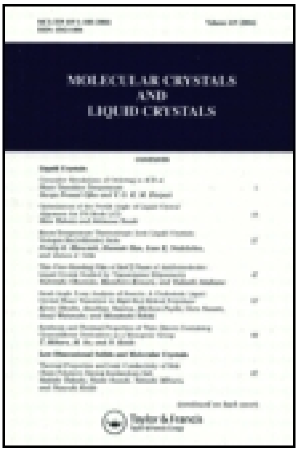

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Hockey Stick Liquid Crystals Based on a 2,5-Asymmetric Disubstituted [1,3,4]Oxadiazole Core

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Hockey Stick Liquid Crystals Based on a 2,5-Asymmetric Disubstituted [1,3,4]Oxadiazole Core

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The article describes the liquid-crystalline properties of some 2,5-asymmetric disubstituted [1,3,4]oxadiazole derivatives containing an azo and an ester linkage obtained through esterification of 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4]oxadiazole with a series of 4-(4-alkoxyphenyl)-benzoic acids containing 6–10 and 18 aliphatic carbon atoms. All reported compounds present liquid-crystalline properties, evidenced by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM), with nematic and smectic C type structures, with very large range of stability of mesophases (between 130°C and 198°C on heating and 134°C and 214°C on cooling).

Keywords asymmetric [1,3,4]oxadiazole; bent-core; hockey stick liquid crystals

Introduction

Discovery of bent-shaped (banana, boomerang, bow) liquid crystals (LCs) opened a very promising area of new mesophases. Despite nonlinear molecules being considered as poor liquid crystals, the synthesis of 1,3-phenylene bis[4-(4-n-octyloxyphenyliminomethyl)benzoate] by Matsunaga and coworkers opened a new era in the field of bent core LCs [1,2]. Since then, many banana-shaped molecules have been synthesized and several reviews have been written [3–7]. As a consequence, the term *banana-shaped mesogens* is used as a synonym for a new field of liquid crystals [8].

The first research in the field of bent-core liquid crystals focused on synthesis and characterization of symmetrical molecules. Their mesomorphic properties were significantly modified by varying the number of aromatic units, lateral substituents of the benzene rings, and types of terminal groups [9–12].

Significant attention was focused on 2,5-disubstituted-[1,3,4]oxadiazole derivatives that contain a symmetric five-membered heterocycle as a central unit. The

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2,5-disubstitution provided a convenient bent shape useful for studying the dependence of the LC properties on the molecular design [13], and several symmetric or asymmetric 2,5-disubstituted-[1,3,4]oxadiazole derivatives have been synthesized [14–18]. The compounds exhibited different types of monotropic or enatiotropic mesophases such as nematic, smectic, or biaxial nematic.

In the last period, a special kind of nonsymmetrical bent-shaped liquid crystal of hockey-stick form was developed, and these compounds are considered at the borderline between bent core and rod-like mesogens [19–22].

The article presents the synthesis, structural characterization, and mesomorphic behavior of a series of hockey-stick-like mesogens based on an [1,3,4]oxadiazole central core and with a strongly nonsymmetrical molecular shape. The new compounds contain five aromatic rings, connected *via* ester and azo groups. One arm of the new mesogens presents three benzene units, with different alkoxy terminal groups, whereas the other one consists of only one 4-methoxy-benzene ring. All synthesized compounds show liquid-crystalline properties. Unexpectedly, taking into account the presence of the azo linking group, the range of stability of mesophases is extremely large (up to 198°C on heating and up to 214°C on cooling). For a better understanding of the liquid-crystalline behavior of the synthesized compounds, molecular simulations were performed using Materials Studio software. The presence of azobenzen moieties can induce photoresponsive properties in the system (due to the capacity to generate *trans-cis* isomerization under ultraviolet-visible [UV–VIS] irradiation) [23].

Experimental

Materials

All reagents, solvents, and starting materials were purchased from Aldrich (Munich, Germany) and Merck (Darmstadt, Germany) and were used without further purification unless otherwise noted. The 4-(4-alkoxyphenylazo)-benzoic acids **(5a-f)** were obtained by adapting literature data [18]. All reactions involving N,N′-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP) were performed in anhydrous dichloromethane, under a dry atmosphere of nitrogen. Silicagel 60 (Merck (Darmstadt, Germany)) was used for column chromatography.

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance DRX 400 MHz spectrometer (Rheinstein, Germany). Chemical shifts were reported in ppm relative to tetramethylsilane (TMS) as internal standard. Infrared (IR) spectra were recorded using a Nicolet (Connecticut, USA) Magna 550 Fourier transform infrared (FTIR) spectrometer (NaCl crystal window). Mass spectra were recorded on a quadrupole time-of-flight mass spectrometer equipped with an electrospray ion source (Agilent 6520 Accurate Mass Q-TOF LC/MS (Santa Clara, CA, USA)). Transition temperatures were determined using a Linkam heating stage and Linksys 32 temperature control unit (Surrey, BC, Canada) in conjunction with a Axioscop 40 Zeiss polarizing optical microscope (Jena, Germany) and Qimaging/Retiga-1000 R camera (Surrey, BC, Canada) for image capture, and the transitions were confirmed by analysis (Mettler-Toledo (Toledo, OH, USA) differential scanning calorimetry (DSC) TGA-SDTA 851e). Heating and cooling cycles were run at rates of 10°C/min under a nitrogen atmosphere, with sample measured in closed-lid aluminum pans. Mesophase type was assigned by visual comparison (under the microscope) with known phase standards.

All thermal analyses were performed on 2.5–4.5 mg samples on a Mettler-Toledo TGA SDTA851^e derivatograph in an N_2 atmosphere, with a flow rate of 20 mL/min and a heating rate of 10°C/min from 25°C to 900°C. In order to obtain comparable data, constant operational parameters were kept for all samples.

The molecular simulations were performed using Materials Studio 4.0. software [24]. The minimum energy conformation was obtained using a molecular mechanics procedure, Forcite module (Dreiding and Compass force fields, alternatively with molecular dynamics, in order to identify the global minimum of the energy value). The dipole moment values corresponding to the oxadiazole derivatives were calculated using the DMol3 module, AM1 method.

Synthesis

4-Methoxybenzoyl Chloride (1). In a round-bottom flask 4-methoxybenzoic acid (10 g, 65.72 mmol) and 200 mL thionyl chloride were refluxed for 1.5 h, after which the thionyl chloride in excess was distillated under vacuum. The acyl chloride was used immediately without purification.

N,N′-bis-(4-Methoxybenzoyl-hydrazine (2). Acid chloride (**1**) was dissolved in 100 mL of anhydrous CH_2Cl_2 and hydrazine hydrate (9.6 mL, 190 mmol) was added using a dropping funnel. After 10 h of refluxing, the reaction mixture was rotary evaporated and the product was purified by recrystallization from methanol. A yellow-white product, yield 5.89 g (60%), was obtained. ^{1}H-NMR δ_H (DMSO): 10.29 (s, 2H, -NH-), 7.90 (d, 4H, Ar), 7.05 (d, 4H, Ar), 3.82 (s, 6H, $-OCH_3$).^{13}C-NMR δ_C (DMSO): 165.39, 161.99, 129.30, 124.78, 113.7, 55.4.

2,5-bis-(4-Methoxyphenyl-[1,3,4]oxadiazole (3). Compound **2** (3 g, 5 mmol) dissolved in 120 mL of anhydrous toluene was heated and stirred at 80°C, $POCl_3$ (10.94 mL, 50 mmol) was added and the mixture was refluxed for 2 h. Reactants conversion was checked by thin-layer chromatography (TLC) (silica gel plates/CH_2Cl_2, the reaction product being strongly fluorescent). After cooling and concentration, the compound was purified by column chromatography (CH_2Cl_2). A white product, yield 2.59 g (74%), was obtained. ^{1}H-NMR δ_H (DMSO): 8.04 (d, 4H, Ar), 7.16 (d, 4H, Ar), 3.85 (s, 6H, $-OCH_3$). ^{13}C-NMR δ_C (DMSO): 163.46, 161.96, 128.40, 115.80, 114.83, 55.52.

2-(4-Methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4]oxadiazole (4). Compound **3** (1 g, 3.54 mmol) and 20 mL HBr (66%) were stirred at 120°C for 30 min under TLC monitoring. The reaction mixture was cooled down and poured into 50 mL H_2O, filtered off, and purified by column chromatography (CH_2Cl_2: ethyl acetate 2:1.2, v/v). A white product, yield 0.52 g (58%), was obtained. ^{1}H-NMR δ_H (DMSO): 10.28 (s, 1H, -OH), 7.97 (d, 4H, Ar), 7.07 (d, 4H, Ar), 3.86 (s, 3H, $-OCH_3$). ^{13}C-NMR δ_C (DMSO): 163.74, 163.49, 161.89, 160.63, 128.54, 128.45, 128.32, 116.13, 114.82, 114.29 (10 C aromatic), 55.51 ($-OCH_3$).

General Method of Esterification

A mixture of 1 equiv. of compound **(4)**, 1 equiv. of aromatic type acid **5,** and a catalytic amount of DMAP, dissolved in dry CH_2Cl_2, was stirred for a few minutes and then 1.1 equiv. of DCC dissolved in dry dichloromethane was added dropwise. The reaction mixture was left under stirring for 24 h at room temperature under an inert atmosphere of nitrogen. After removal by filtration of the dicyclohexylurea (DCU), the solvent was evaporated and the product was purified by column chromatography on silica gel using a mixture of CH_2Cl_2:ethyl acetate = 15:1 as eluent.

5-(4-Methoxyphenyl)-2-(4-hexyloxyphenylazo-4-phenylcarbonyloxy)phenyl-[1,3,4] oxadiazole (6a). Quantities: 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4]oxadiazole (**4**) (0.2 g, 0.746 mmol), 4-(4-hexyloxyphenylazo)-benzoic acid (**5**a) (0.243 g, 0.745 mmol), DCC (0.169 g, 0.819 mmol), DMAP (catalytic), 100 mL dichloromethane. Orange fluffy product, $\eta = 28\%$ (0.12 g), liquid crystal: 148°C (K/LC), 346°C (LC/I), 331°C (I/LC), 117°C (LC/K), ^{1}H-NMR δ_H ppm ($CDCl_3$): 8.32 (d, 2H, Ar), 8.20 (d, 2H, -Ar), 8.07 (d, 2H, Ar), 7.96 (m, 4H, -Ar), 7.43 (d, 2H, Ar), 7.02 (m, 4H, Ar), 4.05 (t, 2H, -O-CH_2), 3.88 (s, 3H, -OCH_3), 1.82 (cv, 2H, -CH_2), 1.49 (cv, 2H, -CH_2), 1.36 (m, 4H, -CH_2), 0.92 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.68 (-C=O esteric), 164.23, 163.58, 162.65, 162.51, 156.12, 153.50, 147.00, 131.31, 129.99, 128.77, 128.30, 125.37, 122.64, 122.56, 121.95, 116.52, 114.94, 114.36, (18 C aromatic), 68.56 (-O-CH_2), 55.49 (OCH_3), 31.58, 29.18, 25.71, 22.60, 14.00 (5 C aliphatic). FTIR (KBr, cm^{-1}): 2929.86, 2866.21 (ν CH, aliphatic), 1734 ($\nu >$C=O), 1604.77 (ν O-C). *m/z* ($CHCl_3$): 576 $[M]^+$.

5-(4-Methoxyphenyl)-2-(4-heptyloxyphenylazo-4-phenylcarbonyloxy)phenyl-[1,3,4] oxadiazole (6b). Quantities: 2-(4-methoxyphenyl)-5-(4-hidroxyphenyl)-[1,3,4] oxadiazole (**4**) (0.2 g, 0.746 mmol), 4-(4-heptyloxyphenylazo) benzoic-acid (5b) (0.253 g, 0.744 mmol), DCC (0.169 g, 0.819 mmol), DMAP (catalytic), 100 mL dichloromethane. Orange fluffy product, $\eta = 34\%$ (0.12 g), liquid crystal: 138°C (K/LC), 293°C (LC/I), 284°C (I/LC), 105°C (LC/K), ^{1}H-NMR δ_H ppm ($CDCl_3$): 8.37 (d, 2H, Ar), 8.24 (d, 2H, -Ar), 8.11 (d, 2H, Ar), 8.01 (m, 4H, -Ar), 7.47 (d, 2H, Ar), 7.06 (m, 4H, Ar), 4.09 (t, 2H, -O-CH_2), 3.92 (s, 3H, -OCH_3), 1.86 (cv, 2H, -CH_2), 1.51 (cv, 2H, -CH_2), 1.36 (m, 6H, -CH_2), 0.93 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.65 (-C=O esteric), 164.26, 163.54, 162.58, 162.43, 156.03, 153.42, 146.88, 131.32, 129.89, 128.75, 128.29, 125.36, 122.62, 122.58, 121.88, 116.40, 114.87, 114.56 (18 C aromatic), 68.49 (-O-CH_2), 55.87 (OCH_3), 31.77, 29.70, 29.17, 25.97, 22.61, 14.08 (6 C aliphatic). FTIR (KBr, cm^{-1}): 2926.01, 2856.57 (ν CH, aliphatic), 1734 ($\nu >$C=O), 1604.77 (ν O-C). *m/z* ($CHCl_3$): 590 $[M]^+$.

5-(4-Methoxyphenyl)-2-(4-octyloxyphenylazo-4-phenylcarbonyloxy)phenyl-[1,3,4] oxadiazole (6c). Quantities: 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4] oxadiazole (**4**) (0.2 g, 0.746 mmol), 4-(4-octyloxyphenylazo)-benzoic acid (**5c**) (0.264 g, 0.745 mmol), DCC (0.169 g, 0.819 mmol), DMAP (catalytic), 100 mL dichloromethane. Orange nacreous product, $\eta = 24\%$ (0.11 g), liquid crystal: 145°C (K/LC), 324°C (LC/I), 321°C (I/LC), 120°C (LC/K), ^{1}H-NMR δ_H ppm ($CDCl_3$): 8.37 (d, 2H, Ar), 8.24 (d, 2H, -Ar), 8.11 (d, 2H, Ar), 8.01 (m, 4H, -Ar), 7.47 (d, 2H, Ar), 7.06 (m, 4H, Ar), 4.09 (t, 2H, -O-CH_2), 3.92 (s, 3H, -OCH_3), 1.86 (cv, 2H, -CH_2), 1.51 (cv, 2H, -CH_2), 1.33 (m, 8H, -CH_2), 0.92 (t, 3H, -CH_3). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.66 (-C=O esteric), 164.26, 163.54, 162.59, 162.43, 156.03, 153.42, 146.88, 131.32, 129.89, 128.75, 128.29, 125.36, 122.62, 122.57, 121.88, 116.40, 114.87, 114.56 (18 C aromatic), 68.50 (-O-CH_2), 55.49 (OCH_3), 31.81, 29.34, 29.33, 29.17, 26.02, 22.66, 14.09 (7 C aliphatic). FTIR (KBr, cm^{-1}): 2926.01, 2854.64 (ν CH, aliphatic), 1734 ($\nu >$C=O), 1612.49 (ν O-C). *m/z* ($CHCl_3$): 604 $[M]^+$.

5-(4-Methoxyphenyl)-2-(4-nonyloxyphenylazo-4-phenylcarbonyloxy)phenyl-[1,3,4] oxadiazole (6d). Quantities: 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4] oxadiazole (**4**) (0.2 g, 0.746 mmol), 4-(4-nonyloxyphenylazo) benzoic acid (**5d**) (0.274 g, 0.746 mmol), DCC (0.169 g, 0.819 mmol), DMAP (catalytic), 100 mL dichloromethane. Orange fluffy product, $\eta = 26\%$ (0.12 g), liquid crystal: 105°C (K/LC), 142°C (LC/LC), 275°C (LC/I), 274°C (I/LC), 112°C (LC/LC), 100°C (LC/K), ^{1}H-NMR δ_H ppm ($CDCl_3$): 8.34 (d, 2H, Ar), 8.22 (d, 2H, -Ar), 8.09 (d, 2H, Ar), 7.98 (m, 4H, -Ar), 7.45 (d, 2H, Ar), 7.04 (m, 4H, Ar), 4.06 (t, 2H, $-O-CH_2$), 3.90 (s, 3H, $-OCH_3$), 1.83 (cv, 2H, $-CH_2$), 1.49 (cv, 2H, $-CH_2$), 1.33 (m, 10H, $-CH_2$), 0.89 (t, 3H, $-CH_3$). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.66 (-C=O esteric), 164.27, 163.55, 162.60, 162.43, 156.04, 153.43, 146.89, 131.32, 129.90, 128.76, 128.30, 125.37, 122.62, 122.58, 121.88, 116.40, 114.88, 114.57 (18 C aromatic), 68.51 ($-O-CH_2$), 55.49 (OCH_3), 31.89, 29.70, 29.53, 29.39, 29.18, 26.01, 22.68, 14.11 (8 C aliphatic). FTIR (KBr, cm^{-1}): 2924.08, 2854.64 (ν CH, aliphatic), 1735.93 ($\nu >$ C=O), 1606.7 (ν O-C). m/z ($CHCl_3$): 618 $[M]^+$.

5-(4-Methoxyphenyl)-2-(4-decyloxyphenylazo-4-phenylcarbonyloxy)phenyl-[1,3,4] oxadiazole (6e). Quantities: 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4] oxadiazole (**4**) (0.2 g, 0.746 mmol), acid 4-(4-decyloxyphenylazo) benzoic (**5d**) (0.285 g, 0.746 mmol), DCC (0.169 g, 0.819 mmol), DMAP (catalytic), 100 mL dichloromethane. Orange fluffy product, $\eta = 42\%$ (0.2 g), liquid crystal: 141°C (K/LC), 313°C (LC/I), 309°C (I/LC), 122°C (LC/K), ^{1}H-NMR δ_H ppm ($CDCl_3$): 8.35 (d, 2H, Ar), 8.22 (d, 2H, -Ar), 8.09 (d, 2H, Ar), 7.98 (m, 4H, -Ar), 7.45 (d, 2H, Ar), 7.04 (m, 4H, Ar), 4.06 (t, 2H, $-O-CH_2$), 3.90 (s, 3H, $-OCH_3$), 1.83 (cv, 2H, $-CH_2$), 1.49 (cv, 2H, $-CH_2$), 1.28 (m, 12H, $-CH_2$), 0.89 (t, 3H, $-CH_3$). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.65 (-C=O esteric), 164.26, 163.54, 162.57, 162.41, 156.01, 153.39, 146.86, 131.31, 129.87, 128.74, 128.29, 125.36, 122.61, 122.57, 121.86, 116.39, 114.86, 114.54 (18 C aromatic), 68.48 ($-O-CH_2$), 55.49 (OCH_3), 31.90, 29.70, 29.55, 29.38, 29.32, 29.17, 26.01, 22.68, 14.12 (9C aliphatic). FTIR (KBr, cm^{-1}): 2920.22, 2850.78 (ν CH, aliphatic), 1735.93 ($\nu >$ C=O), 1606.7 (ν O-C). m/z ($CHCl_3$): 632 $[M]^+$.

*5-(4-Methoxyphenyl)-2-(4-octadecyloxyphenylazo-4-**phenylcarbonyloxy)phenyl-[1,3,4]oxadiazole** (6f).* Quantities: 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4] oxadiazole (4) (0.2 g, 0.746 mmol), acid 4-(4-octadecyloxyphenylazo) benzoic (5d) (0.365 g, 0.745 mmol), DCC (0.169 g, 0.819 mmol), DMAP (catalytic), 100 mL dichloromethane. Light orange nacreous product, $\eta = 20\%$ (0.11 g), liquid crystal: 95°C (K/LC), 137°C (LC/LC), 260°C (LC/I), 258°C (I/LC), 123°C (LC/LC), 77°C (LC/K), ^{1}H-NMR δ_H ppm ($CDCl_3$): 8.34 (d, 2H, Ar), 8.21 (d, 2H, Ar), 8.08 (d, 2H, Ar), 7.87 (m, 4H, Ar), 7.45 (d, 2H, Ar), 7.03 (m, 4H, Ar), 4.06 (t, 2H, $-O-CH_2$), 3.90 (s, 3H, $-OCH_3$), 1.83 (cv, 2H, $-CH_2$), 1.52 (cv, 2H, $-CH_2$), 1.27 (m, 26H, $-CH_2$), 0.88 (t, 3H, $-CH_3$). ^{13}C-NMR δ_C ppm ($CDCl_3$): 164.72 (-C=O esteric), 164.28, 163.62, 162.68, 162.55, 156.18, 153.55, 147.05, 131.34, 130.03, 128.81, 128.34, 125.38, 122.66, 122.58, 122.00, 116.58, 114.98, 114.65 (18 C aromatic), 68.60 ($-O-CH_2$), 55.51 (OCH_3), 31.96, 29.72, 29.68, 29.61, 29.59, 29.53, 29.49, 29.47, 29.40, 29.37, 29.28, 29.24, 29.19, 29.16, 26.05, 22.70, 14.08 (17 C aliphatic). FTIR (KBr, cm^{-1}): 2918.29, 2848.85 (ν CH, aliphatic), 1735.93 ($\nu >$ C=O), 1604.77 (ν O-C). m/z ($CHCl_3$): 742 $[M]^+$.

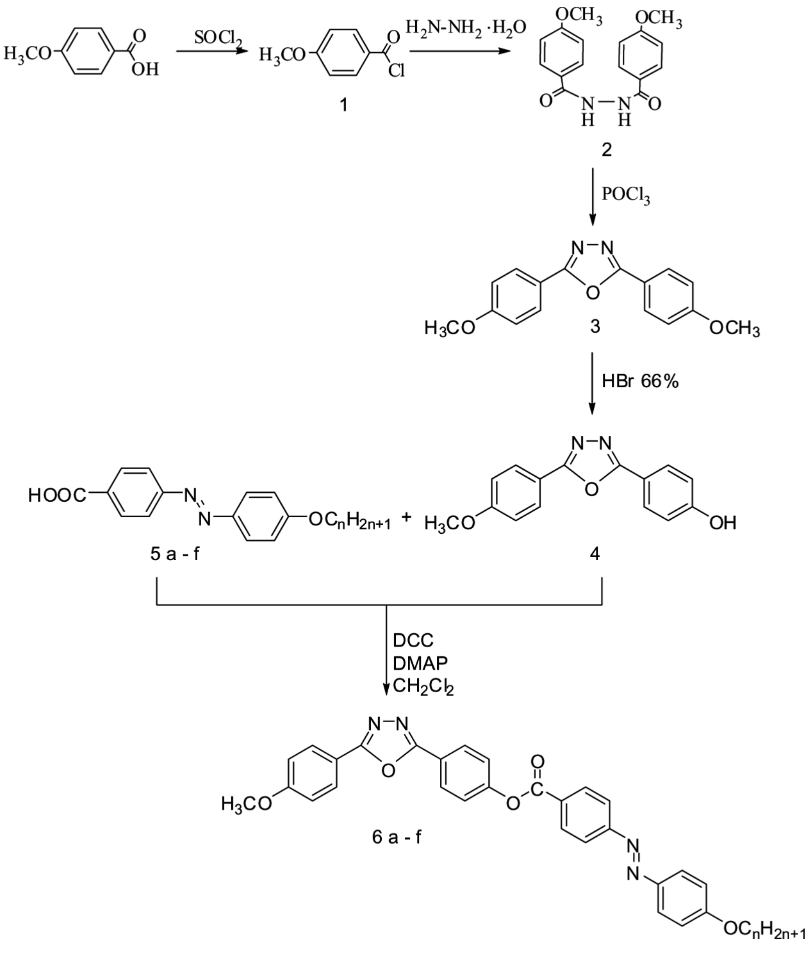
Results and Discussion

Synthesis

The synthetic strategy involved the synthesis of the phenolic asymmetric [1,3,4] oxadiazole core **4** and of the 4-(4-alkoxyphenylazo)-benzoic acids followed by esterification, which provided the final compounds (Scheme 1).

The asymmetric [1,3,4]oxadiazole core was obtained by reacting 4-methoxybenzoyl chloride with hydrazine hydrate in anhydrous dichloromethane to form N,N′-bis-(4-methoxybenzoyl)-hydrazine **2** followed by intramolecular cyclization to form the symmetric 2,5-bis-(4-methoxyphenyl-[1,3,4]oxadiazole **3**. The asymmetric 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4]oxadiazole (**4**) was obtained *via* partial hydrolysis of **3** with 66% HBr (120°C, 30 min). The reaction was monitored by TLC until completion; longer reaction times afforded mainly the symmetric diphenol.

The mesogenic units were obtained through a Williamson reaction by alkylating 4-(4-hydroxyphenylazo)-benzoic acid **5** with alkyl bromides containing 6–10 and 18



Scheme 1. Synthesis of the asymmetric [1,3,4]oxadiazole derivatives: **6a**, n = 6; **6b**, n = 7; **6c**, n = 8; **6d**, n = 9; **6e**, n = 10; **6f**, n = 18.

carbon atoms in KOH alcoholic solution *via* a literature procedure [25]. All (**5a-f**) type compounds exhibited liquid-crystalline properties, evidenced by polarizing optical microscopy (POM) and DSC and confirming the literature data [18].

Esterification of 2-(4-methoxyphenyl)-5-(4-hydroxyphenyl)-[1,3,4] oxadiazole **4** with the 4-(4-alkoxyphenylazo)-benzoic acids (**5a-f**) in the presence of DCC and catalytic quantities of DMAP afforded the final products **6a-f** in 20–42% yield.

Liquid-Crystalline Properties

Investigation of the mesomorphic properties of asymmetric [1,3,4]oxadiazole derivatives **6a-6f** by POM and DSC evidenced enantiotropic liquid-crystalline properties for all compounds.

The asymmetric oxadiazol derivatives exhibited a very large range of mesophases (between 130°C to 198°C on heating and 134°C to 214°C on cooling; Table 1).

Generally, the mesomorphic properties of derivatives **6a-f** were of nematic and smectic C type. Table 2 summarizes the phase transition temperatures of the asymmetric [1,3,4]oxadiazole derivatives **6a-6f**.

All derivatives showed a very good thermal stability, evidenced by thermal analysis studies. Thermogravimetric studies evidenced one or two degradation stages for all **6a-6f** derivatives, the initial temperature at which thermal degradation for the first stage begins (T_{onset}) being situated between 340°C and 360°C (Table 2).

Derivative **6a** containing the smallest number of carbon atoms in the alkyl chain ($n = 6$) showed the largest existence range of the mesophase, both on heating (198°C) and on cooling (214°C), whereas the last compound of the class, **6f** ($n = 18$), showed the smallest one, both on heating (122°C) and on cooling (134°C).

Due to thermostability reasons, in some cases isotropization temperatures were determined only from POM investigations.

Compound **6a** showed the presence of a single phase transition on both heating and cooling cycles: K–LC, LC-I (Figure 1). On heating, compound **6a** presented characteristic nematic Schlieren textures (Figures 1a and 1b) from 148°C up to 346°C when the isotropization occurred.

On cooling, nematic droplets were observed that unified into an extended texture with dark brush Schlieren defects. The nematic domain was clear to about 215°C, when a ribbon-like texture occurred (Figure 1c).

The behavior of compounds **6b**, **6c**, and **6e** are similar to **6a** (Figures 2a and 2b).

Table 1. Range of mesophases corresponding to compounds **6a–6f**

Compounds		Range of mesophases (°C)	
		On heating	On cooling
6a	$n = 6$	148–346	331–117
6b	$n = 7$	138–293	284–105
6c	$n = 8$	145–324	321–120
6d	$n = 9$	142–275	274–112
6e	$n = 10$	141–313	309–122
6f	$n = 18$	137–260	258–123

Table 2. Phase transition temperatures of the asymmetric [1,3,4]oxadiazole derivatives

Compounds		Temperature (°C)/[ΔH] (J/g)						
		K_1/K_2	K_2/LC	LC/I	I/LC	LC/K_2	K_2/K_1	T_{onset}**
6a	n = 6	148 [−66]	—	346* [—]	331* [—]	117 [57]	—	354
6b	n = 7	138 [−27]	—	293* [—]	284* [—]	105 [30]	—	346
6c	n = 8	145 [−48]	—	324* [—]	321* [—]	120 [48]	—	361
6d	n = 9	105 [−18]	142 [−49]	275 [−0.14]	274 [0.06]	112 [40]	100 [1]	351
6e	n = 10	141 [−50]	—	313* [—]	309* [—]	122 [50]	—	360
6f	n = 18	95 [−20]	137 [−37]	260 [−0.28]	258 [0.53]	123 [38]	77 [21]	350

Abbreviations: K, crystal; LC, liquid crystal; I - isotropic.
*Data obtained from POM investigations.
** T_{onse}, temperature at which thermal degradation begins.

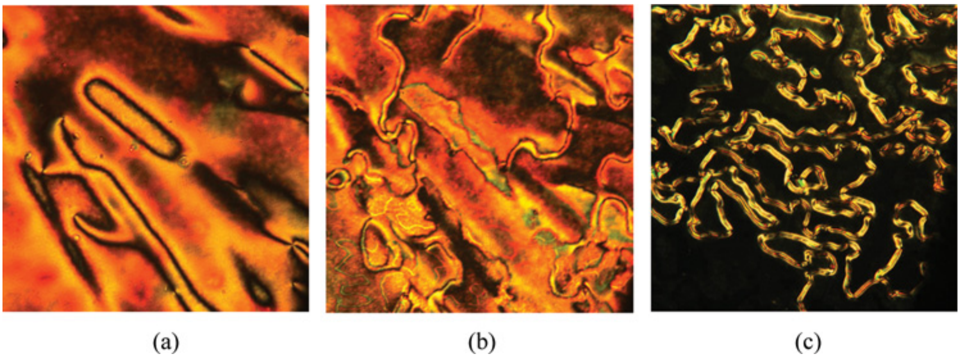

(a) (b) (c)

Figure 1. Optical texture of compound **6a**: (a) 292°C, first heating; (b) 321°C, first cooling; and (c) 215°C, first cooling.

In the case of compound **6e**, DSC curves showed the presence of a single phase transition on both heating and cooling cycles: K-LC and LC-I. Unfortunately, for thermostability reasons, the LC-I/I-LC transitions could not be assigned on DSC heating/cooling curves, but from the microscopy data, the isotropization was observed at 313°C; on cooling the liquid-crystalline ordering started at 309°C and was stable down to 122°C when crystallization occurred.

In the case of compound **6d**, the DSC curves revealed a polymorphism phenomenon both on heating and cooling cycles, due to the reorganization of molecules into a solid state (Figure 3). The nematic mesophase started at 142°C and was stable up to 275°C with specific Schlieren textures (Figure 4).

The mesomorphic behavior of the last compound of the series, **6f**, is different when compared with compounds **6a-e**. This could be explained by the presence of the long aliphatic segment, susceptible to inducing a slight geometric modification in the solid state.

Although the same polymorphism has been observed, on successive heating and cooling cycles, the mesophase texture was different when compared with the other compounds (Figure 5, they are less birefringent and the Schlieren defects suggest a nonpolar smectic C phase).

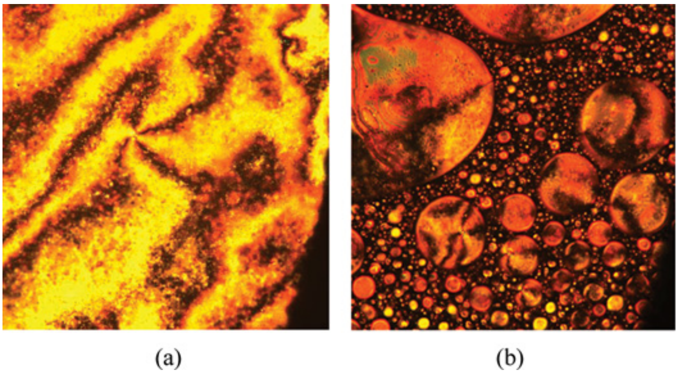

(a) (b)

Figure 2. Optical texture of compound **6b**: (a) 227°C, first heating; and (b) 256°C, first cooling.

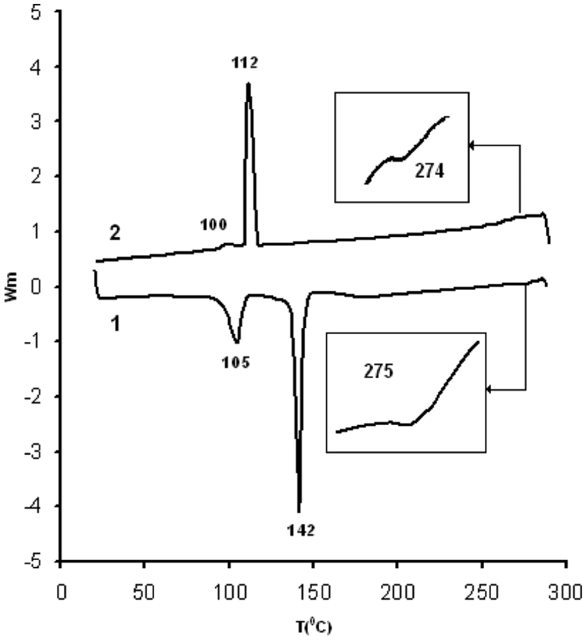


Figure 3. The DSC curves of compound **6d:** 1, first heating, and 2, first cooling, 10°C/min.

The thermal behavior of asymmetric derivatives **6a-6f** varies, both on heating and cooling cycles, as a function of the number of carbon atoms of the alkyl end chain [26], respecting the odd–even effect (Figure 6).

Molecular Modeling Study

For a better understanding of the LC behavior, molecular modeling studies were performed. The geometry of the molecules was described by different parameters,

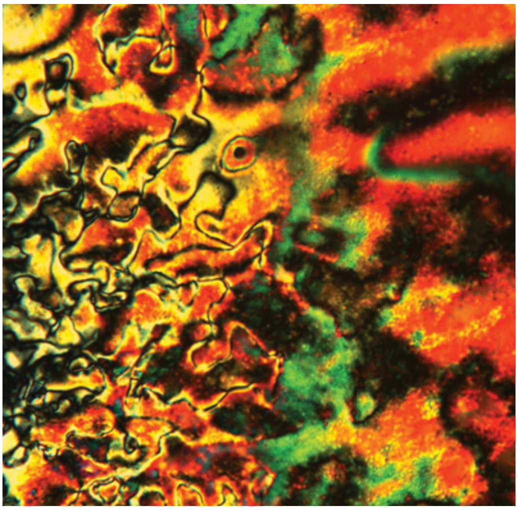


Figure 4. Optical texture of compound **6d** at 255°C, first heating.

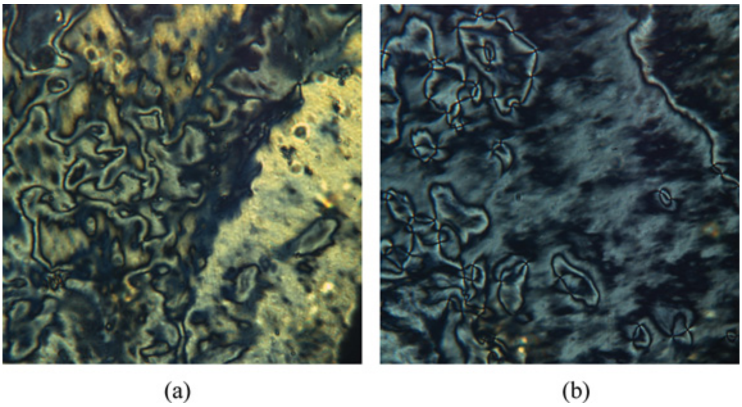


Figure 5. Optical texture of compound **6f**. (a) 192°C, second heating; and (b) 140°C, first cooling.

such as the length of arms (L_{arm}), length between arms (L), diameter (D), and bending angle (ψ); Figure 7).

A first observation is that in the case of the synthesized 2,5-asymmetric disubstituted [1,3,4]oxadiazole derivatives, the molecule curvature is not as pronounced as in the case of a classical banana-shaped LC (Figure 8a). This can explain a better ordering ability, reflected by relatively low values corresponding to the coefficient of asymmetry L/D (Table 3). In the case of compound **6f** one can appreciate that the geometry can be considered almost linear (Figure 8b).

The asymmetric substitution of the oxadiazolic core induces high values of the corresponding dipole moments, situated in the range of 8.4–8.7 D (Table 3). The strong dipolar interactions between molecules can explain the very good stability of the mesophases, which also follows the odd–even effect (Figure 6). We assume that the terminal chains containing an odd number of carbon atoms may generate more disorder in the system and, the because the dipole moment values are similar for all of the synthesized structures, the global effect will be the decreasing of the dipole–dipole interactions.

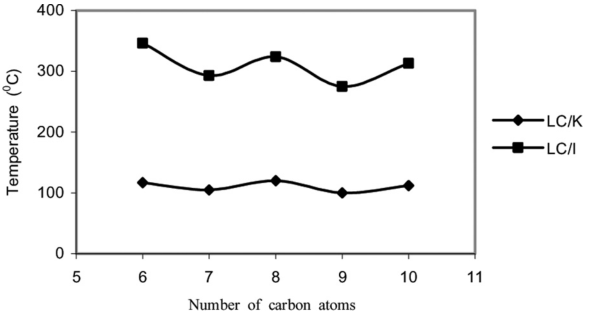


Figure 6. Variation of isotropization and crystallization temperatures as a function of the even–odd number of carbon atoms in the flexible end chain.

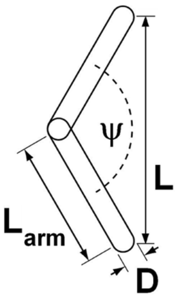
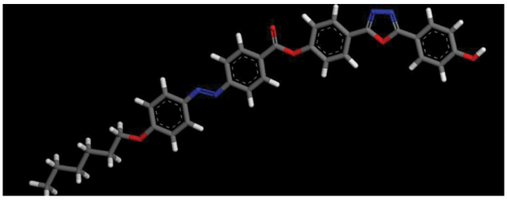
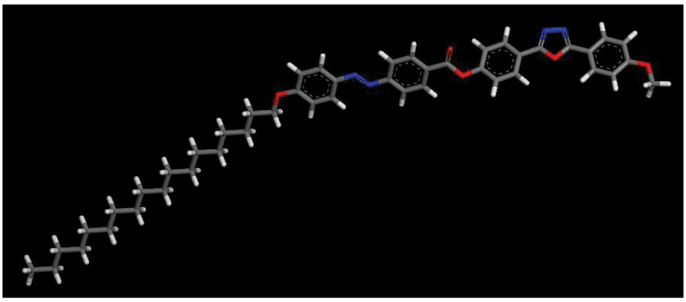


Figure 7. Theoretical model of a banana-shaped molecule.



(a)



(b)

Figure 8. Molecular geometry: (a) compound **6a** and (b) compound **6f**.

Table 3. Geometric characteristics and dipole moments corresponding to compounds **6a-f**

Comp.	Number of carbon atoms	Molecule length (Å)	Diameter (Å)	L/D	Short arm (Å)	Long arm (Å)	Bending angle (°)	Dipole moment (Debye)
6a	6	32.8	6.9	4.7	8.6	26.9	142.1	8.4
6b	7	33.8	7.1	4.8	8.6	28.2	142.3	8.5
6c	8	35.7	7.3	4.9	8.6	29.3	141.0	8.5
6d	9	37.1	7.5	4.9	8.6	30.6	141.2	8.5
6e	10	38.2	7.7	5.0	8.6	31.7	140.0	8.4
6f	18	48.0	8.4	5.7	8.6	41.5	137.1	8.7

Conclusions

The article presents synthesis and structural characterization of some 2,5-asymmetric disubstituted [1,3,4]oxadiazole derivatives containing azo and ester linkages. All of the reported compounds present enantiotropic liquid-crystalline properties, mainly with nematic and smectic C type phase structures, with a very large range of mesophases. The mesophase stability could be explained by the high values of the dipole moment corresponding to the asymmetric substituted derivates. The transition temperatures follow the odd–even effect of the hydrocarbon segment. All compounds show a good thermal stability in the mesophase domain, evidenced by thermal analysis studies.

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