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## Dielectric, calorimetric and mesophase properties of 1"-(2',4-difluorobiphenyl-4'-yloxy)-9"-(4-cyanobiphenyl-4'-yloxy) nonane: an odd liquid crystal dimer with a monotropic mesophase having the characteristics of a twist-bend nematic phase

N. Sebastián,<sup>a</sup> D. O. López,\*<sup>b</sup> B. Robles-Hernández,<sup>ab</sup> M. R. de la Fuente,<sup>a</sup> J. Salud,<sup>b</sup> M. A. Pérez-Jubindo,<sup>a</sup> D. A. Dunmur,<sup>c</sup> G. R. Luckhurst<sup>c</sup> and D. J. B. Jackson<sup>c</sup>

This paper reports a novel liquid crystal phase having the characteristics of a twist-bend nematic phase formed by a non-symmetric ether-linked liquid crystal dimer. The dimer 1"-(2',4-difluorobiphenyl-4'-yloxy)-9"-(4-cyanobiphenyl-4'-yloxy) nonane (FFO9OCB) exhibits two liquid-crystalline phases on cooling at a sufficiently high rate from the isotropic phase. The high temperature mesophase has been reported in the literature as nematic and confirmed in this study. The other mesophase is metastable and can be supercooled giving rise to a glassy state. Its identification and characterization are based on optical textures, broadband dielectric spectroscopy, calorimetry, measurements of both splay and bend elastic constants in the nematic phase and miscibility studies. It is concluded that the low temperature mesophase exhibits the characteristics of a twist-bend nematic phase. Dielectric measurements enable us to obtain the static permittivity and information about the molecular dynamics in the isotropic phase, in the nematic mesophase and across the isotropic-to-nematic phase transition. Two orientations, parallel and perpendicular to the director, have been investigated. In the high temperature nematic mesophase, the dielectric anisotropy is found to be positive. Measurements of the parallel component of the dielectric permittivity are well-explained by the molecular theory of dielectric relaxation in nematic dimers (M. Stocchero, A. Ferrarini, G. J. Moro, D. A. Dunmur and G. R. Luckhurst, J. Chem. Phys., 2004, 121, 8079). The dimer is modelled as a mixture of cis and trans conformers and the model allows an estimate of their relative populations at each temperature. The nematic-to-isotropic phase transition has been exhaustively studied from the accurate evolution of the heat capacity and the static dielectric permittivity data. It has been concluded that the transition is first order in nature, but close to tricritical. The nature of the nematic-to-the novel liquid crystal phase transition is difficult to analyze to the same extent because of insufficient precision. Only observations at cooling rates of 10 K min<sup>-1</sup> or higher were possible because on heating from the glassy state, the twist-bend nematic mesophase crystallizes at temperatures far below the nematic-nematic phase transition.

## 1 Introduction

Liquid crystals are molecular materials in which the type and stability of liquid crystalline phases or mesophases are determined by the molecular shape and anisotropy of the constituent molecules.

<sup>a</sup> Departamento de Física Aplicada II, Facultad de Ciencia y Tecnología, Universidad del País Vasco, Apartado 644, E-48080 Bilbao, Spain

<sup>b</sup> Grup de Propietas Físiques dels Materials (GRPFM), Departament de Física i Enginyeria Nuclear, E.T.S.E.I.B. Universitat Politècnica de Catalunya, Diagonal, 647 08028 Barcelona, Spain. E-mail: david.orencio.lopez@upc.edu

 $^{c}$  School of Chemistry, University of Southampton, Highfield, Southampton, S017 1BJ, UK

Molecular flexibility is one of the most important structural aspects which may influence the average molecular shape. In most liquid crystals, flexible alkyl chains are attached to anisotropic rigid or semi-rigid molecular cores. However, there is a group of liquid crystal-forming molecules in which semirigid pro-mesogenic or mesogenic groups are linked *via* flexible spacers. The simplest of these compounds are the so-called liquid crystal dimers which consist of two pro-mesogenic groups joined by a flexible spacer (the most common spacers are alkyl chains with an odd or even number of carbon atoms). These compounds can be classified into two broad classes: symmetric and non-symmetric. In a symmetric liquid crystal dimer the two pro-mesogenic units are identical, whereas they are different in a non-symmetric dimer.

Liquid crystal dimers have been revealed as a fascinating group of mesogenic materials because of the discovery of unusual properties, some of these in very recent times. It is interesting to cite, among others, the novel alternating and modulated smectic mesophases,<sup>1,2</sup> the new twist-bend nematics (N<sub>TB</sub>), predicted by Dozov<sup>3</sup> and then experimentally identified,<sup>4–7</sup> or the existence of blue phases over an unusually wide range of temperature.<sup>8</sup> An extra motivation is the current interest in liquid crystal dimers with biaxial shapes as potential candidates for thermotropic liquid crystals presenting the elusive biaxial nematic phase (N<sub>B</sub>).<sup>9–13</sup> The existence of nematic–nematic phase transitions in such materials has acquired a renewed interest.<sup>4,14–17</sup>

One of the most exciting examples of the use of liquid crystal dimers having an odd-membered spacer<sup>18</sup> is in flexoelectricbased electro-optic displays first demonstrated by Patel and Lee.<sup>19</sup> The nematic phases formed by dimers offer several advantages over the use of more conventional materials, the most striking of which is the magnitude of the electro-optic response.<sup>20</sup> This is determined by the flexoelastic ratio, e/K, where e is the mean flexoelectric coefficient  $(e_1 + e_3)/2$  and K is the mean elastic constant  $(K_1 + K_3)/2$ ,<sup>21</sup> where  $K_1$  and  $K_3$  are the so-called splay and bend elastic constants. A large value of e/K for the odd dimers is predicted to result not only from the expected large value of  $e_3$  but mainly from the small value of  $K_3$ .<sup>22</sup> This prediction has, subsequently, been confirmed by measurements of the elastic constants  $K_1$  and  $K_3$  for the odd liquid crystal dimer, 1"-(2',4-difluorobiphenyl-4'-yloxy)-9"-(4-cyanobiphenyl-4'-yloxy) nonane (hereafter referred to by the acronym FFO9OCB).<sup>23,24</sup> It has also been shown theoretically that large values of the flexoelastic ratio (e/K) stabilize blue phases over large temperature ranges in chiral doped liquid crystal dimers belonging to the 1"-(2',4-difluorobiphenyl-4'-yloxy)-9"-(4-cyanobiphenyl-4'-yloxy) alkane series (FFOnOCB).25

Liquid crystal dimers exhibit many energetically favoured molecular shapes (*conformers*), the populations of which depend on the parity of the flexible chain, and the population-distribution of conformers is temperature-dependent. In dimers with polar terminal groups this distribution can be partially characterized through the dielectric permittivity. Some experimental studies devoted to the dielectric properties of liquid crystal dimers have already been published.<sup>4,5,12,26-34</sup> Such measurements, besides providing information on the temperature dependence of the conformational distribution, have prompted the development of a new theory<sup>35</sup> for the dielectric relaxation of mesogenic dimers in a nematic phase. It is evident that for the theory to be tested and improved, additional experimental dielectric data for different architectures of liquid crystal dimers are required.

The dielectric behaviour of the FFO9OCB dimer is one of the main aspects on which the present paper will be focused. In order to interpret such dielectric results, the theory<sup>35</sup> will be adapted to the example here, which was not considered previously.

Additionally, the mesomorphic properties of FFO9OCB are presented. Previously, only one enantiotropic nematic mesophase

has been reported<sup>20,23,24</sup> for this material. However, our study reveals the existence of an additional mesophase having the characteristics of a monotropic twist-bend nematic phase, which was not previously reported, and whose nature is an extra motivation for this investigation. This should be taken as understood even though throughout this paper we shall not always add the qualifying phrase 'having the characteristics of the twist-bend nematic phase'. We also identify a glassy  $N_{\rm TB}$  phase linked to the monotropic mesophase, which appears under some cooling regimes.

A further aspect reported in the present work is the N-to-I phase transition of the FFO9OCB dimer. The N-to-I phase transition in liquid crystals attracted considerable attention over many years because of the existing puzzle about its nature.<sup>36–38</sup> Although the phase transition is widely considered to be very weakly first order, some experimental data for a few liquid crystals seem to provide contradictory results and even raise doubts about its first order character. It seems that this apparent puzzle is due to three main factors:<sup>37</sup> fluctuations of the chosen order parameter, the biaxial shape of mesogenic molecules and their flexibility. The first factor appears to be significant in non-linear studies associated with sufficiently strong applied external fields, or for strongly polar mesogens under weak external perturbations. The other two factors are relevant in liquid crystal dimers. Unfortunately, experimental data related to the N-to-I phase transition in such materials with the required precision are very rare.12,13,15

The structure of the paper is as follows. In Section 2 we describe the experimental details of our measurements. In Section 3, we present and discuss our results concerning the overall thermal behaviour on the basis of the heat capacity data and microscopic observations, and dielectric measurements on the isotropic phase and mesophases. Particularly in Section 3.3, we show evidence from optical microscopy and measurements of dielectric and elastic properties for the formation of a twist-bend nematic phase in the ether-linked non-symmetric dimer FFO9OCB. Finally in Section 3.4, very accurate heat capacity as well as static dielectric data through the N-to-I phase transition is analysed to give information on the nature of the phase transition. Our concluding remarks are summarized in Section 4.

## 2 Experimental details

#### 2.1 Materials

The schematic molecular structure of FFO9OCB is



It consists of two mesogenic groups having almost the same shape and size but different chemical structures (named A and B in the schematic) attached by an ether-linked spacer of 9 carbons (O[CH<sub>2</sub>]<sub>9</sub>O). The terminal group B has two

identical dipole moments of about 1.5 D associated with the C-F bond (indicated in the schematic by two thin arrows) leading to a longitudinal component of about 2.25 D and a transverse component of about 1.3 D. The terminal group A has a larger dipole moment ( $\sim 4$  D) along its long axis associated with the nitrile group (indicated in the schematic by a thick arrow).

The non-symmetric liquid crystal dimer, FFO9OCB, was synthesised using the methodology previously used to prepare analogous dimers.<sup>39</sup> The reaction comprises just two steps both of which involve alkylation of a phenol. The first is the preparation of 1-(4-cyanobiphenyloxy)-9-bromononane (CBO9Br). This involves a Williamson alkylation of 4-cyano-4'-hydroxybiphenyl (CBOH) with 1,9-dibromononane (Br9Br) but differs from the standard conditions in that Br9Br is in a tenfold excess. This allows the preparation of CBO9Br without its contamination by the symmetric dimer CBO9OCB. The second step is the alkylation of 3,4'-difluoro-4-hydroxybiphenyl (FFOH) with CBO9Br but now in stoichiometric amounts.

The details of the synthesis of CBO9Br are as follows. To a stirred solution of CBOH (21 mmol, 1 eq.) in freshly distilled acetone (40 ml) solid potassium carbonate (37 mmol, 1.8 eq.) was added in a single portion. The stirred mixture was heated to reflux for 1 h under nitrogen and subsequently allowed to cool to room temperature before Br9Br (204 mmol, 10 eq.) was added in a single portion. The mixture was then heated at reflux for 18 h, cooled, and was subsequently filtered to remove the inorganic salts; these were later washed with DCM. The combined filtrate and washings were concentrated in vacuo to give a crude yellow oil. This was purified by column chromatography (silica gel, 40 mm  $\times$  100 mm; 10-40% DCM/40-60 petroleum), to give a white powder which was crystallised from ethanol to afford CBO9Br with a typical yield of 87%. This sample of CBO9Br was then used in the second stage for the preparation of FFO9OCB.

To a stirred solution of FFOH (1.1 mmol, 1.1 eq.) in dry butanone (40 ml) potassium carbonate (2.2 mmol, 2.2 eq.) was added in one portion and the suspension was heated to reflux for about 20 min under nitrogen. The mixture was allowed to cool prior to the addition of CBO9Br (1 mmol, 1 eq.) in one portion and a catalytic quantity of sodium iodide (80 mg). The reaction mixture was then heated back to reflux for three days, cooled and the solvent was removed *in vacuo*. The off-white solid was partitioned between DCM (50 ml) and water (50 ml). The organic layer was separated and the aqueous layer was washed with DCM (3  $\times$  50 ml). The organic extracts were combined and dried over anhydrous magnesium sulphate. This was then removed by filtration and the filtrate solvent was removed *in vacuo* leaving a white crude product which was purified by column chromatography (silica gel, 40 mm  $\times$ 70 mm; 50–100% DCM/40–60 petroleum) to yield FFO9OCB as a white microcrystalline solid, in a typical yield of 85%.

The structure of FFO9OCB and its purity were determined with a range of analytical techniques. These involved NMR spectroscopy, both <sup>1</sup>H and <sup>13</sup>C. The product gave clean spectra in the sense that only peaks other than those from CHCl<sub>3</sub> and DOH were from the target dimer. The assignment of the spectral lines, listed subsequently, was made on the basis of literature data for analogous compounds. They confirmed the molecular structure and the purity of the sample. The IR bands given are consistent with those expected for this non-symmetric dimer. It did not prove possible to use electrospray (ES) to obtain the mass spectrum of FFO9OCB because there are no protons of sufficient acidity or basicity. Consequently the spectrum contained peaks other than those from the parent ion which masked the purity of the sample. The use of the harder technique of electron impact (EI) resulted in more complex fragmentation patterns. However, the isotope pattern of bromine should be clear and so would allow the presence of CBO9Br which is a likely impurity to be detected; it was not. Thin layer chromatography based on Merck Kieselgel silica gel 60 F<sub>254</sub> using DCM as the mobile phase gave a retardation factor of 0.66. More importantly there was just a single spot consistent with an estimated sample purity of >99%. An additional and complementary indication of the purity of the liquid crystal dimer FFO9OCB was provided by the nematicisotropic transition. First, the sharpness of the transition found, as we shall see in Section 3.4.1, suggests that the dimer is pure. Second, comparison of the N-I transition temperature with values reported in the literature should provide another indication of purity. In fact there are four values of  $T_{\rm NI}$  for FFO9OCB reported in the literature by other workers;<sup>20,23,24,40</sup> surprisingly these vary with time from 388 K,40 to 385 K20 through 382 K<sup>23</sup> to 381 K.<sup>24</sup> No comment is made on this, although the uncertainty in the nematic to isotropic transition temperature seems to be of the order of  $\pm 1$  K. The agreement of our measured transition temperature of 385.5 K with these seems to be reasonable, especially given the differences in the methods used to measure the transition temperature (see Table 1).

<b>Table 1</b> Transition temperatures ( $T_{CrN}$ , $T_{N_{TB}N}$ and $T_{NI}$ ) and associated latent heats ( $\Delta H_{CrN}$ and $\Delta H_{NI}$ )									
$T_{\mathrm{CrN}}\left(\mathrm{K}\right)$	$\Delta H_{ m CrN}  ({ m kJ}  { m mol}^{-1})$	$T_{\rm g}$ (K)	$T_{\mathrm{N}_{\mathrm{TB}}\mathrm{N}}\left(\mathrm{K}\right)$	$T_{\rm NI}$ (K)	$\Delta H_{\rm NI} \left( {\rm kJ \ mol}^{-1} \right)$	Ref.			
323.2 <sup>a</sup>	_	_	_	$385.2^{a}$		20			
$333.2^{a}$	_	_	_	$382.2^{a}$	_	23			
$315.4^{b}$	$17.7^{b,c}$	_	_	$381.2^{b}$	$1.8^{b,c}$	24			
$345.6\pm0.5^{e}$	$31.4\pm0.2^e$	262.2	$\sim$ 323 <sup>d</sup>	$385.5\pm0.5$	$0.44\pm0.05$	This work			

<sup>*a*</sup> Data from optical measurements at 1 K min<sup>-1</sup>. <sup>*b*</sup> Measurements were performed using a Mettler-Toledo DSC823 from DSC traces at 5 K min<sup>-1</sup>. <sup>*c*</sup> From Table 1 of ref. 24 it is said that enthalpies are given in mJ g<sup>-1</sup>. We believe that this is not possible and it has been interpreted as given in J g<sup>-1</sup>. <sup>*d*</sup> From heat capacity measurements under a cooling regime at 10 K min<sup>-1</sup>. <sup>*e*</sup> Data corresponding to the crystal phase obtained by slow cooling.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$ /ppm 7.61 (2H, d, J = 8.6 Hz, C<sub>4</sub>H, C<sub>6</sub>H), 7.55 (2H, d, J = 8.6 Hz, C<sub>3</sub>H, C<sub>7</sub>H), 7.44 (2H, d, J = 9.0 Hz, C<sub>9</sub>H, C<sub>13</sub>H), 7.33–7.41 (2H, m, C<sub>40</sub>H, C<sub>42</sub>H), 7.21 (1H, t, J = 9.2 Hz, C<sub>49</sub>H), 7.02 (2H, t, J = 8.8 Hz, C<sub>39</sub>H, C<sub>43</sub>H), 6.91 (2H, d, J = 8.8 Hz, C<sub>10</sub>H, C<sub>12</sub>H), 6.67 (1H, dd, (J = 8.6 Hz, 2.6 Hz), C<sub>48</sub>H<sub>2</sub>), 6.62 (1H, dd, (J = 12.3 Hz, 2.6 Hz), C<sub>46</sub>H<sub>2</sub>), 3.93 (2H, t, 6.4 Hz, O-C<sub>14</sub>H<sub>2</sub>), 3.90 (2H, t, 6.4 Hz, O-C<sub>22</sub>H<sub>2</sub>), 1.63–1.82 (4H, m, C<sub>15</sub>H<sub>2</sub>, C<sub>21</sub>H<sub>2</sub>), 1.24–1.50 (10H, m, C<sub>16</sub>H<sub>2</sub>, C<sub>17</sub>H<sub>2</sub>, C<sub>18</sub>H<sub>2</sub>, C<sub>19</sub>H<sub>2</sub>, C<sub>20</sub>H<sub>2</sub>).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>):  $\delta_C$ /ppm 163.7 (q,  $C_{45}$ -F(Ar)), 161.9 (q,  $C_{38}$ -F(Ar)), 159.8 (q,  $C_{11}$ (Ar)), 158.5 (q,  $C_{47}$ (Ar)), 145.3 (q,  $C_5$ (Ar)), 132.6 (t,  $C_3$ (Ar),  $C_7$ (Ar)), 131.3 (q,  $C_8$ (Ar)), 130.8 (q,  $C_{44}$ (Ar)), 130.4 (t,  $C_{40}/C_{42}$ (Ar)), 128.3 (t,  $C_4$ (Ar),  $C_6$ (Ar)), 127.1 (t,  $C_9$ (Ar),  $C_{13}$ (Ar)), 119.1 (q,  $C_{41}$ (Ar)), 115.4 (t,  $C_{46}/C_{48}$ (Ar)), 115.2 (t,  $C_{46}/C_{48}$ (Ar)), 115.1 (t,  $C_{10}$ (Ar),  $C_{12}$ (Ar)), 110.9 (t,  $C_{49}$ (Ar)), 110.7 (q,  $C_2$ (Ar)), 102.7 (t,  $C_{43}/C_{39}$ (Ar)), 102.4 (t,  $C_{43}/C_{39}$ (Ar)), 68.4 (s,  $C_{14}$ (OCH<sub>2</sub>)), 29.4 (s,  $C_{15-21}$ (CH<sub>2</sub>)), 29.3 (s,  $C_{15-21}$ (CH<sub>2</sub>)), 29.2 (s,  $C_{15-21}$ (CH<sub>2</sub>)), 29.1 (s,  $C_{15-21}$ (CH<sub>2</sub>)), 29.0 (s,  $C_{15-21}$ (CH<sub>2</sub>)).

IR (solid):  $\nu_{\text{max}}/\text{cm}^{-1}$  2933(m) (*C*-*H*<sub>2</sub>), 2852(m) (*C*-*H*<sub>2</sub>), 2223(m) (*C*=*N*), 1600(s) (*Ar*), 1519(s) (*Ar*), 1492(s) (*Ar*).

EIMS: m/z 525 ([M]<sup>+</sup>, 54%), 330 ([C<sub>23</sub>H<sub>24</sub>NO]<sup>+</sup>, 5%), 206 ([C<sub>15</sub>H<sub>11</sub>O]<sup>+</sup>, 100%), 195 ([C<sub>13</sub>H<sub>9</sub>NO]<sup>+</sup>, 72%), 83 ([C<sub>6</sub>H<sub>11</sub>]<sup>+</sup>, 48%), 69 ([C<sub>5</sub>H<sub>9</sub>]<sup>+</sup>, 28%).

#### 2.2 Experimental techniques

Heat capacity data at atmospheric pressure were obtained by means of a commercial differential scanning calorimeter (DSC-Q2000) from TA-Instruments working in the modulated mode (MDSC). It is important to realize that, like an alternating current (ac) calorimeter, the MDSC technique, besides providing heat capacity data, simultaneously gives phase shift data ( $\phi$ ) that allow the determination of the two-phase coexistence region for weakly first-order phase transitions. In our work, the experimental conditions were adjusted in such a way that the imaginary part of the complex heat capacity data vanished. Similarly, by means of a special calibration procedure in which very precise latent heat data measured for other homologues through adiabatic calorimetry are considered, the MDSC technique is also suitable for quantitative measurements of latent heats of first order transitions, even if they are weak. A more detailed description of the MDSC technique can be found elsewhere.12,13,41

The MDSC measurements were made using two different procedures. The first one was a standard study of the overall thermal behaviour of the sample, consisting of heating runs at 1 K min<sup>-1</sup> from room temperature up to the isotropic phase and cooling runs at several cooling rates to observe the glassy behaviour if possible. The second procedure, designed to study the nature of the N-to-I phase transition, consisted of heating and cooling runs in a temperature interval of about 5 K around the transition at a rate of 0.01 K min<sup>-1</sup>. For both procedures, the modulation parameters (temperature amplitude and oscillation period) were  $\pm 0.5$  K and 60 s in the standard and  $\pm 0.07$  K and 23 s in the other procedure. The sample masses (chosen between 2 and 3 mg) were selected to ensure a uniform thin layer within the aluminium pans.

Measurements of the complex dielectric permittivity defined as  $\varepsilon^*(f) = \varepsilon'(f) - i\varepsilon''(f)$  were performed over the range  $10^{3}$ –  $1.8 \times 10^{9}$  Hz using two impedance analysers: the HP4192A and 4291A. The cell consists of two gold-plated brass electrodes (diameter 5 mm) separated by 50 µm thick silica spacers. A modified HP16091A coaxial test fixture was used as the sample holder. It was held in a cryostat from *Novocontrol* and both temperature and dielectric measurements were computer-controlled. Additional details of the experimental technique can be found elsewhere.<sup>12,29,33,34,37</sup>

Dielectric measurements were performed on heating and on cooling with different temperature steps being stabilized to  $\pm 20$  mK.

Optical textures were studied with an Olympus polarising microscope equipped with a Linkam THMSG-600 hot stage and a Linkam TMS-94 temperature controller.

Capacitance measurements to determine the splay  $K_1$  and bend  $K_3$  elastic constants were carried out using 8 µm antiparallel planar aligned cells. The method consists of inducing the planar to homeotropic Freedericksz transition in the sample by applying an AC signal at a frequency of 5 kHz from an Agilent Precision LRC meter E4890A. The capacitance of the sample was monitored as a function of the applied voltage which is varied from 0.1 V<sub>rms</sub> to 16 V<sub>rms</sub>, with a delay time of 30 s between the application of the AC signal and the acquisition of the capacitance value. Ultimately, values of the splay and bend elastic constants were extracted from the fitting of the entire voltage dependence of the capacitance to the theory.<sup>42</sup>

### 3 Results and discussion

#### 3.1 Thermal behaviour

It was reported by Morris *et al.*<sup>20</sup> that on cooling from the isotropic phase FFO9OCB exhibits a nematic mesophase followed by a solid crystalline state (Cr). Identification of such a phase sequence was made by means of their optical textures, and transition temperatures obtained on cooling are listed in Table 1.

Our optical textures partially confirm the phase sequence found by Morris et al.,<sup>20</sup> although they reveal a more complex phase behaviour that depends strongly on the cooling rate. Fig. 1 shows optical textures seen at different temperatures on cooling the sample from the N-mesophase (light green texture) at 10 K min<sup>-1</sup> (top sequence) and at 15 K min<sup>-1</sup> (bottom sequence), in cells (8 µm thick) with planar alignment. For the former, at about 315-310 K, another mesophase appears (striped texture on a photograph taken at about 310 K) whose identity at this stage is unknown. Subsequent experiments, to be described later, suggest that this phase is the twist-bend nematic phase (the symbol N<sub>TB</sub> will be used, subsequently, to denote this new phase), for which further evidence is provided by miscibility and other studies. At present, there is no particular texture that is identified as an unequivocal signature of the twist-bend nematic phase. However a number of investigations with a variety of materials have revealed that thin film samples of the twist-bend nematic phase in rubbed (planar) cells exhibit a characteristic "rope-like



Fig. 1 Optical textures of FF09OCB obtained from 8  $\mu m$  thick cells with uniform planar alignment at some selected temperatures.

texture". The compound FFO9OCB which is the subject of this paper exhibits this rope texture (see Fig. 9), and a more detailed discussion of the texture is given in Section 3.3.1 of this paper. This texture seemed to persist at low temperatures mixed with what is usually found for a crystalline state. However, when the cooling rate is high enough (bottom sequence), only textures compatible with the N<sub>TB</sub>-mesophase are found. Irrespective of the cooling rate of either 10 or 15 K min<sup>-1</sup>, a subsequent heating from 244 K at 1 K min<sup>-1</sup> (middle sequence) causes the sample to crystallize between 276 and 288 K (photo recorded at 288 K).

Fig. 2 shows the heat capacity as a function of temperature over a wide temperature range for a sample heated at  $1 \text{ K min}^{-1}$  coming from two initial states: after cooling from the I-phase at



**Fig. 2** Heat capacity data as a function of temperature for a sample of FFO9OCB in heating mode at 1 K min<sup>-1</sup> which has been previously cooled from the I-phase at 30 K min<sup>-1</sup> (black symbols) and at 1 K min<sup>-1</sup> (red symbols). The top-left inset shows in a zoom window the characteristic heat capacity jump at the glass transition recorded in heating mode at 1 K min<sup>-1</sup> for samples cooled at different rates ((a) 30 K min<sup>-1</sup>; (b) 15 K min<sup>-1</sup>; (c) 10 K min<sup>-1</sup>). The bottom-right inset shows evidence for the N-N<sub>TB</sub> phase transition through the heat capacity data on cooling the sample at 10 K min<sup>-1</sup>.

1 K min<sup>-1</sup> (red symbols) and after faster cooling at 30 K min<sup>-1</sup> (black open symbols). In the former case, the sample crystallizes on cooling, at about 335 K, and the crystal phase [Cr] is observed at low temperatures. In the second case (cooling rate of 30 K min<sup>-1</sup>), crystallization is prevented and ultimately the mesophase vitrifies. On heating runs, the top-left inset shows the characteristic heat capacity jump of a glass transition for samples cooled at different rates. Cases denoted by (a) and (b) in Fig. 2 provide comparable heat capacity jumps, proving that a cooling rate of about 15 K min<sup>-1</sup> is fast enough to obtain the glassy state. Taking into account the optical information summarized in Fig. 1, the glassy state should correspond to this new  $N_{TB}$  mesophase [( $N_{TB}$ )<sub>gl</sub>]. On cooling, the phase transition N-to-N<sub>TB</sub> is not observed by heat capacity experiments, neither at rates of 30 K min<sup>-1</sup> nor 15 K min<sup>-1</sup>. The bottom-right inset of Fig. 2 shows the heat capacity measured at a cooling rate of 10 K min<sup>-1</sup> in which a small peak (assigned to the N-to-N<sub>TB</sub> phase transition) is observed at about 323 K. It should be stressed that at lower temperatures the sample crystallizes making it impossible to follow the heat capacity of the NTB mesophase down to the glass transition. Even so, subsequent heating of the sample from 250 K at 1 K min<sup>-1</sup> reveals the characteristic heat capacity jump assigned to a glass transition (the case denoted by (c) in the top-left inset of Fig. 2), but smaller than the situations denoted by (a) and (b). This apparently curious fact is understandable since the sample tends to crystallize partially if the cooling rate is not sufficiently high according to the top sequence of Fig. 1. So, the sample is found in an unstable situation in which one part is becoming crystalline and the remainder is becoming glassy. Fig. 2 clearly shows how the sample in the supercooled N<sub>TB</sub> mesophase [(N<sub>TB</sub>)<sub>spc</sub>] crystallizes irreversibly on heating at about 280 K (black symbols), a fact already observed from optical measurements (see the middle sequence of Fig. 1).

In Fig. 2, the N-to-I phase transition is observed to be identical in both experiments (red and black symbols), but this is not the case for the Cr-to-N phase transition. It can be observed that such a phase transition is found to be represented by a single heat capacity peak (at about 345 K) for (a): sample cooled slowly at 1 K min<sup>-1</sup> (red symbols). However, the sample heated from the NTB glassy state (black symbols) which crystallizes on heating exhibits two heat capacity peaks associated with transformation into the nematic mesophase, one at about 345 K and the other at about 357 K. It seems that the crystal phase obtained by slow cooling [Cr] and that from the supercooled N<sub>TB</sub> mesophase [Cr]\* are different. In fact, we believe that [Cr]\* is really a mixture of the crystal phase obtained by slow cooling [Cr] and another metastable crystal phase. The temperatures associated with the glass transition and both Cr-to-N and N-to-I phase transitions, along with the values taken from the literature, are listed in Table 1.

In general terms, the total enthalpy change associated with any transition ( $\Delta H^{\text{TOT}}$ ) can be written as

$$\Delta H^{\rm TOT} = \Delta H + \int \Delta C_{\rm p} \, \mathrm{d}T \tag{1}$$

where the second term on the right-hand side of eqn (1) is the pretransitional fluctuation contribution ( $\Delta C_p$  being the difference  $C_p$ - $C_{p,\text{background}}$  due to the change of orientational order intrinsic

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to this transition) and the latent heat is  $\Delta H$  which vanishes for second-order transitions. In strongly first-order phase transitions, the second term on the right-hand side of eqn (1) can be neglected in comparison with the latent heat and the total enthalpy change is identified with the latent heat associated with the phase transition. The resulting latent heat for the Cr-to-N phase transition (we only consider the crystal phase formed by slow cooling) is also listed in Table 1 together with the value taken from the literature. It should be stressed that both  $T_{\rm CrN}$  and  $\Delta H_{\rm CrN}$  are clearly different from those obtained by us. Even the transition temperatures referred to in studies published by some of the same authors change substantially, as can be seen in Table 1.

#### 3.2 Dielectric behaviour

**3.2.1 Theoretical background.** The dielectric data for conventional liquid crystal monomers<sup>34,37,43,44</sup> have been successfully interpreted using the theories of Maier–Meier<sup>45</sup> for the static permittivity and Nordio–Rigatti–Segre<sup>46</sup> for the molecular dynamics (both approaches assume that the constituent molecules are rigid). However, to interpret the dielectric properties of symmetric and non-symmetric liquid crystal dimers<sup>29</sup> models accounting for molecular flexibility are needed. To achieve this, Stocchero *et al.*<sup>35</sup> proposed a quantitative model with which to understand the observed dielectric properties of nematogenic liquid crystal dimers.

Calculations show how for the liquid crystal dimer, which is considered as a mixture of trans and cis conformers, the transconformer population increases with order and, in addition, the average molecular shape becomes more elongated. As a result, for symmetric dimers the mean square dipole moment decreases with order as does the value of the static permittivity, observed experimentally.<sup>4,29,33,34</sup> For a non-symmetric dimer where only one of the mesogenic units contains a longitudinal dipole moment, the change of the conformation of the molecule has no impact on the mean square dipole moment, and then the static permittivity is predicted to behave as for liquid crystal monomers with positive dielectric anisotropy, as observed experimentally.12,13 For non-symmetric dimers where the two promesogenic units contain different longitudinal dipole moments, an intermediate behaviour is expected. The change in the conformational distribution of the molecules with order is expected to decrease the mean square dipole moment to a certain extent and hence the longitudinal component (the component parallel to the director) of the static permittivity. This is the case considered in the present paper and, as far as we know, the first one investigated with such characteristics for which there are still no experimental results published.

The equilibrium properties of some odd and even symmetric dimers have been calculated using the rotational isomeric state (RIS) model and a model which allows for a continuous torsional potential about the carbon–carbon bonds of the flexible spacer (see ref. 35 for details). It turns out that for flexible dimers the RIS model is not satisfactory and the full torsional potential must be used. Using the latter model, the effective potential of mean torque for the dimer, *i.e.* the energy of a flexible dimer with respect to the director, can be calculated as a function of the



Fig. 3 Schematic representation of the four stable states of non-symmetric dimers, according to Stocchero  $et al's^{35}$  theoretical model.

angles ( $\beta_A$ ,  $\beta_B$ ) made by the mesogenic groups (A, B) of the dimer with the director for different degrees of order. It is found that the potential energy surface has four minima corresponding to parallel or anti-parallel orientations of the groups A, B with respect to the director, and the dimer is assumed to be in one of the four stable states (see Fig. 3). It must be emphasized that the model of dielectric relaxation applied here makes no assumption about the shape of the relaxing molecule, which itself is permitted to explore all possible conformations. Thus the cis and trans states shown in Fig. 3 schematically represent the orientations of the mesogenic groups undergoing rotational relaxation, and the dipoles attached to the mesogenic groups are the components responsible for end-over-end or flip-flop relaxation. The actual geometries corresponding to these energy minima are obtained by detailed calculation over the full conformation space accessible by the flexible relaxing molecules (see ref. 35 for details). This equilibrium model considers that only individual end-over-end rotations of each unit are allowed. The simultaneous rotations of the two rigid units (*i.e.*  $a \leftrightarrow d$  and  $b \leftrightarrow c$  in Fig. 3) are excluded because they are associated with the passage over a potential maximum with too great an activation energy to produce a relevant transition rate. The relative rates for flipping of the different rigid units  $(k_n^{T \to C} \text{ and } k_n^{C \to T}, n \text{ being A or B})$  are determined by their rotational diffusion coefficients and the nematic potential experienced by the terminal groups. A timescale separation is assumed between the slow end-over-end rotations of the terminal groups and other faster processes, at higher frequencies. The latter are not included in the kinetic model, for example rotations around the long molecular axis or the precession around the director.

Calculations according to the model for symmetric dimers predict a single relaxation time for the parallel component of the dielectric permittivity with an intensity that diminishes with decreasing temperature (or increasing orientational order) in quite good agreement with experimental determinations.<sup>29,33,34</sup> The results for non-symmetric dimers depend on the shape, size and dipole moments of the different rigid units. Some of these examples have already been developed in the original paper by Stocchero *et al.*<sup>35</sup> while others must be developed *ad hoc* such as the case treated in the current study.

**3.2.2 Interpretation of the dielectric relaxation data.** Dielectric results for FFO9OCB have been obtained for both parallel and perpendicular alignment of the director in the nematic and isotropic phases. In metallic cells the director spontaneously aligns parallel to the surface allowing us to obtain the perpendicular component of the permittivity ( $\varepsilon_{\perp}$ ). The fact that the material has a positive dielectric anisotropy ( $\Delta \varepsilon = \varepsilon_{\parallel} - \varepsilon_{\perp}$ ),<sup>20,23</sup> allows the parallel component of the permittivity ( $\varepsilon_{\parallel}$ ) to be measured by applying a dc bias voltage (25 V equivalent to an electric field of 0.5 mV m<sup>-1</sup>). Saturation of the parallel alignment of the director in the nematic phase has been confirmed by measuring the capacitance as a function of voltage.

Fig. 4A and B show the imaginary part of the parallel and perpendicular dielectric permittivities, respectively, as a function of frequency and temperature in the isotropic phase and in the nematic mesophase. The dielectric relaxation results show



**Fig. 4** Three-dimensional plot of dielectric loss *versus* temperature and the logarithm of the frequency for FFO9OCB in (A) parallel and (B) perpendicular alignments.

only one mode in the isotropic phase which is believed to correspond to the concerted rotation of the whole dimer, and we denote this as the  $m_1$ -mode.

The parallel component of the permittivity in the nematic mesophase (Fig. 4A) shows three relaxations, one of them at high frequencies and the other two at lower frequencies whose amplitudes seem to be correlated in a similar way to other non-symmetric dimers.<sup>12,29</sup> As cited previously, the latter case was considered explicitly by Stocchero *et al.*,<sup>35</sup> but not the case of the dimer FFO9OCB with two different terminal units, A and B, exhibiting different longitudinal dipole moments. In the following, such a case will be developed according to the model.

The starting point consists in determining the dipole moment correlation function  $(G_{\parallel}(t))$  which is deduced through the calculation of the temporal evolution of the population of each of the four stable states (taken as a four-component vector P(t)) of the dimer (see Fig. 3) as

$$G_{\parallel}(t) = \sum_{\alpha} P_{\alpha}(t) \langle \mu_{\parallel} \rangle_{\alpha} = \boldsymbol{P}(t) \cdot \boldsymbol{v}$$
(2)

The four-component vector  $\boldsymbol{\nu}$  represents the equilibrium average of the longitudinal dipole moment of the dimer in each of the four stable states. The exact analytical solution of P(t) for non-symmetric dimers is too complicated to allow a direct physical interpretation. Alternatively, a simplified strategy is suggested in which well-separated time-scales are assumed for the transition processes of both rigid units A and B. A short time scale of the order of  $1/k_A$ , where  $k_A =$  $\frac{1}{2}(k_A^{T \to C} + k_A^{C \to T})$ , is specified for the independent equilibration of the two pairs of states  $(a \leftrightarrow c)$  and  $(b \leftrightarrow d)$  of the rigid unit A. For this time scale, the rigid unit B does not experience any transition. At a time  $t > 1/k_A$ , the rigid unit B is active with an effective time of  $1/k_{\rm B}$ , where  $k_{\rm B} = 2(P_{\rm C}^{\rm eq}k_{\rm B}^{\rm C \to \rm T}) = 2(P_{\rm T}^{\rm eq}k_{\rm B}^{\rm T \to \rm C})$  for the independent equilibration of the two pairs of states  $(a \leftrightarrow b)$ and  $(c \leftrightarrow d)$  (see Fig. 3). The simplified form for the longitudinal dipole moment correlation function ( $G_{\parallel}(t)$ ) is:<sup>35</sup>

$$G_{\parallel}(t) = G_{\parallel}(\tau^*) e^{-2k_{\rm B}t} + [G_{\parallel}(0) - G_{\parallel}(\tau^*)] e^{-2k_{\rm A}t}$$
(3)

where  $\tau^*$  is a suitable time between the fast and the slow range of time scales  $(1/k_A < \tau^* < 1/k_B^{C \to T})$ . Thus, considering for simplicity that in our case  $\langle \mu_{\parallel} \rangle_B \approx 1/2 \langle \mu_{\parallel} \rangle_A$  and combining the average of each dipole moment the following four-component vector  $\boldsymbol{\nu}$  is obtained:

$$\mathbf{v} = \langle \mu_{\parallel} \rangle_{\mathrm{A}} \begin{vmatrix} 1/2 \\ 3/2 \\ -3/2 \\ -1/2 \end{vmatrix}$$
(4)

leading to

$$G_{\parallel}(t) = 4 \langle \mu_{\parallel} \rangle_{A}^{2} P_{\rm T}^{\rm eq} P_{\rm C}^{\rm eq} e^{-2k_{\rm A}t} + \frac{1}{4} \langle \mu_{\parallel} \rangle_{A}^{2} (P_{\rm T}^{\rm eq} - 3P_{\rm T}^{\rm eq})^{2} e^{-2k_{\rm B}t}$$
(5)

The correlation function given by eqn (5) is associated with two relaxation processes in the dielectric spectra of the parallel component of the permittivity, due to each rigid unit of the dimer. The relaxation at lower frequencies is a consequence of the flip-flop motion of the B-unit (denoted hereafter as the  $m_{1,L}$ -mode). The other relaxation, at higher frequencies, involves a flip-flop of the A-unit (denoted hereafter as the  $m_{1,H}$ -mode). The amplitudes of the modes,  $m_{1,L}$  and  $m_{1,H}$ , depend on  $1/4(P_T^{eq} - 3P_C^{eq})^2$  and  $4P_C^{eq}P_T^{eq}$ , respectively. The *cis*-to-*trans* interchange as the temperature decreases involves a concerted change in the amplitude of the modes: that of the  $m_{1,H}$  decreases while the other increases.

Let us recall Fig. 4A and the relaxation at higher frequencies with a much lower amplitude than the other two relaxations described by eqn (5). Such a relaxation, denoted hereafter as the  $m_{2,\parallel}$ -mode, is not dealt with in the model of Stocchero *et al.*,<sup>35</sup> but is attributed to rotation around the molecular long axis.

The perpendicular component of the permittivity in the nematic mesophase (Fig. 4B) shows, at first glance, a prominent relaxation process, denoted as  $m_{2,\perp}$ , which is believed to be due to the superposition of the precessional motions of the semi-rigid units and the rotation of the dimer around its long molecular axis.

**3.2.3 The static dielectric permittivity.** Measurements of the static dielectric permittivities (limiting low frequency permittivity) of the non-symmetric dimer FFO9OCB are shown in Fig. 5 as a function of temperature. This figure demonstrates that both components of the static permittivity ( $\varepsilon_{\perp}$  and  $\varepsilon_{\parallel}$ ) and the mean permittivity ( $\varepsilon_{mean} = 1/3[\varepsilon_{\parallel} + 2\varepsilon_{\perp}]$ ) change with temperature as expected. The parallel component ( $\varepsilon_{\parallel}$ ) decreases as temperature decreases, as predicted by the equilibrium calculations of Stocchero *et al.*<sup>35</sup> referred to earlier. It is noteworthy that such a decrease is less drastic than that reported for symmetric dimers.<sup>4</sup> According to the simplified kinetic model developed in the previous section for the non-symmetric FFO9OCB, the contribution of the low frequency mode to  $\varepsilon_{\parallel}$  is proportional to  $\left(\frac{9}{4} - 2P_{T}^{eq}\right)$  while in the case of symmetric dimers it is proportional to  $4(1 - P_{T}^{eq}).^{35}$ 



Fig. 5 Static dielectric permittivity behaviour in the I and N phases of FFO9OCB.

The perpendicular component  $(\varepsilon_{\perp})$  also decreases as temperature decreases, saturating at low enough temperatures, as expected<sup>45</sup> for rod-shaped mesogens.

**3.2.4 Dynamic dielectric measurements and analysis.** Fig. 6 is representative of the dielectric response of the dimer FFO9OCB for the real and imaginary parts of the permittivity in the parallel and perpendicular alignments as a function of frequency at two characteristic temperatures, in the I phase (388 K) and in the N mesophase (353 K). The data analysis of the frequency dependence of the permittivity when the different relaxation modes appear partially superimposed (as observed in Fig. 6B or C) is made using the empirical function

$$\varepsilon(\omega) = \sum_{k} \frac{\Delta \varepsilon_{k}}{\left[1 + \left(i\omega\tau_{k}\right)^{\alpha_{k}}\right]^{\beta_{k}}} + \varepsilon_{\infty} - i\frac{\sigma_{\rm dc}}{\omega\varepsilon_{0}} \tag{6}$$

where the summation is extended over all relaxation modes, and each is fitted according to the Havriliak–Negami (H–N) function. In eqn (6),  $\Delta \varepsilon_k$  is the dielectric strength of each relaxation mode,  $\tau_k$  is the relaxation time which is related to the frequency of



**Fig. 6** Frequency dependence of the dielectric permittivity of FFO9OCB in the isotropic phase (T = 388 K) (A) and in the nematic phase (T = 353 K) in both parallel (B) and perpendicular (C) director alignments. Black solid and dashed lines are fittings according to eqn (6). Symbol-lines represent deconvolution into elementary modes. For simplicity, the direct current conductivity contribution ( $\sigma_{dc}$ ) is not drawn, but is considered in the fitting procedure.

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Table 2 Fitting parameters ( $\alpha_k$  and  $\beta_k$ ) according to eqn (6) for the different relaxation modes measured over the temperature range 340–400 K

Modes	$\alpha_k$	$\beta_k$	Phase
$m_1$	0.8	0.8	I
$m_{1,\parallel L}$	1	1	Ν
$m_{1\parallel H}$	1	1	Ν
$m_{2}$	0.8	1	Ν
$m_{2,\perp}^{2,\perp}$	0.7	1	Ν

maximum dielectric loss,  $\alpha_k$  and  $\beta_k$  are the parameters which describe the shape (symmetry and width) of the relaxation spectra ( $\alpha_k = \beta_k = 1$  corresponds to Debye relaxation) and  $\sigma_{dc}$  is the dc conductivity.

The dielectric results in Fig. 6A (I phase) were fitted, according to eqn (6), to a single mode ( $m_1$ -mode). The shape parameters  $\alpha_{m1}$  and  $\beta_{m1}$  were found to be temperature independent over the temperature range of the isotropic phase analysed and are listed in Table 2.

The dielectric results shown in Fig. 6B correspond to the parallel component of the permittivity in the N mesophase at 353 K. As already indicated in Fig. 4A, the results were fitted, according to eqn (6), to three relaxation modes  $(m_{1,L\parallel}, m_{1,H\parallel}, m_{2\parallel})$  and the fitted shape parameters are listed in Table 2.

Fig. 6C shows the dielectric results for the perpendicular component of the permittivity in the N mesophase, also at 353 K. The fittings through eqn (6) require two relaxation modes, one at a frequency similar to that found for parallel alignment ( $m_{1,H\parallel}$ , see Fig. 6B) but with only a few per cent of the strength measured for the latter which is not perceived by the eye in Fig. 4B and 6C. We attribute this mode to an imperfect perpendicular alignment of the director (for consistency we denote this mode as  $m_{1\perp}$ ) and it will not be taken into account for further analyses. The other mode at high frequencies, the most prominent in the perpendicular alignment, is denoted as the  $m_{2\perp}$ -mode. The corresponding shape parameters are listed in Table 2.

Fig. 7 shows the temperature dependence of the dielectric strength for all the aforementioned relaxation modes in both

[N]

т<sub>1,Н|</sub>

355

 $m_1$ 

[I]

 $T_{NI}$ 

375

395



T(K)



**Fig. 8** Arrhenius plot of the relaxation frequencies  $(f_k)$  of the different contributions to the dielectric relaxation for FFO9OCB.

director alignments. For the parallel alignment, the dielectric strengths  $\Delta \varepsilon_{m1,L\parallel}$  and  $\Delta \varepsilon_{m1,H\parallel}$  are related, through eqn (5), with the change of the conformational distribution, being proportional to  $1/4(P_T^{eq} - 3P_C^{eq})^2$  and  $4P_C^{eq}P_T^{eq}$ , respectively. Thus, a decrease in temperature causes  $\Delta \varepsilon_{m1,L\parallel}$  to increase, that is,  $P_T^{eq}$  increases (note that  $P_T^{eq} + P_C^{eq} = 1$ ). At the same time,  $\Delta \varepsilon_{m1,H\parallel}$  decreases as the temperature decreases. The dielectric strength of the  $m_{2\parallel}$ -mode ( $\Delta \varepsilon_{m2\parallel}$ ) decreases on entering the N-mesophase stabilizing at a nearly constant value at lower temperatures as previously reported for other dimers in which the same mode has been identified.<sup>12,33,34</sup> For perpendicular alignment of the director, the most prominent contribution ( $\Delta \varepsilon_{m2\perp}$ ) evolves with temperature, to a certain extent, similar to  $\Delta \varepsilon_{m2\parallel}$ , as expected.

Fig. 8 shows, in an Arrhenius plot, the temperature dependence of the characteristic relaxation frequencies associated with each mode for both N and I phases. Activation energies for the  $m_{1,L\parallel}$  ( $E_{a}^{m1,L\parallel}$ ) and  $m_{1,H\parallel}$  ( $E_{a}^{m1,H\parallel}$ ) relaxation modes are 90 kJ mol<sup>-1</sup> and 65 kJ mol<sup>-1</sup>, respectively. The ratio ( $E_{a}^{m1,H\parallel}/E_{a}^{m1,L\parallel}$ ) is about 0.7, a value certainly somewhat lower than that found for other non-symmetric dimers (of about 0.8) with only one long-itudinal dipole moment located in the smaller semi-rigid unit.<sup>12,29,47</sup> Regarding the so-called  $m_{2,\parallel}$  or  $m_{2,\perp}$  relaxation modes, the corresponding activation energies ( $E_{a}^{m2\parallel}$  or  $E_{a}^{m2\perp}$ ) are close to each other, with a value of about 35 kJ mol<sup>-1</sup>, a value similar to that found for the same modes in other non-symmetric dimers.<sup>12,47</sup>

**3.2.5 Conformational distribution.** The temperature dependence of the conformational distribution of the molecules in the nematic mesophase for the FFO9OCB dimer can be estimated by applying the model of Stocchero *et al.*<sup>35</sup> According to eqn (5), the ratio of dielectric strengths for both  $m_{1,L\parallel}$  and  $m_{1,H\parallel}$  modes can be expressed as a function of the equilibrium population of *trans* conformers ( $P_{T}^{eq}$ ) as

$$\frac{\Delta \varepsilon_{m1,\text{L}\parallel}}{\Delta \varepsilon_{m1,\text{H}\parallel}} = \frac{\left(4P_{\text{T}}^{\text{eq}} - 3\right)^2}{16P_{\text{T}}^{\text{eq}}\left(1 - P_{\text{T}}^{\text{eq}}\right)} \tag{7}$$

From eqn (7),  $P_T^{eq}$  is obtained as a function of temperature with values ranging from about 0.94 (94% of *trans*-conformers)

5

4

3

2

1

 $m_{1,L_{II}}$ 

 $m_{2,\perp}$ 

 $0^{\lfloor m_2 \rfloor}$ 

335

Dielectric strength ( $\Delta \epsilon$ )

at the N-to-I phase transition to 0.98 (98% of *trans*-conformers) at temperatures 45 K lower in the nematic phase. It should be stressed that these values have been calculated following some simplifying assumptions detailed in Section 3.2.2. While it is true that eqn (5) provides valuable assistance in the interpretation of our dielectric measurements, quantitative calculations such as the conformational distribution of the molecules should be taken with caution. By way of illustration, for the non-symmetric dimer 1"-(4-cyanobiphenyl-4'-yloxy)-9"-(4-decylaniline-benzylidene-4'-oxy) nonane (with the same ether-linked spacer as FFO9OCB), the calculated  $P_{\rm T}^{\rm eq}$  ranges from 0.74 at  $T_{\rm NI}$  to 0.84 at 45 K below  $T_{\rm NI}$ .<sup>29</sup>

#### 3.3 The nature of the monotropic mesophase

It has been reported that certain liquid crystal dimers exhibit the recently discovered twist-bend nematic phase ( $N_{TB}$ ), predicted by Dozov.<sup>3</sup> The first compounds to exhibit this phase were methylenelinked odd-membered dimers,<sup>4,6,7,48–50</sup> but recently an ether-linked twist-bend phase has been reported.<sup>51</sup> Our observations on FFO9OCB, the subject of this paper, strongly suggest that it forms a monotropic twist-bend nematic phase.

A virtual twist-bend nematic-nematic transition has been observed for a mixture of five ether-linked odd liquid crystal dimers; this mixture was denoted by the letters KA.<sup>52</sup> The mixture was designed, in part, to produce a system of dimers with relatively low transition temperatures and so facilitate the experimental investigation of the twist-bend nematic phase. The nematic-isotropic transition temperature for KA is 348 K and the virtual NTB-N transition temperature has been located at 295 K.<sup>52</sup> The shifted virtual transition temperature,  $T_{\rm NI}$ - $T_{\rm N_{res}N}$ , is 53 K which is smaller than that found for the single component system, FFO9OCB, explored here of 62 K. The larger value determined for the single component is consistent with its long spacer whereas for the mixture which contains odd dimers heptane as well as nonane spacers<sup>52</sup> it is expected that  $T_{\rm NI}$ - $T_{\rm N_{TP}N}$ will be smaller. This follows from calculations of the bend elastic constants which show that for the odd dimers. FFOnOCB, the shifted transition temperature decreases with reduction in the length of the spacer.<sup>22</sup>

Further evidence for the assignment of the lower temperature nematic phase of FFO9OCB as a twist-bend nematic has been provided by miscibility studies with CB7CB.<sup>53</sup> The latter dimer has been extensively examined using X-ray<sup>4,6</sup> and freeze fracture transmission electron microscopy<sup>6,7</sup> and its assignment as  $N_{TB}$  is not in doubt. Our mixture phase diagram is given in Fig. 9, and the continuous mixing shown in the  $N_{TB}$ phase is a consequence of this phase for FFO9OCB and CB7CB having the same structural symmetry.

**3.3.1 Optical textures.** We now consider in detail some selected optical textures at three temperatures within the proposed  $N_{TB}$  mesophase which are shown in Fig. 10. These were obtained on cooling the sample from the I-phase at 15 K min<sup>-1</sup> in cells (8 µm thick, with an anti-parallel alignment layer from Instec) with a defined planar alignment direction. Under these conditions a characteristic striped texture with the stripes parallel to the surface alignment direction is obtained. A periodicity of the



**Fig. 9** Phase diagram for FFO9OCB + CB7CB mixtures. Full symbols (circles, squares, diamonds and stars) correspond to heat capacity measurements recorded on heating at 1 K min<sup>-1</sup>. The open diamond is related to the monotropic N<sub>TB</sub>–N-phase transition of pure FFO9OCB from heat capacity measurements recorded on cooling at 10 K min<sup>-1</sup> (see Table 1). Note that the full square for pure FFO9OCB corresponds to the Cr–N phase transition (see Table 1).

order of 16  $\mu$ m (2*d*, where *d* is the thickness of the cell) perpendicular to the stripes direction can be observed. On cooling the sample such a periodicity is maintained but tilted bands across the stripes are developed giving rise to a rope-like texture at 270 K.<sup>4,14,52</sup> It has also been observed that consecutive stripes show reversed optical birefringence on opposite rotation. All these features were already observed in the optical textures of the CB7CB dimer which was the first compound to be identified as forming a twist-bend nematic phase.<sup>4</sup>

3.3.2 Dielectric measurements. Fig. 11 shows the perpendicular component of the dielectric loss at two temperatures close to each other, one in the N mesophase and the other in the NTB mesophase. It can be observed how the amplitude of the  $m_{1\perp}$ -mode sharply increases in the NTB mesophase, a fact already reported for the N<sub>TB</sub> of the CB7CB dimer.<sup>4</sup> This is consistent with the formation of a phase in which the director tilts away from the planar alignment direction defined in the precursor nematic phase. In the absence of any evidence of a tilted smectic C phase, we attribute this dielectric feature to the formation of a twist-bend nematic phase. It should be stressed that the amplitude of the  $m_{2\perp}$ -mode abruptly decreases, in fact much more than expected,<sup>4</sup> which is believed to be due to the partial crystallization of the sample. It should be remembered that this mesophase is highly metastable and must be obtained by using high cooling rates making dielectric measurements difficult.

**3.3.3** Splay and bend elastic constants. The essence of the Landau or elastic model proposed by Dozov<sup>3</sup> for the formation of the twist-bend nematic phase is the bent shape of the constituent molecules. Under certain conditions the ground-state remains in a state of permanent bend, and accompanying the bend distortion there is also a twist.



**Fig. 10** Optical textures at three temperatures obtained from 8  $\mu$ m thick cells (anti-parallel alignment from Instec). Red arrows correspond to the direction of the rubbing and crossed arrows indicate the direction of the polarizer axes. The width of all pictures is 144  $\mu$ m and D = 2d.

The twist is not spontaneous, assuming no intrinsic chirality, but is imposed by the bend to enable topological continuity. In the theory it was assumed that the bent-core or banana mesogenic molecules had a fixed geometrical bend, but the first compound reported to form the twist-bend nematic phase was the flexible odd-membered liquid crystal dimer CB7CB.<sup>4</sup> This mesogen has a flexible core which can give rise to a variety of molecular shapes. The conformationally averaged shape depends on the type of the phase, temperature and degree of order, but in general is also bent. In the twist-bend nematic phase, the director distribution is both bent and twisted.



Fig. 11 Frequency dependence of the imaginary part of the perpendicular component of the permittivity at two temperatures, one (T = 319 K) in the N phase and the other (T = 313 K) in the N<sub>TB</sub> phase.

For this structure there are two defining features, the tilt of the director with respect to the helix axis,  $\theta_0$ , and the wave vector,  $k = 2\pi/p$  where *p* is the pitch of the helix. The main assumption in Dozov's model is that in the twist-bend nematic phase the coefficient of the bend distortion in the free energy should be negative. This assumption does not apply to the high temperature uniform nematic phase, but it is tempting to speculate that nematic phases with low values of the bend elastic constant might have a predisposition to form a twistbend nematic phase, although for any particular example, other factors may intervene.

We now turn to the elastic constants in the uniform nematic phase of dimer liquid crystals. It is to be expected, and indeed found, that for the odd dimers the splay  $K_1$  and twist  $K_2$  elastic constants behave normally, namely  $K_1 > K_2$ , and in addition both increase with decreasing temperature and hence orientational order.<sup>22</sup> In marked contrast, theory<sup>4,22</sup> and experiment<sup>23,50,52</sup> reveal that the bend  $K_3$  elastic constant is small and decreases with decreasing temperature. The bend and splay elastic constants have been measured for FFO9OCB<sup>23</sup> and the results show that  $K_1$ increases with decreasing temperature while  $K_3$  is significantly smaller than  $K_1$  and decreases slightly with decreasing temperature. They are found to be in accordance with earlier theoretical predictions.<sup>22</sup> The lowest reduced temperature for which the experimental results are available is ~0.93 which is significantly higher than the monotropic N<sub>TB</sub>–N transition at ~0.83.

We have determined the splay ( $K_1$ ) and bend ( $K_3$ ) elastic constants for FFO9OCB over a more extended range of temperature. Our results are given in Fig. 12 as a function of reduced temperature ( $T/T_{\rm NI}$ ) along with values measured by Atkinson *et al.*<sup>23</sup> over a shorter temperature range. As regards  $K_1$ , there is a reasonable agreement between the two sets of measurements over the common temperature range. As regards  $K_3$ , a certain difference is observed in absolute values between the two sets of measurements. However, and despite this difference,  $K_3$  is significantly smaller than  $K_1$  at temperatures close to the N<sub>TB</sub>–N phase transition and a similar behaviour is observed as the temperature decreases on approaching the transition to the proposed N<sub>TB</sub> phase.



**Fig. 12** Temperature dependence of the splay ( $K_1$ ) and bend ( $K_3$ ) elastic constants in the nematic phase for FFO9OCB.  $\bigcirc$  – our results for  $K_1$ ;  $\blacklozenge$  – results for  $K_1$  from ref. 23;  $\diamondsuit$  – our results for  $K_3$ ;  $\blacklozenge$  – results for  $K_3$  from ref. 23.

#### 3.4 The nematic-to-isotropic phase transition

One of the simplest theoretical descriptions of the N-to-I phase transition is that offered by the Landau-de Gennes free energy expansion in terms of the second-rank symmetric traceless order parameter tensor Q. In the simplest case for uniaxial nematic phases, the tensor Q can be substituted by a scalar order parameter  $Q_N (Q_N = 1/2 \langle (3\cos^2 \theta - 1) \rangle)$ . In such a situation the free energy density expansion for the nematic phase up to sixth order can be written as

$$F_{\rm N} = F_{\rm I} + \frac{1}{2}AQ_{\rm N}^2 - \frac{1}{3}BQ_{\rm N}^3 + \frac{1}{4}CQ_{\rm N}^4 + \frac{1}{6}DQ_{\rm N}^6 \tag{8}$$

where A, B, C, and D are the expansion coefficients and  $F_{I}$  is the free energy density of the isotropic phase. It is usual to define A as  $a_0(T - T^*)$  with  $a_0 > 0$  and  $T^*$  the spinodal temperature accounting for the metastable limit of the I-phase. The other terms B, C, and D are assumed to be temperature independent and among them, the term *B*, the so-called cubic invariant, is responsible for the first-order character of the N-to-I phase transition. If the molecules forming the uniaxial nematic phase are flexible and/or biaxial, then the absolute value of B is diminished.<sup>36</sup> When *B* is very small and the other parameters A and C become simultaneously zero, the N-to-I phase transition becomes strictly tricritical.<sup>36,54</sup> In such a situation the heat capacity critical exponent  $\alpha$  in both N and I phases must be 1/2and the  $Q_{\rm N}$  critical exponent  $\beta$  must be 1/4. From an experimental point of view, such parameters can be obtained from very accurate heat capacity data combined with static dielectric determinations through the N-to-I phase transition. In addition, indications about the magnitude of B can be obtained from the determination of the spinodal temperatures  $T^*$  and  $T^{**}$  ( $T^{**}$  accounts for the metastable limit of the N mesophase) and from the magnitude of the latent heat as well.

**3.4.1 Heat capacity measurements and the order parameter.** Fig. 13 shows the heat capacity together with the  $\phi$ -phase shift data around the N-to-I phase transition. The sharp-peak in the  $\phi$ -phase shift data at the transition temperature is a signature of



**Fig. 13** Heat capacity data ( $\bigcirc$ ) as a function of temperature near the N-to-I phase transition of FFO9OCB. Phase shift angle ( $\phi$ ) data ( $\Delta$ ) are included to define the limits of the heat capacity coexistence region (area delimited by the vertical dashed lines). Grey solid lines are fittings according to eqn (9a) and (9b). The inset shows  $Q_N'$  data according to eqn (11) as a function of temperature together with the fitting curve (grey line) according to eqn (12).

the first order character of the N-to-I phase transition and will be used to determine the limits of the coexistence region indicated by dashed lines in Fig. 13.

Let us consider the analysis of the heat capacity data through the standard expressions:<sup>36-38</sup>

$$C_{\rm p,I} = B_{\rm C} + D_{\rm C} \left[ \frac{T}{T^*} - 1 \right] + A_{\rm C,I} \left| \frac{T}{T^*} - 1 \right|^{-\alpha} \quad T > T_{\rm NI} = T^* + \Delta T^*$$
(9a)

$$C_{\rm p,N} = B_{\rm C} + D_{\rm C} \left[ \frac{T}{T^{**}} - 1 \right] + A_{\rm C,N} \left| \frac{T}{T^{**}} - 1 \right|^{-\alpha} \quad T < T_{\rm NI} = T^{**} - \Delta T^{**}$$
(9b)

Both eqn (9a) and (9b) are assumed to be valid in a region of no more than  $\pm 3$  K around  $T_{\rm NI}$ , but excluding all the points in the coexistence region. The exponent  $\alpha$  (the same in the I and N phases), both spinodal temperatures  $T^{**}$  and  $T^*$ , the  $B_{\rm C}$  and  $D_{\rm C}$ terms corresponding to the so-called heat capacity background and the corresponding amplitudes  $A_{\rm C,N}$  and  $A_{\rm C,I}$  are found by fitting the experimental data of Fig. 13 according to eqn (9a) and (9b). In the methodology followed, the common parameters in both phases ( $B_{\rm C}$ ,  $D_{\rm C}$  and  $\alpha$ ) have been simultaneously refined after a previous independent fitting. The most significant parameters ( $A_{\rm C,N}/A_{\rm C,I}$ , ( $T^{**} - T^*$ ) and  $\alpha$ ) that characterize the nature of the N-to-I phase transition are listed in Table 3. All the fitted parameters are consistent with the measured heat capacity data, as indicated by the  $\chi^2$  values and as shown in Fig. 13 where both eqn (9) are drawn.

The latent heat associated with the N-to-I phase transition is calculated using eqn (1) over the heat capacity data of Fig. 13

through a previous careful calibration.<sup>12,13,37</sup> Our value is listed in Table 1.

In this work, the critical behaviour of the scalar order parameter  $Q_N$  around the N-to-I phase transition has been estimated from very precise measurements of the heat capacity shown in Fig. 13 according to the procedure given by Iannacchione and Finotello.<sup>55</sup> The methodology was applied successfully by us<sup>38,56</sup> and is based on the Landau-de Gennes approach given by eqn (8). The square of the scalar order parameter is defined as

$$Q_{\rm N}^2(T) = \frac{2\rho}{a_0} \left[ \int_{T_0}^{T_{\rm CI}} \frac{\Delta C_{\rm p}}{T} + \frac{\Delta H_{\rm NI}}{T_{\rm NI}} + \int_{T_{\rm CN}}^{T} \frac{\Delta C_{\rm p}}{T} \right]$$
(10)

where  $\rho$  is the density of the liquid crystal and the constant  $a_0$  is the first coefficient in eqn (8) ( $A = a_0(T - T^*)$  with  $a_0 > 0$ ). The integration is done numerically on cooling from  $T_0$  in the I-phase, well above  $T_{\rm NI}$ , at which  $Q_{\rm N}$  could be considered zero down to temperature T in the N-mesophase. Both temperatures  $T_{\rm CI}$  and  $T_{\rm CN}$  are the limiting temperatures of the coexistence region in the isotropic and nematic phases, respectively. The terms  $\Delta H_{\rm NI}$  and  $\Delta C_{\rm p}$  are the latent heat and the difference between the heat capacity and the heat capacity background, respectively. Assuming that the density of the liquid crystal is constant in the integrated temperature range, we can write  $Q_{\rm N}'$  as

$$Q_{\rm N}'(T) = Q_{\rm N} \left[ \frac{a_0}{2\rho} \right]^{\frac{1}{2}} = \left[ \int_{T_0}^{T_{\rm CI}} \frac{\Delta C_{\rm p}}{T} + \frac{\Delta H_{\rm NI}}{T_{\rm NI}} + \int_{T_{\rm CN}}^{T} \frac{\Delta C_{\rm p}}{T} \right]^{\frac{1}{2}} \quad (11)$$

where  $Q_{\rm N}'$  is not strictly the scalar order parameter but is a proportional quantity which displays the same critical behaviour at the N-to-I phase transition. Such a critical behaviour is usually parameterized, according to the Landau-de Gennes theory,<sup>36,57,58</sup> as a generic expression

$$Q_{N}' = Q_{N}'^{**} + K |T - T^{**}|^{\beta} \quad T < T^{**} - \Delta T^{*} \quad (12)$$

where  $T^{**}$  has the same meaning as in eqn (9b). The critical exponent  $\beta$  and K and  $Q_N'^{**}$  are parameters obtained from fits of the  $Q_N'$  data calculated using eqn (11). The inset of Fig. 13 shows the calculated  $Q_N'$  data and the fitting according to eqn (12) (grey line). The value of the critical exponent  $\beta$  is listed in Table 3 together with the fitting  $\chi^2$  value.

**3.4.2 Static dielectric permittivity measurements.** Fig. 14 shows the static permittivity data ( $\varepsilon_{\text{mean}}$  and  $\varepsilon_{\text{iso}}$ ) around the N-to-I phase transition in more detail than in Fig. 5. The data analysis at the N-to-I phase transition has been carried out according to the equations<sup>12,13,57</sup>

$$\varepsilon_{\rm iso} = \varepsilon^* + a_{\rm I} |T - T^*| + A_{\varepsilon,{\rm I}} |T - T^*|^{1-\alpha} \quad T > T_{\rm NI} = T^* + \Delta T^*$$
(13a)

 Table 3
 Results of the fittings for the N-to-I phase transition



**Fig. 14** Behaviour of the mean static dielectric permittivity in the nematic phase ( $\bigcirc$ ) and the static dielectric permittivity in the isotropic phase ( $\bigcirc$ ) for FFO9OCB. Grey solid lines are fittings according to eqn (13a) and (13b). The inset shows the derivative of the static dielectric permittivity (left *y*-axis and open symbols) and heat capacity data (right *y*-axis and grey points) both as a function of temperature.

$$\varepsilon_{\text{mean}} = \varepsilon^{**} + a_{\text{N}} |T - T^{**}| + A_{\varepsilon,\text{N}} |T - T^{**}|^{1-\alpha} \quad T < T_{\text{NI}} = T^{**} - \Delta T^{**}$$
(13b)

where  $\alpha$  is the specific heat critical exponent;  $T^*$  and  $T^{**}$  have the same meaning as in eqn (9);  $\varepsilon^*$  and  $\varepsilon^{**}$  are the extrapolated values of  $\varepsilon_{iso}$  and  $\varepsilon_{mean}$  at  $T^*$  and  $T^{**}$ , respectively; both  $a_I$  and  $a_{\rm N}$  are the static dielectric permittivity background;  $A_{\varepsilon,\rm I}$  and  $A_{\varepsilon,\rm N}$ are the corresponding dielectric amplitudes. All these parameters have been obtained by fitting the dielectric data and the most significant values  $(A_{\varepsilon,N}/A_{\varepsilon,I}, (T^{**} - T^*) \text{ and } \alpha)$  are listed in Table 3. In our fitting strategy, the star symbols in Fig. 14 have been removed from the fitting according to the scaling relationship between the derivative of the static dielectric permittivity  $(d\varepsilon_{\text{mean}}/dT \text{ and } d\varepsilon_{\text{iso}}/dT)$  and the heat capacity (see the inset of Fig. 14) around the phase transition as was theorized earlier by Mistura.<sup>59</sup> It may be emphasised that both  $d\varepsilon_{mean}/dT$  and  $d\varepsilon_{iso}/dT$ have been obtained numerically by distortion-sensitive derivative analysis of the static permittivity data according to the procedure given elsewhere.<sup>12,57,58</sup>

Both eqn (13a) and (13b) with the corresponding fitting parameters portray almost perfectly our experimental data as shown in Fig. 14 and also as indicated by the  $\chi^2$ -value listed in Table 3 which is indicative of the quality of the fitted results.

**3.4.3** The critical behaviour. From our analysis using highresolution heat capacity measurements, it has been clearly demonstrated that the N-to-I phase transition is first order in nature. The latent heat  $(\Delta H_{\rm NI})$  (see Table 1) is estimated to be

Physical property	$A_{ m N}/A_{ m I}$	$T^{**} - T^{*}$ (K)	$\Delta T^{**} / \Delta T^{*}$	α	β	$\chi^2 \times 10^4$	
Heat capacity	$2.4\pm0.1$	$0.59^{a}$	0.83	$0.50\pm0.05$	_	1	
Static permittivity	$-0.6\pm0.1$	$3.97^{a}$	0.46	$0.5\pm0.1$	_	0.5	
$Q_{\rm N}'$	_	—	—	_	$0.25 \pm 0.02$	1	

<sup>*a*</sup> The error is estimated to be about 50% of the absolute magnitude of  $(T^{**} - T^*)$ .

4 times lower than the one reported by Atkinson *et al.*<sup>24</sup> Such discrepancies are usually observed in other liquid crystals for which latent heats are determined from standard DSC measurements at 5 or 10 K min<sup>-1</sup>.

The width of the metastable region  $(T^{**} - T^*)$ , that is linked with the magnitude of the cubic invariant B, has been found to be non-zero and positive (see Table 3). The value of  $(T^{**} - T^*)$ obtained from static dielectric permittivity is higher than that found from heat capacity measurements, as usually occurs.<sup>12,58,60</sup> It was thought that such differences are caused by a non-perfect experimental scaling between the heat capacity and the derivative of the static dielectric permittivity, as shown in the inset of Fig. 14. The ratio  $\Delta T^{**}/\Delta T^{*}$  (see Table 3) ranges from 0.8 (heat capacity) to about 0.5 (static dielectric permittivity). It is noteworthy that  $\Delta T^{**}/\Delta T^{*}$  of about 0.5 agrees with the tricritical hypothesis of the N-to-I phase transition.<sup>60–64</sup> In addition, the heat capacity critical exponent  $\alpha$  is found to be 0.5 whatever the technique used (either heat capacity or static dielectric data). The  $\beta$ -critical exponent of the order parameter through  $Q_{\rm N}'$  is found to be 0.25. Both critical exponents are also compatible with the tricritical hypothesis. The heat capacity amplitude ratio  $(A_{C,N}/A_{C,I})$  and even the dielectric amplitude ratio  $(A_{\varepsilon,N}/A_{\varepsilon,I})$  (see Table 3) are in quite good agreement with the values obtained for the tricritical behaviour in other liquid crystals.<sup>12,58,61</sup> Noteworthy is the validation of the approximate scaling relation  $A_{\varepsilon,N}/A_{\varepsilon,I} \approx 1 - 4\alpha$ .

### 4 Conclusions

The study reported in this paper is an extensive investigation of the non-symmetric liquid crystal dimer FFO9OCB. So far, our dielectric relaxation and heat capacity measurements are the first measurements performed in compounds of the FFOnOCB series.

In the nematic phase, the temperature dependence of the static dielectric permittivity is qualitatively similar to that exhibited by symmetric liquid crystal dimers,<sup>4,29,33,34</sup> but the parallel component decreases with temperature to a lesser extent. Dielectric relaxation results have been obtained over a wide range of frequencies from  $10^3$  to  $10^9$  Hz. The model of Stocchero *et al.*<sup>35</sup> has allowed us to identify and interpret the molecular processes that are responsible for the two different longitudinal dielectric relaxations observed at low frequencies. Both relaxations are a consequence of flip-flop motions of the terminal groups of the dimer. On the basis of the model, the conformational distribution of the molecules in the N mesophase has been estimated as a function of temperature.

The N-to-I phase transition has been characterized as firstorder in nature from heat capacity as well as static dielectric permittivity measurements. The measured latent heat and transitional entropy change ( $\Delta S/R = 0.14$ ) associated with the N-to-I phase transition is found to be much lower than the value previously reported in the literature<sup>24</sup> and is in agreement with the very weakly first order character of the transition evidenced by the small value of the width of the metastable region. The magnitude of  $Q_N'$ , which is proportional to the scalar orientational order parameter, has been obtained from the heat capacity data. The associated critical exponent is found to be 0.25, the tricritical value which supports other strong evidence arising from calorimetric and dielectric measurements suggesting that the N-to-I phase transition exhibits a tricritical behaviour.

In relation to the mesomorphism of the FFO9OCB the main unpublished result is the discovery of a new metastable nematic phase formed when the sample is cooled at sufficiently high rates (at least 10 K min<sup>-1</sup>). Evidence for identifying this phase as a twist-bend nematic phase (NTB) comes from optical textures, dielectric measurements close to the N-to-NTB phase transition and the temperature dependence of both  $K_1$  and  $K_3$ elastic constants. This assignment is confirmed by miscibility studies with CB7CB. Thus, the FFO9OCB dimer constitutes an example of a pure ether-linked dimer exhibiting the twist-bend nematic mesophase. Additionally, the FFO9OCB dimer exhibits a glassy state when the sample is cooled at 10 K min<sup>-1</sup> or higher, and it has been shown that this glassy state corresponds to the vitrification of this new N<sub>TB</sub> mesophase. Unfortunately, the fact that the  $N_{TB}$  mesophase is metastable (it crystallizes on cooling even at high cooling rates) prevents the possibility of performing a detailed investigation, by dielectric spectroscopy, of the motions involved in the glass transition<sup>5</sup> and to apply the most advanced procedures<sup>65,66</sup> to characterize the glass transition in the light of critical phenomena.

Our earlier claim<sup>4</sup> to have discovered a new liquid crystalline phase has rightly been subjected to critical review in the literature.<sup>67</sup> The theoretical possibility for such a phase has been raised in the past by a number of authors,<sup>68,69</sup> and most recently by Dozov.<sup>3</sup> A conical nematic phase has been reported in a lyotropic suspension of helical flagella<sup>70</sup> and other groups have reported additional examples of the twist-bend nematic phase in thermotropic systems.<sup>67,51</sup>

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