2001, 13(18), 1398. 17 18 C. V. Yelamaggad, S. Anitha Nagamani, U. S. Hiremath, D. S. Shankar Rao and S. Krishna Prasad, Liq. Cryst., 2001,
- **28**(10), 1581. C. T. Imrie, D. Stewart, C. Remy, D. W. Christie, I. W. Hamley and R. Harding, J. Mater. Chem., 1999, 9, 2321. 19
- 20 J. Watanabe and M. Hayashi, Macromol., 1988, 21, 278.