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Online publication date: 06 August 2010

To cite this Article Dingemans, Theo J. and Samulski, Edward T.(2000) 'Non-linear boomerang-shaped liquid crystals derived from 2,5-bis(p-hydroxyphenyl)-1,3,4-oxadiazole', Liquid Crystals, 27: 1, 131 — 136

To link to this Article: DOI: 10.1080/026782900203308

URL: http://dx.doi.org/10.1080/026782900203308

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 1, 131–136

Non-linear boomerang-shaped liquid crystals derived from 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole

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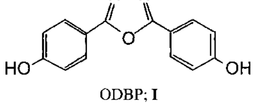
(*Received 17 May 1999; accepted 11 August 1999*)

Boomerang-shaped liquid crystals based on 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) having a ~ 134° bend in the mesogenic cores were synthesized and their properties investigated by optical microscopy and differential scanning calorimetry. Substituting the nonlinear ODBP mesogenic core with *p*-dodecyloxyphenyl tails resulted in a non-linear mesogen that exhibited five distinct mesophases and a clearing temperature of 204°C. The highest temperature phase appears to be nematic followed by a smectic C phase. The latter phase in freely suspended films does not appear to exhibit polar order. The highest temperature phase of 4,4′(1,3,4-Oxadiazole-2,5-diyl) di-*p*-heptylbenzoate shows a schlieren texture with a 2-brush pattern exclusively.

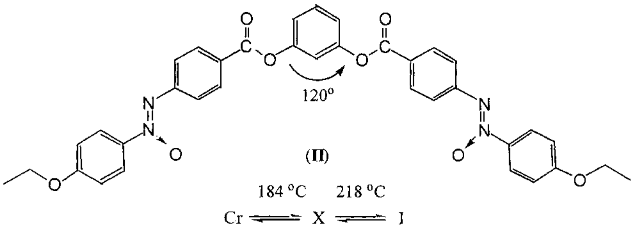
1. Introduction

Herein we report the synthesis, thermal transitions and optical properties of boomerang-shaped calamitic mesogens, nonlinear molecules derived from 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP; **I**). The new liquid crystals (LCs) were prepared by esterifying ODBP. This class of non-linear calamitics possesses a multiplicity of smectic-like phases at readily accessible temperatures. These new materials are examples from the continuing effort to explore the limits of molecular shapes compatible with liquid crystallinity, an endeavour which may be traced to the school of Vorländer. Seventy years ago Vorländer [1] considered non-linear mesogens prepared from a *meta*-substituted benzene, 1,3-bis-[4-(4-ethoxyphenylazoxy)-benzoyloxy]benzene (**II**). The Vorländer mesogen **II** is referred to as 'banana-shaped.' The origin of the non-linear shape is the *meta*-substituted central ring; i.e. the 1,3-benzene substitution pattern of the central ring of **II** has an exocyclic bond angle ε = 120°. The qualifier 'statistically bent' is often used when characterizing the shape of **II** in order to emphasize the inherent flexibility of the ester linkages at its central ring and the associated variability of the core's non-linearity. The average over the mesogen's internal degrees of freedom will result in a statistically non-linear mesogen with an average bend that derives from ε. We use the term 'boomerang-shaped' mesogen to characterize the more rigid and better defined non-linearity in the ODBP core with a larger exocylic bond angle (ε ~ 134°). An informal chronology of the polar attributes of non-linear mesogens may be found in the introduction of a recent paper by Pelzl *et al.* [2], and a tabulation of the types of structures exhibited by such mesogens is given by Diele *et al.* [3].



ODBP; I

Structure **I**



Structure **II**

A decade ago interest in molecular-structure/mesophase-property relationships prompted Cai and Samulski [4] to explore non-linear molecular shape effects in symmetric *para*-substituted phenyl esters of 2,5-thiophene-dicarboxylic acid, a mesogenic core derived from the sulphur-containing heterocycle having ε ~ 148°. Nematic, smectic A (SmA) and smectic C (SmC) phases were observed for mesogens such as **III**. They also reported that while ester homologues derived from 2,5-thiophene dicarboxylic acid were mesomorphic, similar analogues of isophthalic acid (ε = 120°) did not exhibit liquid crystallinity. It was in this same spirit of defining the envelope of viable mesogen geometries that Semmler

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*Author for correspondence.

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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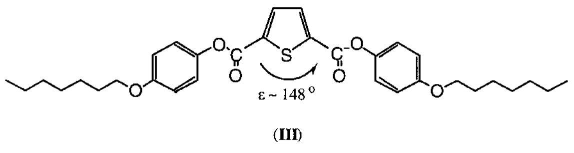
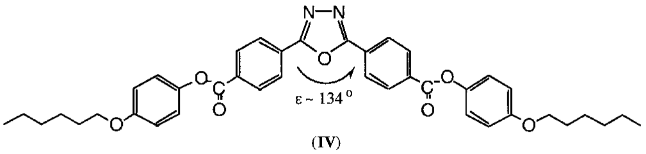


(III)

$$\mathrm{Cr} \xrightleftharpoons{125\,^\circ\mathrm{C}} \mathrm{SmC} \xrightleftharpoons{127\,^\circ\mathrm{C}} \mathrm{N} \xrightleftharpoons{135^\circ\mathrm{C}} \mathrm{I}$$

Structure **III**

et al. considered non-linear molecules having an exocylic bond angle (ε ~ 134°) by utilizing the oxadiazole heterocycle in the mesogenic core [5]. Those mesogens were derived by esterifying 4,4′-(1,3,4-oxadiazole-2,5-diyl)-bisbenzoic acid (ODCA), and conoscopic evidence for a biaxial, orthogonal smectic phase was reported in the 4-hexyloxyphenol ester (**IV**). The latter observation suggests that the (dynamic) packing constraint operative in the ODCA-based LC in its nominally uniaxial SmA phase conspire to order the boomerang shapes rotationally about their molecular long-axis—the horizontal direction in the structure of **IV**—which in turn, is orthogonal to the smectic layers. This biased rotational order transforms the uniaxial SmA phase to an optically biaxial smectic symbolized by the abbreviation SmC [6]. Semmler *et al.* were not able to differentiate between the apolar, biaxial McMillan phase ($\mathrm{SmC_M}$), and a ferroelectric supramolecular structure ($\mathrm{SmC_P}$ phase) having the boomerang's (polar) C_2 axes aligned along a common direction within the smectic layers. A thorough characterization of the biaxial packing in **IV** (e.g. via X-ray diffraction, NMR, etc.) was precluded by the inconveniently high mesophase transition temperatures exhibited by the ODCA mesogen. The transition temperatures of the mesophases reported here make these new ODBP boomerang mesogens candidates for more extensive physical characterization; as a prelude to such characterization we report on their thermodynamic and optical properties.



(IV)

$$\mathrm{Cr} \xrightleftharpoons{220\,^\circ\mathrm{C}} \mathrm{SmC} \xrightleftharpoons{235\,^\circ\mathrm{C}} \mathrm{SmA} \xrightleftharpoons{295\,^\circ\mathrm{C}} \mathrm{I}$$

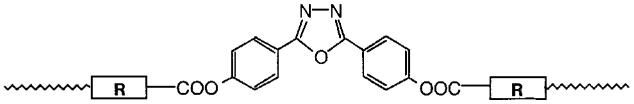
Structure **IV**

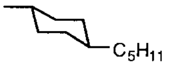
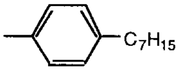
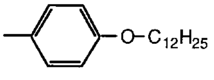
2. Results and discussion

Several boomerang-shaped liquid crystals were synthesized using standard esterification techniques: 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) was coupled with the corresponding acid chlorides in the presence of pyridine to obtain the pure ester compounds 4,4′(1,3,4-oxadiazole-2,5-diyl) di-*trans*-pentylcyclohexane (ODBP-*t*-CH-C_5), 4,4′(1,3,4-oxadiazole-2,5-diyl) di-*p*-heptylbenzoate (ODBP-Ph-C_7), and 4,4′(1,3,4-oxadiazole-2,5-diyl) di-*p*-dodecyloxybenzoate (ODBP-Ph-O-C_{12}) (see the table). The structures of all three compounds were confirmed by mass spectroscopy, proton/carbon nuclear magnetic resonance (^{1}H/^{13}C NMR), and infrared spectroscopy.

The new ODBP-based mesogens reported here differ from the ODCA-materials of Semmler *et al.* simply by the directional sense of the ester linkage in the LC core.

Table. Transition temperatures (°C) and enthalpies (kJ mol^{-1}) (in italic) for the ODBP-based liquid crystals (cooling).



R	Cr		Cr′	SmZ		SmY		SmX		SmC		N		I
 ODBP-*t*-CH-C_5 (**V**)	•	76 *− 9.3*	•								201 − 22.6	?	242 *− 0.6*	•
 ODBP-Ph-C_7 (**VI**)	•	148 *− 25.3*								?	173 *− 10.8*	?	222 *− 0.7*	•
 ODBP-Ph-O-C_{12} (**VII**)	•	104 *− 25.5*		•	141 *− 0.3*	•	148 *− 0.3*	•	184 *− 0.1*	•	193 *− 4.7*	•	204 *− 0.9*	•

But this seemingly innocuous reversal of the carboxyl group sense from ODCA to ODBP has rather dramatic consequences. First, the new ODBP mesogens have transition temperatures significantly lower than those found for ODCA analogues—contrast the thermal properties of **IV** with ODBP-Ph-C$_7$ (entry **VI** in the table). Second we can observe a multiplicity of smectic-like phases in ODBP mesogens having long alkyl 'tails' (see properties of ODBP-Ph-O-C$_{12}$, entry **VII** in the table).

In figure 1 we show the DSC heating and cooling scans for the polymesomorphic ODBP-Ph-O-C$_{12}$ mesogen. Five distinct mesophases for this boomerang are observed. The two high temperature phases appear to be very fluid and are reminiscent of conventional calamitic behaviour. The high temperature phase looks like a nematic and there is preliminary X-ray evidence for smectic C fluctuations therein, i.e. cybotactic behaviour [7]. The diffraction pattern from the penultimate phase is suggestive of a SmC phase and the latent heat associated with the transition between the two highest temperatures phases (4.7 kJ mol^{-1}) is also consonant with a N–SmC transition. The three viscous lower temperature 'smectic' phases are denoted SmX, SmY, and SmZ, as the detailed nature of the supramolecular packing of the ODBP boomerangs in these phases is uncertain at this time.

The mesophase transitions apparent in the DSC traces are accompanied by profound changes in the textures observed with polarizing microscopy. Figure 2 illustrates typical textures observed during cooling ODBP-Ph-O-C$_{12}$ from the isotropic melt. The temperature of the mesophases photographs in figure 2 are indicated by the vertical arrows (labelled 1–6) on the DSC trace in figure 1. The first two textures in figures 2.1 and 2.2 are derived from the nematic and SmC mesophases (arrows labelled 1 and 2, respectively, in figure 1). Both are schlieren textures and appear to respond to mechanical perturbations like conventional calamitic phases [8]. The textures of the three lower temperature mesophases (SmX, SmY, and SmZ) are shown in figures 2.3, 2.4 and 2.5, respectively; SmZ is extremely viscous and is hard to shear. Figure 2.6 shows the texture for the crystalline (Cr) phase of **VII**.

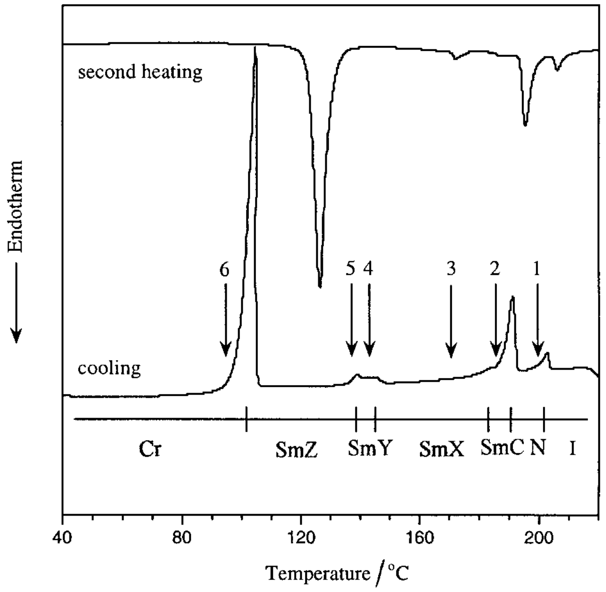


Figure 1. Second heating and cooling trace of ODBP-Ph-O-C$_{12}$ (**VII**). The thermal ranges of the two low viscosity phases tentatively identified as N and SmC and three unidentified smectic-like phases SmX, SmY and SmZ, are indicated.

An examination of the electro-optic response of freely suspended thin films of the smectic-like phases of ODBP-Ph-O-C$_{12}$ by Link [9] suggests that the SmC phase is not ferroelectric, i.e. it is not a SmC$_P$ phase as there was no field response, irrespective of domain layer-number parity. In SSFLC cells the planar-aligned focal conic textures of the SmC phase (with smectic layers aligned locally normal to the cell walls) do not respond to driving fields as high as 25 V/μm. And the brush orientations in the two bistable SSFLC domains suggest that the optic axis is tilted ~45° with respect to the layer normal, accounting for the large in-plane optical anisotropy exhibited by the thin, freely suspended films [9].

The possibility of two nematic phases, the normal uniaxial phase (N) and a biaxial phase (N$_B$) remains an intriguing but as yet an elusive possibility in thermotropics generally. (Earlier claims of N$_B$ phases in low molar mass calamitics have been shown to be in error [10].) The boomerang shape of the ODBP mesogens would make these molecules candidates for a N$_B$ phase. To this end it is worth noting that the high temperature phase of ODBP-Ph-C$_7$, wherein the ODBP core is substituted with *p*-heptylbenzoate 'tails', exhibits a schlieren texture which displays only two-brush patterns under crossed polars (figure 3.1), i.e. the texture has an absence of disclinations of unit strength, $|s| = 1$. Although this kind of texture was suggested by Chandrasekhar *et al.* [11] to be indicative of a biaxial nematic phase, this single characteristic is not sufficient for confirming the N$_B$ phase [8]. (The low viscosity of this phase has thus far prevented us from confirming biaxiality via conoscopy of freely suspended films.) The two-brush texture of ODBP-Ph-C$_7$ is readily observed on the first cooling run, but as the high temperature phase is cooled the two-brush texture appears to break locally into small domains. In figure 3.2 we show the growth of the lower temperature phase into the high temperature phase. The low temperature phase has a dark appearance under crossed polars and does not show a conoscopic interference pattern. As the temperature is lowered further,

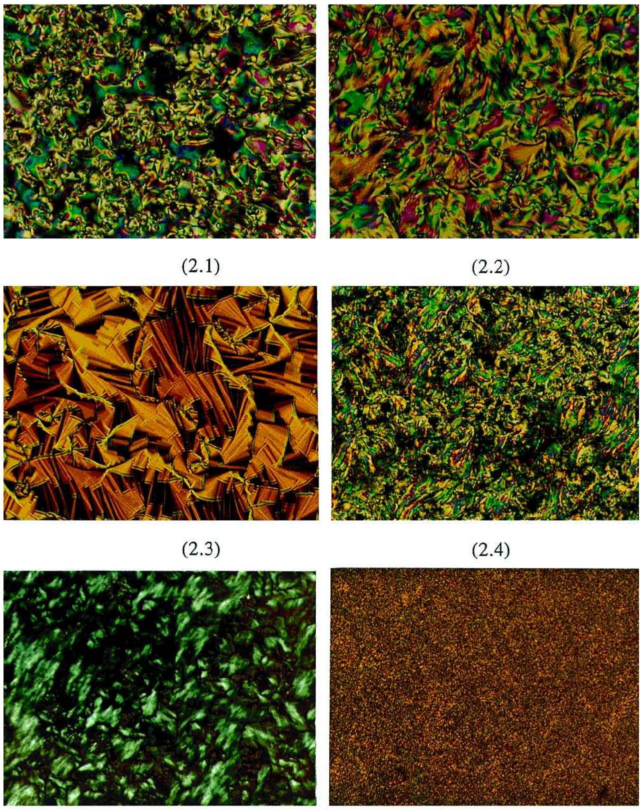
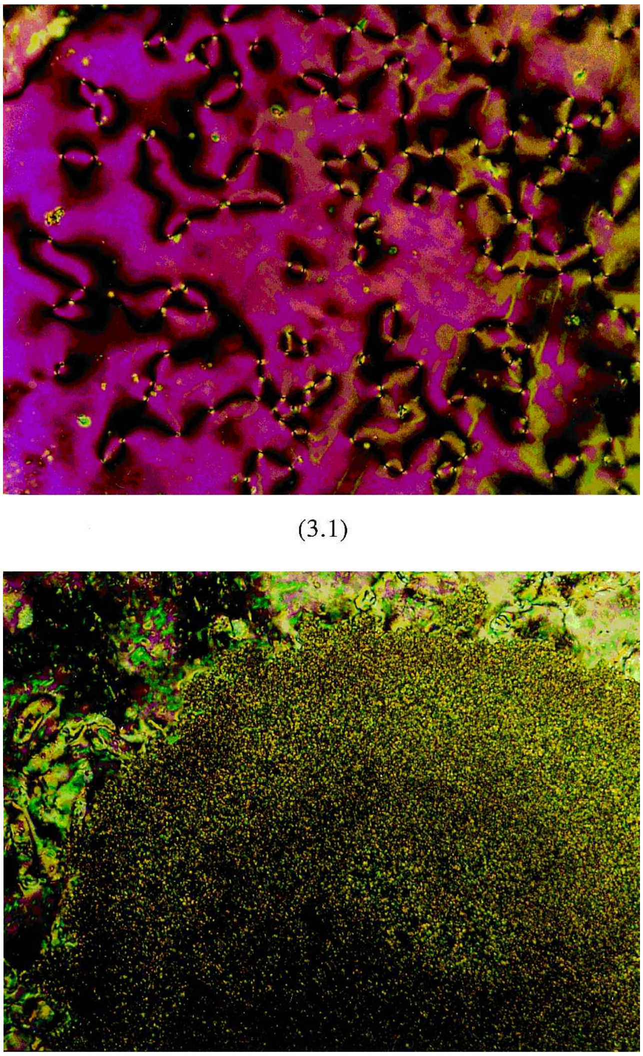

(2.1) (2.2)
(2.3) (2.4)
(2.5) (2.6)

Figure 2. Mesophase textures of ODBP-Ph-O-C_{12} (**VII**). Photomicrograph 2.1 was recorded at 201°C (N); 2.2 at 190°C (SmC); 2.3 at 170°C (SmX); 2.4 at 146°C (SmY); 2.5 at 139°C (SmZ); 2.6 at 95°C (Cr): crossed polars and 20X.

at 150°C, a birefringent Cr phase grows into the dark field of the ODBP-Ph-C_7 intermediate texture. The cyclohexyl derivative of ODBP ODBP-*t*-CH-C_5 (**V**) exhibits only a single mesophase and what appears to be a crystal–crystal transition in its solid state (table, entry **V**).

3. Concluding remarks

Much of the current interest in non-linear mesogens is motivated by the report by Niori *et al.* [12] of ferroelectricity in a smectic phase consisting of the Vorländer banana-shaped mesogen, an achiral molecule. Generally ferroelectricity is a property exclusively associated with smectics formed from chiral molecules, although Brand *et al.* had postulated that spontaneously polar smectics might arise from packing considerations of non-linear mesogens [13]. In subsequent theoretical modelling [14] these workers have, in the context of a general tilted smectic phase, suggested that different packing motifs of non-linear mesogens might lead to a variety of smectic phases distinguished by subtle differences in properties.


(3.1)

(3.2)

Figure 3. Mesophase textures of ODBP-Ph-C_7 (**VI**). Photomicrograph 3.1 at 202°C, two-brush schlieren texture; 3.2 at 177°C, transition from the high temperature phase to the optically dark phase: crossed polars and 20X.

In summary, the 1996 report from Takezoe's laboratory [12] has stimulated a mini-renaissance in experimental studies of nonlinear mesogens and a variety of properties, including chiral supramolecular arrangements fabricated from the achiral banana-shaped mesogens, have been observed [15]. We find evidence of a multiplicity of smectic-like phases in long-tail derivatives of the boomerang core ODBP. More importantly, the transition temperatures of the ODBP mesogens are considerably lower than related ODCA mesogens synthesized earlier [5]. This latter attribute may have practical ramifications as the accessibility of ODBP mesophases at more convenient temperatures provides a route to non-linear LC materials with large dipole moments (e.g. the dipole bisecting the oxadiazole ring in **I** is 3.78 D). Studies of such polar boomerangs should afford a more comprehensive understanding of electro-optic phenomena in liquid crystals consisting of non-linear mesogens.

4. Experimental

4.1. *Materials*

2,5-Bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) was provided by Hoechst Celanese Corporation and used as received. *p*-Heptylbenzoyl chloride, *trans*-pentylcyclohexanebenzoic acid, and *p*-dodecyloxybenzoic acid were purchased from Aldrich, and used as received. Pyridine was dried over, and distilled twice from calcium hydride.

4.2. *Measurements*

4.2.1. *Structure determinations*

The structures of the final products were confirmed by ^{1}H NMR (Bruker WM250, 250 MHz) and ^{13}C NMR (Varian Gemini 2000-300, 75.46 MHz). All of the two-dimensional NMR experiments were carried out with a Bruker Avance 500 spectrometer. Infrared spectra were obtained with a Bio-rad FTS-7 spectrometer and mass spectra were recorded on a Waters Integrity MS system.

4.2.2. *Thermodynamic properties*

Transition temperatures were determined by using a Seiko DSC 120 differential scanning calorimeter, calibrated with indium (99.99%) (m.p. 156.5°C, $\Delta H = 28.315$ J g^{-1}) and tin (99.99%) (m.p. 232.0°C, $\Delta H = 54.824$ J g^{-1}). The second heating (10°C min^{-1}) as well as the cooling scans (10°C min^{-1}) were recorded.

4.2.3. *Optical microscopy*

Optical investigations were performed on a Nikon Microphot-FX polarizing light microscope with orthoscopic and conoscopic equipment. Samples were investigated between glass cover slides.

4.3. *Synthesis*

4.3.1. *Representative procedure for the synthesis of 4,4′(1,3,4-oxadiazole-3,5-diyl) di-trans-pentylcyclohexane benzoate (**V**) (ODBP-t-CH-C$_5$)*

A 100 ml 2-neck flask was charged with 5 mmol of *trans*-4-pentylcyclohexane carboxylic acid, 25 ml of SOCl$_2$, and two drops of dimethylformamide (DMF). This mixture was heated under reflux for 6 h and the excess SOCl$_2$ removed by distillation. Dried pyridine (15 ml), and 2 mmol 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) were added and this mixture heated at reflux overnight. After cooling the reaction mixture to room temperature, 50 ml of water was added and the resulting solids were filtered and washed with an Na$_3$CO$_3$ solution (1M) and excess water. The resulting off-white product was dried under vacuum at 40°C and recrystallized three times from ethanol; an 87% yield of the title compound was obtained. ^{1}H NMR (CDCl$_3$) δ (ppm): 8.13 (d, 3-Ar$\underline{\text{H}}$), 7.24 (d, 4-Ar$\underline{\text{H}}$), 2.49 (tt, α-C$\underline{\text{H}}$), 1.24 (m, δ-C$\underline{\text{H}}$), 1.19 (m, ε-C$\underline{\text{H}}_2$), 1.24 (m, η-C$\underline{\text{H}}_2$), 1.87, 0.97 (dd, dq, γ-C$\underline{\text{H}}_2$), 2.13, 1.55 (dd, dq, β-C$\underline{\text{H}}_2$), 1.27 (m, ξ-C$\underline{\text{H}}_2$), 1.29 (m, ν-C$\underline{\text{H}}_2$), 0.87 (t, ω-C$\underline{\text{H}}_3$). ^{13}C NMR (CDCl$_3$) δ (ppm): 164.03 (C1), 153.58 (C2), 128.27 (C3), 122.46 (C4), 121.22 (C5), 43.64 (α-$\underline{\text{C}}$H), 37.10 (ε-$\underline{\text{C}}$H), 36.87 (δ-$\underline{\text{C}}$H$_2$), 32.13 (η-$\underline{\text{C}}$H$_2$), 32.20 (γ-$\underline{\text{C}}$H$_2$), 28.95 (β-$\underline{\text{C}}$H$_2$), 26.51 (ξ-$\underline{\text{C}}$H$_2$), 22.67 (ν-$\underline{\text{C}}$H$_2$), 14.10 (ω-$\underline{\text{C}}$H$_2$), 174.20 ($\underline{\text{C}}$=O). IR (KBr): v 2923, 2852, 1751 (C=O stretch), 1610, 1491, 1207, 1163, 1129, 1013, 870, 696, 513 cm^{-1}. MS (*m*/*z*): 615 (M +), 435, 254, 181, 153.

4.3.2. *Analytical data for 4,4′(1,3,4-oxadiazole-2,5-diyl) di-p-heptylbenzoate (**VI**) (ODBP-Ph-C$_7$)*

The final product was recrystallized three times from hexane/ethyl acetate (75/25), yield 92%. ^{1}H NMR (CDCl$_3$) δ (ppm): 0.87 (t, ω-C$\underline{\text{H}}_3$), 1.18–1.49 (m, γ, δ, ε, ζ−(C$\underline{\text{H}}$)$_2$−CH$_3$), 1.56–1.71 (m, β-C$\underline{\text{H}}_2$), 2.69 (t, α-C$\underline{\text{H}}_2$), 7.32 (d, 4-Ar$\underline{\text{H}}$), 7.4 (d, 9-Ar$\underline{\text{H}}$), 8.1 (d, 3-Ar$\underline{\text{H}}$), 8.2 (d, 8-Ar$\underline{\text{H}}$). ^{13}C NMR (CDCl$_3$) δ (ppm): 13.96 (ω-$\underline{\text{C}}$H$_3$), 22.52 (ζ-$\underline{\text{C}}$H$_2$), 29.02, 29.11, 31.02 (β, γ, δ-$\underline{\text{C}}$H$_2$), 31.67 (ε-$\underline{\text{C}}$H$_2$), 36.01 (α-$\underline{\text{C}}$H$_2$), 121.5 (C5), 122.8 (C4), 126.5 (C7), 128.4 (C3), 128.8 (C9), 130.4 (C8), 149.9 (C10), 153.8 (C2), 164.2 (C1), 165.4 ($\underline{\text{C}}$=O). IR (KBr): v 2922, 2849, 1724 (C=O stretch), 1597, 1483, 1267, 1200, 1065, 1013, 870, 696, 513 cm^{-1}. MS (*m*/*z*): 658 (M +), 288, 203.

4.3.3. *Analytical data for 4,4′(1,3,4-oxadiazole-2,5-diyl) di-p-dodecyloxybenzoate (**VII**) (ODBP-Ph-O-C$_{12}$)*

The final product was recrystallized three times from acetone/tetrahydrofuran (75/25), yield 79%. ^{1}H NMR (CDCl$_3$) δ (ppm): 0.88 (t, ω-C$\underline{\text{H}}_3$), 1.18–1.53 (m, γ, δ, ε, ζ, η, θ, ι, κ, λ−(C$\underline{\text{H}}$)$_2$−CH$_3$), 1.73–1.88 (m, β-C$\underline{\text{H}}_2$), 4.05 (t, α-C$\underline{\text{H}}_2$), 6.97 (d, 9-Ar$\underline{\text{H}}$), 7.39 (d, 4-Ar$\underline{\text{H}}$), 8.13 (d, 3-Ar$\underline{\text{H}}$), 8.19 (d, 8-Ar$\underline{\text{H}}$). ^{13}C NMR (CDCl$_3$) δ (ppm): 14.09 (ω-$\underline{\text{C}}$H$_3$), 22.65 (λ-$\underline{\text{C}}$H$_2$), 25.94, 29.04, 29.15, 29.21, 29.32, 29.55, 29.61, (δ, ε, ζ, η, θ, ι, κ−$\underline{\text{C}}$H$_2$), 29.77 (γ-$\underline{\text{C}}$H$_2$), 31.88 (β-$\underline{\text{C}}$H$_2$), 68.34 (α-$\underline{\text{C}}$H$_2$), 114.4 (C9), 120.9 (C7), 121.3 (C5), 122.7 (C4), 128.3 (C3), 132.4 (C8), 153.8 (C2), 163.8 (C10), 164.0 (C1), 164.4 ($\underline{\text{C}}$=O). IR (KBr): v 2919, 2851, 1730 (C=O stretch), 1606, 1509, 1490, 1255, 1209, 1171, 1078, 1021, 852, 762, 686, 628 cm^{-1}. MS (*m*/*z*): 355, 289, 251, 166.

We are indebted to a referee who enabled us to place these findings into a more general context. This work was supported by the National Science Foundation Grant DMR-9412701. The authors would like to thank Dr Chi-Duen Poon for performing the two-dimensional

NMR experiments and Drs Darren Link, Noel Clark, and Satyendra Kumar for making unpublished work on the ODBP boomerangs available to us.

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