

# Enantioselective segregation in achiral nematic liquid crystals†

Verena Görtz and John W. Goodby

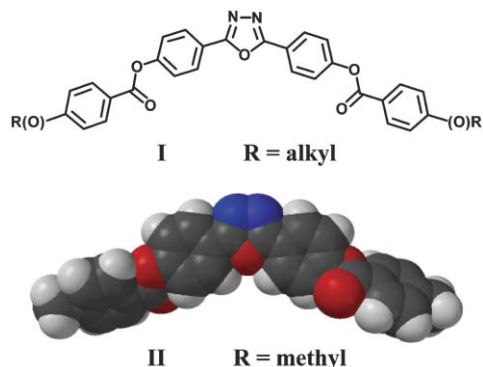
Received (in Cambridge, UK) 15th March 2005, Accepted 18th April 2005

First published as an Advance Article on the web 13th May 2005

DOI: 10.1039/b503846d

The elusive biaxial nematic liquid crystal phase was recently discovered in a family of substituted oxadiazoles. Our investigations of these materials show that the achiral biaxial nematic phase can segregate into chiral domains of opposite handedness, thereby demonstrating that the liquid-like nematic phase exhibits the properties of a conglomerate.

The possibility of the occurrence of a biaxial nematic phase was highlighted, in 1970, in an article by Freiser.<sup>1</sup> However, it was only recently that Samulski *et al.*<sup>2</sup> and Kumar *et al.*<sup>3</sup> reported on low molecular mass materials, based on the oxadiazole motif, which exhibited thermotropic biaxial nematic phases. The biaxial order parameter however was found to be relatively small, with a value of approximately 0.1. The materials themselves have molecular structures that are bent; the bend being associated with the bis(phenyl)oxadiazole moiety located at the centre of the aromatic core, as shown by structure I.



The structures and accompanying phase transitions of these first examples of low mass materials possessing thermotropic biaxial nematic phases are shown in Scheme 1 and Table 1 (compounds **8a** and **8g**).

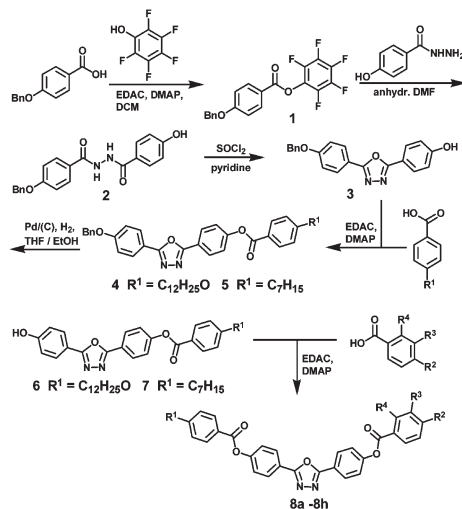
Although the materials have very high temperature nematic phases, we nevertheless repeated their syntheses. In addition, we also prepared dissimilarly substituted bis(phenyl)oxadiazole materials with differing aliphatic chain lengths, and fluoro-substituents incorporated in the outer phenyl rings in order to moderate and reduce melting points and clearing points, thereby making nematic phases accessible at lower temperatures. Scheme 1 shows the route we established to synthesize the materials. Further details of the syntheses are given in the supplementary information.†

With the exception of compound **8f** we found the nematic phase to have a broader temperature range for the dissimilarly

substituted compounds in comparison to the symmetric parent systems **8a** and **8g**; the nematic to smectic phase transitions occur at lower temperatures, and the melting points are reduced. The phase transition temperatures given in Table 1 are the onset temperature values for transitions observed in first DSC cooling cycles at a cooling rate of 10 °C min<sup>-1</sup> (first values are reported as the materials undergo thermal degradation). Although we are mainly concerned with the nematic phase, Table 1 also lists the higher ordered, lower temperature, phases which have undefined structures. Following the terminology used by Samulski *et al.*,<sup>2,4</sup> we denote the unidentified phases as smectic X, Y, and Z, however we also note the lettering is not consistent with the phase identity across the series of compounds.

Upon examination of compound **8g**, which was reported previously by Samulski *et al.*<sup>2,4</sup> and Kumar *et al.*,<sup>3</sup> pristine samples sandwiched between a slide and a cover slip gave unusual textures when examined by thermal, polarized light optical microscopy (POM), as shown in Fig. 1 (a and b). Under crossed polarizers, an apparently normal nematic phase was formed first on cooling from the isotropic liquid. The nematic phase separated in the form of a *schlieren* texture exhibiting Brownian motion. However, the mesophase also exhibited domains, with walls separating one domain from another. Upon rotation of the analyser of the microscope, the domains which were dark became light and *vice versa*, as shown in the figure. This result indicates the domains are helical, and that they have the opposite handedness.

The novel, dissimilarly substituted, bis(phenyl)oxadiazoles were also examined by thermal, polarized light optical microscopy to see if they too displayed helical domains. Fig. 2 shows that the nematic mesophase of compound **8b**, sandwiched between a slide and a

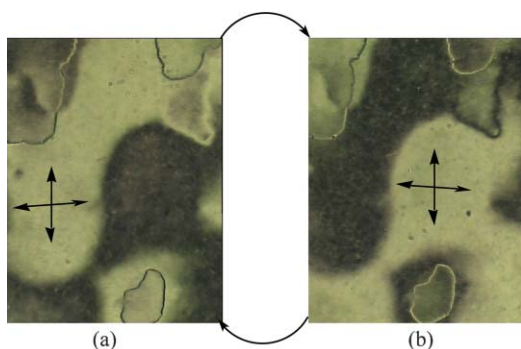


**Scheme 1** Synthesis of similarly and dissimilarly substituted bis(phenyl)oxadiazoles.

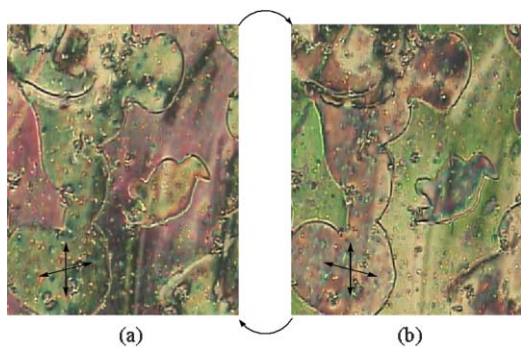
† Electronic supplementary information (ESI) available: detailed synthetic procedures, NMR data, mass spectra, and elemental analyses of final compounds. See <http://www.rsc.org/suppdata/cc/b5/03846d/>

**Table 1** Phase transition temperatures of compounds **8a–h**. Reported are the onset temperature values for transitions observed in DSC cooling cycles at  $10\text{ }^{\circ}\text{C min}^{-1}$

N <sup>o</sup>	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	Phase transitions ( $^{\circ}\text{C}$ )
<b>8a</b>	C <sub>12</sub> H <sub>25</sub> O	C <sub>12</sub> H <sub>25</sub> O	H	H	Iso 203 N 192 SmC 184 SmX 143 SmY 138 SmZ 104 Cr
<b>8b</b>	C <sub>12</sub> H <sub>25</sub> O	C <sub>9</sub> H <sub>19</sub> O	H	H	Iso 210 N 182 SmX 157 SmY 149 SmZ 91 Cr
<b>8c</b>	C <sub>12</sub> H <sub>25</sub> O	C <sub>8</sub> H <sub>17</sub> O	H	H	Iso 213 N 176 SmX 162 SmY 152 SmZ 77 Cr
<b>8d</b>	C <sub>12</sub> H <sub>25</sub> O	C <sub>5</sub> H <sub>11</sub>	H	H	Iso 215 N 160 SmX 91 Cr
<b>8e</b>	C <sub>12</sub> H <sub>25</sub> O	C <sub>9</sub> H <sub>19</sub> O	H	F	Iso 205 N 168 SmX 135 SmY 125 SmZ 72 Cr
<b>8f</b>	C <sub>12</sub> H <sub>25</sub> O	C <sub>9</sub> H <sub>19</sub> O	F	F	Iso 210 N 197 SmC 186 SmX 155 SmY 150 SmZ 100 Cr
<b>8g</b>	C <sub>7</sub> H <sub>15</sub>	C <sub>7</sub> H <sub>15</sub>	H	H	Iso 222 N 173 SmX 151 Cr
<b>8h</b>	C <sub>7</sub> H <sub>15</sub>	C <sub>5</sub> H <sub>11</sub>	H	H	Iso 232 N 164 SmX 149 Cr



**Fig. 1** The *schlieren* texture of the nematic phase of compound **8g** at  $222\text{ }^{\circ}\text{C}$  on cooling from the isotropic, where (a) shows an anticlockwise rotation and (b) a clockwise rotation of the analyser ( $\times 100$ ).



**Fig. 2** Defect texture of the nematic phase of compound **8b** at  $202\text{ }^{\circ}\text{C}$ , where (a) shows an anticlockwise rotation and (b) a clockwise rotation of the analyser ( $\times 100$ ).

cover slip, exhibited domains that also reversed colour upon rotation of the analyser of the microscope. The walls separating the domains from one another are clearly visible in the figure.

Remarkably, uncovered regions of the nematic phase of compound **8f** showed fingerprint textures similar to the chiral nematic phase as depicted in Fig. 3. The photomicrograph of the nematic phase was taken at a temperature of  $189\text{ }^{\circ}\text{C}$ , which is lower than the transition to the smectic C phase obtained on first cooling due to slight sample decomposition. In this texture the equidistant parallel lines could be manifestations of the helical structure of a chiral mesophase with the distance between the lines being equivalent to half the pitch of the helix. Unlike conventional chiral nematic phases where the pitch is constant at constant temperature, the line-separation in this case varied from one domain to the next. Typically it varied from approximately  $5$  to  $12\text{ }\mu\text{m}$  in different domains.



**Fig. 3** The texture of the nematic phase of compound **8f** in an uncovered region on a glass slide at  $189\text{ }^{\circ}\text{C}$  ( $\times 100$ ).

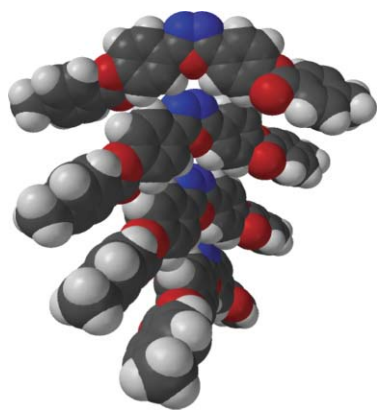
In investigations of the textures exhibited by compound **8h** we observed intense and extensive dynamical motion in uncovered regions of the nematic phase. Fig. 4 shows lines in the nematic phase which occur well above the transition to the smectic X phase. At constant temperature well within the temperature range of the nematic phase, defect lines appear and flow rapidly across the *schlieren* texture of the phase, rather like Williams domains or possibly Rayleigh Bénard thermal instabilities.

In conclusion the results appear to indicate the formation and separation of enantiomeric species during the generation of the nematic phase. Furthermore the observation of what appears to be different pitch lengths in different domains for compound **8f** indicates that the proposed enantioselective segregation is not homogeneous, suggesting that the process is kinetically driven.

Differential scanning calorimetry of the compounds for the first cooling, at slow scanning rates of  $0.2\text{ }^{\circ}\text{C min}^{-1}$  (Mettler DSC 822<sup>o</sup>), indicates that there is a thermal event in the liquid state at a temperature slightly above that of the clearing point. Although the continuous drop in transition temperatures on further cycles shows



**Fig. 4** Lines in the nematic phase of compound **8h** in an uncovered region on a glass slide at  $173\text{ }^{\circ}\text{C}$  ( $\times 100$ ).



**Fig. 5** Cartoon of the proposed formation of a helix *via* the self-assembly of twisted conformers of the bent core molecules.

that the materials undergo decomposition, these results suggest that the liquid is structured at temperatures just above the formation of the liquid-crystalline state, and consequently it is possible that the molecules undergo a process of self-assembly before self-organization into the mesophase occurs.

The results described for the nematic phases of the materials studied strongly suggest the formation of chiral domains characterized by the generation of a helical macrostructure. In each case the formation of helical domains was dependent on the thermal and mechanical history of the sample, indicating that domain formation was kinetically based rather than thermodynamic. Such results are of relevance to the observation made that compound **8g** exhibits a biaxial nematic phase.<sup>2,3</sup> In addition the results challenge our very understanding of the concept of liquid crystallinity, where molecular diffusion, rotation and flipping would suppress the formation of helical domains of opposite handedness in a fluid-like nematic phase.

It is possible to speculate on the results in the following way. For the bis(phenyl)oxadiazole molecules, chiral conformational isomers such as **II** and its mirror image might be expected to exist in the bond rotational profile of a molecule. At the clearing point the conformers could self-select to give the most stable self-assembled structure. This means that the nucleation of the nematic phase could occur through a process of self-assembly where conformers of one hand pack together to give a helical macrostructure which in turn stabilizes conformer formation. Such helical structures assemble into spiralling ribbons, which then self-organize into chiral nematic phases, and because of the sizes of the ribbons, domains are formed by segregation.

Fig. 5 shows how the self-assembly of chiral conformers such as **II** might occur. The chirality of the conformational structure **II** is generated from the two ester linkages being rotated in opposite directions with respect to the bis(phenyl)oxadiazole core. When molecules in this twisted conformation are packed one on top of another a helical self-assembled structure results. The self-organization of the self-assembled structures would result in the formation of a chiral nematic phase. An inverted rotation of the two ester linkages produces the enantiomeric form of conformer **II**, which would assemble to give a helix of opposite handedness. Such self-assembled structures would be dynamically fluctuating with up and down domains as a function of time and external influences such as surface pinning and mechanical disturbances.

This structural speculation would satisfy the criterion that the process is kinetically driven; that the energy barrier to conformational flipping is raised through the self-assembly, and that the pitch length of the helix could vary from one domain to another. In addition, helix formation can be suppressed by external forces such as surface interactions. Furthermore, the length scales of the self-organized structures are such that diffusion probably does not easily occur thereby stabilising the formation of helical domains.

Thus we propose that the bis(phenyl)oxadiazole materials studied could be examples of self-assembling-self-organizing nematogens where the conformational forms can spontaneously segregate into chiral domains.

Although it is thus apparently possible to have enantioselective segregation in the nematic phase of achiral bent-core systems, it is interesting that Strigazzi *et al.*<sup>6,7</sup> also evoke a comparable model to explain their observation of chiral domains in the nematic phases of achiral 4-alkyl(oxy)benzoic acids. In their case twisted open dimers formed *via* hydrogen bonding are the suggested source for the formation of helical structures.<sup>6</sup>

Takezoe *et al.*<sup>8</sup> also showed that the addition of an achiral bent-core solute to a conventional chiral nematic phase reduces the pitch, thereby indicating that the achiral dopant has a strong chiral effect on the local helical packing of the molecules.

Lastly we also note that Pelzl *et al.*<sup>9</sup> reported on the formation of chiral domains in the nematic phase of another achiral bent-core system. Thus with our work on biaxial nematogens we can state that it seems to be a more general phenomenon that nematic phases of certain achiral materials are capable of exhibiting chiral ordering. Pelzl *et al.* also refer to a computer simulation study by Memmer<sup>10</sup> that suggests the helical superstructure occurs due to conical twist-bend deformations, which as a result reduces the overall flexoelectric effect. However it is also possible to devise a chiral twisted conformer similar to **II** for the bent-core molecule studied by Pelzl *et al.* This emphasises again the possibility of self-assembly in a quasi-liquid phase driving enantioselective separations similar to those found in the solid state.

We wish to thank Andrew Stipetic, Kenneth M. Fergusson, and Alan W. Hall for the supply of alkyl(oxy)benzoic acids and the European research training network SAMPA for financial support. We also acknowledge the input of a referee.

**Verena Görtz and John W. Goodby**

*Liquid Crystal Group, Department of Chemistry, University of York, Heslington, York, UK YO10 5DD. E-mail: vg501@york.ac.uk; jwg500@york.ac.uk; Tel: +44 (0)1904 432539*

## Notes and references

- 1 M. J. Freiser, *Phys. Rev. Lett.*, 1970, **24**, 1041.
- 2 L. A. Madsen, T. J. Dingemans, M. Nakata and E. T. Samulski, *Phys. Rev. Lett.*, 2004, **92**, 145505.
- 3 B. R. Acharya, A. Primak and S. Kumar, *Phys. Rev. Lett.*, 2004, **92**, 145506.
- 4 T. J. Dingemans and E. T. Samulski, *Liq. Cryst.*, 2000, **27**, 131.
- 5 P. Oswald and P. Pieranski, *Nematic and cholesteric liquid crystals*, Taylor and Francis, London, 2005.
- 6 S. I. Torgova, L. Komitov and A. Strigazzi, *Liq. Cryst.*, 1998, **24**, 131.
- 7 S. I. Torgova, M. P. Petrov and A. Strigazzi, *Liq. Cryst.*, 2001, **28**, 1439.
- 8 J. Thisayukta, H. Niwano, H. Takezoe and J. Watanabe, *J. Am. Chem. Soc.*, 2002, **124**, 3354.
- 9 G. Pelzl, A. Eremin, S. Diele, H. Kresse and W. Weissflog, *J. Mater. Chem.*, 2002, **12**, 2591.
- 10 R. Memmer, *Liq. Cryst.*, 2002, **29**, 483.