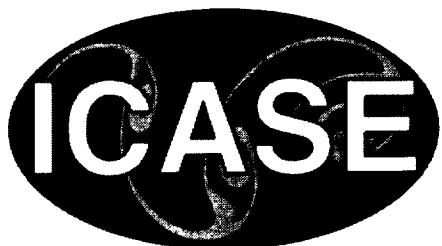


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ICASE Report No. 2002-37



**A Deuterium NMR Study of Bent-core Liquid Crystals
I. Synthesis and Characterization of Deuterium-labeled
Oxadiazole-containing Liquid Crystals**

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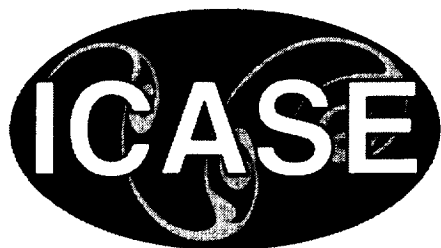
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A DEUTERIUM NMR STUDY OF BENT-CORE LIQUID CRYSTALS I. SYNTHESIS AND CHARACTERIZATION OF DEUTERIUM-LABELED OXADIAZOLE-CONTAINING LIQUID CRYSTALS

THEO J. DINGEMANS^{*}, LOUIS A. MADSEN[§] AND EDWARD T. SAMULSKI[§]

Abstract. We have synthesized two deuterated boomerang-shaped liquid crystals based on 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (ODBP). Deuterium was introduced in the rigid 2,5-diphenyl-1,3,4-oxadiazole core and in the aromatic ring of the terminal 4-dodecyloxyphenyl moiety using standard acid catalyzed deuterium exchange conditions. Both compounds, ([4,4'(1,3,4-oxadiazole-2,5-diyl-*d*₄)] di-4-dodecyloxybenzoate; ODBP-*d*₄-Ph-O-C₁₂) and ([4,4'(1,3,4-oxadiazole-2,5-diyl)] di-4-dodecyloxybenzoate-*d*₄; ODBP-Ph-*d*₄-O-C₁₂) were investigated by nuclear magnetic resonance, optical microscopy and differential scanning calorimetry. The optical textures and thermal behavior of both compounds were found to be identical to the non-deuterated analog [4,4'(1,3,4-oxadiazole-2,5-diyl)] di-4-dodecyloxybenzoate (ODBP-Ph-O-C₁₂) which we reported earlier. These compounds exhibit behavior indicative of a biaxial nematic liquid crystal phase, which we hope to confirm using deuterium NMR spectroscopy in the next phase of this study.

Key words. boomerang-shaped liquid crystals, oxadiazole, deuterated liquid crystals, deuterium NMR

Subject classification. Structures and Materials

1. Introduction. Theoretical predictions with respect to the possible existence of biaxial thermotropic phases date back to the early 70's.[1] Although unambiguously proven in lyotropic systems by Saupe *et al.*[2] in 1980, biaxiality in thermotropic liquid crystals is still a subject of great controversy. Since the molecular prerequisites for biaxial thermotropic systems are not well understood, the search remains largely a challenge for synthetic organic chemists. Many claims with respect to thermotropic systems have been found to be erroneous, mostly due to misinterpretation of textures or because samples under investigation appeared thermally unstable. A good review on the subject of biaxial phases in thermotropic liquid crystals is available in Praefcke *et al.*[3]

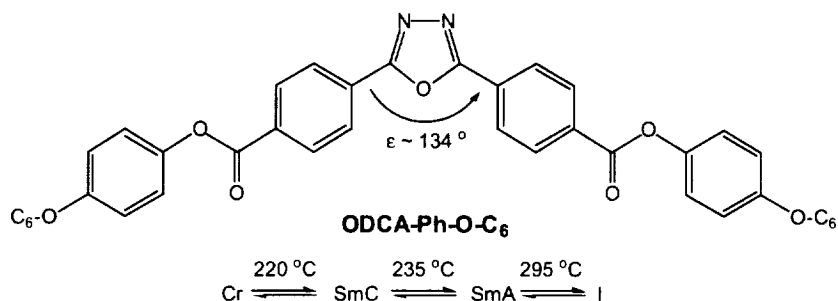
Recently we have published results on a series of boomerang-shaped mesogens derived from 4,4'-(1,3,4-oxadiazole-2,5-diyl)-bisbenzoic acid (ODCA) and 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (ODBP).[4,5] Both ODCA and ODBP based mesogens have a 1,3,4-oxadiazole heterocycle in the center of the rigid core, which results in a non-linear mesogen with a 134° bend, or kink, as shown in Structure I.

Oxadiazole based mesogens form very stable compounds and exhibit a rich variety of mesophases. In ODCA-Ph-O-C₆ (I), we found conoscopic evidence of a biaxial, orthogonal smectic phase. Unfortunately, the high melting temperature of this compound made further characterization such as X-ray diffraction experiments difficult, so we synthesized a new series of lower melting oxadiazole containing mesogens. These new ODBP based mesogens, for example ODBP-Ph-O-C₁₂ (Structure II), melts considerably lower and in this case displays five different mesophases. The supramolecular arrangements of the lower temperature smectic phases denoted SmX, SmY, and SmZ has not been elucidated at this time. Temperature dependent X-ray diffraction experiments performed on these

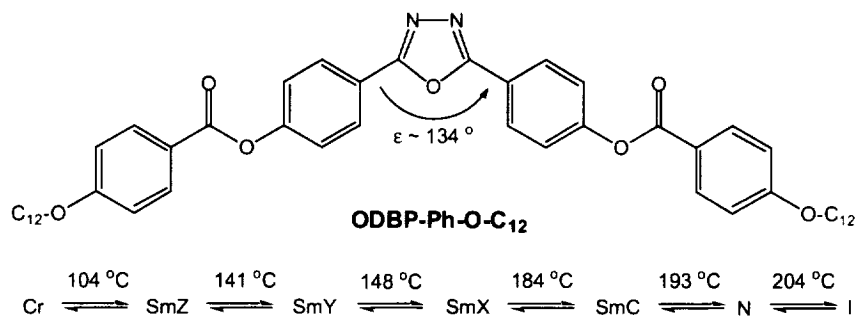
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compounds by Acharya *et al.* confirmed the high temperature N and SmC phase, and they found some evidence that the low temperature SmZ phase may be consistent with a cubic phase.[6] This was corroborated by recent optical microscopy studies.[7] X-ray studies on aligned samples suggest the presence of a biaxial nematic phase in these boomerang shaped liquid crystals.



Structure I

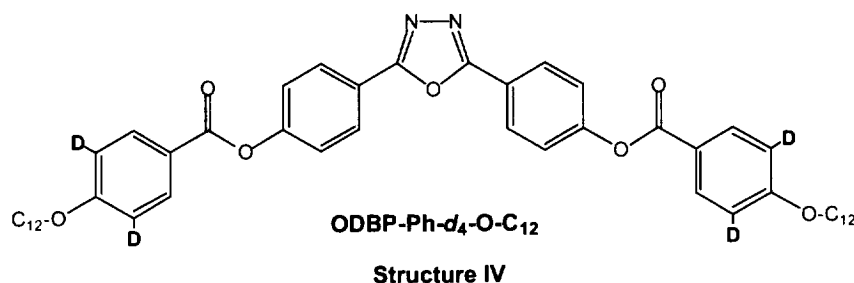
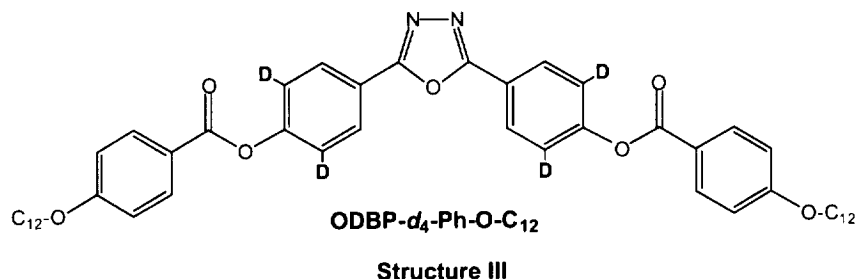


Structure II

In order to unambiguously determine whether biaxial phases exist in these oxadiazole based mesogens, we are undertaking a series of ²H-NMR experiments. Deuterium NMR spectroscopy provides a highly versatile and specific method for studying liquid crystal order and dynamics. Two research groups have developed an experimental method incorporating sample spinning orthogonal to the NMR static field, along with a detailed formalism, to unambiguously study the biaxiality of nematic phases using deuterium quadrupole splittings.[8, 9] Using this method, the symmetry of the partially averaged quadrupole tensor may be determined for liquid crystals with mesogens labeled at one or more chemically distinct sites, such as the deuterium labeled molecules described here. It is possible to observe the phase biaxiality in the 2-D powder spectra that may be obtained by rotating the aligned nematic about an axis perpendicular to the spectrometer magnetic field. A fit to the NMR spectrum of such a rotating sample yields a biaxiality parameter, which provides a measure of the order along an axis normal to the major director, and is analogous to the standard nematic order parameter.

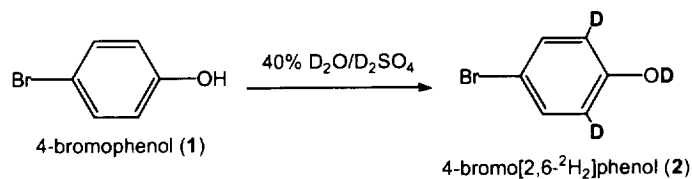
Here we report the synthesis and characterization of two deuterium-labeled oxadiazole-based liquid crystals, that we will study using deuterium NMR. Both mesogens, shown below, are deuterated analogs of our previously reported ODBP-Ph-O-C₁₂ (II) compound.[5] ODBP-*d*₄-Ph-O-C₁₂ (III) has four equivalent deuterons in the central oxadiazole core, and ODBP-Ph-*d*₄-O-C₁₂ (IV) has four equivalent deuterons in the terminal dodecyloxybenzoic acid moiety. The ODBP-Ph-O-C₁₂ mesogens are build around a rigid 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) core. When coupled with 4-

dodecyloxybenzoic acid, the resulting di-ester exhibits a typical boomerang shape with a maximum molecular length of ~ 53 Å. Placing deuterium in the rigid 2,5-diphenyl-1,3,4-oxadiazole core, as in the case of ODBP- d_4 -Ph-O-C₁₂ (**III**), allows us to investigate the molecular dynamics of the central oxadiazole core as a function of temperature, whereas placing deuterium in the terminal 4-dodecyloxybenzoate moiety allows us to study the dynamic behavior of the terminal phenyl rings.



2. Synthetic Approach. In order to label the oxadiazole bent core we initially attempted to exchange the protons *ortho* to the phenol functionality in 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) using deuterated acids and appropriate solvents, unfortunately, without success. Deuterium exchange reactions usually require refluxing the phenolic substrate for 24-48 h. in the presence of strong deuterated acids, which in most cases results in a 90% deuterium-hydrogen exchange *ortho* to the alcohol functionality.[10] It appeared in our case, that the oxadiazole core was not resistant to these harsh conditions, and using dilute acidic conditions did not result in any deuterium exchange.

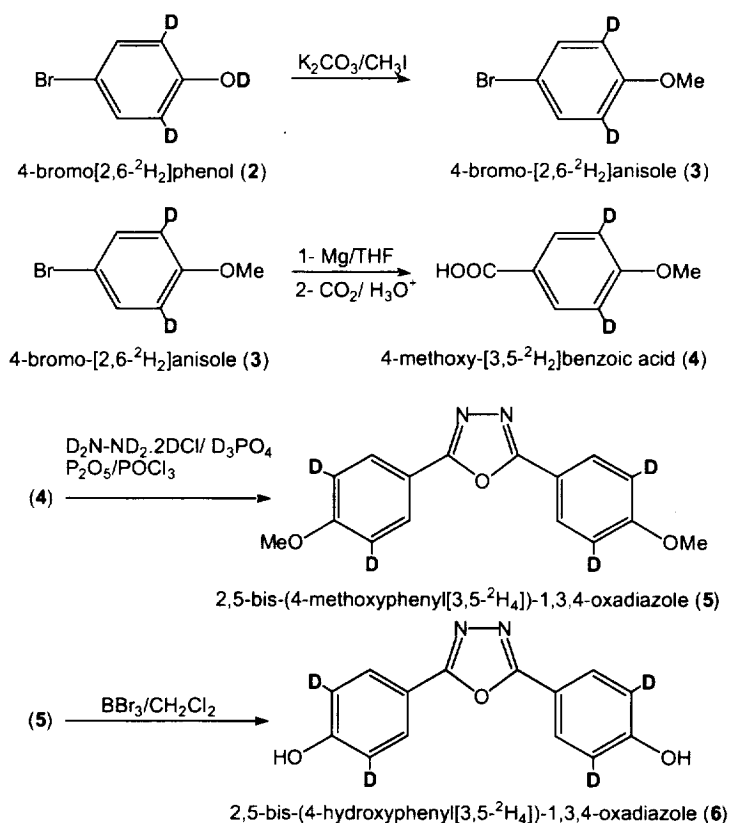
In order to circumvent these problems we choose an alternate route. The synthesis of both ODBP- d_4 -Ph-O-C₁₂ (**III**) and ODBP-Ph- d_4 -O-C₁₂ (**IV**) started with 4-bromo-[2,6-²H₂]phenol (**2**) as the common starting material, which was obtained by refluxing 4-bromophenol (**1**) in 40% D₂O/D₂SO₄ (Scheme 1).[11]



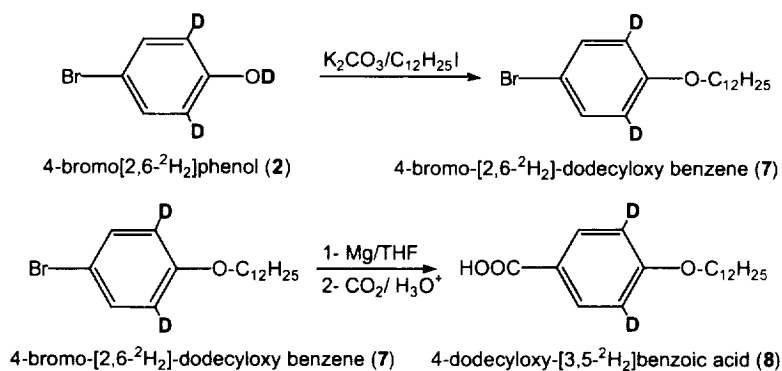
SCHEME 1. Synthesis of 4-bromo[2,6-²H₂]phenol (**2**).

2,5-Bis-(4-hydroxyphenyl)[3,5-²H₄]-1,3,4-oxadiazole (**6**), or ODBP- d_4 , was synthesized as shown in Scheme 2. 4-Bromo-[2,6-²H₂]phenol (**2**) was first protected as its methoxy ether (**3**) using standard etherification conditions. 4-Methoxy-[3,5-²H₂]benzoic acid (**4**) was obtained by quenching the Grignard

reagent of (3) with carbon dioxide. Because the synthesis of symmetrical 2,5-disubstituted 1,3,4-oxadiazoles requires strong acidic conditions, back exchange reactions needed to be minimized. We adopted a novel route towards the synthesis of 2,5-diaryl-1,3,4-oxadiazoles as presented by Bentiss and Lagrenée.[12] 4-Methoxy-[3,5-²H₂]benzoic acid (4) was treated with hydrazine-*d*₄-dideuteriochloride in the presence of orthophosphoric acid (85 wt% in D₂O), phosphoroylchloride, and phosphorus pentoxide to give 2,5-bis-(4-methoxyphenyl-[3,5-²H₄])-1,3,4-oxadiazole (5) in high yields and without back exchange. Treatment with BBr₃ in CH₂Cl₂ gave the desired 2,5-bis-(4-hydroxyphenyl[3,5-²H₄])-1,3,4-oxadiazole (6).



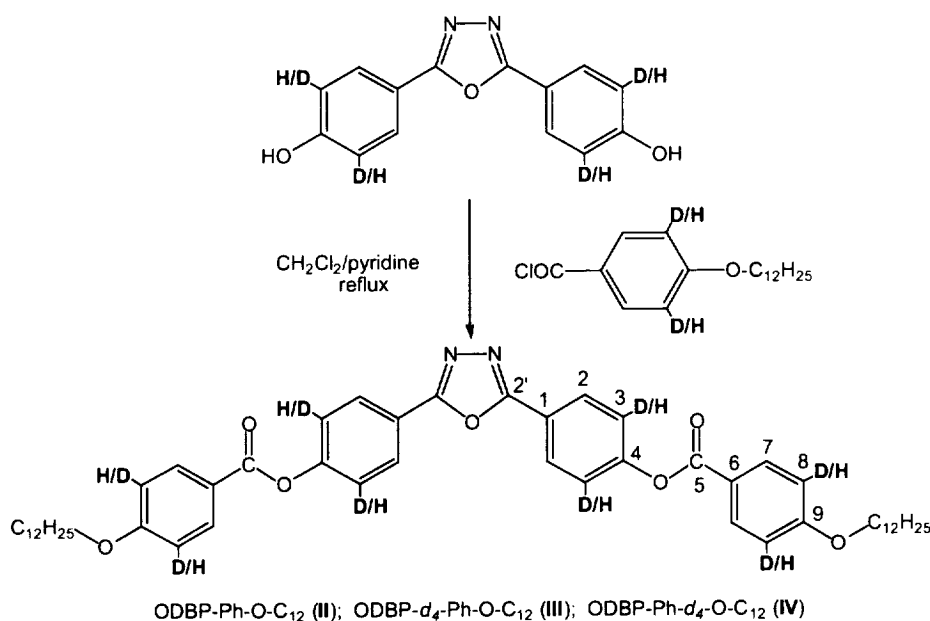
SCHEME 2. Synthesis of 2,5-bis-(4-hydroxyphenyl[3,5-²H₄])-1,3,4-oxadiazole (6).



SCHEME 3. Synthesis of 4-dodecyloxy[3,5-²H₂]benzoic acid (8).

4-Dodecyloxy-[3,5- $^2\text{H}_2$]benzoic acid (**8**) was synthesized in a similar fashion as 4-bromo-[2,6- $^2\text{H}_2$]anisole (**3**). This procedure is summarized in Scheme 3.

All three oxadiazole-based liquid crystals were synthesized using standard esterification techniques as shown in Scheme 4. The appropriate 4-dodecyloxybenzoic acid was converted to its acid chloride using SOCl_2 and subsequently coupled with 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole in the presence of pyridine to obtain ODBP-Ph-O- C_{12} (**II**), ODBP- d_4 -Ph-O- C_{12} (**III**), and ODBP-Ph- d_4 -O- C_{12} (**IV**).



SCHEME 4. Synthesis of the deuterated and non-deuterated oxadiazole based liquid crystals.

3. Results and Discussion. All three oxadiazole based liquid crystals were obtained in good yields. The deuterium labeling appeared successful and back exchange could not be observed during the multi-step synthetic routes. Proton NMR experiments show that both labeled analogs, ODBP- d_4 -Ph-O- C_{12} (**III**), and ODBP-Ph- d_4 -O- C_{12} (**IV**) have deuterium contents of approximately 95%. Figure 1 shows the aromatic region of the NMR spectra of the three liquid crystals. The protons are labeled consistent with the structure shown in Scheme 4. ODBP-Ph-O- C_{12} (**II**), as shown in Figure 1, exhibits four doublets which correspond to the 8-ArH, 3-ArH, 7-ArH, and 2-ArH protons respectively. Labeling of the oxadiazole core in ODBP- d_4 -Ph-O- C_{12} (**III**) results in a 95% reduction of the 3-ArH doublet intensity (7.40 ppm) and the adjacent 2-ArH doublet (8.20 ppm) is reduced to a singlet since the direct spin-spin coupling between 3-ArH and 2-ArH is effectively removed. The same is observed when the terminal phenyl rings are labeled as shown in compound ODBP-Ph- d_4 -O- C_{12} (**IV**). The intensity of the 8-ArH doublet (6.97 ppm) is reduced with 95%, and the adjacent 7-ArH protons (8.14 ppm) show a singlet structure only. Addition proof for the proposed labeled structures can be found in the ^{13}C spectra (section 5.2), where the carbon signals from the C-D bonds result in a triplet, as the C,D coupling is not eliminated by the ^1H broad-band decoupling.

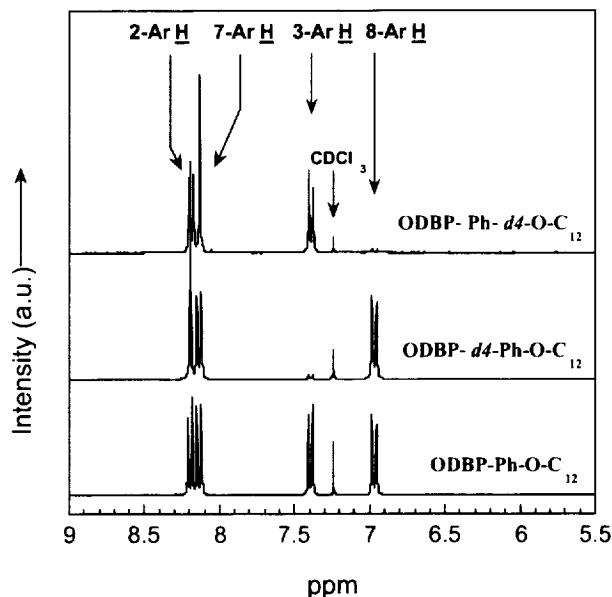


FIG. 1. Proton NMR spectra of the aromatic region of ODBP-Ph-O-C₁₂ (**II**), ODBP-*d*₄-Ph-O-C₁₂ (**III**), and ODBP-Ph-*d*₄-O-C₁₂ (**IV**).

In Table 1 we have summarized the differential scanning calorimetry (DSC) results of ODBP-Ph-O-C₁₂ (**II**), ODBP-*d*₄-Ph-O-C₁₂ (**III**), and ODBP-Ph(*d*₄)-O-C₁₂ (**IV**). All phase transition temperatures and their associated enthalpies are approximately the same, which proves that all three compounds are identical. The only difference we noted is that ODBP-*d*₄-Ph-O-C₁₂ (**III**) crystallizes somewhat faster than ODBP-Ph-O-C₁₂ (**II**) and ODBP-Ph-*d*₄-O-C₁₂ (**IV**).

TABLE 1.
Transition temperatures (°C) and enthalpies (kJ.mol⁻¹) (*Italic*) for the ODBP based liquid crystals.

Compound	Cr	S _z	S _y	S _x	S _c	N	I						
II	•	102.9	•	144.5	•	149.2	•	182.9	•	191.6	•	203.2	•
		<i>(-21.5)</i>		<i>(-0.7)</i>		<i>(-0.7)</i>		<i>(-0.1)</i>		<i>(-4.9)</i>		<i>(-1.0)</i>	
III	•	106.7	•	142.1	•	146.3	•	186.6	•	193.4	•	204.6	•
		<i>(-23.5)</i>		<i>(-0.7)</i>		<i>(-0.7)</i>		<i>(-0.1)</i>		<i>(-5.2)</i>		<i>(-0.8)</i>	
IV	•	104.7	•	136.8	•	141.7	•	182.0	•	189.8	•	201.7	•
		<i>(-25.3)</i>		<i>(-0.7)</i>		<i>(-0.7)</i>		<i>(-0.1)</i>		<i>(-5.1)</i>		<i>(-0.9)</i>	

Figure 2 shows the DSC cooling scans (10 °C/min) for ODBP-Ph-O-C₁₂ (**II**), ODBP-*d*₄-Ph-O-C₁₂ (**III**), and ODBP-Ph-*d*₄-O-C₁₂ (**IV**). All compounds show essentially identical thermograms.

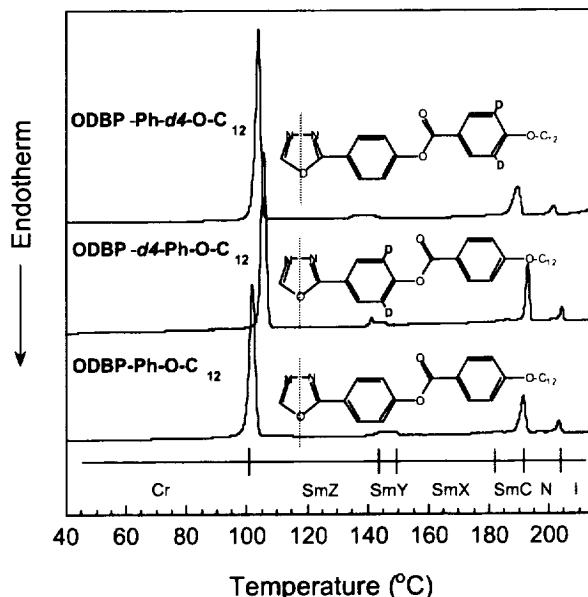


FIG. 2. Second cooling trace ($10\text{ }^{\circ}\text{C}/\text{min}$) of ODBP-Ph-O- C_{12} (II), ODBP- d_4 -Ph-O- C_{12} (III), and ODBP-Ph- d_4 -O- C_{12} (IV).

The melt behavior of the three samples was also investigated using hot-stage polarizing microscopy. All samples show identical mesophase textures, and the textures of ODBP- d_4 -Ph-O- C_{12} (III) are shown in Figure 3.

The textures were observed during cooling ($5\text{ }^{\circ}\text{C}/\text{min}$) from the isotropic phase. Figure 3.1 shows the formation of a nematic Schlieren texture at the I to N transition at $204.6\text{ }^{\circ}\text{C}$. This texture almost immediately transformed into a low viscous, marble type nematic texture as shown in Figure 3.2 at $199\text{ }^{\circ}\text{C}$. When cooling was continued, an unusual finger print type texture could be observed as shown in Figure 3.3, that marked the transition from the N to S_c phase. This texture, which we did not notice before, is only stable over a short ($0.1\text{ }^{\circ}\text{C}$) temperature range and immediately transformed to the S_c texture shown in Figure 3.4. The tilt of the mesogens in the smectic C phase appears to be $\sim 45^{\circ}$ from optical microscopy experiments and increases to $\sim 50^{\circ}$ on cooling into a lower temperature smectic-C-like phase.[7] These optical microscopy conclusions appear to be consonant with the X-ray findings. The lower temperature phases were hard to identify by optical microscopy only, and are therefore preliminary labeled as S_x , S_y and S_z . The texture at $160\text{ }^{\circ}\text{C}$, labeled S_x and shown in Figure 3.5, displays an unusual fan shaped texture consisting of rectangular planes which are separated by bright disclinations. Although the change in texture from S_c to S_x is dramatic, the transition is accompanied by a very low transition enthalpy ($0.1\text{ kJ}\cdot\text{mol}^{-1}$, Table 1) and is indicative of a subtle change in molecular arrangement. At $144\text{ }^{\circ}\text{C}$, this texture changes abruptly into the texture shown in Figure 3.6. This texture labeled S_y , shows similar fan shaped regions, but transverse striations have appeared. Upon cooling, this phase slowly evolves into the S_z phase, shown in Figure 3.7, which is extremely viscous and hard to shear. Although X-ray diffraction experiments seem to indicate the presence of a cubic phase[6], we note that the texture and the highly viscous nature of this mesophase agrees with what has been observed for the rare SmBlue phase, or B_4 phase.[13] Finally, the sample crystallizes at $106\text{ }^{\circ}\text{C}$ and the texture of the crystal phase is shown in Figure 3.8.

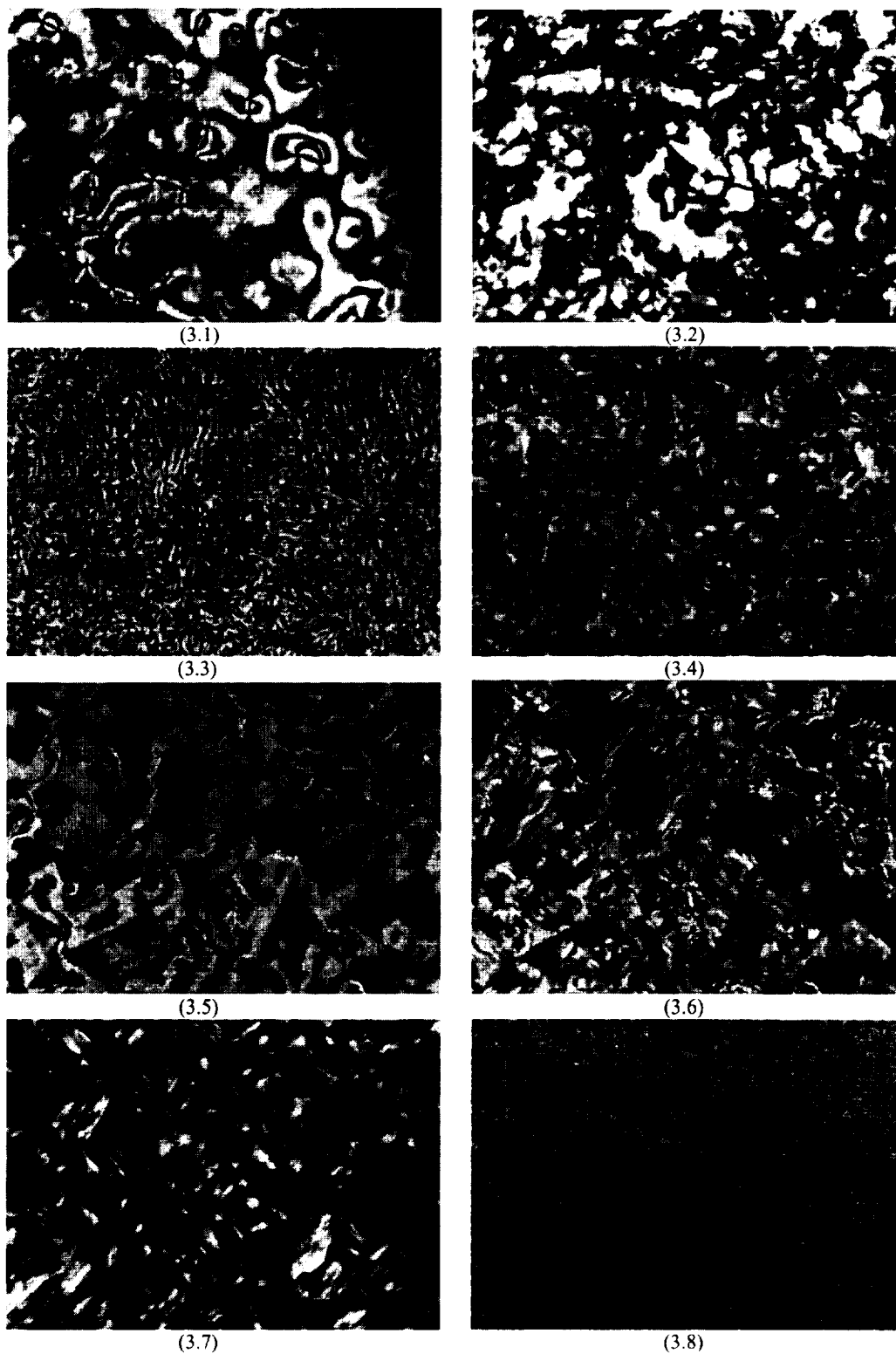


FIG. 3. Mesophase textures of ODBP- d_4 -Ph-O-C₁₂ (III). Microphotograph 3.1 shows the I to N transition at 204.6 °C; 3.2 N at 199 °C; 3.3 N to S_c at 193.4 °C; 3.4 S_c at 190 °C; 3.5 S_x at 160 °C; 3.6 S_y at 144 °C; 3.7 S_z at 130 °C; 3.8 Cr at 100 °C.

4. Conclusions. We have successfully synthesized two deuterium-labeled boomerang-shaped liquid crystals, *i.e.* ODBP-*d*₄-Ph-O-C₁₂ (**III**), and ODBP-Ph-*d*₄-O-C₁₂ (**IV**). Both compounds were synthesized in high yields using standard acid-catalyzed deuterium exchange procedures. The melt and phase behavior of both compounds, as determined by DSC and hot-stage optical microscopy, was identical to its non-deuterated analog, ODBP-Ph-O-C₁₂ (**II**). ¹H-NMR analysis showed that ~95% of the protons at the desired positions were successfully exchanged for deuterium. ODBP-*d*₄-Ph-O-C₁₂ (**III**), and ODBP-Ph-*d*₄-O-C₁₂ (**IV**) are currently under investigation using deuterium NMR spectroscopy.

5. Experimental.

5.1. Materials. All start materials were purchased from Aldrich, and used as received. Dichloromethane and pyridine were dried over, and distilled from CaH₂ before use. Thin-layer chromatography (TLC) was carried out on pre-coated silica gel plates (silica gel 60F 254, layer thickness 0.2 mm, Riedel de Haen). The final products were purified on a 30 cm silica gel column (d=2.5 cm) using silica gel (Merck, grade 60, 230-400 mesh, 60Å).

5.2. Measurements.

5.2.1. Structure determinations. All intermediate and final products were confirmed using ¹H and ¹³C-NMR spectroscopy. The spectra were collected with a Bruker Avance 300 spectrometer (300 MHz), and the infrared spectra were collected using a Nicolet Magna-IR Spectrometer 750. Mass spectra (MS) were obtained using a Waters Integrity MS system; M⁺ representing the molecular ion.

5.2.2. Thermodynamic properties. Transition temperatures were determined using a Perkin Elmer Pyris differential scanning calorimeter, calibrated with indium (99.99%) (mp 156.5 °C, ΔH=28.315 J/g) and tin (99.99%) (mp 232.0 °C, ΔH=54.824 J/g). Both heating and cooling scans were recorded at 10 °C/min. Mesophases were identified with an Olympus BH-2 optical microscope, equipped with a Mettler Toledo FP82H hot stage. Samples were examined between glass microscope cover slides.

5.3. Synthesis.

5.3.1. 4-Bromo-[2,6-²H₂]phenol (2**)** A 150 mL two-neck flask fitted with a reflux condenser and nitrogen inlet was charged with 4-bromophenol (10 g, 58 mmol) and 100 mL D₂SO₄/D₂O (40%). This suspension was refluxed for 2 days and cooled to room temperature. The reaction mixture was extracted with diethyl ether (3 x 50 mL), washed with water (3X), dried over MgSO₄, and concentrated to obtain pure 4-bromo-[2,6-²H₂]phenol (**2**). Yield: 9.4 g (94%); ¹H-NMR (CDCl₃) δ (ppm): 5.45 (s, -OH), 6.71 (d, 2-ArH, *J*=9.2Hz), 7.33 (s, 3-ArH); ¹³C-NMR (CDCl₃) δ (ppm): 113.14 (C4), 117.19 (t, C2), 132.66 (C3), 154.60 (C1).

5.3.2. 4-Bromo-[2,6-²H₂]anisole (3**)** To a solution of 4-bromo-[2,6-²H₂]phenol (**2**) (7.0 g, 40 mmol) in dry acetone (80 mL) was added K₂CO₃ (11.1 g, 80 mmol) and methyl iodide (8.52 g, 60 mmol), and this mixture was refluxed for 12h. The reaction mixture was filtered, and the acetone solution was concentrated. Water (100 mL) was added to the crude product and stirred for 1 h., followed by extraction with hexane (3X). The organic layer was dried over MgSO₄ and concentration gave pure 4-bromo-[2,6-²H₂]anisole (**3**) as a colorless oil. Yield: 6.75 g (89%); TLC (90/10 hexane/ethyl acetate) *t*_r=0.16; ¹H-NMR (CDCl₃) δ (ppm): 3.76 (s, -OMe), 6.77 (d, 2-ArH, *J*=9.4Hz), 7.36 (s, 3-ArH); ¹³C-NMR (CDCl₃) δ (ppm): 55.58 (OCH₃), 112.93 (C4), 115.63 (t, C2), 132.34 (C3), 158.78 (C1).

5.3.3. 4-Methoxy-[3,5-²H₂]benzoic acid (4**)** A 150 mL 2-neck flask equipped with reflux condenser and nitrogen inlet was charged with 4-bromo-[2,6-²H₂]anisole (**3**) (6.0 g, 32 mmol), magnesium turnings (0.83 g, 34 mmol), and dry THF (50 mL). The mixture was gently heated to initiate the reaction. When the reaction started, the reaction mixture was heated at reflux for 2 h. The Grignard

reagent was cooled to room temperature and slowly added to a sludge of dry-ice in dry THF. After complete addition, the mixture was allowed to warm to room temperature, and at 0 °C a 10 % HCl solution was slowly added. 4-Methoxy-[2,6-²H₂]benzoic acid (**4**) was collected by filtration, washed with water, and vacuum dried at 80 °C. Yield: 6.75 g (70%); ¹H-NMR (DMSO-*d*₆) δ (ppm): 3.81 (s, -OMe), 7.00 (d, 3-ArH, *J*=9.2Hz), 7.89 (s, 2-ArH), 12.63 (s, COOH); ¹³C-NMR (DMSO-*d*₆) δ (ppm): 55.43 (OCH₃), 113.56 (t, C3), 122.96 (C1), 131.24 (C2), 162.77 (C4), 167.04 (COOH).

5.3.4. 2,5-Bis-(4-methoxyphenyl)[3,5-²H₄]-1,3,4-oxadiazole (5**)** A 150 mL 2-neck flask equipped with reflux condenser and nitrogen inlet was charged with 4-methoxy-[3,5-²H₂]benzoic acid (**4**) (3.08 g, 20 mmol), hydrazine-*d*₄ dideuteriochloride (1.11 g, 10 mmol), phosphoric acid-*d*₃ (85 wt% in D₂O) (5.4 mL), and P₂O₅ (8.52 g, 60 mmol). To this suspension was slowly added POCl₃ (3.1 g, 20 mmol), and the viscous solution was stirred at 140 °C for 2h. The reaction was cooled to room temperature and slowly poured over crushed ice. The solids were collected by filtration, washed with water, and dried under vacuum at 80°C. Pure 2,5-bis-(4-methoxyphenyl)[3,5-²H₄]-1,3,4-oxadiazole (**5**) was obtained after crystallization from ethanol. Yield: 1.9 g (66%); ¹H-NMR (DMSO-*d*₆) δ (ppm): 3.85 (s, -OMe), 7.15 (d, 3-ArH, *J*=9.2Hz), 8.02 (s, 2-ArH); ¹³C-NMR (DMSO-*d*₆) δ (ppm): 55.53 (OCH₃), 114.88 (t, C3), 115.78 (C1), 128.30 (C2), 161.90 (C4), 163.48 (C2').

5.3.5. 2,5-Bis-(4-hydroxyphenyl)[3,5-²H₄]-1,3,4-oxadiazole (6**)** A 100 mL two-neck flask equipped with reflux condenser and nitrogen inlet was charged with 2,5-bis-(4-methoxyphenyl)[3,5-²H₄]-1,3,4-oxadiazole (**5**) (1 g, 35 mmol) and 20 mL of a 1M solution BBr₃ in CH₂Cl₂. This mixture was stirred at room temperature for 2 hours, after which the solution was heated at reflux for 12 h. When the reaction mixture was cooled to room temperature, the reaction was quenched in 10 mL ice-water and the precipitate was collected by filtration and dried under vacuum at 80 °C. Yield: 0.85 g (93%); TLC (90/10 CH₂Cl₂/THF) *t*_r=0.05; ¹H-NMR (DMSO-*d*₆) δ (ppm): 6.97 (d, 3-ArH, *J*=9.1Hz), 7.93 (s, 2-ArH), 10.29 (s, OH); ¹³C-NMR (DMSO-*d*₆) δ (ppm): 114.29 (C1), 116.16 (t, C3), 128.36 (C2), 160.56 (C4), 163.51 (C2').

5.3.6. 4-Bromo-[2,6-²H₂]dodecyloxy benzene (7**)** To a solution of 4-bromo-[2,6-²H₂]phenol (**2**) (5.0 g, 29 mmol) in dry acetone (50 mL) was added K₂CO₃ (8.0 g, 58 mmol) and 1-iodododecane (10.4 g, 35 mmol), and this mixture was refluxed for 12h. The reaction mixture was filtered, and the acetone solution was concentrated. Water (100 mL) was added to the crude product and stirred for 1 h., followed by extraction with hexane (3X). The organic layer was dried over MgSO₄ and pure 4-bromo-[2,6-²H₂]dodecyloxy benzene (**7**) was obtained after removing the un-reacted start materials by vacuum distillation. Yield: 7.93 g (80%); TLC (90/10 hexane/ethyl acetate) *t*_r=0.31; ¹H-NMR (CDCl₃) δ (ppm): 0.87 (t, ω-CH₃, *J*=6.5Hz), 1.10-1.54 (m, γ-λ-CH₂), 1.75 (q, β-CH₂), 3.89 (t, α-CH₂, *J*=6.6Hz), 6.75 (d, 2-ArH, *J*=9.4Hz), 7.35 (s, 3-ArH); ¹³C-NMR (CDCl₃) δ (ppm): 14.34 (ω-CH₃), 22.91 (λ-CH₂), 26.22 (γ-CH₂), 29.39, 29.58, 29.60, 29.79, 29.82, 29.86, 29.88 (β, δ-ι-CH₂), 32.14 (κ-CH₂), 68.45 (α-CH₂), 112.71 (C4), 116.22 (t, C2), 132.30 (C3), 158.38 (C1).

5.3.7. 4-Dodecyloxy[3,5-²H₂]benzoic acid (8**)** A 100 mL 2-neck flask equipped with reflux condenser and nitrogen inlet was charged with 4-bromo-[2,6-²H₂]dodecyloxy benzene (**7**) (3.43 g, 10 mmol), magnesium turnings (0.27 g, 11 mmol), and dry THF (50 mL). The mixture was gently heated to initiate the reaction. When the reaction started, the reaction mixture was heated at reflux for 3 h. The Grignard reagent was cooled to room temperature and slowly added to a sludge of dry-ice in dry THF. After complete addition, the mixture was allowed to warm to room temperature, and at 0 °C a 15 % HCl solution was slowly added. 4-Dodecyloxy[3,5-²H₂]benzoic acid (**8**) was collected by filtration, washed with water, vacuum dried at 80 °C, and recrystallized from acetone. Yield: 2.75 g (89%); ¹H-NMR (DMSO-*d*₆) δ (ppm): 0.85 (t, ω-CH₃, *J*=6.6Hz), 1.10-1.70 (m, γ-λ-CH₂), 1.73 (q, β-CH₂), 4.01 (t, α-CH₂, *J*=6.6Hz), 6.98 (d, 3-ArH, *J*=9.4Hz), 7.87 (s, 2-ArH), 12.61 (s, COOH); ¹³C-NMR (DMSO-*d*₆) δ (ppm):

13.93 (ω -CH₃), 22.10 (λ -CH₂), 25.42 (γ -CH₂), 28.51, 28.72, 28.98, 29.02(β , δ - τ -CH₂), 31.30 (κ -CH₂), 67.72 (α -CH₂), 114.17 (t, C3), 122.86 (C1), 131.19 (C2), 162.16 (C4), 167.09 (COOH).

5.3.8. Representative procedure for the synthesis of 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole based liquid crystals; 4,4'-(1,3,4-oxadiazole-2,5-diyl)di-4-dodecyloxybenzoate (ODBP-Ph-O-C₁₂; II). A 100 mL flask was charged with 4-dodecyloxybenzoic acid (2.76 g, 9 mmol) and 10 mL SOCl₂. The reaction mixture was heated to reflux for 2 h. and the excess SOCl₂ was removed by distillation. 4-Dodecyloxybenzoyl chloride was diluted with 50 mL dry CH₂Cl₂ and 2,5-bis(4-hydroxyphenyl)-1,3,4-oxadiazole (1.02 g, 4 mmol) was added, followed by dry pyridine (0.6 g, 8 mmol). This mixture was stirred at room temperature for 1 h, and refluxed for 12 h. under a nitrogen atmosphere. The reaction was quenched with 50 mL water, and the CH₂Cl₂ was removed by distillation. The off-white product was collected by filtration, washed with water, and vacuum dried at 80 °C. The crude product was dissolved in a minimum amount of CHCl₃ and chromatographed over silica-gel with CHCl₃/THF (90/10) as eluent. When the solvent was removed, pure 4,4'-(1,3,4-oxadiazole-2,5-diyl)di-4-dodecyloxybenzoate (ODBP-Ph-O-C₁₂; II) was obtained as colorless platelets after one recrystallization from acetone/THF (70/30) at 0 °C. Yield: 2.75 g (83%); TLC (90/10) CHCl₃/THF t_r =0.77; ¹H-NMR (CDCl₃) δ (ppm): 0.87 (t, ω -CH₃, J =6.5Hz), 1.24-1.70 (m, γ - λ -CH₂), 1.81 (q, β -CH₂), 4.04 (t, α -CH₂, J =6.6Hz), 6.97 (d, 8-ArH, J =9.0Hz), 7.40 (d, 3-ArH, J =8.8Hz), 8.14 (d, 7-ArH, J =8.9Hz), 8.20 (d, 2-ArH, J =8.8Hz); ¹³C-NMR (CDCl₃) δ (ppm): 14.35 (ω -CH₃), 22.92 (λ -CH₂), 26.20 (γ -CH₂), 29.31, 29.58, 29.78, 29.81, 29.86, 29.88 (β , δ - τ -CH₂), 32.14 (κ -CH₂), 68.62 (α -CH₂), 114.65 (C8), 121.18 (C6), 121.54 (C1), 122.96 (C3), 128.57 (C2), 132.63 (C7), 154.05 (C4), 164.05 (C9), 164.33 (C2'), 164.65 (C5).

5.3.9. Analytical data for 4,4'-(1,3,4-oxadiazole-2,5-diyl)[3,5-²H₄]di-4-dodecyloxybenzoate (ODBP-d₄-Ph-O-C₁₂; III) Yield: 1.32 g (75%); TLC (90/10) CHCl₃/THF t_r =0.77; ¹H-NMR (CDCl₃) δ (ppm): 0.87 (t, ω -CH₃, J =6.5Hz), 1.24-1.70 (m, γ - λ -CH₂), 1.81 (q, β -CH₂), 4.04 (t, α -CH₂, J =6.6Hz), 6.97 (d, 8-ArH, J =9.0Hz), 7.39 (d, 3-ArH, J =8.8Hz), 8.14 (d, 7-ArH, J =8.9Hz), 8.19 (s, 2-ArH); ¹³C-NMR (CDCl₃) δ (ppm): 14.34 (ω -CH₃), 22.91 (λ -CH₂), 26.19 (γ -CH₂), 29.30, 29.57, 29.78, 29.81, 29.85, 29.87 (β , δ - τ -CH₂), 32.14 (κ -CH₂), 68.61 (α -CH₂), 114.64 (C8), 121.17 (C6), 121.51 (C1), 122.63 (t, C3), 128.44 (C2), 132.63 (C7), 153.94 (C4), 164.04 (C9), 164.32 (C2'), 164.63 (C5).

5.3.10. Analytical data for 4,4'-(1,3,4-oxadiazole-2,5-diyl)di-4-dodecyloxy[3,5-²H₄]benzoate (ODBP-Ph-d₄-O-C₁₂; IV) Yield: 0.77 g (62%); TLC (90/10) CHCl₃/THF t_r =0.77; ¹H-NMR (CDCl₃) δ (ppm): 0.87 (t, ω -CH₃, J =6.5Hz), 1.24-1.70 (m, γ - λ -CH₂), 1.81 (q, β -CH₂), 4.03 (t, α -CH₂, J =6.6Hz), 6.97 (d, 8-ArH, J =9.0Hz), 7.39 (d, 3-ArH, J =8.8Hz), 8.13 (s, 7-ArH), 8.20 (d, 2-ArH, J =8.8Hz); ¹³C-NMR (CDCl₃) δ (ppm): 14.33 (ω -CH₃), 22.90 (λ -CH₂), 26.18 (γ -CH₂), 29.29, 29.56, 29.77, 29.80, 29.84, 29.86 (β , δ - τ -CH₂), 32.12 (κ -CH₂), 68.60 (α -CH₂), 114.60 (t, C8), 121.12 (C6), 121.51 (C1), 122.93 (C3), 128.53 (C2), 132.50 (C7), 154.03 (C4), 163.95 (C9), 164.29 (C2'), 164.61 (C5).

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