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INVITED ARTICLE

Asymmetric oxadiazole mesogens as candidates for low-temperature biaxial nematics

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We report the synthesis and properties of a homologous series of asymmetric, mesogenic derivatives of 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP). Benzyloxy (BnO-), alkoxy benzoate ester derivatives BnO-ODBP-Ph-O-C_n, where $n = 4, 5, 6, 7, 8, 9, 12$, were studied by ^{2}H-NMR, X-ray diffraction and polarising microscopy in order to ascertain if the lower temperature nematic phases exhibited biaxiality. Deuterium nuclear magnetic resonance (NMR) of labelled probes in these asymmetric mesogens does not show evidence of biaxiality. The absence of biaxiality is discussed in terms of the statistical non-linearity of these asymmetric ODBP mesogens.

Keywords: biaxial nematics; oxadiazole derivatives; structure-property relationship

1. Introduction

Mesomorphism was first reported for non-linear, symmetric, alkyl and alkoxy benzoate ester derivatives of the 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) core in 2000 (*1*). In this class of so-called bent-core mesogens, the non-linear moiety is the central 2,5-disubstituted oxadiazole heterocycle, which has an exocyclic bond angle of 134 degrees (*2*). The symmetric ODBP mesogen with a generic structure R-Ph-ODBP-Ph-R (denoted ODBP-Ph-R) also has a large transverse electric dipole moment (~5 Debye) bisecting the oxadiazole ring and hence bisecting the mesogenic core's boomerang-like shape. Nuclear magnetic resonance (NMR) evidence suggested that the high temperature (~200°C) mesophases of the symmetric mesogens ODBP-Ph-C_7 and ODBP-Ph-OC_{12} were biaxial nematic phases (*3*, *4*). If the transverse electrostatic dipole moment is dominant at low frequencies and leads to a negative dielectric anisotropy, biaxial nematic phases in ODBP mesogens would make these compounds candidates for putative fast switching phenomena: facile, in-plane E-field-driven reorientation of a minor director about an anchored primary director (*5*). Herein we characterise the nematic phases of a homologous series of asymmetric ODBP mesogens R'-ODBP-Ph-R wherein the terminal substituents are different and therefore break the symmetry of these non-linear mesogens. The syntheses described here were motivated by a desire to lower the temperature range of the nematic phase in ODBP mesogens and thereby enable more in-depth studies of the still-elusive biaxial nematic phase.

Recently, Paraskos and Swager (*6*) discovered in asymmetric, thiophene-based, bent-core mesogens that packing frustration in the supramolecular organisation led to broader mesophases. In efforts to lower the onset of the biaxial nematic phase in the ODBP mesogens, we synthesised a series of asymmetric compounds R'-ODBP-Ph-R, having the usual alkoxy benzoate ester (-Ph-OC_n) on one end of the ODBP core and a benzyloxy (BnO-) terminus, a prototypical 'blocking group', on its other end (i.e. R' = BnO-). We report the synthesis and explore the phase behaviour of several asymmetric BnO-ODBP-Ph-OC_n (**5**) where $n = 4, 5, 6, 7, 8, 9, 12$. These asymmetrical compounds were studied by ^{2}H-NMR, X-ray diffraction and electro-optical measurements, with a goal of seeking lower temperature biaxial nematic phases.

2. Synthetic strategy

The route we employ to the BnO-ODBP-Ph-OC_n series is illustrated in scheme 1. Synthesis of the symmetric ODBP core was previously reported by Dingemans (*1*). Here we focus on derivatising 1,3,4-oxadiazole asymmetrically. The parent compound **4** is prepared by coupling 4-(benzyloxy)benzoyl chloride with the reactive 4-hydroxybenzohydrazide in nearly quantitative yield to give **3**, which is then dehydrated using $SOCl_2$ to afford the five-membered oxadiazole heterocycle. The final compounds **5a–g** are made by the equimolar addition of the appropriate 4-alkoxy($n = 4, 5, 6, 7, 8, 9, 12$) benzoic acid to **4** under EDC/DMAP coupling conditions. The yields are high, so the final compounds can readily be purified by recrystallisation.

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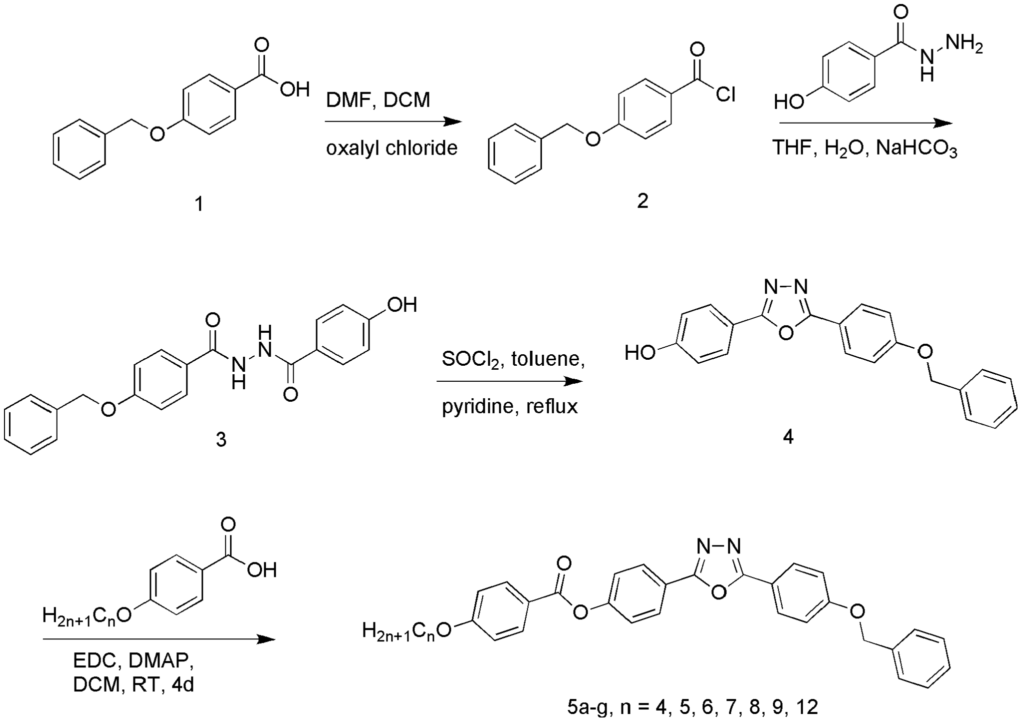

Scheme 1. Synthesis of asymmetric benzyloxy (BnO-)/phenylalkoxy (-Ph-OC$_n$) derivatised ODBP liquid crystals, BnO-ODBP-Ph-OC$_n$.

3. Results and discussion

We originally set out to make the biaxial nematic phase of the symmetric phenylalkyl mesogen ODBP-Ph-C$_7$ more accessible by modest asymmetric substitutions via differentiating the aliphatic termini in this class of non-linear mesogens. But during the course of that effort, Gortz and Goodby (*7*) reported asymmetrically substituted ODBP cores with varying aliphatic chain lengths. They started from the asymmetrically protected cpds **4** and **5**, and using **5** as an intermediate, prepared different alkyl chain lengths for asymmetric, alkoxy benzoate ester derivatives of ODBP. However, they observed only a small reduction in the nematic onset temperatures of the asymmetric mesogens. This suggested that such modest asymmetrical structural changes on the periphery of the mesogenic core are unable to markedly lower phase transition temperatures. However, having already started down the path of appending dissimilar tails on the ODBP mesogenic core, we decided to look for mesogenicity in the precursors to the asymmetric aliphatic mesogens, namely, cpd **5** itself. To that end we synthesised a homologous series of asymmetric BnO-ODBP-Ph-OC$_n$ molecules where one bent-core terminus is the conventional alkyloxybenzoic ester of ODBP and the other is the benzyloxy group.

3.1 Thermal analysis

The DSC results of the homologous series BnO-ODBP-Ph-OC$_n$, where n ranges from 5 to 12, are presented in Figure 1. All compounds are liquid crystalline, containing at least one enantiotropic nematic phase. The mesophase onset temperatures for this series of compounds is significantly lower than the earlier reported symmetric analogues, the ODBP-Ph-OC$_n$ series. These onset temperatures, as well as the clearing points, decrease slightly with an odd–even alternation as the aliphatic chain increases in length. The **5a** mesogen shows a crystal to crystal transition observable by optical microscopy at 50°C; the **5b–f** mesogens exhibit only nematic phases. The last compound in the series, BnO-ODBP-Ph-OC$_{12}$ (**5g**), has multiple mesophases; optical microscopy and X-ray studies indicate both a smectic A phase as well as a higher ordered smectic, perhaps a G, J or even a tilted phase.

3.2. Texture analysis

We used polarising optical microscopy to study the melt behaviour of BnO-ODBP-Ph-OC$_{12}$ in order to gain insight into the phase type and phase stability as a function of the temperature. Observations were initiated by heating into the isotropic phase then cooling at a rate of 5°C min^{-1}. At 140°C a nematic

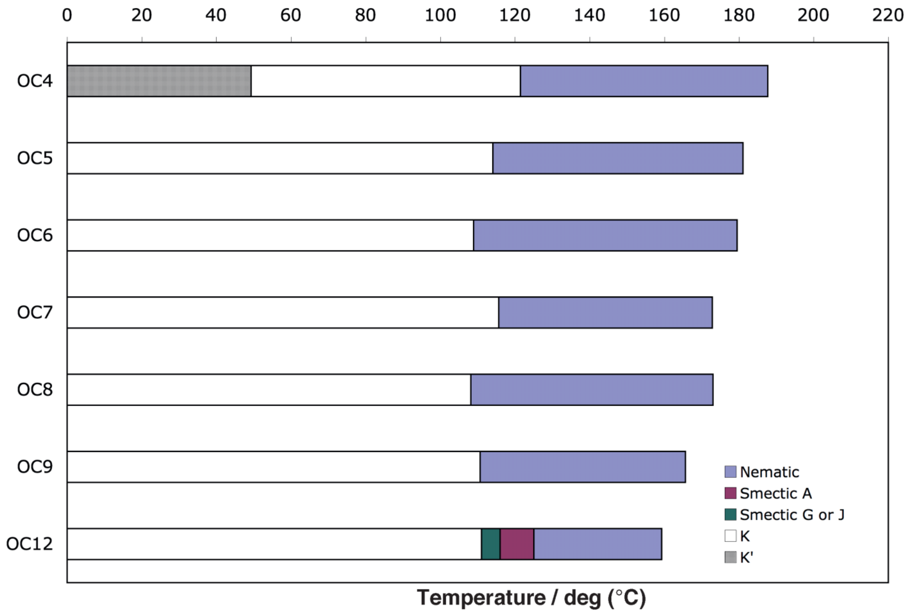

Figure 1. Transition maps showing the phase behaviour of the BnO-ODBP-Ph-OC$_n$ liquid crystals.

Schlieren texture appears, one that exhibits mainly two-brush disclinations (Figure 2(a)). On continued cooling, a focal conic texture indicative of the SmA phase was observed (Figure 2(b)). The SmA phase transformed into a higher ordered smectic phase with unusually low birefringence (Figure 2(c)). This phase, however, is only stable over a 5°C temperature range above the crystal melting point. The liquid crystal textures are summarised in Figure 2.

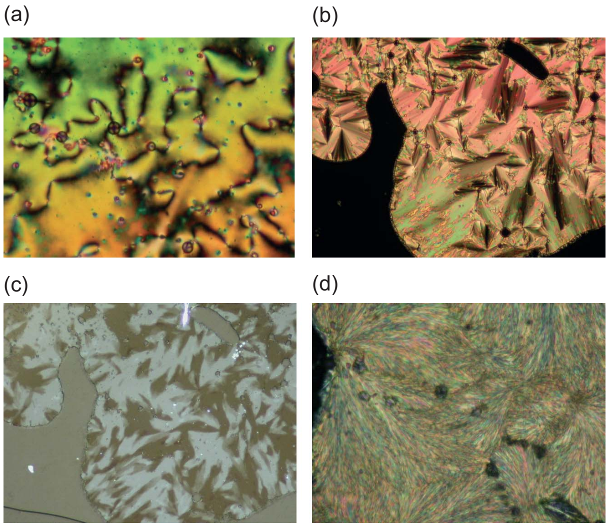

Figure 2. Microphotographs of BnO-ODBP-Ph-OC$_{12}$, between crossed polarisers: (a) nematic Schlieren texture at 140°C; (b) focal conic texture of the SmA phase at 117°C; (c) highly ordered Sx phase (J or G) at 115°C; (d) the crystal phase at 110°C.

3.3 X-ray analysis

BnO-ODBP-Ph-OC$_{12}$ was investigated using temperature-dependent small-angle X-ray diffraction. A 1.0 mm quartz capillary was charged with the LC sample, sealed and placed in a graphite furnace. The sample was heated to the isotropic phase and slowly cooled.

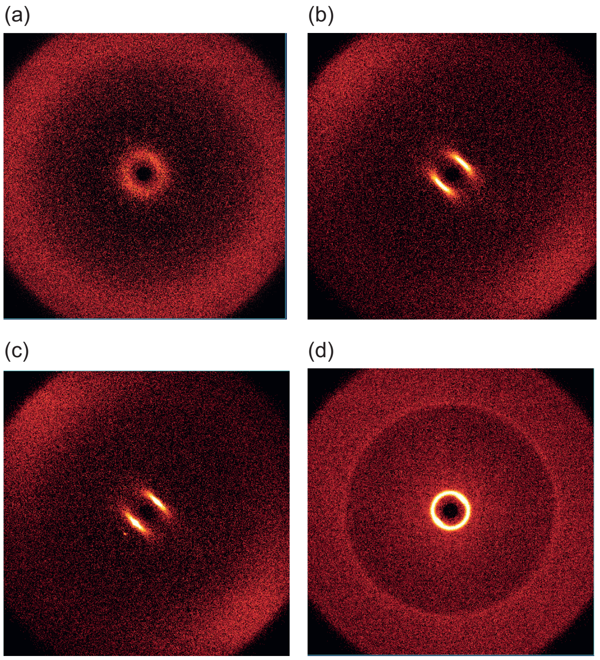

Figure 3. Diffraction patterns of BnO-ODBP-Ph-OC$_{12}$: (a) the isotropic phase at 170°C; (b) the nematic phase at 140°C; (c) the SmA phase at 117°C; (d) SmX phase (J or G) at 115°C.

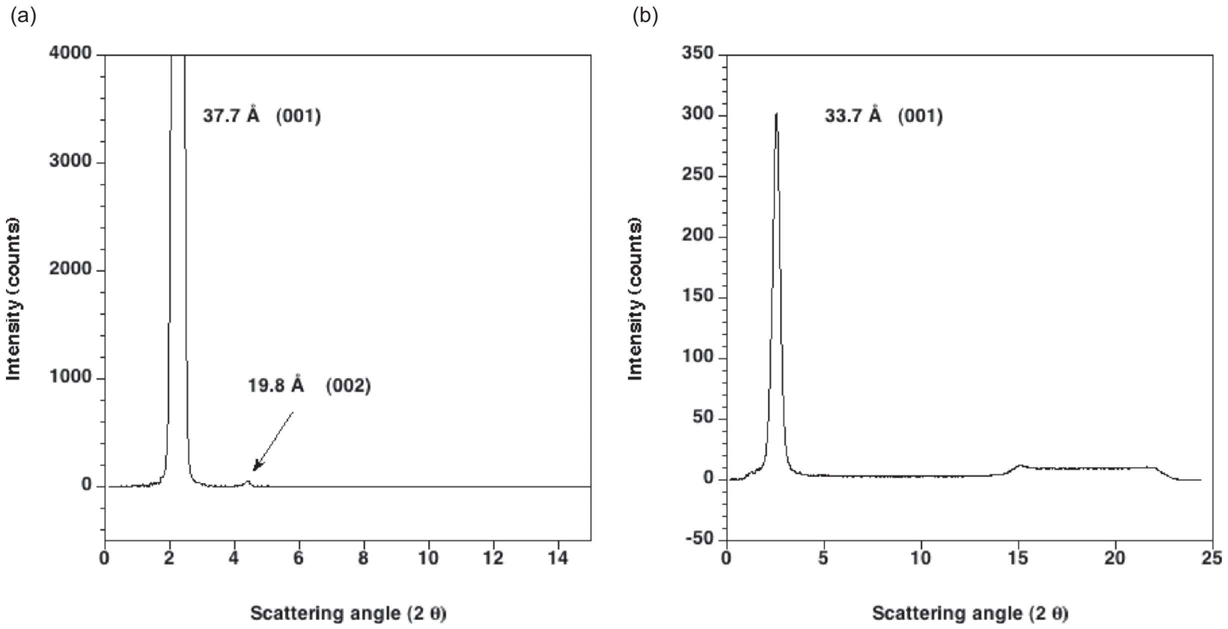

Figure 4. X-ray diffraction of BnO-ODBP-Ph-OC$_{12}$: (a) SmA$_1$ phase at 117°C; (b) SmX phase at 115°C.

A permanent magnet of ~4 T was used to align the liquid crystal phase and the sample was kept in this field throughout the duration of the experiment.

The X-ray diffraction results are summarised in Figures 3 and 4. Upon cooling, a nicely aligned nematic phase forms (Figure 3(b)) and shows signs of a cybotactic structure, but no evidence of the small-angle four-spot pattern reported for symmetric ODBP mesogens (*8*). When cooling is continued, the nematic phase transforms into a well-aligned SmA phase exhibiting a small-angle reflection ($2\theta \sim 2°$) that translates into a layer spacing with d = 37.7 Å (Figure 3(c)). This d spacing corresponds to the molecular length of the BnO-ODBP-Ph-OC$_{12}$Bz mesogen in its most extended conformation. The SmA phase can therefore be indexed as a SmA$_1$ monolayer. The SmA$_1$ phase on further cooling transforms into an unaligned liquid crystal phase, with a (001) reflection corresponding to a layer spacing of 33.7Å (Figure 3(d)), indicating a partially interdigitated smectic phase (possibly a G or J phase) or a tilted phase. Due to the lack of alignment of this phase it is difficult to be more specific about the exact nature of this phase, hence we have labelled it SmX. It should be noted that this SmX phase appears to be chiral and hence suggestive of a tilted phase since rotating the analyser slightly from the orthogonal position causes a reversal of the dark and lighter domains (see Figure 5). This has been interpreted in the past to be indicative of locally chiral domains (*7*).

3.4 Deuterium NMR

Our initial goal with this homologous series of compounds was to synthesise a biaxial nematic liquid crystal at temperatures lower than the previously reported symmetric ODBP mesogens. We selected BnO-ODBP-Ph-OC$_5$ for ^{2}H-NMR spectroscopy studies.

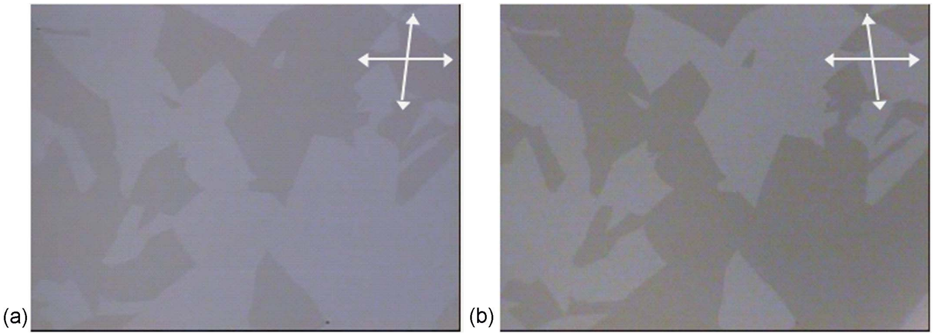

Figure 5. Microphotographs of the highly ordered SmX phase of BnO-ODBP-Ph-OC$_{12}$ between crossed polarisers at 116°C. The analyser (vertical double arrow) is rotated: (a) +10° and (b) –10° from the orthogonal setting (10 × magnification).

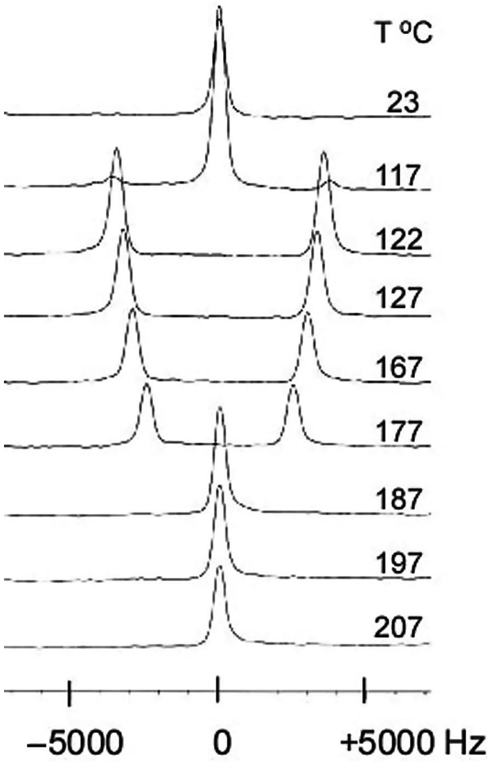

Figure 6. NMR data for a static sample of BnO-ODBP-Ph-OC_5Bn/HMB-d_{18} at temperatures ranging from 207°C (lower) to 23°C (upper).

BnO-ODBP-Ph-OC_5 is not deuterated, so the NMR experiments were conducted by doping the sample with 1–2 wt% hexamethylbenzene-d_{18} (HMB-d_{18}), which acts as a solute probe molecule and indirectly reflects the symmetry of the phase. The temperature dependence of the static spectra of HMB-d_{18} dissolved in BnO-ODBP-Ph-OC_5 is shown in Figure 6 (from 480°C to 280°C). The ^{2}H NMR spectra of the isotropic phase (480–450°C) are singlets, corresponding to the completely motionally averaged quadrupolar interaction. In the nematic phase of the doped BnO-ODBP-Ph-OC_5 mesogen (~ 445–380°C) a quadrupolar splitting is exhibited by the HMB-d_{18} probe molecule, as it is partially oriented as it diffuses among the aligned mesogens. This splitting increases as the temperature is lowered and the orientational order improves; eventually the sample crystallises, characterised by a single peak in the ^{2}H NMR spectrum (e.g. the 280°C spectrum) suggesting that the probe phase separates from the crystalline mesogen and diffuses isotropically.

When the sample was rotated about an axis normal to the magnetic field $\mathbf{B}_0$ at a rate of 166 Hz at 395 K (122°C), the lower end of the nematic range, the NMR spectrum exhibits a two-dimensional 'powder' pattern – a weighted average of the quadrupolar spectra for a planar distribution of $\boldsymbol{n}$. In a biaxial nematic we would expect to see a secondary alignment of the X component to minimise the magnetic free energy. However, we observed a uniaxial nematic with equivalent $X = Y = ½ Z$ components. This is evident in Figure 7 where we have overlaid the experimentally determined spectrum with the simulated spectrum. We measured a biaxiality parameter $\eta = 0.00 \pm 0.03$ for BnO-ODBP-Ph-OC_5/HMB. This is too close to the experimental uncertainty in our measurements (*4*) so we concluded that for BnO-ODBP-Ph-OC_5 $\eta = 0$ and this class of asymmetric ODBP mesogens exhibit uniaxial nematic phases.

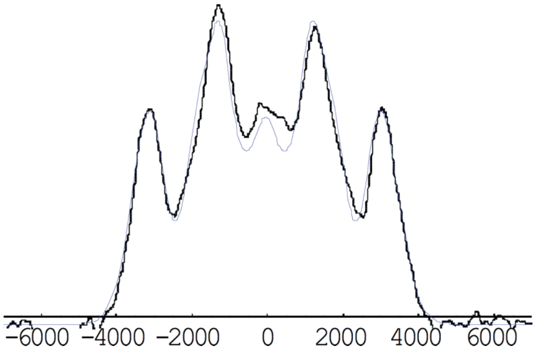

Figure 7. NMR data (thick line) and simulation (thin line) for a rotating uniaxial nematic BnO-ODBP-Ph-OC_5 (the x-axis is in Hz). Best fit obtained with biaxiality $\eta = 0.00 \pm 0.03$.

We rationalise this observation in terms of molecular structural considerations as follows. While BnO-ODBP-Ph-OC_5 can adopt a bent-core shape, rotations about the benzyloxy ether bonds (Figure 8) transform this mesogenic core into a more rod-like calamitic molecular structure. This in turn would reduce the

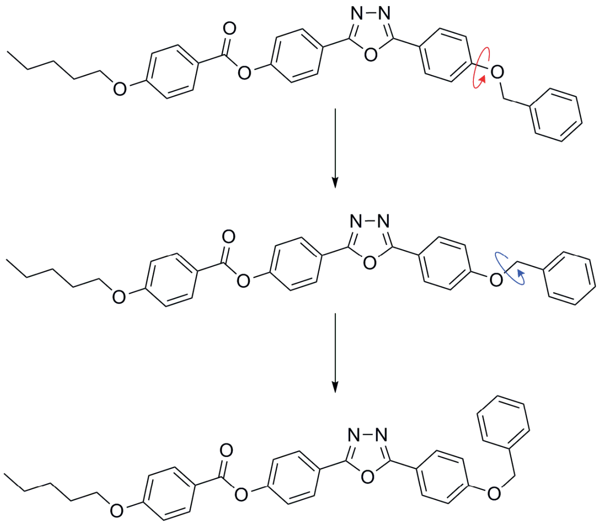

Figure 8. Schematic representation of the rotation about the benzyloxy ether bonds, leading to more rodlike conformations of the BnO-ODBP-Ph-OC_5 mesogen.

biaxial shape and thereby decrease the proclivity for the formation of a biaxial nematic phase in the strict sense of molecular-shape driven biaxiality.

4. Concluding remarks

We have successfully synthesised a homologous series BnO-ODBP-Ph-OC$_n$ of asymmetric ODBP mesogens with aliphatic tails on only one end of the mesogen. Thermal analyses indicate that all compounds (with a singular alkyl terminus ranging from butyloxy to dodecyloxy chains) exhibit nematic phase behaviour in the range between 115°C and 170°C; the nematic window decreases slightly with increasing alkyl chain length. The longest alkyl chain derivative, BnO-ODBP-Ph-OC$_{12}$, exhibits smectic phases and was characterised by optical microscopy and wide-angle X-ray diffraction. Its low temperature Sm-X phase exhibited chiral domains and may be a tilted phase. We picked BnO-ODBP-Ph-OC$_5$, with low nematic onset temperature and wide nematic range, as a representative mesogen of this series and searched for biaxiality with ^{2}H-NMR. Within the experimental uncertainty of the NMR measurements with a labelled probe, we see no evidence for phase biaxiality. Although the depiction of the chemical formulae of BnO-ODBP-Ph-OC$_n$ mesogens can be rendered with a bent-core shape (Scheme 1), unlike the symmetric ODBP-Ph-C7 originally reported to exhibit a probe biaxiality ($\eta \sim 0.1$), the pendant benzyloxy group can freely rotate and yield statistical molecular shapes that are more calamitic like.

The absence of biaxiality in the BnO-ODBP-Ph-OC$_n$ mesogens reinforces the subtle array of intermolecular interactions that must be required to observe macroscopic biaxiality in the nematic phase. If one considers the findings reported here in the context of recent suggestions that the earlier observed biaxial phase in symmetric ODBP mesogens may derive from cybotacticity (O. Francescangeli, private communication, 2008) – the formation of clusters of stratified, tilted mesogens with intrinsic biaxiality –then it may be useful to speculate about the differences between smectic supramolecular arrangements of symmetric ODBP mesogens versus that in the asymmetric BnO-ODBP-Ph-OC$_n$ mesogens. One perspective on the origin of tilt (inherent biaxiality) in smectics is that this supramolecular arrangement is driven by the obtuse junction of the tails to the mesogenic core (*9*) – the segregation of extended aliphatic chains into strata on either side of the cores forces the core to tilt to accommodate the tails so that the flexible chains are able to persist in a direction normal to the strata. This constraint would be relaxed considerably in the single-tail BnO-ODBP-Ph-OC$_n$ mesogens and may account for the normal (untilted) Sm-A phase observed in BnO-ODBP-Ph-OC$_{12}$. While the X-ray data show evidence for cybotacticity in the nematic phase of BnO-ODBP-Ph-OC$_{12}$, biaxial cybotactic clusters (*10*) – tilted mesogen arrangements within clusters – would be less probable in this nematic relative to the symmetric ODBP mesogens like ODBP-Ph-OC$_{12}$, which were reported to exhibit biaxiality (*3*).

5. Method

5.1 Synthesis of BnO-ODBP-Ph-OC$_n$ series

5.1.1 General

Tetrahydrofuran (THF) and toluene were dried over and distilled from sodium prior to use. Pyridine was dried over and distilled from calcium hydride. Dichloromethane (CH_2Cl_2) was dried over molecular sieves. All other solvents and reagents were purchased from Aldrich and used without further purification. All of the reactions were carried out under argon with the use of standard inert-atmosphere Schlenk techniques.

5.1.2. Synthesis of 4-(benzyloxy)benzoyl chloride (2)

4-benzyloxybenzoic acid (1) (2.4 g, 10.5 mmol) was dissolved in anhydrous CH_2Cl_2 (30 ml) and anhydrous DMF (3 drops) at 0°C to which 2 N oxalyl chloride in dichloroethane (10.5 ml, 20.9 mmol) was added dropwise over 25 minutes. The reaction mixture was stirred at room temperature under Ar atmosphere for 5 hours. Solvent and excess reagents were removed under reduced pressure and the product was used without further purification and characterisation for the next step.

5.1.3 Synthesis of 4-(benzyloxy)-N′-(4-hydroxybenzoyl)benzohydrazide (3)

4-(benzyloxy)-benzoyl chloride (**2**) from the above reaction and 4-hydroxybenzohydrazide were treated with $NaHCO_3$ (0.98 g, 10.5 mmol) in a mixture of dry THF (20 ml) and distilled H_2O (25 ml) for 4 hours at room temperature. The white precipitate formed, was filtered, washed thoroughly with H_2O and dried to give the final product **3** (3.7 g, 97% overall yield). ^{1}H NMR (DMSO-d_6): 10.24 (s, 1H), 10.16 (s, 1H), 10.10 (s, 1H), 7.88 (d, 2H), 7.78 (d, 2H), 7.48–7.33 (m, 5H), 7.12 (d, 2H), 6.83 (d, 2H), 5.18 (s, 2H).

5.1.4 Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenol, BnO-ODBP-OH (4)

A mixture of 4-(benzyloxy)-N′-(4-hydroxybenzoyl)-benzohydrazide (3.7 g, 10.1 mmol), thionyl chloride

(7.3 ml), pyridine (0.2 ml) and toluene (5 ml) was refluxed under Ar atmosphere for 8 hours. The reaction mixture was cooled to room temperature, quenched over ice, and stirred for about 1 hour. The resulting colourless precipitate was filtered, washed with H_2O and dried. Final product **4** was recrystallised from ethanol (2.5 g, 73% yield). ^{1}H NMR (DMSO-d_6): 10.31 (s, 1H), 8.03 (d, 2H), 7.93 (d, 2H), 7.49–7.34 (m, 5H), 7.23 (d, 2H), 6.96 (d, 2H), 5.22 (s, 2H).

5.1.5 Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(propyloxy)-benzoate, BnO-ODBP-Ph-OC$_4$ (5a)

Compounds **5a–g** were all synthesised in the same manner as ODBP-Ph-OC$_4$Bn. 4-propyloxybenzoic acid (0.14 g, 0.73 mmol) and BnO-ODBP-OH 4 (0.25 g, 0.73 mmol) were treated with 1-(3-(dimethylamino)propyl)-3-ethylcarbodiimide hydrochloride (EDC) (0.14 g, 1 equiv.) and 4-(dimethylamino)pyridine (DMAP) (0.020 g, 20 mol%) in CH_2Cl_2 (50 ml) and were allowed to stir under Ar atmosphere at room temperature for 4 days. Solvent was removed under reduced pressure and the crude was recrystallised from CH_2Cl_2/MeOH to afford the final colourless product **5a** (0.33 g, 88%). ^{1}H NMR ($CDCl_3$): δ8.17 (d, 2H), 8.14 (d, 2H), 8.07 (d, 2H), 7.46–7.34 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.05 (t, 2H), 1.80 (quintet, 2H), 1.50 (sextet, 2H), 0.98 (t, 3H).

5.1.6 Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(pentyloxy)-benzoate, BnO-ODBP-Ph-OC$_5$ (5b)

Reaction of **4** (0.50 g, 1.5 mmol) with 4-pentyloxybenzoic acid (0.30 g, 1.5 mmol) gave **5b** (0.56 g, 72%). ^{1}H NMR ($CDCl_3$): 8.17 (d, 2H), 8.14 (d, 2H), 8.07 (d, 2H), 7.45–7.34 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.04 (t, 2H), 1.81 (quintet, 2H), 1.53 – 1.39 (m, 2H), 1.35 – 1.25 (m, 2H), 0.93 (t, 3H).

5.1.7 Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(hexyloxy)-benzoate, BnO-ODBP-Ph-OC$_6$ (5c)

Reaction of **4** (0.25 g, 0.73 mmol) with 4-hexyloxybenzoic acid (0.16 g, 0.73 mmol) gave **5c** (0.35 g, 87%). ^{1}H NMR ($CDCl_3$): δ8.17 (d, 2H), 8.14 (d, 2H), 8.07 (d, 2H), 7.45–7.34 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.04 (t, 2H), 1.81 (quintet, 2H), 1.53–1.42 (m, 2H), 1.37–1.32 (m, 4H), 0.90 (t, 3H).

5.1.8 Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(heptyloxy)-benzoate, BnO-ODBP-Ph-OC$_7$ (5d)

Reaction of **4** (0.25 g, 0.73 mmol) with 4-heptyloxybenzoic acid (0.16 g, 0.73 mmol) gave **5d** (0.35 g, 86%). ^{1}H NMR ($CDCl_3$): δ8.17 (d, 2H), 8.14 (d, 2H), 8.07 (d, 2H), 7.46–7.33 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.04 (t, 2H), 1.81 (quintet, 2H), 1.49–1.41 (m, 2H), 1.40–1.28 (m, 6H), 0.89 (t, 3H).

5.1.9 Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(octyloxy)-benzoate, BnO-ODBP-Ph-OC$_8$ (5e)

Reaction of **4** (0.25 g, 0.73 mmol) with 4-octyloxybenzoic acid (0.16 g, 0.73 mmol) gave **5e** (0.36 g, 86%). ^{1}H NMR ($CDCl_3$): 8.17 (d, 2H), 8.14 (d, 2H), 8.07 (d, 2H), 7.46–7.34 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.04 (t, 2H), 1.81 (quintet, 2H), 1.48–1.42 (m, 2H), 1.41–1.23 (m, 8H), 0.88 (t, 3H).

5.1.10. Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(nonyloxy)-benzoate, BnO-ODBP-Ph-OC$_9$ (5f)

Reaction of **4** (0.25 g, 0.73 mmol) with 4-nonyloxybenzoic acid (0.16 g, 0.73 mmol) gave **5f** (0.37 g, 86%). ^{1}H NMR ($CDCl_3$): 8.17 (d, 2H), 8.11 (d, 2H), 8.07 (d, 2H), 7.45–7.34 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.04 (t, 2H), 1.81 (quintet, 2H), 1.50–1.42 (m, 2H), 1.39–1.23 (m, 10H), 0.87 (t, 3H).

5.1.11. Synthesis of 4-(5-(4-(benzyloxy)phenyl)-1,3,4-oxadiazol-2-yl)phenyl-4-(dodecyloxy)-benzoate, BnO-ODBP-Ph-OC$_{12}$ (5g)

Reaction of **4** (0.25 g, 0.73 mmol) with 4-dodecyloxybenzoic acid (0.16 g, 0.73 mmol) gave **5g** (0.41 g, 89%). ^{1}H NMR ($CDCl_3$): 8.17 (d, 2H), 8.14 (d, 2H), 8.07 (d, 2H), 7.45–7.34 (m, 7H), 7.10 (d, 2H), 6.97 (d, 2H), 5.14 (s, 2H), 4.04 (t, 2H), 1.81 (quintet, 2H), 1.50–1.42 (m, 2H), 1.40–1.21 (m, 16H), 0.90 (t, 3H).

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References

(1) Dingemans, T.J.; Samulski, E.T. *Liquid Crystals* **2000**, *27*, 131–136.
(2) Dingemans, T.J.; Murthy, N.S.; Samulski, E.T. *J. Phys. Chem. B* **2001**, *105*, 8845–8860.

(3) Madsen, L.A.; Dingemans, T.J.; Nakata, M.; Samulski, E.T. *Phys. Rev. Lett.* 92 **2004**, *14*, 145505.

(4) Dingemans, T.J.; Madsen, L.A.; Zafiropoulos, N.A.; Lin, W.; Samulski, E.T. *Philos. Trans. R. Soc. Lond. A* **2006**, *364*, 2681–2696.

(5) Luckhurst, G.R. *Thin Solid Films* **2001**, *393*, 40.

(6) P Paraskos, A.J.; Swager, T.M. *Chem. Mater.* **2002**, *14*, 4543–4549.

(7) Gortz, V.; Goodby, J.W. *Chem. Comm.* **2005**, *26*, 3262–3264.

(8) Acharya, B.R.; Primak, A.; Kumar, S. *Phys. Rev. Lett.* **2004**, *92*, 14506-1–14506-4.

(9) Vanakaras, A.G.; Photinos, D.J.; Samulski, E.T. *Phys. Rev. E* **1998**, *57*, R4875–R4878.

(10) Vanakaras, A.G.; Photinos, D.J. *J. Chem. Phys.* **2008**, *128*, 154512.