Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Towards Room Temperature Biaxial Nematics

Lori L. Cooper [a], Edward T. Samulski [a] & Eric Scharrer [b]

[a] Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA

[b] Department of Chemistry, University of Puget Sound, Tacoma, WA, USA

Version of record first published: 05 Oct 2009

To cite this article: Lori L. Cooper, Edward T. Samulski & Eric Scharrer (2009): Towards Room Temperature Biaxial Nematics, Molecular Crystals and Liquid Crystals, 511:1, 203/[1673]-217/[1687]

To link to this article: http://dx.doi.org/10.1080/15421400903053826

Mol. Cryst. Liq. Cryst., Vol. 511, pp. 203/[1673]–217/[1687], 2009

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400903053826

Towards Room Temperature Biaxial Nematics

Lori L. Cooper[1], Edward T. Samulski[1], and Eric Scharrer[2]
[1]Department of Chemistry, University of North Carolina, Chapel Hill, NC, USA
[2]Department of Chemistry, University of Puget Sound, Tacoma, WA, USA

A series of new liquid crystalline compounds based on the 2,5-bis-(p-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) core was synthesized in an effort to access the biaxial nematic phase at low temperatures. Derivatives with secondary terminal alkoxy groups and derivatives with either two or four lateral methyl groups were prepared. Secondary alkoxy terminal groups either suppressed mesophase formation altogether or increased the nematic onset temperature relative to primary groups. The dimethylated derivatives showed significant reductions in the nematic onset temperatures compared to the previously reported unmethylated compounds. The tetramethylated analogs generally possessed low clearing temperatures, but exhibited only monotropic mesomorphism.

Keywords: biaxial nematic phase; lateral methylation; oxadiazole containing liquid crystals

INTRODUCTION

Freiser's biaxial nematic phase [1], posited for *monomeric* calamitic liquid crystals—molecules with a single, biaxially-shaped mesogenic core—has, for the most part, eluded liquid crystallographers. Initially chemists tried to induce the *Nb* phase by exaggerating the core's shape biaxiality with, in retrospect, no apparent success [2]. Sidechain

We thank Drs. Dingemans, Madsen, and Zafiropoulos for helpful conversations. This work was supported by NSF grant DMR-9971143. Eric Scharrer also wishes to acknowledge the University of Puget Sound for a Lantz Sabbatical Award that allowed him to spend the 2006–07 academic year at the University of North Carolina.

Address correspondence to Edward T. Samulski, Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290, USA. E-mail: et@unc.edu

polymer-based liquid crystals, on the other hand, readily exhibited *Nb* phases [3]. Previously, we reported a family of nonlinear, symmetric alkyl and alkoxy benzoate ester mesogens based on the disubstituted 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) core of which OC_{12}-Ph(ODBP), **1b**, and C_7-Ph(ODBP), **1c**, were shown to exhibit a high temperature (>170°C) biaxial nematic phase (Fig. 1) [4].

The nonlinear oxadiazole heterocycle has an exocyclic bond angle of 134° and additionally possesses a large electric dipole moment (~5 Debye) bisecting the mesogenic core's boomerang-like shape. The resulting negative dielectric anisotropy of the ODBP core makes these compounds putative candidates for fast switching phases [5]. Since the initial report confirming the presence of a biaxial nematic phase, we, and others, have investigated a variety of structural modifications (for oxadiazole and other liquid crystals) in an attempt to access this unique phase in a more useful temperature range [6]; achieving this goal should allow for more in-depth studies of the biaxial nematic phase. Our initial attempts focused on the incorporation of terminal

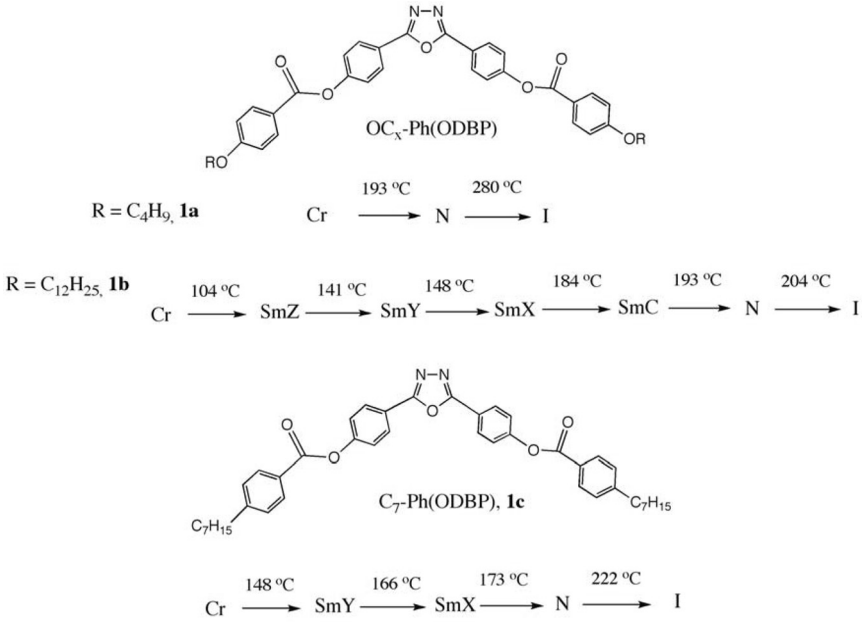


FIGURE 1 Previously prepared oxadiazole liquid crystals. **1b** and **1c** were shown to exhibit a biaxial nematic phase with conoscopy and deuterium NMR spectroscopy; SmX, SmY, and SmZ represent smectic phases that have not been fully characterized.

alkyl chains possessing tertiary groups, but this led to elimination of all liquid crystallinity [6h].

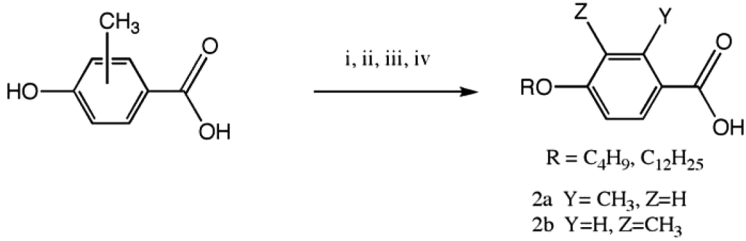
It is well known that modest substitutions (e.g., halogens, short alkyl groups, etc.) on the mesogenic core can change the mesophase transition temperatures [7]. Generally, if small changes in the core's shape are not overcompensated for by directional electrostatic interactions, the transition temperature can be lowered without loss of the mesophase. To that end, we have explored the introduction of methyl groups on the aromatic rings of the ODBP mesogens as well as the incorporation of secondary terminal alkyl chains, and we report the effects of such changes herein.

RESULTS AND DISCUSSION

Synthesis

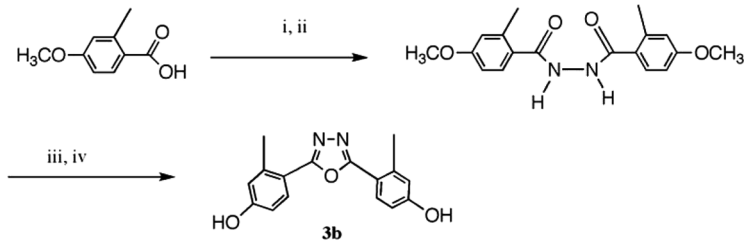
The preparation of the target compounds with lateral methyl groups requires access to various methylated alkoxybenzoic acids. Such compounds are not commercially available and were prepared as shown in Scheme 1. The appropriate 4-hydroxybenzoic acid was esterified using ethanol, and the phenol was then alkylated in the presence of KOH and butyl iodide or dodecyl iodide. Hydrolysis of the ester under basic conditions followed by acidification led to the substituted benzoic acid derivatives, **2**.

The synthesis of the unsubstituted bisphenol oxadiazole, 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole, **3a**, has been described elsewhere [8], but the synthesis of 2,5-bis-(4-hydroxy-2-methylphenyl)-1,3,4-oxadiazole, **3b**, was carried out as shown in Scheme 2. This method represents an adaptation of a procedure to prepare a related compound [6e]. 2-methyl-4-methoxy benzoic acid was converted to the acid



i: EtOH, H_2SO_4, reflux; ii: RX (1.1 equiv), KOH (2 equiv.), DMSO;
iii: 2M KOH, EtOH; iv: 6M HCl

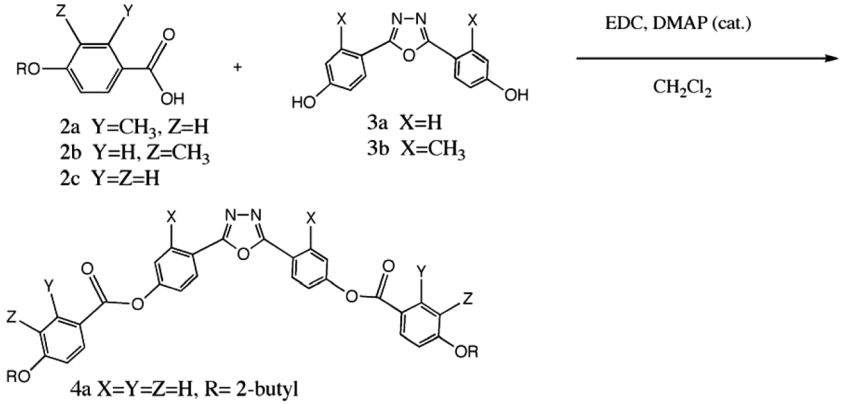
SCHEME 1 Synthesis of methylated 4-alkoxybenzoic acids.



SCHEME 2 Synthesis of the oxadiazole bisphenol core.

chloride and then reacted with 0.45 equivalents of hydrazine which led to the formation of the amide linkage. Ring closure to give the oxadiazole was effected by using a large excess of thionyl chloride. Demethylation to give the bisphenol was carried out with BBr_3.

The general synthesis of the target oxadiazole derivatives, **4–9**, involved the reaction of the appropriately substituted benzoic acid, **2**, with the appropriate oxadiazole bisphenol core, **3**, in the presence of ethyl dimethylaminopropylcarbodiimide hydrochloride (EDC) and catalytic 4-(dimethylamino)pyridine (DMAP) (Scheme 3). In addition to assigning compound numbers, we have also provided a simplified



SCHEME 3 Synthesis of liquid crystalline oxadiazole derivatives.

nomenclature system to facilitate discussion. For example OC_4-2MePh(ODBP) refers to a compound that has butoxy chains and possesses methyl groups at the 2-position of both outer benzene rings and no methyl groups on the interior benzene rings. OC_{12}-Ph(2MeODBP) refers to a compound with dodecyloxy groups, no methyl groups on the outer benzene rings and methyl groups at the 2-position of both inner benzene rings.

Phase Behavior

Effects of Modifying the Terminal Alkyl Groups

As described earlier, ODBP derivatives with tertiary alkyl groups did not exhibit mesomorphism. This led us to investigate the effects of incorporating alkyl groups with secondary carbons. The symmetric derivative with (S) 2-butoxy groups, **4a**, was prepared as shown in Scheme 3 [9]. However, this compound melted directly to the isotropic state at 193°C (Fig. 2). Clearly, the presence of the branch point so close to the aromatic core has a strongly detrimental effect on the formation of a mesophase. Therefore, an isomeric derivative, **4b**, possessing isobutyloxy groups was prepared. The separation of the branch point from the core via a methylene spacer restored the liquid crystallinity. However, the nematic onset occurred at 225°C (0.81 kJ/mol) with a range of only 5 degrees (Fig. 2). It is evident that the mesophase behavior of the ODBP derivatives is extremely sensitive to any changes in the nature of the terminal aliphatic groups. Based on the relatively high clearing points of the latter two derivatives, it appears that the transition temperatures are controlled by the typical electrostatic and van der Waals attractions in combination with a presumed unique packing arrangement in the crystal. It is remarkable that variations in the nature of the aliphatic chains for the isomeric C_4H_9 derivatives would have such a strong impact on the very stable nematic phase (87°C range) exhibited by the *n*-butyl parent compound, **1a**.

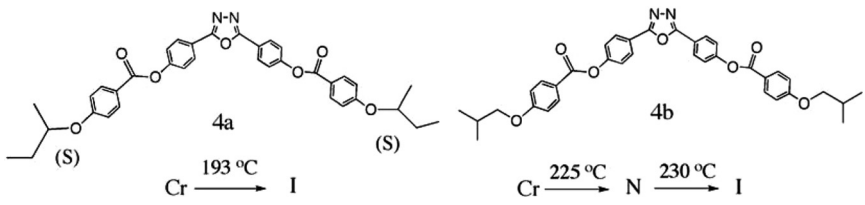


FIGURE 2 Phase behavior of ODBP derivatives with secondary alkoxy groups.

Effects of Lateral Methyl Substitution

The incorporation of lateral methyl groups on benzene rings has been demonstrated to lower phase transition temperatures in rod-like liquid crystals [7,10]. This structural modification also proved to be successful for the bent-core oxadiazole derivatives, **5–7**; the onset temperatures were significantly reduced relative to the non-methylated analogs, and good mesophase ranges were maintained. The phase transition temperatures and enthalpies of the dimethylated derivatives are given in Table 1.

With the derivatives in which the methyl groups are on the outer benzene rings, the butoxy 2-methyl derivative, **6a**, OC_4-2MePh(ODBP), exhibits a nematic onset at 130°C and a nematic range of 56°C. The corresponding 3-methyl derivative, **5a**, OC_4-3MePh(ODBP), has a nematic range of 55°C. In both cases, the clearing temperatures are comparable with the nematic onset temperature (193°C) of the unsubsituted OC_4 derivative, **1a**. However, the nematic range is compressed by about 30 degrees in the case of the dimethylated derivatives.

For the corresponding dodecyloxy derivatives, the nematic onset temperature is lowered by 56°C for the 3-methyl derivative, **5b**, OC_{12}-3MePh(ODBP), compared to the unsubstituted compound, **1b**, while the nematic range of 10°C is nearly identical to that of the unsubstituted version. For the 2-methyl derivative, **6b**, OC_{12}-2MePh(ODBP), the nematic onset is lowered by a remarkable 87°C and the nematic range of 28°C is significantly larger than that of

TABLE 1 Phase Transition Temperatures and Enthalpies of Oxadiazole Derivatives, **5–9**

	Transition temperature to indicated phase **T [°C]**[a]			
Compound	Cr_2 (Enthalpy [kJ/mol])	Smectic X[b] (Enthalpy [kJ/mol])	Nematic (Enthalpy [kJ/mol])	Isotropic (Enthalpy [kJ/mol])
5a, OC_4-3MePh(ODBP)	—	—	150.0 (50.7)	205.1 (0.96)
5b, OC_{12}-3MePh(ODBP)	—	123.1 (85.0)	137.3 (6.3)	147.7 (0.79)
6a, OC_4-2MePh(ODBP)	—	—	130.6 (38.1)	186.1 (0.95)
6b, OC_{12}-2MePh(ODBP)	92.3 (7.9)	99.5 (60.3)	106.6 (1.9)	134.3 (0.79)
7a, OC_4-Ph(2MeODBP)	112.8 (9.2)	—	129.3 (52.5)	180.1 (1.35)
7b, OC_{12}-Ph(2MeODBP)	70.2 (23.9)	[111.6 (3.18)][c]	117.3 (67.1)	130.5 (1.41)

[a]All temperatures and enthalpies are based on the second DSC heating run.
[b]This represents an uncharacterized smectic phase.
[c]Temperatures in brackets indicate a monotropic transition.

the unsubstituted compound. This onset temperature of 106°C represents the lowest nematic onset temperature of any of our dimethylated ODBP compounds.

The derivatives in which the methyl groups are located on the interior benzene rings do not exhibit phase behavior which deviates much from that of the derivatives described above. The butoxy derivative, **7a**, OC_4-Ph(2MeODBP), has a nematic range of 51°C with a nematic onset temperature only 1 degree lower than that of **6a**, OC_4-2MePh(ODBP). The dodecyloxy derivative, **7b**, OC_{12}-Ph(2MeODBP), gives a nematic range of 13 degrees with an onset temperature in between that observed for **6b**, OC_{12}-2MePh(ODBP), and **5b**, OC_{12}-3MePh(ODBP). The clearing temperatures of **7a** and **7b** are slightly lower than the clearing temperatures for the derivatives with the methyl groups on the outer rings. A direct comparison of the phase transition temperatures of all dimethylated derivatives with those of the unmethylated analogs can be seen in Figure 3.

To summarize the impact of lateral methylation for the dimethylated derivatives described above, the lowest onset temperature was observed for **6b**, OC_{12}-2MePh(ODBP) at 106°C. All dodecyloxy derivatives showed a nematic range at least as large as that of the unmethylated analog with compound **6b** possessing a nematic range almost three times as large as this. In contrast, all the butoxy derivatives

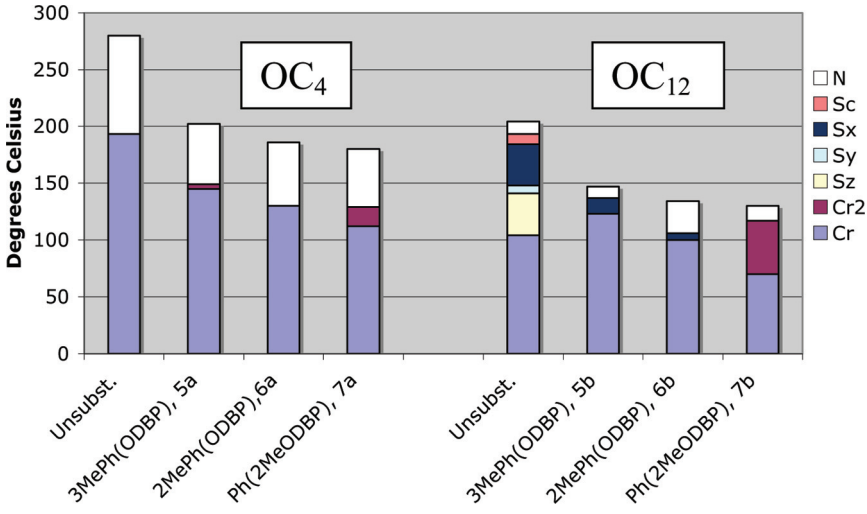


FIGURE 3 A comparision of the phase transition temperatures for all dimethylated ODBP derivatives with those of the unmethylated analogs.

demonstrated compressed nematic ranges (by about 30 degrees) compared to the unmethylated derivative.

When the compounds described here are examined under polarized light, all show a preponderance of 2 brush disclinations. An example of this can be seen in a micrograph for **7a**, OC_4-Ph(2MeODBP) (Fig. 4). Moreover, when attempts were made to generate homeotropically aligned samples, the material remained birefringent. However, neither of these observations is sufficient evidence of biaxiality, and detailed conoscopic studies and ^2H NMR spectroscopy are in progress in an effort to quantitate the degree of biaxiality that might be present.

While the incorporation of two lateral methyl groups was successful in terms of lowering onset temperatures, the nematic onset temperatures remained above 100°C. In an effort to further lower the phase transition temperatures, the related series of tetramethylated compounds, with methyl groups on both the inner and outer benzene rings, was prepared: **8a** OC_4-3MePh(2MeODBP), **8b** OC_{12}-3MePh(2-MeODBP), **9a** OC_4-2MePh(2MeODBP), and **9b** OC_{12}-2MePh(2-MeODBP). While the clearing temperatures are reduced significantly relative to the dimethylated derivatives (Fig. 5), none of these compounds exhibit enantiotropic liquid crystalline behavior.

However, all of these compounds do exhibit complex monotropic mesomorphism. In the case of the OC_{12} derivatives, crystal growth into the liquid crystal phase occurs almost immediately after mesophase formation. With the OC_4 derivatives, rapid cooling appears to

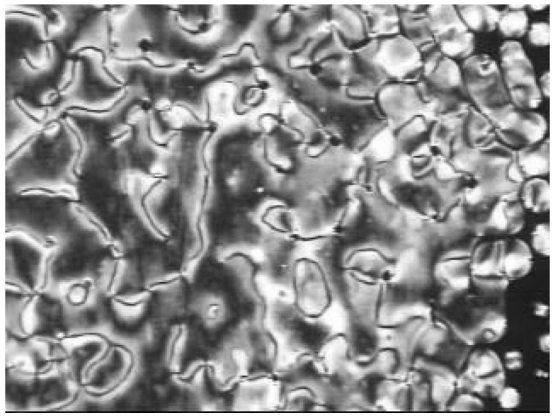


FIGURE 4 Nematic texture of OC_4-Ph(2MeODBP), 179°C, crossed polars, 20X.

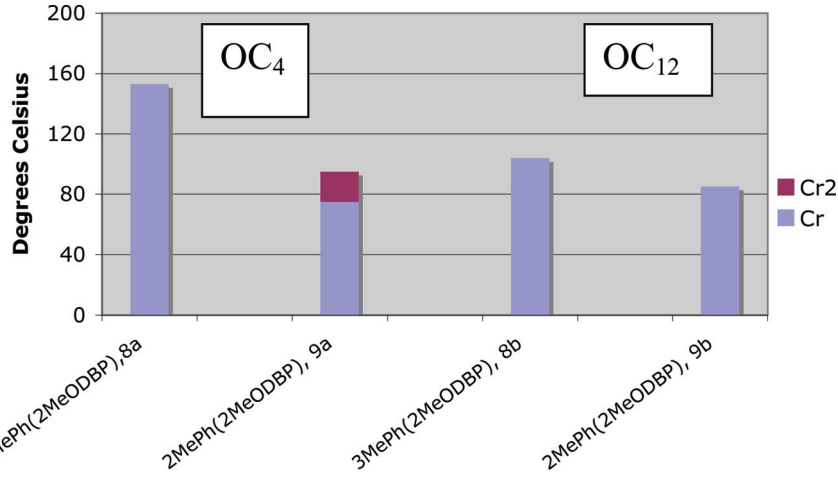


FIGURE 5 Phase transition temperatures of tetramethylated oxadiazole derivatives (All temperatures are from the initial DSC heating run).

lock the mesophase into a glassy state which persists to room temperature. The complex phase behavior of the tetramethylated derivatives is illustrated with the DSC thermograms for OC_4-3MePh(2MeODBP), **8a** (Fig. 6). On the initial heating, the material clears directly to a liquid at 153°C. Upon cooling, a monotropic nematic phase forms at 89°C

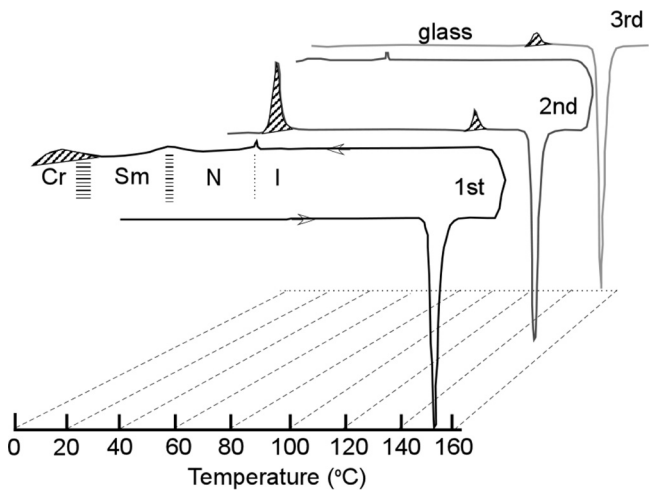


FIGURE 6 DSC thermograms of OC_4-3MePh(2MeODBP), **8a**.

(0.86 kJ/mol). With a cooling rate of 10°/min., a slow transition to a viscous, presumably smectic phase occurs at 58°C. When a sample is examined by polarized light microscopy with slower cooling rates, the formation of crystallites interspersed in the smectic phase is evident. This crystallization is kinetically controlled and tends to be incomplete (crystallization slows as the sample is cooled further). Evidence of this partial crystallization can be seen in the form of a broad exotherm at 19°C during the first DSC cooling trace. If any of the crystallite regions do form on cooling, then during the subsequent heating, the crystallization continues as shown by an exothermic peak at 41°C (24.5 kJ/mol) (2nd trace). This is followed by a second exothermic transition at 127°C (4.65 kJ/mol) to a highly birefringent crystalline state. This new crystal phase persists until the clearing point and is always observed on subsequent heatings. However, if the material is cooled quickly only to room temperature (2nd cooling trace), a glassy smectic phase persists indefinitely. No crystallization occurs, and as can be observed in the 3rd heating trace, the exothermic crystallization peak at 41°C is absent.

SUMMARY

In conclusion, the incorporation of terminal secondary alkoxy chains in the oxadiazole derivatives led to the elimination of liquid crystallinity or dramatic reduction of the nematic phase range. However, inclusion of two lateral methyl groups on the benzene rings in the target compounds led to a substantial reduction in nematic onset temperatures and these derivatives also showed reasonably robust nematic ranges. Attempts to further lower the nematic onset temperature by incorporating four lateral methyl groups were unsuccessful; the tetramethyl compounds melted directly to the isotropic state. Research on the related, asymmetrically methylated derivatives is currently underway.

EXPERIMENTAL

General

All materials were purchased from Sigma-Aldrich or Fisher and used as received. Column chromatography was carried out using Fisher brand Silica gel (230–400 mesh) and fractions were analyzed using Aluminum backed TLC plates with fluorescent indicator purchased from Fluka. The syntheses of 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole [8], 4-(2-butoxy)benzoic acid [11], and 4-isobutyloxybenzoic

acid [12] have been described elsewhere. Nuclear Magnetic Resonance Spectroscopy was carried out using either a Bruker AMX 300 MHz NMR Spectrometer or a Bruker AV 400 MHz Widebore NMR Spectrometer. Chemical Shifts are given relative to TMS and coupling constants are reported in Hz. Thermal analysis was carried out using a Seiko DSC 220 C and a Nikon Microphot-FX polarizing microscope equipped with a Mettler FP82HT Hot Stage and a Mettler Toledo FP90 Central Processor. Video of the microscopy was acquired using a Sony CCD-IRIS color video camera and the video was processed using Roxio Dell Movie Studio software.

4-Butoxy-3-Methylbenzoic Acid, OC_4-2b

4-hydroxy-3-methylbenzoic acid (2.97 g, 19.5 mmol) was dissolved in absolute ethanol (30 mL) and ca. 1 mL sulfuric acid was added. The reaction flask was equipped with a water condenser and heated under reflux for 17 hours. After the reaction flask was cooled, ethanol was removed by rotary evaporation. Water (100 mL) and diethyl ether (50 mL) were added to the residue and this was transferred to a separatory funnel. The organic layer was washed a total of three times with water and the combined aqueous washings were backextracted once with fresh diethyl ether. The combined ether extracts were dried over $MgSO_4$. After filtration and removal of solvent by rotary evaporation, ethyl 4-dodecyloxy-3-methylbenzoate (3.10 g, 88%) was obtained as a white crystalline material and used without further purification.

A slurry of ethyl 4-hydroxy-3-methylbenzoate (1.0 g, 5.55 mmol), iodobutane (1.45 g, 7.88 mmol), and pulverized KOH (0.74 g, 13.1 mmol) was stirred in DMSO (40 mL) for 42 hours. To this mixture was added water (80 mL) and diethyl ether (40 mL). After stirring for 15 minutes, the solution was transferred to a separatory funnel and the organic layer was washed a total of three times with water. The combined aqueous washes were backextracted once with fresh diethyl ether. The combined ether extracts were dried over $MgSO_4$. After filtration and removal of solvent by rotary evaporation, an oily product was obtained. This was hydrolyzed directly by stirring for 18 hours in the presence of 20 mL of 2 M KOH (in ethanol). The solution was poured into water (80 mL) and then acidified with 6 M HCl which led to the formation of a white precipitate. This powder was collected via Buchner filtration and it was then recrystallized using 2:1 ethanol:water to give the acid (0.66 g, 57%) as a fluffy white solid. (Found: C, 69.18; H, 7.82. $C_{12}H_{16}O_3$ requires C, 69.21; H 7.74); δ_H (399.73 MHz; $CDCl_3$; Me_4Si) 7.96 (d, 1H, J = 8.5 Hz, Ar), 7.91 (s, 1H, Ar), 6.86 (d, 1H, J = 8.6 Hz, Ar), 4.06 (t, 2H, J = 6.4 Hz, OCH_2CH_2), 2.27 (s, 3H, CH_3), 1.83 (pentet, 2H, J = 6.5 Hz, OCH_2CH_2), 1.55 (sextet, 2H, J = 7.5 Hz,

TABLE 2 Yields and Elemental Analyses for Compound **2**

Compound	Percent yield	C% calc. (found)	H% calc. (found)
2a-OC$_4$	48	69.21 (69.35)	7.74 (7.78)
2a-OC$_{12}$	58	74.96 (75.00)	10.06 (9.90)
2b-OC$_4$	57	69.21 (69.18)	7.74 (7.82)
2b-OC$_{12}$	31	74.96 (74.83)	10.06 (9.96)

$CH_2CH_2CH_3$), 1.01 (t, 3H, J = 7.4 Hz, CH_2CH_3); δ_C (100.55 MHz; $CDCl_3$; Me_4Si) 172.2, 161.8, 132.5, 130.1, 126.8, 120.6, 109.9, 67.8, 31.2, 19.2, 16.1, 13.8.

All other alkoxybenzoic acids were prepared in the same manner and the yields (from the phenol) and elemental analysis data are compiled in Table 2.

2,5-Bis-(4-Hydroxy-2-Methylphenyl)-1,3,4-Oxadiazole, 3b

To a 100 mL flask equipped with a Claisen adapter was added 4-methoxy-2-methylbenzoic acid (3.00 g, 18.0 mmol). This was placed under an Argon atmosphere and dissolved in 15 mL dry dichloromethane. The flask was placed in an ice bath and 18.1 mL of 2.0 M oxalyl chloride (36.1 mmol) was slowly added. After several minutes, a few drops of dry DMF were added which led to vigorous gas evolution. The reaction mixture was allowed to stir overnight at which point the solvent and excess oxalyl chloride were removed under vacuum. The acid chloride was isolated as a white solid (2.38 g, 71%) and used without further purification.

The acid chloride (2.38 g, 12.9 mmol) was dissolved in 15 mL dry THF and cooled to 0°C. In a different flask, hydrazine hydrate (0.28 mL, 5.81 mmol) and triethylamine (1.62 mL, 11.6 mmol) were dissolved in 15 mL dry THF. The acid chloride solution was slowly added to the hydrazine solution which led to the formation of large amounts of precipitate. The reaction mixture was allowed to stir for 12 hours. Water (100 mL) was added to the reaction flask and the solid product was isolated using Buchner filtration. The filter cake was washed with additional water and then dried under vacuum. The solid was recrystallized from ethanol/acetone to give a bright white powder (1.54 g, 80.6%) δ_H (399.73 MHz; DMSO; Me_4Si) 9.95 (s, 2H), 7.44 (d, 2H), 6.86–6.78 (mult., 4H), 3.76 (s, 6H), 2.40 (s, 6H).

The amide (1.54 g, 4.69 mmol) was placed in a 100 mL round bottom flask equipped with a reflux condenser. Thionyl chloride (17.1 ml, 235 mmol) was added and the reaction was heated at reflux for 3 hours. The hot reaction mixture was poured onto 75 g ice which led

to the formation of an off white precipitate. After the ice had completely melted, the granular solid was isolated by Buchner filtration and washed with 100 mL water. The product (2,5-bis-(4-methoxy-2-methylphenyl)-1,3,4-oxadiazole) was recrystallized from ethanol to give fine, colorless needles (1.24 g, 86%). δ_H (399.73 MHz; DMSO; Me_4Si) 7.96 (d, 2H), 7.04–6.92 (mult., 4H), 3.83 (s, 6H), 2.66 (s, 6H).

2,5-bis-(4-methoxy-2-methylphenyl)-1,3,4-oxadiazole (1.07 g, 3.45 mmol) was added to a 100 mL round bottom flask equipped with a Claisen adapter and the reaction vessel was placed under an Argon atmosphere. Dichloromethane (15 mL) was added and the reaction mixture was cooled to 0°C. BBr_3 (3.02 g, 12.1 mmol) was added dropwise over a period of 15 minutes and the mixture was allowed to stir for 15 hours. The reaction mixture was then poured over 100 g of ice which gave a white precipitate. This solid was collected by Buchner filtration and then washed with additional water. The product was recrystallized from ethanol/acetone to give colorless plates, and used without further purification (0.76 g, 79%). δ_H (399.73 MHz; DMSO; Me_4Si) 10.14 (br. singlet, 2H, OH), 7.84 (d, 2H, J = 9.1 Hz, Ar), 6.80–6.74 (mult., 4H, Ar), 2.57 (s, 6H, CH_3); δ_C (100.55 MHz;$CDCl_3$; Me_4Si) 163.84, 160.36, 157.03, 140.05, 131.11, 118.71, 114.05, 22.24.

2,5-Bis-(4-(4-Butoxy-3-Methylbenzoyloxy)-Phenyl)-1,3,4-Oxadiazole, 5a

A 250 mL two neck round bottom flask was charged with 4-butoxy-3-methylbenzoic acid (0.382 g, 1.84 mmol) and 2,5-bis-(4-hydroxyphenyl)-1,3,4-oxadiazole (0.262 g, 1.03 mmol). The flask was placed under an Argon atmosphere and 35 mL dry dichloromethane was added. Then, 4-(dimethylamino)pyridine (0.063 g, 0.52 mmol) and ethyl dimethylaminopropylcarbodiimide HCl (0.406 g, 2.12 mmol) were added and the reaction was allowed to stir for 2 days at which point, TLC analysis (2:1:1 hexanes:dichloromethane:acetone) showed that the reaction had gone to completion. Additional dichloromethane and 50 mL water were added to the reaction flask. The mixture was stirred vigorously for 10 minutes and then transferred to a separatory funnel. The organic layer was washed twice with water and once with 1 M HCl. The combined aqueous washes were backextracted once with fresh dichloromethane and the combined organic extracts were then dried over $MgSO_4$, filtered, and concentrated by rotary evaporation to give a white solid. The crude product was purified using flash chromatography (3:2:1 hexanes:dichloromethane:ethyl acetate) to give a white solid which was recrystallized from ethanol and a minimal

TABLE 3 Yields and Elemental Analysis Data for the ODBP Derivatives, **4–9**

Compound	Percent yield	C% calc. (found)	H% calc. (found)	N% calc. (found)
4a	77	71.27 (71.38)	5.65 (5.58)	4.62 (4.63)
4b	39	71.27 (71.11)	5.65 (5.57)	4.62 (4.56)
5a	57	71.91 (71.78)	6.03 (6.03)	4.41 (4.44)
5b	89	75.49 (75.26)	8.21 (7.87)	3.26 (3.33)
6a	71	71.91 (71.77)	6.03 (5.89)	4.41 (4.43)
6b	78	75.49 (75.14)	8.21 (8.24)	3.26 (3.16)
7a	76	71.91 (71.58)	6.03 (5.80)	4.41 (4.36)
7b	63	75.49 (75.12)	8.21 (8.13)	3.26 (3.18)
8a	65	72.49 (72.11)	6.39 (6.28)	4.23 (4.17)
8b	60	75.81 (75.43)	8.41 (8.16)	3.16 (3.08)
9a	55	70.56 (70.57)	7.02 (6.63)	3.83 (3.88)
9b	41	75.81 (75.54)	8.41 (8.64)	3.16 (3.08)

amount of chloroform to give the product (0.34 g, 57%). Found (C, 71.78; H, 6.03; N, 4.44. $C_{38}H_{38}N_2O_7$ requires C, 71.91; H, 6.03; N, 4.41); δ_H (399.73 MHz; $CDCl_3$; Me_4Si) 8.24 (d, 4H, J = 8.8 Hz, Ar), 8.07 (d 2H, J = 8.6 Hz, Ar), 8.02 (s, 2H, Ar), 7.43 (d, 4H, J = 8.8 Hz, Ar), 6.92 (d, 2H, J = 8.7 Hz, Ar), 4.10 (t, 4H, J = 6.4 Hz, OCH_2CH_2), 2.31 (s, 6H, CH_3), 1.87 (pentet, 4H, J = 6.9 Hz, OCH_2CH_2), 1.58 (sextet, 4H, J = 7.5 Hz, $CH_2CH_2CH_3$), 1.04 (t, 6H, J = 7.3 Hz, CH_2CH_3). δ_C (100.55 MHz; $CDCl_3$; Me_4Si) 164.2, 164.1, 161.9, 153,8, 132.5, 130.2, 128.3, 127.1, 122.7, 121.2, 120.2, 110.1, 67.9, 31.1, 19.2, 16.2, 13.8.

All other target compounds (**4–9**) were prepared in an analogous manner. Yields and elemental analysis data are shown in Table 3.

REFERENCES

[1] Freiser, M. J. (1970). *Phys. Rev. Lett.*, *24*, 1041.

[2] (a) Hughes, J. R., Kothe, G., Luckhurst, G. R., Malthete, J., Neubert, M. E., Shenouda, I., Timimi, B. A., & Tittlebach, M. (1997). *J. Chem. Phys.*, *107*, 9252–9263; (b) Galerne, Y. (1998). *Mol. Cryst. Liq. Cryst.*, *311*, 211–229.

[3] (a) Leube, H. F. & Finkelmann, H. (1990). *Makromol. Chem.*, *191*, 2707–2715; (b) Severing, K. & Saalwachter, K. (2004). *Phys. Rev. Lett.*, *92*, 124501/1–124501/4.

[4] (a) Madsen, L. A., Dingemans, T. J., Nakata, M., & Samulski, E. T. (2004). *Phys. Rev. Lett.*, *92*, 14505/1–14505/4; (b) Acharya, B. R., Primak, A., & Kumar, S. (2004). *Phys. Rev. Lett.*, *92*, 14506/1–14506/4.

[5] Lee, J.-H., Lim, T.-K., Kim, W.-T., & Jin, J.-L. (2007). *J. Appl. Phys.*, *101*, 034105-1–034105-9.

[6] (a) Yelamaggad, C. V., Prasad, S. K., Nair, G. G., Shashikala, I. S., Rao, D. S. S., Lobo, C. V., & Chandrasekhar, S. (2004). *Angew. Chem. Int. Ed.*, *43*, 3429–3432; (b) Figueirinhas, J. L., Cruz, C., Filip, D., Feio, G., Ribeiro, A. C., Frere, Y., Meyer, T. & Mehl, G. H. (2005). *Phys. Rev. Lett.*, *94*, 107802-1–107802-4; (c) Gortz, V., & Goodby, J. W. (2005). *Chem. Commun.*, 3262–3264; (d) Prasad, V., Kang, S.-W.,

Suresh, K. A., Joshi, L., Wang, Q., & Kumar, S. (2005). *J. Am. Chem. Soc.*, *127*, 17224–17227; (e) Kang, S., Saito, Y., Watanabe, N., Tokita, M., Takanishi, Y., Takezoe, H., & Watanabe, J. (2006). *J. Phys. Chem. B*, *110*, 5205–5214; (f) Apreutesei, D. & Mehl, G. H. (2007). *J. Mater. Chem.*, *17*, 4711–4715; (g) Martin, P. J. & Bruce, D. W. (2007). *Liq. Cryst.*, *34*, 767–774; (h) Dingemans, T. J., Madsen, L. A., Zafiropoulos, N. A., Lin, W., & Samulski, E. T. (2006). *Phil. Trans. R. Soc. A*, *364*, 2681–2696; (i) Lehmann, M., Kang, S.-W., Kohn, C., Haseloh, S., Kolb, U., Schollmeyer, D., Wang, Q. B., & Kumar, S. (2006). *J. Mater. Chem.*, *16*, 4326–4334.

[7] Demus, D. (1998). Chemical structure and mesogenic properties. In: *Handbook of Liquid Crystals, Fundamentals*, Demus, D., Goodby, J., Gray, G. W., Speiss, H.-W., & Vill, V. (Eds.), Wiley, VCH: Weinheim, Vol. 1, Chap. VI, 151–153.

[8] Dingemans, T. J., Murthy, N. S., & Samulski, E. T. (2001). *J. Phys. Chem. B*, *105*, 8845–8860.

[9] Note: the optical purity of the parent (S)-2-butoxybenzoic acid was not tested as the target compound was not liquid crystalline. The assignment of the configuration is based on the fact that it was prepared using the Mitsunobu reaction between ethyl 4-hydroxybenzoate and (R) 2-butanol and the Mitsunobu reaction is known to occur with inversion of configuration. Mitsunobu, O. (1981). *Synthesis*, *1*, 1–28.

[10] (a) Kaspar, M., Hamplova, V., Pakhomov, S. A., Stibor, I., Sverenyak, H., Bubnov, A. M., Glogarova, M., & Vanek, P. (1997). *Liq. Cryst.*, *22*, 557–561; (b) Prajapati, A. K. (2000). *Liq. Cryst.*, *27*, 1017–1020.

[11] Hino, K., Maeda, K., & Okamoto, Y. (2000). *J. Phys. Org. Chem.*, *13*, 361–367.

[12] Pierce, J. S., Salsbury, J. M., & Fredericksen, J. M. (1942). *J. Am. Chem. Soc.*, *64*, 1691–1694.