The effects of lateral halogen substituents on the low-temperature cybotactic nematic phase in oxadiazole based bent-core liquid crystals

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We have previously demonstrated that the incorporation of lateral methyl groups on oxadiazole-based liquid crystals leads to relatively low-temperature cybotactic nematic phases which, in some cases, supercool to room temperature. We report here the synthesis and phase behaviour of related compounds that possess lateral halogen groups and in some cases, lateral methyl groups as well. Derivatives with three lateral substituents (one halogen and two methyl groups) in a specific pattern supercool in the nematic phase to room temperature. As was the case with the previously reported trimethylated derivatives, the low-temperature nematic phase is glassy in nature. Two of the new trisubstituted derivatives (with bromo and chloro groups) remain in the nematic phase upon subsequent heating until transitioning to the isotropic phase indicating that the low-temperature nematic phase may be more stable than that shown by the trimethylated analogue. Preliminary X-ray diffraction analysis confirms the presence of a tilted cybotactic nematic phase. In addition, the splitting observed in the wide-angle scattering feature is indicative of enhanced local biaxial packing.

**Keywords:** cybotactic; oxadiazole-based liquid crystals; biaxiality; low-temperature nematic phase; lateral halogen groups

1. Introduction

Since it was first proposed in 1970,\(^{[1]}\) there has been a great deal of interest in the biaxial nematic (N\(_b\)) phase due to the potential for enhancements to display applications such as faster electro-optic switching and improved viewing angles.\(^{[2–5]}\) Evidence from \(^2\)H NMR spectroscopy, conoscopic microscopy, and X-ray diffraction (XRD) was originally thought to be proof for the N\(_b\) phase in bent-core liquid crystals derived from a 1,3,4-oxadiazole bisphenol (ODBP) moiety.\(^{[6,7]}\) However, more recent work (on oxadiazoles and other bent-core mesogens (BCM)) indicates that the unique behaviour observed may be field induced and due to the presence of cybotactic (smectic-like) clusters within the nematic phase (designated N\(_\text{Cybc}\) or N\(_\text{Cyba}\)).\(^{[8–20]}\) Further evidence of the cluster model has been found by examining the effects of an applied electric or magnetic field on the nematic phase in BCM.\(^{[21–24]}\) Dramatic shifts in transition temperatures (up to 11 K) were observed as the strength of the field was increased. Such substantial shifts can be best accounted for by considering that the applied field is coupling to biaxial clusters rather than simply to individual molecules. As additional proof, smectic layers within a nematic phase of a BCM have been imaged using cryo-transmission electron microscopy.\(^{[25]}\) The cluster model has also been used to explain some other interesting features of BCM, such as the fact that chiral domains are observed when the sample is viewed by polarising microscopy (POM),\(^{[26–32]}\) and ferroelectric switching behaviour in the nematic phase of 1,2,4-oxadiazole-based liquid crystals.\(^{[33–37]}\) However, some differences of opinion regarding the precise cause of the observed behaviour in the nematic phase remain.\(^{[38–41]}\) Clearly, there continues to be much to learn about the fundamentals of how the bent-core molecules are interacting to establish supramolecular structures in the nematic phase and this is being investigated using a variety of techniques.\(^{[42–49]}\) Moreover, several recent studies suggest that fast electro-optical switching about the minor director of a BCM in a field-induced N\(_b\) phase is possible, so continued investigations into this unique liquid crystal phase hold technological promise.\(^{[50–52]}\)

One of the challenges in studying these types of compounds is that most of the derivatives that show the unique N\(_\text{Cyb}\) phase do so at very high temperatures. In order to more fully comprehend details about the phase (and to be able to exploit possible practical applications), it is necessary to prepare derivatives that exhibit this phase closer
to room temperature. Currently, there are only a handful of derivatives that show a cybotactic nematic phase at relatively low temperatures including some cyanoresorcinol based derivatives, [13] fluorenone- or thiadiazone-based derivatives with pendant alkoxy groups,[53–60] and low molar mass organosilosane multipodes.[61,62] Some of these derivatives supercool in the nematic phase to room temperature or below. In these instances, the low-temperature phase tends to be very viscous or glass-like.

Our approach to lowering transition temperatures has been to incorporate lateral methyl groups on the aromatic rings of the oxadiazole system.[63–67] This has led to considerably lower transition temperatures compared to the non-methylated analogues; derivatives with three lateral methyl groups supercool to room temperature in the nematic phase (Figure 1) and XRD studies indicate the presence of cybotactic clusters. In the case of the compound shown below, OC4 2MePh(mono3MeODBP), the nematic phase persists at room temperature for nearly 24 hours before crystallisation occurs. In addition, at room temperature, the nematic phase was no longer fluid but glassy. This result is consistent with the phase behaviour observed in other bent-core systems that show supercooling of a nematic phase to low temperatures. The supercooling effect can be attributed to two factors which are both related to the presence of lateral substituents and prevent facile crystallisation: (1) restricted internal rotation allows for the presence of a variety of conformers and (2) rotation about the long axes of the molecules is slowed. Recently, we reported a novel splitting of the wide-angle XRD pattern in bent-core molecules. It represents the first XRD evidence of local biaxial order in this class of nematogens. This behaviour is only present in the trimethylated derivatives that supercool in the nematic phase to room temperature and is suggestive of enhanced biaxial ordering in the cybotactic clusters of such mesogens.[65,66]

The effects of lateral polar groups (halogens, cyano, etc.) on BCM have also been investigated. [5,13,26,27,68–74] This is of interest because such groups will exaggerate the electrostatic profile (molecular dipole), and computational studies indicate that increasing the transverse dipole might stabilise the biaxial nematic phase (this idea has been investigated experimentally as well).[75–78] It has been demonstrated that subtle changes in the nature of the lateral groups can alter both the stability and types of liquid crystalline phases observed. For example, in resorcinol based bent-core liquid crystals, the presence of a lateral cyano group at the central benzene ring leads to the formation of a nematic phase, while a derivative with a lateral methyl group in the same position shows no nematic phase.[13]

Given these precedents, we were interested to learn how lateral halogen substituents would affect the nematic phase in oxadiazole-based liquid crystals. The steric effects of these groups can be compared using the van der Waals (VDW) volumes of each substituent. A fluoro group has a VDW volume of 6.20 cm$^3$/mol, Cl (12.24 cm$^3$/mol), and Br (14.60 cm$^3$/mol).[79] Therefore, the steric effects of the chloro and bromo groups on the phase behaviour should be comparable to that of the methyl group (which has a VDW volume of 13.67 cm$^3$/mol), while the fluoro group should create a much weaker steric effect. Of course, the halogen substituents will alter the molecular dipoles, so both steric and electronic effects must be considered. In this paper, we will discuss the phase behaviour of oxadiazole-based liquid crystals that possess a lateral halogen substituent (F, Cl, or Br) on one of the inner benzene rings.

![Figure 1. Phase behaviour of a trimethylated ODBP derivative.](image-url)

**2. Results and discussion**

**2.1. Synthesis**

The target compounds were prepared as shown in Scheme 1 using methodology previously described.[16a] The appropriately substituted 4-hydroxybenzoic acid is reacted with 4-hydroxybenzyldrazide in the presence of a carbodiimide coupling agent (EDC) and HOBt, to give compound 1. Ring closure with an excess of thionyl chloride yields the oxadiazole bisphenol core, 2. This synthetic intermediate can then be reacted with the appropriate benzoic acid using carbodiimide coupling to yield the target compound, 3.
Nine derivatives have been prepared which differ only in the position of lateral methyl groups (if any) and the identity of the halogen (in all cases the halogen is at the 3 position of one of the inner benzene rings). In the past, we have prepared derivatives that possess a very long terminal alkoxy group or a very short alkoxy group. Given that we were interested in the nematic phases of these compounds, we focused solely on short chain derivatives. Therefore, all of the derivatives described in this paper have two butoxy end chains. Figure 2 shows a representative structure along with the short-hand nomenclature. The chloro and bromo derivatives are named in a similar fashion with the exception that the core is designated (mono3ClODBP) or (mono3BrODBP).

2.2. Phase behaviour

A table showing all transition temperatures and enthalpies on the initial heating run is provided in Supplemental Material Table S1. The phase behaviour (heating and cooling) of the derivatives with no methyl group (OC4 Ph(mono3XODBP)) and a methyl group at the 3 position of the outer benzene rings (OC4 3MePh(mono3XODBP)) is shown in Figure 3.

For the compounds without a lateral methyl group, the fluoro derivative (OC4 Ph(mono3FODBP)) exhibits a wide nematic range of over 100°C with a clearing point of 280°C. This is approximately the same clearing temperature as observed for the originally reported (unsubstituted) oxadiazole derivative but the fluorine analogue has a larger nematic range. The presence of the fluorine obviously causes very little steric disruption and seems to stabilise the nematic phase somewhat compared with the non-halogenated species, as the onset temperature in the former compound is lower by 40°C. The chloro derivative (OC4 Ph(mono3ClODBP)) has a slightly lower clearing temperature than the

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**Scheme 1.** Synthesis of halogenated oxadiazole derivatives.

**Figure 2.** General structure and short-hand nomenclature for the halogenated oxadiazole derivatives.

**Figure 3.** (colour online) Phase transition temperatures of OC4 Ph(mono3XODBP) and OC4 3MePh(mono3XODBP); heating and cooling rates of 10°C/minute.
fluro derivative, but it too has a large nematic range of about 120°C. The bromo derivative (OC4 Ph (mono3BrODBP)) has about the same nematic onset temperature as the fluoro derivative, but a slightly shorter nematic range. The fluoro derivative shows only a small amount of supercooling in the nematic phase, but this effect is considerably larger for the bromo and chloro derivatives with both crystallising below 100°C.

For derivatives with a methyl group at the 3 position of both outer rings (OC4 3MePh (mono3XODBP)), the clearing points are reduced considerably compared to the non-methylated analogues, and the nematic ranges are reduced as well (Figure 3). The bromo derivative (OC4 3MePh (mono3BrODBP)) exhibits the shortest nematic range (18°C) and lowest clearing point (183°C). All three of these compounds supercool in the nematic phase with crystallisation occurring below 100°C.

As expected, based on our studies with trimethylated analogues, the trisubstituted derivatives with methyl groups at the 2 position of the outer benzene rings (OC4 2MePh(mono3XODBP)) show the most promising phase behaviour. All three of these derivatives show lower nematic onset and clearing temperatures than the other halogenated analogues. In addition, all of them supercool in the nematic phase to room temperature. A bar graph illustrates this phase behaviour (Figure 4); an additional segment is included for the subsequent heating run.

While the fluoro analogue crystallises upon heating, as was observed for the previously reported trimethylated derivatives, the bromo and chloro derivatives do not and remain in the nematic phase all the way to the isotropisation point. This is illustrated in Figure 5 which shows a differential scanning calorimetry (DSC) thermogram of the chloro derivative, OC4 2MePh(mono3ClODBP), including both the first and second heating and cooling cycles. However, if this compound is held at 70°C in the nematic phase for several hours, slow recrystallisation is observed. Thermograms for the fluoro and bromo derivatives can be found in the Supplemental Material (Figures S1 and S2).

As was the case for the previously described trimethylated derivative, OC4 2MePh (mono3MeODBP), all of the halogenated derivatives with the same substitution pattern form a viscous nematic glass at room temperature. But while the previously reported trimethylated compound crystallises after 24 hours at room temperature, the chloro and bromo derivatives remain in the nematic phase at room temperature for up to 2 weeks before crystallising. Attempts to observe a \( T_g \) by DSC have been challenging as this transition is known to be a weak event for low molar mass (monomeric) species. However, we were able to observe a possible \( T_g \) at 66°C for OC4 2MePh(mono3ClODBP) when a large sample size and rapid heating rate were used (see Figure 5).
Figure S3). This result is consistent with microscopy studies as the nematic phase of this compound seems to lose most of its fluidity by 60°C upon cooling.

When these derivatives are studied by POM, the nematic phase shows a mixture of 4 and 2 brush disclinations (Figure 6) as was observed for the related compounds with lateral methyl groups described in [63].

In comparing the phase behaviour of the three halogenated derivatives, OC4 2MePh (mono3XODBP), both steric and electronic effects must be considered. Since the dipole can be altered considerably depending upon the conformation of the outer benzene rings, we have chosen to calculate the dipoles for simplified molecules (the 2,5-diphenyl-1,3,4-oxadiazole unit) using Spartan ’10 DFT B3LYP parameters (Figure 7).

The fact that the fluorine substituent is so much smaller than the chlorine and bromine is likely the reason for the higher clearing temperature of the fluoro derivative. The steric effects of the bigger chloro and bromo substituents are also likely responsible for the fact that these compounds remain in the nematic phase upon heating from the supercooled nematic phase while the fluoro derivative crystallises upon heating in the glassy nematic phase. The larger groups can more effectively restrict intramolecular flexibility and rotation of the molecules about their long axes thereby kinetically preventing crystallisation by disrupting packing. If the larger dipoles for the chloro and bromo derivatives were responsible for the phase behaviour, we might then expect the clearing temperatures for these compounds to be higher as well.

It is more difficult to rationalise the difference in phase behaviour between the chloro, bromo, and trimethylated derivative (OC4 2MePh (mono3MeODBP), Figure 1) given that all three of the substituents are similar in size. Since the trimethylated analogue crystallises upon heating from the supercooled nematic phase while the bromo and chloro derivatives do not, it seems unlikely that steric differences can account for this behaviour. However, the dipoles mentioned above for the bromo and chloro derivatives are higher than for the trimethylated analogue (3.14 D). The direction of the dipole is different as well; for the halogenated compounds, the dipole angles across the oxadiazole moiety in the general direction of the halogen, while for the trimethylated derivative, the dipole generally bisects the oxadiazole moiety. It may be that these electronic factors conspire to stabilise the nematic phase for the chloro and bromo compounds or act to raise the barrier to rotation, thus slowing the crystallisation process.

Figure 6. (colour online) POM texture for OC4 2MePh (mono3ClODBP) at 156°C on cooling (100× magnification).

Figure 7. Calculated dipole moments (and dipole direction) for substituted 2,5-diphenyl-1,3,4-oxadiazoles.
2.3. X-ray diffraction studies

Preliminary XRD measurements were performed on OC4 2MePh(mono3ClODBP). The small-angle XRD patterns taken on cooling from the isotropic melt under an aligning magnetic field (horizontal in all figures) are shown in Figure 8. They show the typical four-spot feature indicative of the tilted, i.e. smectic C-like, cybotactic nematic (N_{CybC}) phase. We verified that the cooled sample retained a nearly unchanged pattern after being kept on the shelf at room temperature for 24 hours (Figure 8f). The q-space position of the intensity maxima [4a,b] in the pattern at T = 100°C corresponds to a molecular length L = 35.6 ± 0.3 Å, a smectic layer spacing d = 23.8 ± 0.4 Å and a tilt angle β = 48° ± 2°. These values are very similar to those previously reported for the trimethylated analogue,[63] as expected from the similar steric attributes of chloro and methyl groups.

In the wake of the recent observation of a splitting in the wide-angle XRD diffuse feature of trimethylated BCM,[65,66] we performed additional wide-angle measurements on the chloro derivative. Selected patterns taken on cooling under magnetic field are shown in Figure 9(a)–(c). Similarly to what was observed in the trimethylated counterparts, the equatorial wide-angle diffuse feature can be resolved into two diffraction peaks, labelled p1 and p2 in Figure 9(d)–(f), corresponding to distinct transverse intermolecular distances d_1 = 4.7 Å and d_2 = 3.8 Å. These values can be associated with the in-plane width of aromatic rings and the face-to-face distance between stacked π-systems, respectively, providing direct XRD evidence of (local) biaxial ordering. Overall, the splitting was comparable to that previously reported for the trimethylated analogue, the effect being stronger at low temperatures but still clearly detectable close to the clearing point. The possibility to resolve such a minor difference in the transverse intermolecular distances, a peculiarity of this class of trisubstituted BCMs, confirms an enhanced local biaxial packing of these mesogens compared to other BCMs studied so far. Further investigation is ongoing to elucidate the specific roles played by steric hindrance and dipole interactions in restricting rotation.

3. Experimental

3.1. General methods

All experiments were performed at room temperature and atmospheric pressure unless otherwise stated. All chemicals were acquired from Sigma-Aldrich Company in Milwaukee, Wisconsin and used without further purification unless otherwise stated. NMR spectra were obtained using a JEOL ECA-400 MHz FT-NMR with sample changer and auto tuning probe. A TA Instruments Model 2920 DSC and a Nikon Labophot-2-Pol microscope equipped with a Mettler Toledo Hot Stage FP82HT and a FP90 Central Processor were used for thermal analysis.

Figure 8. Small-angle XRD patterns of OC4 2MePh(mono3ClODBP) taken on cooling from the isotropic melt under a horizontal aligning magnetic field. Pattern (f) was taken after keeping the sample on the shelf (at room temperature with no magnetic field) for 24 hours.
Silica Gel 60 (230–400 mesh) from EMD, and Ottawa Sand Standard, 20–30 mesh, were used for column chromatography. All non-commercially available alkoxybenzoic acid derivatives were prepared according to published procedures.[64] Elemental analyses were carried out by Atlantic Microlab, Inc. (Norcross, GA). XRD measurements were performed at the European Synchrotron Radiation Facility (ESRF), Grenoble, France, on the BM26B DUBBLE beamline. Samples were studied in glass capillaries (1 mm diameter) mounted into a temperature-controlled sample holder allowing application of a static magnetic field (1 T for small-angle measurements, 2.2 T for wide-angle measurements) orthogonal to the X-ray beam. The beam energy was 12 keV (\(\lambda = 1.03\ \text{Å}\)), while the sample-to-detector distance was 1.286 m for small-angle measurements (a vacuum chamber was inserted between the sample and the detector to reduce air scattering) and 0.189 m for wide-angle measurements.

### 3.2. General synthetic procedures

Examples of each type of representative synthetic step are given below. Details for all other derivatives (including elemental analyses (Table S2)) are provided in the Supplemental Material.

**3-fluoro-4-hydroxy-N-(4-hydroxybenzoyl) benzhydrazide** 3-fluoro-4-hydroxybenzoic acid (0.502 g, 3.21 mmol), 4-hydroxybenzhydrazide (0.488 g, 3.20 mmol), and 1-hydroxybenzotriazole (HOBt) (0.446 g, 3.30 mmol) were added to a 250 mL three-neck round bottom flask equipped with a stir bar, and dissolved in dimethylformamide (DMF) (15 mL). The reaction mixture was then put under a nitrogen atmosphere. Upon dissolution, N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC HCL) (0.632 g, 3.29 mmol) was added. The solution was allowed to stir for 3 days, after which it was slowly pipetted into stirring DI water (200 mL). A white precipitate formed which was collected by Buchner filtration (0.749 g, 81.1% yield) and used without further purification.

**1H NMR (400 MHz, DMSO-d_6)** \(\delta 10.61\ (1\text{H}, \text{br s}), 10.22\ (1\text{H}, \text{s}), 10.16\ (1\text{H}, \text{s}), 10.09\ (1\text{H}, \text{s}), 7.75\ (2\text{H}, \text{d}, J = 8.70), 7.67\ (1\text{H}, \text{d}, J = 8.5), 7.01\ (1\text{H}, \text{t}, J = 8.4\ \text{Hz}), 6.81\ (2\text{H}, \text{d}, J = 8.5\ \text{Hz}).

2-(4-hydroxy-3-fluorophenyl)-5-(4-hydroxyphenyl)-1,3,4-oxadiazole 3-fluoro-4-hydroxy-N-(4-hydroxybenzoyl) benzhydrazide (0.749 g, 2.60 mmol) and thionyl chloride (7.5 mL, 103 mmol) were added to a 50 mL round bottom flask which was fitted with a reflux condenser and a water trap. The creamy white solution was refluxed for 20 minutes before it turned amber in colour, and this was then refluxed for an additional 2 hours. The solution was then poured onto ice which resulted in the formation of a yellow precipitate. The product was collected by Buchner filtration (0.749 g, 81.1% yield) and used without further purification.

**1H NMR (400 MHz, DMSO-d_6)** \(\delta 10.61\ (1\text{H}, \text{br s}), 10.22\ (1\text{H}, \text{s}), 10.16\ (1\text{H}, \text{s}), 10.09\ (1\text{H}, \text{s}), 7.75\ (2\text{H}, \text{d}, J = 8.70), 7.67\ (1\text{H}, \text{d}, J = 8.5), 7.01\ (1\text{H}, \text{t}, J = 8.4\ \text{Hz}), 6.81\ (2\text{H}, \text{d}, J = 8.5\ \text{Hz}).

Figure 9. (a–c) Wide-angle XRD patterns of OC4 2MePh(monodClOBDP) taken on cooling from the isotropic under a horizontal aligning magnetic field. Because of the pattern symmetry, only the upper equatorial feature is shown. (d–f) Fit of the corresponding \(q\)-scans along the equatorial axis by means of three Pearson VII lineshapes (note that \(p_0\), the low hump in the small \(q\) region, is just peripheral scattering from the four-spot feature).
filtration and washed with cold water, and then was recrystallised using a 3:2 ethanol:water solution to give a pale yellow solid (0.5239 g, 74.1% yield). $^{1}$H NMR (400 MHz, DMSO-d$_6$) δ 10.80 (1H, s), 10.31 (1H, s), 7.91 (2H, AA’BB’), 7.81 (1H, dd, J = 11.7, 2.0), 7.71–7.75 (1H, m), 7.12 (1H, t, J = 8.7 Hz), 6.93 (2H, AA’BB’).

OC$_4$ 2MePh(mono3FODBP) 2-(4-hydroxy-3-fluorophenyl)-5-(4-hydroxyphenyl)-1,3,4-oxadiazole (0.152 g, 0.551 mmol), DMAP (0.034 g, 0.28 mmol), and 4-butoxy-2-methyl benzoic acid (0.232 g, 1.12 mmol) were added to a 2-neck round bottom flask equipped with a stir bar and dissolved in dry dichloromethane (25 mL). This solution was then put under a nitrogen atmosphere. After stirring for 5 minutes EDC HCl (0.216 g, 1.14 mmol) was added and the reaction mixture was allowed to stir for 3 days, after which TLC indicated that the reaction was complete (2:1 Hexane:DCM:Acetone, $R_f$ = 0.62). DI water (25 mL) and dichloromethane (25 mL) were then added and the solution allowed to stir for 5 minutes before being transferred to a separatory funnel. The organic extract was then washed once with water (25 mL), once with brine (25 mL), and once with 2 M HCl (25 mL). The combined aqueous washings were backextracted with dichloromethane. The combined organic extracts were dried over magnesium sulphate, filtered, and solvent removed by rotary evaporation resulting in a white powder. The crude product was then purified using flash column chromatography (20:10:1.5 dichloromethane:hexanes:ethyl acetate, $R_f$ = 0.16). Solvent was then removed by rotary evaporation to give a white solid. The product was recrystallised using 1:30 chloroform:ethanol to give a white crystalline solid (0.214 g, 59.6% yield). $^{1}$H NMR (400 MHz, CDCl$_3$) δ 8.16–8.22 (4 H, m), 7.99 (2H, d, J = 8.4), 7.44 (1H, t, J = 8.0), 7.39 (2H, AA’BB’), 6.80–6.84 (4H, m), 4.04 (4H, t, J = 6.6 Hz), 2.67 (3H, s), 2.66 (3H, s), 1.73–1.83 (4H, m), 1.46–1.56 (4H, m), 0.99 (6H, t, J = 7.3 Hz). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 164.72, 164.47, 163.68, 163.35, 163.15, 162.97, 154.07 (d, J = 240 Hz), 154.07 (overlapping), 145.05, 144.82, 141.60 (d, J = 13 Hz), 134.12, 133.86, 128.48, 125.36, 123.36, 123.06, 122.60 (d, J = 7.7 Hz), 121.06, 119.69, 118.96, 117.92, 115.50 (d, J = 22 Hz), 111.87, 111.82, 67.99, 31.23, 22.70, 22.62, 19.29, 13.93.

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No potential conflict of interest was reported by the authors.

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Supplemental data
Supplemental data for this article can be accessed here.

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