Supplementary information

Synthesis, characterization and mesomorphic behaviors of non-symmetrically substituted 1,2,4- and 1,3,4-oxadiazole derivatives

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2. Experimental section

2.1. Materials and techniques

All the starting materials required for the synthesis were produced from sigma-Aldrich Company and used as received without further purification. **Most the intermediate compounds in this study were prepared according to the procedures in our references [20] and [21] with a few simple modifications.** The structures of all intermediates and more of final products were characterized by spectroscopic methods. FT-IR spectra of solid sample in ATR technique were recorded on Shimadzu 8400S, ¹H NMR spectra were obtained with Bruker spectrophotometer model ultra-shield at 300 MHz using tetramethylsilane (TMS) as interval standard and CDCl₃, DMSO-*d*₆ as solvents. Elemental analysis for carbon, hydrogen and nitrogen were conducted using a Perkin-Elmer model 2400 instrument. Mass spectra of some compounds were recorded on Shimadzu QP1000EX using (SCI) mode. Investigation the liquid crystals properties of the final compounds

were carried out by polarized optical microscopy (POM) model PW-BK 5000 PR equipped with a hot-stage system of HS-400 (KER 3100-08S). Phase transition temperatures were recorded by differential scanning calorimetry (DSC) model Linseis instrument STA PT-1000, Ramp rate: 5 °C/ min. on heating and cooling, temperature and heat flow calibrated with standard indium with heating and cooling rates of 5 °C/min⁻¹.

2.2. Synthesis

2.2.1. Methyl *p*-toluate [A]

This compound was prepared by classical esterification method described by Chiang et al. [22].

Yield (93%); mp: 32-34 °C.

2.2.2. *p*-Toluichydrazide [B]

This compound was prepared according to the method that described by Reddy et al. [23]. Yield (91%); mp: 117-118 °C.

2.2.3. *p*-Butoxybenzoic acid [C]

4-Hydroxybenzoic acid (0.1 mol, 13.8 g) was dissolved in (100 mL) of methanol at 25 °C with stirring. After the acid was dissolved, (0.46 mol, 25.8 g) of potassium hydroxide in (20 mL) of distilled water was added drop wise. The reaction mixture was heated at reflux for 30 min., then (0.12 mol, 16.5 g) of 1-bromobutane was added over 1h and the reaction mixture was refluxed overnight. As the reaction proceeded, potassium bromide precipitated and (50 mL) of methanol from the mixture was removed by evaporation. The remained of reaction mixture was cooled to 25 °C and then added (250 mL) of distilled water then (25 mL) of hexane was added to extract organic impurities, after discarding the organic phase, the aqueous phase was heated near 40 °C and neutralized with 20% HCl. The precipitate product during the neutralization was collected by filtration and purified by recrystallization from ethanol, yield (87%); mp: 140-145 °C; FT-IR (ATR, cm⁻¹), ν_{max} : (3100-2551, broad O-H), (2953, 2872, C-H aliph.), (1674, C=O); elemental

analysis: calculated for $C_{11}H_{14}O_3$ (194.23 g/mol): C 68.02, H 7.27, O 24.71., found C 68.12, H 7.54, O 24.99

2.2.4. 2-(4-Butoxyphenyl)-5-(p-tolyl)-1,3,4-oxadiazole [D]

Compound B (0.01 mol, 1.5 g) and compound C (0.01 mol, 1.94 g) were refluxed with phosphorous oxychloride (5 mL) overnight and the reaction mixture was treated with cold water carefully and made basic by adding concentrated $NaHCO_3$ solution. The resulting product was filtered, washed with water, dried and recrystallized from ethanol. Yield (81%); mp: 94-95 °C, lit 95-96 °C [31]; FT-IR (ATR, cm^{-1}), ν_{max} : (2953, 2872, C-H aliph.), (1608, C=N), (1249, 1172, C-O-C sym. and asym.); 1H NMR ($CDCl_3$), δ , ppm: 8.04-8.07 (d, 2H, Ar-H attached to butoxy group, $J = 8.7$ Hz), 8.00-8.02 (d, 2H, Ar-H attached to methyl group, $J = 8.3$ Hz), 7.31-7.34 (d, 2H, Ar-H attached to methyl group, $J = 8.3$ Hz), 7.00-7.03 (d, 2H, Ar-H attached to butoxy group, $J = 8.7$ Hz), 4.02-4.07 (t, 2H, OCH_2), 2.44 (s, 3H, CH_3), 1.79-1.83 (m, 2H, CH_2), 1.45-1.49 (m, 2H, CH_2), 0.97-1.02 (t, 3H, CH_3); MS (SCI) (relative intensity %): $m/z = 308$ (M^+ , 100%); elemental analysis: calculated for $C_{19}H_{20}N_2O_2$ (308.37 g/mol): C 74.00, H 6.54, N 9.08., found C 74.11, H 6.61, N 9.17.

2.2.5. 4-(5-(4-Butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoic acid [E]

Potassium permanganate (0.02 mol, 3.33g) in (10 mL) water was added dropwise to a stirred solution of compound D (0.0025 mol, 0.77 g) in (20 mL) pyridine at 70 °C. The mixture was then heated under reflux overnight, then (25 mL) of water was added to the mixture and the hot solution was filtered, the acid [E] was precipitated by acidification the filtrate with (2 M HCl), the product was filtered, washed with water and dried at 100 °C. Yield (79%); mp: 259-260 °C; FT-IR (ATR, cm^{-1}), ν_{max} : (3100-2546, broad O-H), (2956, 2874, C-H aliph.), (1691, C=O), (1610, C=N), (1251, 1174, C-O-C sym. and asym.); 1H NMR ($DMSO-d_6$), δ , ppm: 13.35-13.48

(s, 1H, br., COOH), 8.19-8.22 (d, 2H, Ar-H attached to carboxy group, $J = 9.0$), 8.14-8.16 (d, 2H, Ar-H attached to butoxy group, $J = 6.1$), 8.04-8.07 (d, 2H, Ar-H, $J = 9.0$), 7.15-7.17 (d, 2H, Ar-H, $J = 6.0$), 4.06-4.11 (t, 2H, CH₂O), 1.72-1.77 (m, 2H, CH₂), 1.44-1.48 (m, 2H, CH₂), 0.95-0.99 (t, 3H, CH₃).; MS (SCI) (relative intensity %): $m/z = 338$ (M^+ , 100%); elemental analysis: calculated for C₁₉H₁₈N₂O₄ (338.36 g/mol): C 67.44, H 5.36, N 8.28., found C 67.48, H 5.35, N 8.32.

2.2.6. Alkyl- 4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F_I - F_{II}].

A mixture of compound E (0.0005 mol, 0.17 g), **n-alkyl alcohol** (0.0005 mol), N,N'-dicyclohexylcarbodiimide (DCC) (0.00054 mol, 0.11 g), 4-dimethylaminopyridine (DMAP) (0.0005 mol, 0.06 g) in dry dichloromethane (DCM) (20 mL) was stirred for 7 days at room temperature. The precipitated filtered off and filtrate dilute with DCM (10 mL). The resulted solution was washed with 5% acetic acid (10 mL) and twice with water (25 mL) then evaporated the solvent. The resulting solid was recrystallized from ethanol and dried to obtain the ester.

2.2.6.1. Methyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F_I].

Yield (59%); mp: 143-145 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2855, C-H aliph.), (1720, C=O), (1608, C=N); MS (SCI) (relative intensity %): $m/z = 352$ (M^+ , 100%); elemental analysis: calculated for C₂₀H₂₀N₂O₄ (352.38 g/mol): C 68.17, H 5.72, N 7.95., found C 68.26, H 5.78, N 8.01.

2.2.6.2. Ethyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F_2].

Yield (61%); mp: 114-116 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2870, C-H aliph.), (1720, C=O), (1606, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.21-8.24 (d, 2H, Ar-H attached to ether linkage, $J = 9.11$), 8.09-8.11 (d, 2H, Ar-H attached to ester linkage, $J = 6.10$), 7.24-7.27 (d, 2H, Ar-H attached to ether linkage, $J = 9.13$), 7.07-7.09 (d, 2H, Ar-H, $J = 6.11$), 4.41-4.48 (t, 2H, CH₂O),

4.05-4.09 (t, 2H, CH₂O), 1.78-1.85 (m, 2H, CH₂), 1.50-1.58 (m, 2H, CH₂), 1.44-1.48 (t, 3H, CH₃), 0.98-1.04 (t, 3H, CH₃); elemental analysis: calculated for C₂₁H₂₂N₂O₄ (366.16 g/mol): C 68.84, H 6.05, N 7.65., found C 68.92, H 6.15, N 7.71.

2.2.6.3. Propyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₃].

Yield (60%); mp: 131-133 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2958, 2874, C-H aliph.), (1720, C=O), (1608, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.22-8.25 (d, 2H, Ar-H attached to ether linkage, J = 9.14), 8.12-8.10 (d, 2H, Ar-H attached to ester linkage, J = 6.16), 7.25-7.28 (d, 2H, Ar-H attached to ether linkage, J = 9.12), 7.05-7.08 (d, 2H, Ar-H, J = 6.13), 4.31-4.36 (t, 2H, CH₂O), 4.04-4.08 (t, 2H, CH₂O), 1.78-1.87 (m, 4H, 2×CH₂), 1.50-1.55 (m, 2H, CH₂), 1.05-1.08 (t, 3H, CH₃), 0.96-1.03 (t, 3H, CH₃); elemental analysis: calculated for C₂₂H₂₄N₂O₄ (380.17 g/mol): C 69.46, H 6.36, N 7.36., found C 69.55, H 6.41, N 7.43.

2.2.6.4. Butyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₄].

Yield (64%); mp: 125-127 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2956, 2872, C-H aliph.), (1718, C=O), (1608, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.19-8.21 (d, 2H, Ar-H attached to ether linkage, J = 9.10), 8.08-8.11 (d, 2H, Ar-H attached to ester linkage, J = 6.11), 7.25-7.27 (d, 2H, Ar-H attached to ether linkage, J = 9.11), 7.03-7.05 (d, 2H, Ar-H, J = 6.12), 4.37-4.41 (t, 2H, CH₂O), 4.04-4.08 (t, 2H, CH₂O), 1.78-1.87 (m, 4H, 2×CH₂), 1.50-1.54 (m, 4H, 2×CH₂), 1.05-1.08 (t, 3H, CH₃), 0.96-1.04 (t, 3H, CH₃); elemental analysis: calculated for C₂₃H₂₆N₂O₄ (394.46 g/mol): C 70.03, H 6.64, N 7.10., found C 70.11, H 6.71, N 7.17.

2.2.6.5. Bentlyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₅].

Yield (58%); mp: 113-115 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2868, C-H aliph.), (1720, C=O), (1608, C=N); MS (SCI) (relative intensity %): m/z = 408 (M⁺, 100%); elemental analysis:

calculated for C₂₄H₂₈N₂O₄ (408.20 g/mol): C 70.57, H 6.91, N 6.86., found C 70.63, H 7.00, N 6.92.

2.2.6.6. Hexyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₆].

Yield (64%); mp: 99-101 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2860, C-H aliph.), (1720, C=O), (1610, C=N); elemental analysis: calculated for C₂₅H₃₀N₂O₄ (422.22 g/mol): C 71.07, H 7.16, N 6.63., found C 71.15, H 7.22, N 6.71.

2.2.6.7. Heptyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₇].

Yield (57%); mp: 96-98 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2854, C-H aliph.), (1722, C=O), (1608, C=N); elemental analysis: calculated for C₂₆H₃₂N₂O₄ (436.24 g/mol): C 71.53, H 7.39, N 6.42., found C 71.64, H 7.44, N 6.51.

2.2.6.8. Octyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₈].

Yield (61%); mp: 97-99 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2854, C-H aliph.), (1722, C=O), (1608, C=N); elemental analysis: calculated for C₂₇H₃₄N₂O₄ (450.57 g/mol): C 71.97, H 7.61, N 6.22., found C 72.05, H 7.68, N 6.33.

2.2.6.9. Nonyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₉].

Yield (66%); mp: 86-88 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2956, 2852, C-H aliph.), (1722, C=O), (1608, C=N); elemental analysis: calculated for C₂₈H₃₆N₂O₄ (464.27 g/mol): C 72.39, H 7.81, N 6.03., found C 72.44, H 7.89, N 6.09.

2.2.6.10. Decyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₁₀].

Yield (67%); mp: 95-97 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2958, 2852, C-H aliph.), (1716, C=O), (1608, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.19-8.21 (d, 2H, Ar-H attached to ether linkage, J = 9.12), 8.08-8.11 (d, 2H, Ar-H attached to ester linkage, J = 6.13), 7.25-7.27 (d, 2H, Ar-H attached to ether linkage, J = 9.10), 7.03-7.05 (d, 2H, Ar-H, J = 6.11), 4.33-4.39 (t, 2H, CH₂O),

4.03-4.08 (t, 2H, CH₂O), 1.77-1.87 (m, 4H, 2×CH₂), 1.30-1.52 (m, 16H, 8×CH₂), 0.98-1.04 (t, 3H, CH₃), 0.88- 0.92 (t, 3H, CH₃); elemental analysis: calculated for C₂₉H₃₈N₂O₄ (478.28 g/mol): C 72.77, H 8.00, N 5.85., found C 72.83, H 8.09, N 5.91.

2.2.6.11. Dodecyl-4-(5-(4-butoxyphenyl)-1,3,4-oxadiazol-2-yl)benzoate [F₁₁].

Yield (64%); mp: 107-109 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2848, C-H aliph.), (1716, C=O), (1610, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.18-8.20 (d, 2H, Ar-H attached to ether linkage, J = 9.12), 8.07-8.10 (d, 2H, Ar-H attached to ester linkage, J = 6.10), 7.24-7.27 (d, 2H, Ar-H attached to ether linkage, J = 9.12), 7.03-7.05 (d, 2H, Ar-H, J = 6.12), 4.34-4.39 (t, 2H, CH₂O), 4.04-4.09 (t, 2H, CH₂O), 1.76-1.86 (m, 4H, 2×CH₂), 1.29-1.50 (m, 20H, 10×CH₂), 0.99-1.04 (t, 3H, CH₃), 0.86- 0.90 (t, 3H, CH₃); elemental analysis: calculated for C₃₁H₄₂N₂O₄ (506.31 g/mol): C 73.94, H 8.36, N 5.53., found C 73.60, H 8.42, N 5.55.

2.2.7. 4-Butoxybenzonitril [G]

A mixture of (0.087 mol, 10.36 g) of 4-cyanophenol, (0.087 mol, 12.00 g) of potassium carbonate and (75 mL) of dimethylformamide was heated for several minutes, after cooling, (0.13 mol, 14 mL) of 1-bromobutane was added dropwise and the reaction mixture was refluxed for 24 h, potassium bromide was precipitated, after cooling, (50 mL) of water and (50 mL) of diethyl ether were added. The mixture was extracted and the organic layer was collected and washed with (25 mL) of 10% sodium hydroxide solution then with (100 mL) of water, dried the ether layer over anhydrous magnesium sulfate overnight, after filtration and evaporation the solvent, the oil residue obtained yielded (92%) FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2958, 2874, C-H aliph.), (2224, C≡N), (1604, 1506, C=C), (1255, 1170, C-O-C sym. and asym.); elemental analysis: calculated for C₁₁H₁₃NO (175.23 g/mol): C 75.40, H 7.48, N 7.99., found C 75.47, H 7.55, N 8.08.

2.2.8. (Z)-4-Butoxy-N'-hydroxybenzimidamide [H]

A mixture of (0.134 mol, 23.5 g) of nitrile [G], (0.144 mol, 10 g) of hydroxylamine hydrochloride and (0.15 mol, 6 g) of sodium hydroxide in (200 mL) of ethanol with (50 mL) of water is stirred for 24 hours at boiling temperature, then concentrated the mixture in vacuum. The residue was poured in (500 mL) of cold water, filtered, washed with water and dried, the product was purified by washing with hot n-hexane and recrystallized from ethanol. Yield (87%); mp: 97-100 °C; FT-IR (ATR, cm^{-1}), ν_{max} : (3437, 3344, N-H), (3169, O-H), (1643, C=N); ^1H NMR (DMSO- d_6), δ , ppm: 9.43 (s, 1H, OH), 7.60-7.57 (d, 2H, Ar-H, $J = 8.7$ Hz), 6.92-6.89 (d, 2H, Ar-H, $J = 8.7$ Hz), 5.70 (s, 2H, NH₂), 4.03-3.95 (t, 2H, CH₂O), 1.71-1.65 (m, 2H, CH₂), 1.49-1.37 (m, 2H, CH₂), 0.95-0.90 (t, 3H, CH₃); elemental analysis: calculated for C₁₁H₁₆N₂O₄ (208.12 g/mol): C 63.44, H 7.74, N 13.45., found C 63.48, H 7.81, N 13.51.

2.2.9. 3-(4-Butoxyphenyl)-5-(p-tolyl)-1,2,4-oxadiazole [I]

A mixture of (0.013 mol, 2.7 g) of compound [H] and (0.013 mol, 1.95 g) of ester [A] dissolved in sodium ethoxide solution (prepared from dissolving 0.014 mol, 0.32 g of sodium metal in 27 mL absolute ethanol), then the reaction mixture was heated under reflux for 48 hours and the hot solution was filtrated, off-white crystals were collected by filtration the cold solution and dried, the product was crystallized from ethanol. Yield (69%); mp: 108-110 °C; FT-IR (ATR, cm^{-1}), ν_{max} : (2956, 2870, C-H aliph.), (1608, C=N), (1591, C=C), (1247, 1176, C-O-C sym. and asym.), (923, N-O); ^1H NMR (DMSO- d_6), δ , ppm: 8.08-8.05 (d, 2H, Ar-H attached to butoxy group, $J = 8.1$ Hz), 8.03-8.02 (d, 2H, Ar-H attached to methyl group, $J = 9.0$ Hz), 7.48-7.45 (d, 2H, Ar-H attached to methyl group, $J = 8.1$ Hz), 7.14-7.11 (d, 2H, Ar-H attached to butoxy group, $J = 9.0$ Hz), 4.08-4.04 (t, 2H, CH₂O), 2.43 (s, 3H, CH₃), 1.75-1.71 (m, 2H, CH₂), 1.49-

1.42 (m, 2H, CH₂), 0.97-0.92 (t, 3H, CH₃); elemental analysis: calculated for C₁₉H₂₀N₂O₂ (308.37 g/mol): C 74.00, H 6.54, N 9.08., found C 74.11, H 6.59, N 9.18.

2.2.10. 4-(3-(4-Butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoic acid [J]

This compound was prepared by the same procedure that described for compound [E]. Yield (81%); mp: 260-261 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (3100-2544, O-H), (2949, 2875, C-H aliph.), (1693, C=O), (1608, C=N), (1247, 1176, C-O-C sym. and asym.); ¹HNMR (DMSO-d₆), δ , ppm: 13.12-14.22 (s, 1H, br., COOH), 8.26-8.29 (d, 2H, Ar-H attached to carboxy group, $J = 7.9$), 8.16-8.19 (d, 2H, Ar-H attached to carboxy group, $J = 8.0$), 8.01-8.04 (d, 2H, Ar-H attached to butoxy group, $J = 8.4$ Hz), 7.12-7.14 (d, 2H attached to butoxy group, Ar-H, $J = 8.4$), 4.04-4.08 (t, 2H, CH₂O), 1.71-1.75 (m, 2H, CH₂), 1.42-1.49 (m, 2H, CH₂), 0.92-0.97 (t, 3H, CH₃); MS (SCI) (relative intensity %): $M/Z = 338$ (M^+ , 56%); elemental analysis: calculated for C₁₉H₁₈N₂O₄ (338.36 g/mol): C 67.44, H 5.36, N 8.28., found C 67.61, H 5.44, N 8.37.

2.2.11. Alkyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K_I-K_{II}]

These compounds were prepared by the same procedure that described for compounds [F₁-F₁₁].

2.2.11.1. Methyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K_I].

Yield (68%); mp: 91-93 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2953, 2872, C-H aliph.), (1716, C=O), (1612, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.28 (d, 2H, Ar-H attached to ester linkage, $J = 6.83$), 8.23-8.20 (d, 2H, Ar-H attached to ester linkage, $J = 6.82$), 8.11-8.08 (d, 2H, Ar-H attached to ether linkage, $J = 6.91$), 7.02-6.99 (d, 2H, Ar-H attached to ether linkage, $J = 6.90$), 4.06-4.02 (t, 2H, CH₂O), 3.97 (s, 3H, COOCH₃), 1.92-1.76 (m, 2H, CH₂), 1.56-1.46 (m, 2H, CH₂), 1.02-0.97 (t, 3H, CH₃); MS (SCI) (relative intensity %): $M/Z = 352$ (M^+ , 100%); elemental analysis: calculated for C₂₀H₂₀N₂O₄ (352.38 g/mol): C 68.17, H 5.72, N 7.95., found C 68.31, H 5.81, N 8.04.

2.2.11.2. Ethyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K₂].

Yield (65%); mp: 96-98 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2960, 2872, C-H aliph.), (1722, C=O), (1608, C=N); ¹HNMR (DMSO-d₆), δ , ppm: 8.32-8.29 (d, 2H, Ar-H attached to ester linkage, J = 7.22), 8.20-8.18 (d, 2H, Ar-H attached to ester linkage, J = 7.21), 8.02-8.01 (d, 2H, Ar-H attached to ether linkage, J = 6.91), 7.14-7.11 (d, 2H, Ar-H attached to ether linkage, J = 6.91), 4.40-4.34 (t, 2H, OCH₂), 4.08-4.04 (q, 2H, COOCH₂), 1.75-1.71 (m, 2H, CH₂), 1.49-1.40 (m, 2H, CH₂), 1.38-1.33 (t, 3H, CH₃), 0.96-0.92 (t, 3H, CH₃); elemental analysis: calculated for C₂₁H₂₂N₂O₄ (366.16 g/mol): C 68.84, H 6.05, N 7.65., found C 68.90, H 6.17, N 7.79.

2.2.11.3. Propyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K₃].

Yield (68%); mp: 116-118 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2958, 2872, C-H aliph.), (1720, C=O), (1610, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H attached to ester linkage, J = 6.81), 8.22-8.20 (d, 2H, Ar-H attached to ester linkage, J = 6.82), 8.11-8.08 (d, 2H, Ar-H attached to ether linkage, J = 6.91), 7.02-6.99 (d, 2H, Ar-H attached to ether linkage, J = 6.91), 4.36-4.32 (t, 2H, OCH₂), 4.06-4.02 (t, 2H, COOCH₂), 1.87-1.82 (m, 2H, CH₂), 1.81-1.76 (m, 2H, CH₂), 1.53-1.46 (m, 2H, CH₂), 1.08-1.04 (t, 3H, CH₃), 1.02-0.97 (t, 3H, CH₃); elemental analysis: calculated for C₂₂H₂₄N₂O₄ (380.17 g/mol): C 69.46, H 6.36, N 7.36., found C 69.59, H 6.48, N 7.42.

2.2.11.4. Butyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K₄].

Yield (66%); mp: 111-113 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2870, C-H aliph.), (1718, C=O), (1610, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, J = 8.6), 8.22-8.20 (d, 2H, Ar-H, J = 8.6), 8.11-8.08 (d, 2H, Ar-H, J = 8.9), 7.02-6.99 (d, 2H, Ar-H, J = 8.9), 4.4-4.35 (t, 2H, CH₂O), 4.06-4.02 (t, 2H, CH₂O), 1.95-1.74 (m, 4H, 2×CH₂), 1.54-1.44 (m, 4H, 2×CH₂), 1.03-

0.98 (t, 6H, 2×CH₃); elemental analysis: calculated for C₂₃H₂₆N₂O₄ (394.46 g/mol): C 70.03, H 6.64, N 7.10., found C 70.17, H 6.77, N 7.22.

2.2.11.5. *Bentyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K₅].*

Yield (69%); mp: 94-96 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2872, C-H aliph.), (1720, C=O), (1608, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, J = 6.5), 8.22-8.20 (d, 2H, Ar-H, J = 6.5), 8.11-8.08 (d, 2H, Ar-H, J = 6.8), 7.02-6.99 (d, 2H, Ar-H, J = 6.8), 4.4-4.35 (t, 2H, CH₂O), 4.06-4.02 (t, 2H, CH₂O), 1.85-1.72 (m, 4H, 2×CH₂), 1.53-1.42 (m, 6H, 3×CH₂), 1.02-0.98 (t, 6H, 2×CH₃); elemental analysis: calculated for C₂₄H₂₈N₂O₄ (408.20 g/mol): C 70.57, H 6.91, N 6.86., found C 70.60, H 7.04, N 6.91.

2.2.11.6. *Hexyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K₆].*

Yield (70%); mp: 85-87 °C; FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2953, 2870, C-H aliph.), (1714, C=O), (1610, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, J = 8.6), 8.22-8.20 (d, 2H, Ar-H, J = 8.6), 8.11-8.08 (d, 2H, Ar-H, J = 8.9), 7.02-6.99 (d, 2H, Ar-H, J = 8.9), 4.39-4.34 (t, 2H, CH₂O), 4.06-4.02 (t, 2H, CH₂O), 1.83-1.78 (m, 4H, 2×CH₂), 1.41-1.33 (m, 8H, 4×CH₂), 1.02-0.97 (t, 3H, CH₃), 0.95-0.88 (t, 3H, CH₃); elemental analysis: calculated for C₂₅H₃₀N₂O₄ (422.22 g/mol): C 71.07, H 7.16, N 6.63., found C 71.18, H 7.20, N 6.74.

2.2.11.7. *Heptyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [K₇].*

Yield (68%); FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2854, C-H aliph.), (1716, C=O), (1610, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, J = 6.5), 8.22-8.19 (d, 2H, Ar-H, J = 6.5), 8.11-8.07 (d, 2H, Ar-H, J = 6.8), 7.02-6.98 (d, 2H, Ar-H, J = 6.8), 4.4-4.34 (t, 2H, CH₂O), 4.06-4.01 (t, 2H, CH₂O), 1.85-1.76 (m, 4H, 2×CH₂), 1.42-1.31 (m, 10H, 5×CH₂), 1.03-0.97 (t, 3H, CH₃), 0.93-0.88 (t, 3H, CH₃); elemental analysis: calculated for C₂₆H₃₂N₂O₄ (436.24 g/mol): C 71.53, H 7.39, N 6.42., found C 71.62, H 7.47, N 6.58.

2.2.11.8. Octyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [*K*₈].

Yield (61%); FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2922, 2850, C-H aliph.), (1722, C=O), (1608, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, *J* = 7.1), 8.22-8.19 (d, 2H, Ar-H, *J* = 7.1), 8.11-8.07 (d, 2H, Ar-H, *J* = 8.7), 7.02-6.99 (d, 2H, Ar-H, *J* = 8.7), 4.38-4.33 (t, 2H, CH₂O), 4.06-4.02 (t, 2H, CH₂O), 1.84-1.76 (m, 4H, 2×CH₂), 1.46-1.29 (m, 12H, 6×CH₂), 1.02-0.96 (t, 3H, CH₃), 0.93-0.88 (t, 3H, CH₃); MS (SCI) (relative intensity %): *m/z* = 450 (*M*⁺, 100%); elemental analysis: calculated for C₂₇H₃₄N₂O₄ (450.57 g/mol): C 71.97, H 7.61, N 6.22., found C 72.15, H 7.73, N 6.39.

2.2.11.9. Nonyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [*K*₉].

Yield (73%); FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2850, C-H aliph.), (1724, C=O), (1612, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, *J* = 8.5), 8.22-8.19 (d, 2H, Ar-H, *J* = 8.6), 8.11-8.08 (d, 2H, Ar-H, *J* = 8.9), 7.02-6.99 (d, 2H, Ar-H, *J* = 8.9), 4.4-4.34 (t, 2H, CH₂O), 4.06-4.02 (t, 2H, CH₂O), 1.83-1.75 (m, 4H, 2×CH₂), 1.48-1.28 (m, 14H, 7×CH₂), 1.02-0.98 (t, 3H, CH₃), 0.93-0.88 (t, 3H, CH₃); elemental analysis: calculated for C₂₈H₃₆N₂O₄ (464.27 g/mol): C 72.39, H 7.81, N 6.03., found C 72.49, H 7.86, N 6.13.

2.2.11.10. Decyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl)benzoate [*K*₁₀].

Yield (68%); FT-IR (ATR, cm⁻¹), $\nu_{\max}$: (2955, 2850, C-H aliph.), (1722, C=O), (1610, C=N); ¹HNMR (CDCl₃), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, *J* = 8.1), 8.22-8.19 (d, 2H, Ar-H, *J* = 8.0), 8.11-8.08 (d, 2H, Ar-H, *J* = 8.9), 7.03-6.99 (d, 2H, Ar-H, *J* = 8.9), 4.4-4.34 (t, 2H, CH₂O), 4.06-4.02 (t, 2H, CH₂O), 1.83-1.75 (m, 4H, 2×CH₂), 1.49-1.29 (m, 16H, 8×CH₂), 1.02-0.97 (t, 3H, CH₃), 0.91-0.85 (t, 3H, CH₃); MS (SCI) (relative intensity %): *m/z* = 478 (*M*⁺, 100%); elemental analysis: calculated for C₂₉H₃₈N₂O₄ (478.28 g/mol): C 72.77, H 8.00, N 5.85., found C 72.87, H 8.03, N 5.99.

2.2.11.11. Dodecyl-4-(3-(4-butoxyphenyl)-1,2,4-oxadiazol-5-yl) benzoate [K11].

Yield (71%); FT-IR (ATR, cm^{-1}), ν_{max} : (2953, 2851, C-H aliph.), (1724, C=O), (1610, C=N); ^1H NMR (CDCl_3), δ , ppm: 8.30-8.27 (d, 2H, Ar-H, $J = 8.3$), 8.22-8.19 (d, 2H, Ar-H, $J = 8.3$), 8.11-8.08 (d, 2H, Ar-H, $J = 8.7$), 7.03-6.99 (d, 2H, Ar-H, $J = 8.6$), 4.38-4.34 (t, 2H, CH_2O), 4.06-4.02 (t, 2H, CH_2O), 1.83-1.75 (m, 4H, $2 \times \text{CH}_2$), 1.49-1.28 (m, 20H, $10 \times \text{CH}_2$), 1.02-0.97 (t, 3H, CH_3), 0.89-0.84 (t, 3H, CH_3); MS (SCI) (relative intensity %): $m/z = 506$ (M^+ , 100%); elemental analysis: calculated for $\text{C}_{31}\text{H}_{42}\text{N}_2\text{O}_4$ (506.60 g/mol): C 73.94, H 8.36, N 5.53., found C 73.63, H 8.45, N 5.59.

Figure 1. ^1H NMR spectra of compounds **F2** (Top) and **F11** (Down)

Figure 2. ^1H NMR spectra of compounds **K₁** (Top) and **K₉** (Down)

Figure 3. Crystals to isotropic transition temperatures as a function of the length of terminal alkoxy chain in compounds **F1-F11**.

Figure 4. (Color online) DSC thermo-grams of compounds **K7-K11**.

Figure 5. Transition temperatures in cooling (I –N) and (N-Cr) against the number of carbon atoms in the last five homologues **K7-K11**.

Figure 6. (Color online) The transition Mesophase textures of **K₁₁** on cooling from nematic to crystal phases: (A) transition from isotropic to nematic droplets with Schlieren texture at 63 °C; (B) Schlieren texture at 57 °C; (C) transition from nematic (N) to crystal phase at 54 °C; (D) the end of nematic phase (N) at 52 °C.