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Synthesis and characterization of new mesogenic esters derived from 1,2,4-oxadiazole and study the effect of alkoxy chain length in their liquid crystalline properties

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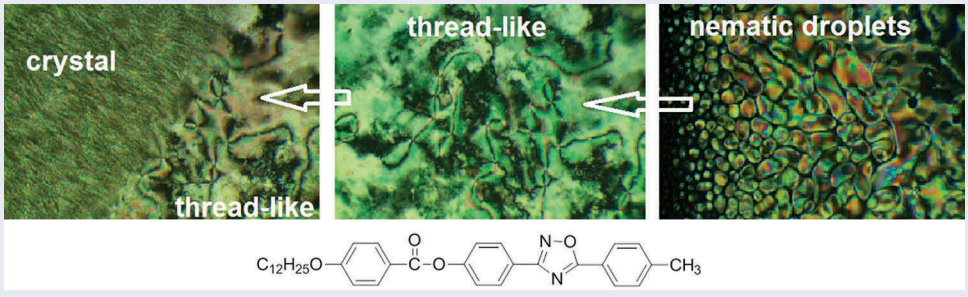
ABSTRACT

In this study, a new series of non-symmetrically 3,5-disubstituted of 1,2,4-oxadiazole derivatives, 4-[5-(4-methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-alkoxybenzoate (G_1–G_{11}), which containing ether and ester linkages in the same molecule, is synthesized using different synthetic procedures and their structures are confirmed by several spectroscopic techniques (FT-IR and ^{1}H nuclear magnetic resonance). The mesomorphic properties of these compounds are studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM); all these derivatives exhibited as mesogens and displayed an enantiotropic liquid crystal with nematic texture, the nematogenic phase of these materials was appeared in wide temperature ranges on heating and cooling cycles that were observed by POM and DSC. The influence of 1,2,4-oxadiazole ring and the elongation of alkyl chain in the mesomorphic properties of this series were investigated. The mesogenic behaviour of this series was compared with the compounds possessing a somewhat similar structure.



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1,2,4-Oxadiazole; mesomorphic; liquid crystalline; ester mesogens

1. Introduction

Liquid crystals (LCs) are the materials that represent an intermediate state of matter which combine between the crystalline solid and isotropic liquid. These mesogens have wide-developed applications in various industrial fields, especially in optical and biological [1–5]. The correlation between chemical structure and liquid crystalline behaviour of these molecules is one of the most important problems in LCs science. This influence has made many chemists interest in designing novel thermotropic mesogens to study the effect of their chemical structures, through the selection of suitable core, linkage group, terminal group and the length of flexible chain, on their liquid crystalline properties [6–10].

Among the common compounds used in the field of LCs are heterocycles [11–13], this system of compounds reduced the symmetry in the overall molecule and a change in the polarity, polarizibility and geometry of the molecule; this changes to insertion heteroatoms (S, O and N) that are more polarizable than carbon atom, which in turn affect the type of mesophase, phase transition temperatures, dielectric constants and other properties of the mesogens [14,15].

1,2,4-Oxadiazole is asymmetrical five-membered aromatic heterocyclic ring containing two nitrogens and one oxygen atom, it has exhibited non-linearity ring and their derivatives were used as mesogens, the mesomorphic properties of the 1,2,4-oxadiazole derivatives strongly depend on the substitution at both C_3 and C_5 positions in the ring and they are different than the liquid crystalline properties produced by other oxadiazole isomers like 1,3,4- and 1,2,3-

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oxadiazole [16–19]. Mesomorphic behaviours of the 1,2,4-oxadiazole derivatives are studied briefly in the recently reported, particularly rod-like molecules [20–24].

In view of these details and as a part of our continuing research in the synthesis, characterization and development of new mesogenic materials, we planned in this work to synthesize new series based on 1,2,4-oxadiazole core with variety alkoxy chain lengths in the one terminus of the molecules, differential scanning calorimetry (DSC) and polarized optical microscopy (POM) techniques were used to study their optical and thermal properties; the structure–property relationships will be discussed on the basis of the experimental results.

2. Experimental section

2.1. Techniques

All the chemicals that are used to prepare all the derivatives of this work were furnished by Sigma-Aldrich company and polarized without purification. Some of 4-alkoxybenzoic acids (F_n) were prepared previously by Bradfield et al. [25], the same method of preparation was used in this work to prepare all (F_n) compounds. The FT-IR spectra were carried out by Shimadzu spectrophotometer, type 8400S with (ATR) technique. ^{1}H nuclear magnetic resonance (NMR) spectra were applied by Bruker, model ultra-shield at 300 MHz in ppm (δ); dmso-*d*6 and $CDCl_3$ were used as solvents of the compounds with Tetramethylsilane as an internal standard. The optical behaviours and texture types of the mesogens were screened by using polarized optical microscopy (POM), model (PW-BK 5000 PR) built with a hot stage, type HS-400. The thermal behaviours of the compounds were studied by DSC, type STA PT-1000 LINSIS in 5°C/min heating and cooling rates; standard indium is used to calibrate the temperatures and heat flow in DSC.

2.2. Preparation methods of compounds (a-G_n)

2.2.1. Methyl 4-methylbenzoate (A)

This compound was prepared by the classical esterification method of 4-methylbenzoic acid with absolute methanol using sulphuric acid as catalyst [26]. Yield (95%); mp: 32–35°C.

2.2.2. 4-Methoxybenzonitrile (B)

This compound was prepared using the method that reported by Gallardo and Begnini [15] with some differences. A mixture of 4-cyanophenol (0.084 mol, 10 g), potassium carbonate (0.084 mol, 11.6 g) in 100 mL of dimethylformamide was heated for 10 min; after cooling, 0.13 mol, 18.5 mL of iodomethane was added dropwise with a quiet stirring, then the reaction mixture was refluxed for 72 h. After cooling, potassium iodide was precipitated and the mixture was poured into water. The resulting solid product was washed with 50 mL of 10% sodium hydroxide solution, filtered, washed with water several times and dried to yield (97%); mp: 57–59°C; FT-IR (ATR, cm^{-1}), υ_{max}: (2953, 2845, C–H aliph.), (2216, C≡N), (1604, 1508, C=C) (1255, 1174, C–O–C sym. and asym.).

2.2.3. 4-Methoxy-n-hydroxylbenzenecarboximidamide (C)

This compound was prepared using the procedure that reported in Ref. [27]. A mixture of nitrile (B) (0.11 mol, 14.63 g), hydroxylamine hydrochloride (0.14 mol, 9.73 g) and sodium hydroxide (0.144 mol, 5.76 g) in 200 mL of ethanol with 50 mL of water was stirred overnight at reflux temperature. After cooling, the mixture was concentrated under vacuum, then 500 mL of cold water was added to the mixture, filtered, washed with water, dried and purified by washing with hot *n*-hexane then recrystallized from ethanol. Yield (90%); mp: 116–118°C; FT-IR (ATR, cm^{-1}), υ_{max}: (3439, 3350, N–H), (3211, O–H), (1645, C=N); ^{1}H NMR (dmso-*d*6), δ, ppm: 3.76 (s, 3*H*, $-OCH_3$), 5.73 (s, 2*H*, $-NH_2$), 7.62–7.59 and 6.93–6.90 (2d, 4*H*, Ar–H, –ph–), 9.47 (s, 1*H*, OH).

2.2.4. 3-(4-Methoxyphenyl)-5-(p-methylphenyl)-1,2,4-oxadiazole (D)

This compound was recrystallized according to the method reported by Parra et al. [28]. Sodium ethoxide solution (0.06 mol, 1.38 g of sodium metal in 20 mL of ethanol absolute) was added dropwise with stirring to a mixture of amidoxime (C) (0.03 mol, 5.0 g) and ester (A) (0.03 mol, 4.5 g) over 5 min, then the reaction mixture was heated under reflux for 48 h; after the reaction is complete, the mixture was filtrated and the filtration was evaporated to result the product. The solid product was boiled with 100 mL of water about 30 min, then the hot mixture was filtrated, yellow crystal was obtained, collected by filtration, dried and recrystallized from ethanol. Yield (78%); mp: 109–111°C; FT-IR (ATR, cm^{-1}), υ_{max}: (2951, 2852, C–H aliph.), (1610, C=N), (1591, C=C), (968, N–O); (1251, 1170, C–O–C sym. and asym.); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.12–8.09 (d, 2*H*, Ar–H, CH_3O–ph–, J = 8.85 Hz), 8.11–8.08 (d, 2*H*, Ar–H, CH_3–ph–, J = 7.98 Hz), 7.36–7.34 (d, 2*H*, Ar–H, CH_3–ph–, J = 7.93 Hz), 7.03–7.00 (d, 2*H*, Ar–H, CH_3O–

ph–, J = 8.86 Hz), 3.88 (s, 3*H*, –OCH_3), 2.46 (s, 3*H*, –CH_3).

2.2.5. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenol (E)

The demethylation procedure of the compound (D) was reported in Ref. [29]. Compound (D), *3-(4-methoxyphenyl)-5-(p*-methylphenyl*)-1,2,4-oxadiazole* (0.0113 mol, 3.0 g), was dissolved in 10 mL of benzene and the solution was stirred for 10 min, then 0.045 mol, 6.0 g of anhydrous aluminium trichloride was added to the solution as a demethylation agent. The resulting mixture was heated under reflux for 24 h. After cooling, the solvent was evaporated by rotary evaporator, 100 mL of distillation water was added carefully to the crude product, the mixture was filtered off and the precipitate was dissolved in 100 mL of 30% aqueous sodium hydroxide solution to remove the residue of a compound (D) and the filtrate was acidified with concentrated hydrochloric acid to give brown solid product. The precipitate was filtered, washed with water and dried to yield (85%); mp: 117–119°C; FT-IR (ATR, cm^{-1}), υ_{max}: (3244, OH), (1610, C=N), (1595, C=C), (1236, 1172, C–O–C sym. and asym.); ^{1}H NMR (dmso-*d*6), δ, ppm: 10.16 (s, 1*H*, –OH); 8.07–8.05 (d, 2*H*, Ar–H, CH_3–ph–, J = 8.14 Hz); 7.93–7.90 (d, 2*H*, Ar–H, HO–ph–, J = 8.65 Hz); 7.48–7.45 (d, 2*H*, Ar–H, CH_3–ph–, J = 7.96 Hz); 6.96–6.93 (d, 2*H*, Ar–H, HO–ph–, J = 8.67 Hz), 2.43 (s, 3*H*, –CH_3).

2.2.6. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-alkoxybenzoate (G_n)

These derivatives were prepared using the coupling procedure that was reported by Tomi et al. [30]. A mixture of 4-[5-(4-methylphenyl)-1,2,4-oxadiazol-3-yl] phenol (E), 0.0005 mol, 0.126 g, 4-alkoxybenzoic acid (F_n), 0.0005 mol, *N,N′*-dicyclohexylcarbodiimide (DCC), 0.00054 mol, 0.11 g and 4-dimethylaminopyridine (DMAP), 0.0005 mol, 0.06 g in 25 mL dry dichloromethane (DCM) was stirred for 7 days at room temperature. The precipitated dicyclohexylurea (DCU) was filtered off and the filtrate was diluted with 10 mL of DCM. The resulted solution was washed with 10 mL of 5% aqueous acetic acid solution, then with 25 mL of water. After the solution was extracted, the organic layer (DCM) was evaporated to give the crude product of esters (G_n). The esters were recrystallised from ethanol and dried.

2.2.6.1. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-methoxybenzoate (G_1).

Yield (85%); FT-IR (ATR, cm^{-1}), υ_{max}: (2928, 2842, C–H aliph.), (1735, C=O), (1606, C=N), (1581, C=C), (1263, 1177, asym. and sym. C–O–C) (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.26–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.69), 8.19–8.16 (d, 2*H*, Ar–H, –Ph–OCH_3, J = 8.90), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.08), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.02–6.99 (d, 2*H*, Ar–H, –ph–OCH_3), J = 8.90), 3.91 (s, 3*H*, –OCH_3), 2.46 (s, 3*H*, –CH_3).

2.2.6.2. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-ethoxybenzoate (G_2).

Yield (81%); FT-IR (ATR, cm^{-1}), υ_{max}: (2929, 2852, C–H aliph.), (1734, C=O), (1604, C=N), (1579, C=C), (1259, 1170, asym. and sym. C–O–C), (966, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.26–8.23 (d, 2*H*, Ar–H, central –ph–), J = 8.70), 8.18–8.15 (d, 2*H*, Ar–H, –ph–OR_2, J = 8.86), 8.13–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.16), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –ph–OR_2, J = 8.86), 4.17–4.12 (q, 2*H*, –CH_2O–), 2.47 (s, 3*H*, CH_3), 1.49–1.45 (t, 3*H*, –CH_3).

2.2.6.3. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-propoxybenzoate (G_3).

Yield (83%); FT-IR (ATR, cm^{-1}), υ_{max}: (2930, 2899, C–H aliph.), (1732, C=O), (1606, C=N), (1579, C=C), (1263, 1168, asym. and sym. C–O–C), (970, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.26–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.58), 8.17–8.14 (d, 2*H*, Ar–H, –ph–OR_3, J = 8.82), 8.13–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.02), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.01–6.97 (d, 2*H*, Ar–H, –ph–OR_3, J = 8.82), 4.04–4.00 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, CH_3), 1.91–1.80 (m, 2*H*, –CH_2), 1.10–1.05 (t, 3*H*, –CH_3).

2.2.6.4. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-butoxybenzoate (G_4).

Yield (85%); FT-IR (ATR, cm^{-1}), υ_{max}: (2928, 2872, C–H aliph.), (1726, C=O), (1602, C=N), (1579, C=C), (1255, 1161, asym. and sym. C–O–C), (964, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, central–ph–, J = 8.42), 8.17–8.14 (d, 2*H*, Ar–H, –ph–OR_4, J = 8.66), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.05), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –ph–OR_4, J = 8.64), 4.08–4.04 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.86–1.77 (m, 2*H*, –CH_2CH_2O–), 1.58–1.46 (m, 2*H*, –CH_2CH_3), 1.02–0.97 (t, 3*H*, –CH_3).

2.2.6.5. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-pentyloxybenzoate (G_5).

Yield (87%); FT-IR (ATR, cm^{-1}), υ_{max}: (2949, 2864, C–H aliph.), (1732, C=O), (1606, C=N), (1579, C=C), (1267, 1168, asym.

and sym. C–O–C), (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.26–8.23 (d, 2*H*, Ar–H, central–ph–, J = 8.66), 8.17–8.14 (d, 2*H*, Ar–H, –ph–OR_5, J = 8.81), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.18), 7.37–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –ph–OR_5, J = 8.85), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.86–1.79 (m, 2*H*, –CH_2CH_2O–), 1.49–1.39 (m, 4*H*, 2 –CH_2–), 0.97–0.92 (t, 3*H*, –CH_3).

2.2.6.6. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-hexyloxybenzoate (G_6). Yield (84%); FT-IR (ATR, cm^{-1}), υ_{max}: (2943, 2862, C–H aliph.), (1728, C=O), (1602, C=N), (1577, C=C), (1259, 1165, asym. and sym. C–O–C), (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.69), 8.17–8.14 (d, 2*H*, Ar–H, –ph–OR_6, J = 8.83), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.16), 7.37–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –ph–OR_6, J = 8.86), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.88–1.78 (m, 2*H*, –CH_2CH_2O–), 1.52–1.44 (m, 2*H*, –CH_2), 1.38–1.34 (m, 4*H*, 2-CH_2), 0.95–0.90 (t, 3*H*, –CH_3).

2.2.6.7. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-heptyloxybenzoate (G_7). Yield (81%); FT-IR (ATR, cm^{-1}), υ_{max}: (2924, 2858, C–H aliph.), (1732, C=O), (1604, C=N), (1579, C=C), (1253, 1165, asym. and sym. C–O–C), (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, Ar–H, central –ph–, J = 8.51), 8.17–8.14 (d, 2*H*, –ph–OR_7, J = 8.87), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 7.94), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –ph–OR_7, J = 8.75), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.87–1.79 (m, 2*H*, –CH_2CH_2O–), 1.52–1.47 (m, 2*H*, –CH_2), 1.40–1.26 (m, 6*H*, 3-CH_2), 0.93–0.89 (t, 3*H*, –CH_3).

2.2.6.8. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-octyloxybenzoate (G_8). Yield (87%); FT-IR (ATR, cm^{-1}), υ_{max}: (2920, 2858, C–H aliph.), (1734, C=O), (1604, C=N), (1579, C=C), (1263, 1166, asym. and sym. C–O–C), (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.67), 8.17–8.14 (d, 2*H*, Ar–H, –Ph–OR_8, J = 8.85), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.23), 7.37–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –Ph–OR_8, J = 8.89), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.87–1.80 (m, 2*H*, –CH_2–CH_2O–), 1.48–1.42 (m, 2*H*, CH_2), 1.33–1.25 (m, 8*H*, 4-CH_2), 0.92–0.87 (t, 3*H*, –CH_3).

2.2.6.9. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-nonyloxybenzoate (G_9). Yield (83%); FT-IR (ATR, cm^{-1}), υ_{max}: (2939, 2848, C–H aliph.), (1728, C=O), (1604, C=N), (1577, C=C), (1273, 1166, asym. and sym. C–O–C), (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.55), 8.17–8.14 (d, 2*H*, Ar–H, –Ph–OR_9, J = 8.74), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.03), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –Ph–OR_9, J = 8.73), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.86–1.78 (m, 2*H*, –CH_2CH_2O–), 1.48–1.46 (m, 2*H*, CH_2), 1.39–1.25 (m, 10*H*, 5-CH_2), 0.91–0.87 (t, 3*H*, –CH_3).

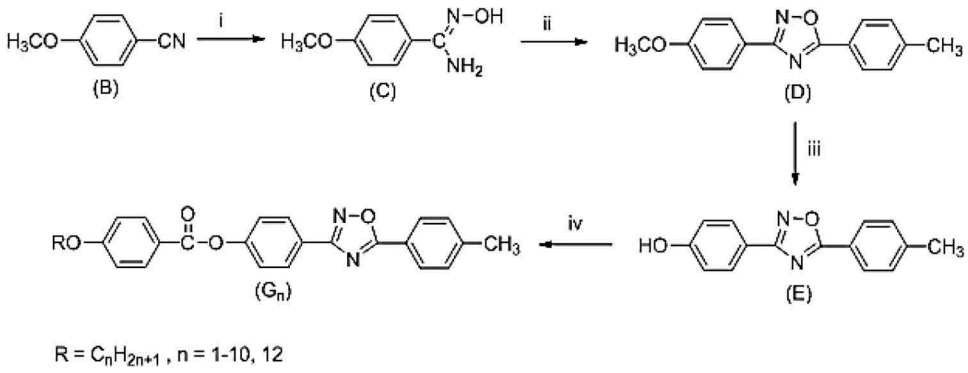
2.2.6.10. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-decyloxybenzoate (G_{10}). Yield (82%); FT-IR (ATR, cm^{-1}), υ_{max}: (2922, 2847, C–H aliph.), (1728, C=O), (1604, C=N), (1579, C=C), (1273, 1168, asym. and sym. C–O–C), (977, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.70), 8.17–8.14 (d, 2*H*, Ar–H, –Ph–OR_{10}, J = 8.87), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.18), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –Ph–OR_{10}, J = 8.89), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.87–1.76 (m, 2*H*, –CH_2CH_2O–), 1.50–1.44 (m, 2*H*, –CH_2), 1.34–1.26 (m, 12*H*, 6-CH_2), 0.90–0.86 (t, 3*H*, –CH_3).

2.2.6.11. 4-[5-(4-Methylphenyl)-1,2,4-oxadiazol-3-yl]-phenyl-4-dodecyloxybenzoate (G_{11}). Yield (81%); FT-IR (ATR, cm^{-1}), υ_{max}: (2918, 2848, C–H aliph.), (1730, C=O), (1604, C=N), (1579, C=C), (1273, 1165, asym. and sym. C–O–C), (968, N–O); ^{1}H NMR ($CDCl_3$), δ, ppm: 8.25–8.23 (d, 2*H*, Ar–H, central –ph–, J = 8.63), 8.17–8.14 (d, 2*H*, Ar–H, –Ph–OR_{12}, J = 8.81), 8.12–8.10 (d, 2*H*, Ar–H, –ph–CH_3, J = 8.17), 7.38–7.35 (2d, overlapping, 4*H*, Ar–H, –ph–CH_3 and central –ph–), 7.00–6.97 (d, 2*H*, Ar–H, –Ph–OR_{12}, J = 8.83), 4.07–4.03 (t, 2*H*, –CH_2O–), 2.46 (s, 3*H*, –CH_3), 1.86–1.79 (m, 2*H*, –CH_2CH_2O–), 1.50–1.43 (m, 2*H*, –CH_2), 1.33–1.24 (m, 16*H*, 8-CH_2), 0.90–0.87 (t, 3*H*, –CH_3).

3. Result and discussion

3.1. Synthesis

The synthesis of asymmetrical compounds (G_1–G_{11}) was illustrated in Scheme 1. Firstly, standard esterification and alkylation methods were used to recrystallized the starting compounds (A and B), respectively. Compound (B) was treated with hydroxylamine hydrochloride in ethanol and water mixture to give a good yield of *N*-hydroxy-4-methoxybenzimidamide (C). The cyclization reaction between ester



Scheme 1. Reaction and reagents: (i) $NH_2OH{\cdot}HCl$, NaOH, ethanol, H_2O; (ii) methyl 4-methylbenzoate (A), Na, absolute ethanol; (iii) benzene, $AlCl_3$; and (iv) 4-alkoxybenzoic acids (F_n), DCC, DMAP, DCM.

(A) and amidoxime (C) was occurred in the presence of sodium ethoxide solution to yield compound (D), 3-(4-methoxyphenyl)-5-(4-methylphenyl)-1,2,4-oxadiazole, which was treated with anhydrous aluminium chloride as a demethylation agent in benzene solvent to obtain the compound (E), 4-[5-(4-methylphenyl)-1,2,4-oxadiazol-3-yl]-phenol. On the other hand, 4-alkoxybenzoic acids (F_n) were prepared by alkylation reaction of 4-hydroxybenzoic acid and *n*-alkyl bromides, these acids were condensed with compound (E) in the presence of DCC as a condensation agent and DMAP as catalyst in dichloromethane at room temperature to yield about 81–87% of final 1,2,4-oxadiazole esters (G_n) in the Scheme 1. The chemical structures of these mesogens were identified by FT-IR and ^{1}H NMR spectroscopies. The FT-IR spectra of these materials exhibited a sharp stretching peak between 1726 and 1735 cm^{-1} which were assigned to the C=O of the ester group in the compounds (G_n), As well as, the increase in the length of the stretching vibrations of C–H band was a very clear indication of success the coupling reaction between a compound (E) and the acids (F_n). ^{1}H NMR spectra of these compounds shows the presence of a new signal of doublet to doublet of the aromatic protons which were assigned to the new benzene moiety which have been introduced into the chemical composition of these compounds; also, the appearance of aliphatic protons in the ^{1}H NMR spectra of these esters is further proof to confirm the structure of the esters (G_n). Figure S1 shows some ^{1}H NMR spectra of the esters (G_n) as examples.

3.2. Liquid crystalline properties

The optical behaviours and mesophases formed for these mesogens (G_1–G_{11}) were examined by POM that is connected to a hot stage; the films of the samples were sandwiched between a glass plate and their cover slip. The thermal properties and transition temperatures were studied by DSC. The results show that all these materials exhibited enantiotropic mesomorphisim with a nematic phase. The mesophases textures were identified and checked depending on the textures that reported by Dierking [31]. Schlieren, thread-like, marble and nematic droplets textures of the nematic phase were observed in both heating and/or cooling runs. Figure 1 displays POM micrographs of some compounds in the series (G_n) as examples obtained by heating the crystalline solid and cooling their isotropic liquids; also, Figure 2 showed the transition from isotropic phase to crystalline phase of the compound (G_{11}).

The DSC investigations of the (G_n) series showed that all these mesogens were involved in showing two transitions in heating cycle and also two transitions in cooling cycle; the two transitions in the heating scan were assigned to crystal–nematic (Cr–N) and nematic–isotropic (N–I); on the other hand, the opposite transitions (I–N) and (N–Cr) were very clear in cooling cycle. Also, some of the compounds in this series, such as G_1, G_3, G_8, G_9, G_{10} and G_{11}, showed crystal–crystal transition in heating cycle in their DSC thermograms. The changes in enthalpy and entropy data in addition to the transition temperatures between the phases are listed in Table 1. It is significant that the ΔS values of the N–I transition were starting with lower value of the first member and somewhat increases as the number of alkyl chain increases; lower values may be interpreted in terms of the bent molecular structure, enhanced molecular biaxiality. With increasing the chain length, the flexibility of the chain reduces the biaxiality which make the entropy increase [32–34]. The transition between mesophases assignments according to DSC curves is in good agreement with the corresponding POM

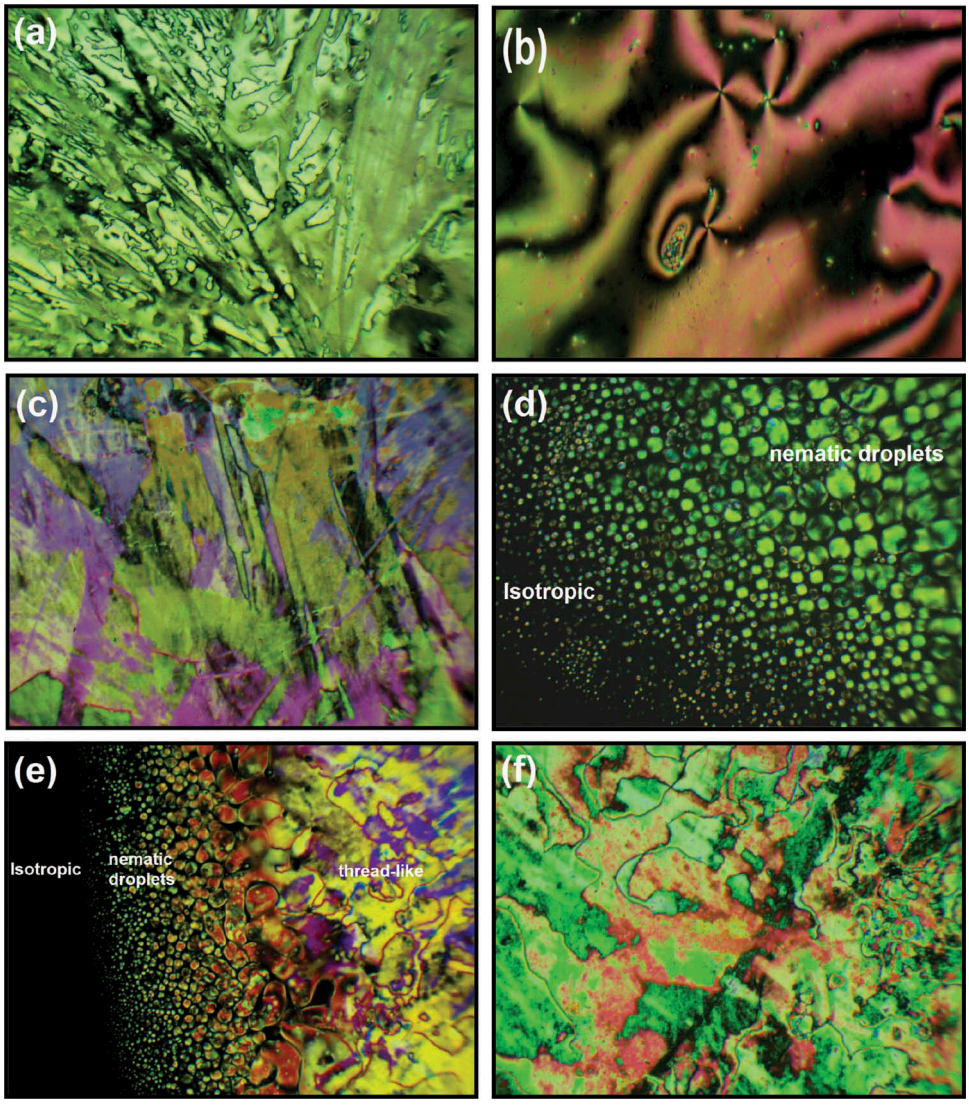


Figure 1. (Colour online) (a) Schlieren texture of nematic phase for compound (G_1) on first heating at 145°C, (b) thread-like texture of the nematic phase exhibited in the first heating cycle for compound (G_2) at 219°C, (c) marble texture of the nematic phase for compound (G_6) on first heating at 220°C, (d) isotropic melt to nematic droplets of the nematic phase for compound (G_7) on first cooling at 218°C, (e) isotropic melt to nematic droplets to thread-like textures of the nematic phase for compound (G_8) on first cooling at 213°C, and (f) marble texture of the nematic phase of compound (G_{10}) on first cooling at 181°C.

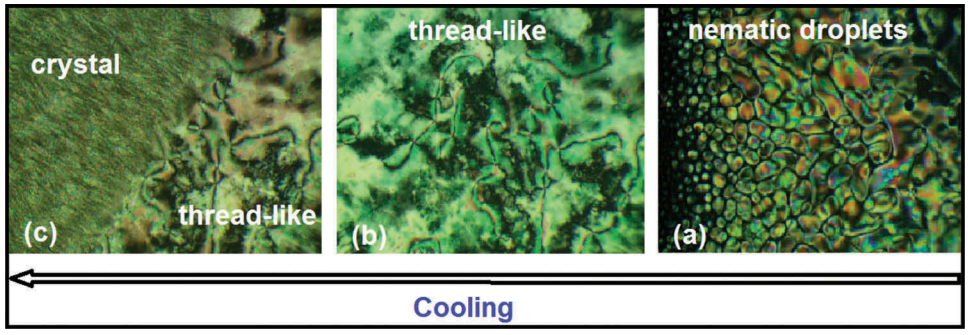


Figure 2. (Colour online) transition from isotropic to crystal phases of compound (G_{12}) at (a) 185, (b) 157, and (c) 56°C.

Table 1. Transition temperatures (T [°C]), ΔH (kJ mol^{-1}) and ΔS (J mol^{-1} K^{-1}) of the mesogens (G_n) both in first heating and cooling scans from (DSC) experiments.

Symbols	n	Phase transitions T (°C), ΔH and ΔS on first heating	Phase transitions T (°C), ΔH and ΔS on first cooling
G_1	1	Cr–Cr_1 118.45 (3.33) [8.50] Cr_1–N 139.85 (24.91) [60.34] N–I 279.70 (0.59) [1.07]	I–N 276.50 (−0.78) [−1.42] N–Cr 79.85 (−15.32) [−43.44]
G_2	2	Cr–N 194.50 (44.52) [95.23] N–I 269.40 (0.61) [1.129]	I–N 264.60 (−0.79) [−1.48] N–Cr 85.40 (−15.86) [−44.26]
G_3	3	Cr–Cr_1 150.15 (5.03) [11.89] Cr_1–N 167.45 (30.08) [68.31] N–I[a]	I–N[a] N–Cr 108.85 (−20.51) [−53.71]
G_4	4	Cr–N 155.00 (29.39) [68.66] N–I 242.9 (1.42) [2.72]	I–N 243.35 (−1.18) [−2.29] N–Cr[a]
G_5	5	Cr–N 142.75 (31.62) [76.07] N–I 230.50 (0.80) [1.59]	I–N 225.50 (−0.77) [−1.55] N–Cr 100.40 (−26.60) [−71.24]
G_6	6	Cr–N 141.30 (30.20) [72.90] N–I 228.00 (0.90) [1.81]	I–N 223.25 (−1.20) [−2.41] N–Cr 80.95 (−23.40) [−66.13]
G_7	7	Cr–N 121.60 (21.67) [54.92] N–I 217.15 (0.86) [1.76]	I–N 209.90 (−1.03) [−2.15] N–Cr 95.00 (−17.61) [−47.86]
G_8	8	Cr–Cr_1 94.05 (6.67) [18.19] Cr_1–N 119.75 (19.17) [48.81] N–I 211.80 (0.98) [2.03]	I–N 206.75 (−1.10) [−2.29] N–Cr 67.70 (−17.08) [−50.13]
G_9	9	Cr–Cr_1 106,25 (4.95) [13.05] Cr_1–N 119.80 (20.55) [52.32] N–I 204.15 (0.94) [1.97]	I–N 198.40 (−1.21) [−2.57] N–Cr 59.25 (−19.80) [−59.59]
G_{10}	10	Cr–Cr_1 101.35 (2.55) [6.83] Cr_1–N 116.05 (27.96) [71.88] N–I 199.20 (0.94) [2.00]	I–N 193.30 (−1.55) [−3.33] N–Cr 61.95 (−28.48) [−85.05]
G_{11}	12	Cr–Cr_1 93.0 (2.44) [6.67] Cr_1–N 100.90 (12.51) [33.46] N–I 186.25 (0.68) [1.49]	I–N 183.55 (−0.43) [−0.95] N–Cr 59.20 (−19.72) [−59.37]

Cr, Cr_1: Crystal phases; N: nematic phase; I: isotropic phase.
[a]Observed on OPM only.

observation. Figure 3 shows the DSC thermographs of compounds G_1, G_5, G_7 and G_{10}.

Now, we discuss here the effect of the number of carbon atoms in the terminal alkoxy chain on the temperature range of the nematic phase (ΔT_N), that's defined as the difference between temperature that start the nematic phase and the temperature recorded at the end of this phase, which is known as the thermal

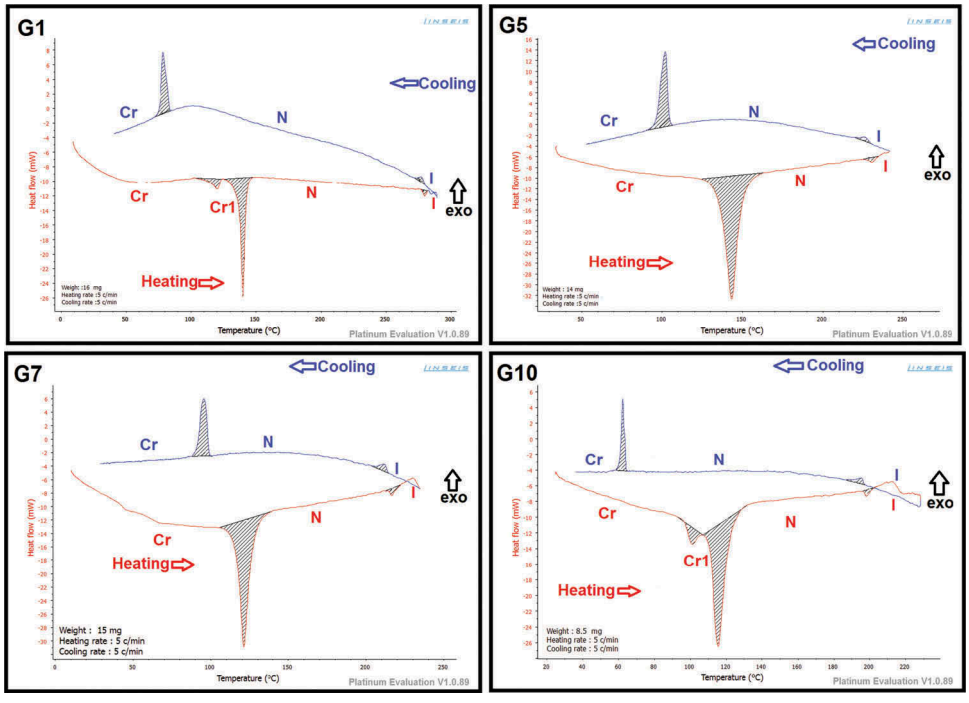


Figure 3. (Colour online) DSC thermographs of the compounds (G_1, G_5, G_7 and G_{10}) as examples of series (G_n).

stability of this phase. Results from the heating scan of DSC and POM results showed that all compounds in this series showed an almost equal range of the nematic phase (ΔT_N = 79.39°C as an average), except the first compound (G_1) where is the highest nematic range in the series (134.6°C), while the results recorded in cooling scan were different; we found that the ΔT_N of the first five compounds (G_1–G_5) decreased as the length of the alkyl chain increased, whereas the rest compounds of this series showed relatively close nematogenic ranges. These results are almost compatible with Refs. [35,36]. Table 2 shows ΔT_N of the series (G_n) both in heating and cooling scans depending on the DSC results.

Through these results, the compound (G_1), contains a shorter alkoxy chain (–OCH_3), exhibited wider mesomorphic temperature ranges both in heating and cooling scans than all mesogens of the series (G_n). This behaviour is convincing because the carbon atom of the methoxy group in compound (G_1) forms a small dihedral angle relative to other members of the series, which is about 1.55°, it is worth noting that the homologue (G_1) is the mesogenic 1,2,4-oxadiazole derivative with the shortest alkoxy and alkyl chains, which has the largest nematogenic range in the heating and cooling cycles. Also, increasing in terminal length in the other corresponding compounds is often helpful to enhance dipole–dipole interaction between the molecules and facilitate the formation of mesophase.

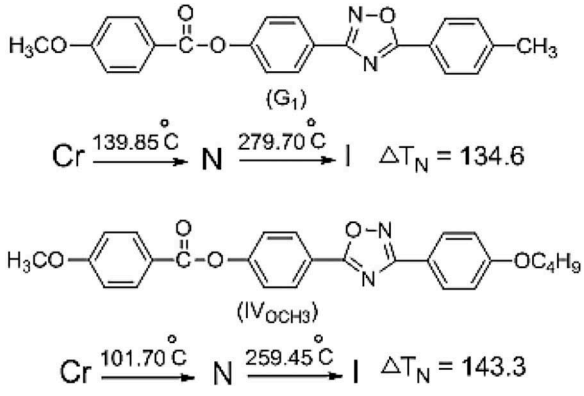
In literature, we did not find compounds that have structure-like to compare their liquid crystalline properties with those prepared in this study; so, the mesomorphic results of some derivatives in G_n series were compared with fairly similar compounds, the derivative (IV_{OCH_3}) that prepared in our previous work [37], (2.2) and (2.3) compounds which were reported by Girdziunaite et al. [38]. The mesomorphic properties of the first homologous in this series (G_1) were compared to compound (IV_{OCH_3}) which is different in terminal group (–OC_4H_9) instead of the (–CH_3) group as well as replacement of oxygen and carbonyl in the ester linkage. The LC results were highly compatible in both compounds (G_1) and (IV_{OCH_3}), where displayed enantiotropic nematic phase, the range of the nematic phase of the compound (IV_{OCH_3}) was slightly higher than the compound (G_1). This is very reasonable, where the –OC_4H_9 classified as a strong electron-donating group compared to the methyl group; also, the length of the alkyl chain in this group also affects in the mesogenic properties of this compound, which makes it appear in higher range than the compound (G_1). Scheme 2 shows the comparison between the mesomorphic behaviours of compounds (G_1 and IV_{OCH_3}).

On the other hand, the liquid crystalline properties of other two compounds in this series (G_4 and G_8) were compared with the two compounds (2.2 and 2.3) which differ from the compounds (G_4 and G_8) in the heterocyclic ring and in the nature of the one terminus group, where the two compounds (2.2 and 2.3) have a 1,3,4-oxadiazole ring and alkoxy terminal group instead of a 1,2,4-oxadiazole ring and methyl terminal group in the compounds (G_4 and G_8). All compounds (G_4, G_8, 2.2 and 2.3) have been shown only nematic phase while they differ in the extent of this phase, where the nematic phase of the compounds (G_4 and G_8) appeared in a higher range (about double) compared to the two compounds (2.2 and 2.3), the main reason for this difference in the liquid crystalline range is their difference in the type of heterocyclic ring, the compounds containing 1,2,4-oxadiazole ring possessing linearity more than the compounds containing 1,3,4-oxadiazole ring due to their differences in the exocyclic angle, 134° and 140° for 1,3,4- and 1,2,4-oxadiazole isomers, respectively [39,40]. The comparison between the liquid crystalline properties of compounds (G_4, G_8, 2.2 and 2.3) shows in Scheme 3.

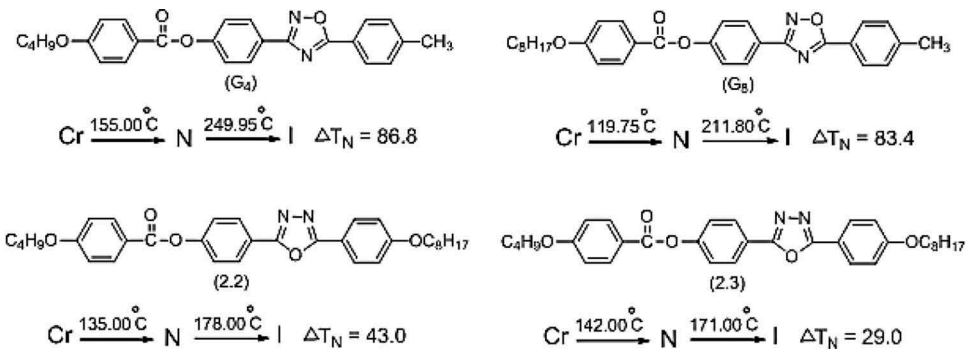
Table 2. Nematogenic ranges (ΔT_N, T [°C]) of all mesogens (G_n) resulted from first heating and cooling scan in (DSC) technique.

	Heating scan	Cooling scan
Comp.	*N*	*N*
G_1	134.60	189.30
G_2	69.00	169.70
G_3	80.50[a]	142.40[a]
G_4	86.80	138.10
G_5	77.10	116.80
G_6	78.80	138.20
G_7	87.50	107.10
G_8	83.4	134.70
G_9	76.60	133.90
G_{10}	75.10	126.00
G_{11}	79.10	121.30

[a]Determined by (OPM) observations.



Scheme 2. The mesomorphic behaviour of compounds (G_1 and IV_{OCH_3}).



Scheme 3. The comparison between the liquid crystalline properties of the compounds (G_4, G_8, 2.2 and 2.3).

4. Conclusion

In summary, new 1,2,4-oxadiazole derivatives were designed and synthesized in good yields, 81–87% by many organic methods. The structures of these compounds were confirmed by usual spectroscopic methods like FT-IR and ^{1}H NMR. Their mesomorphic properties were investigated by POM and DSC. All the compounds in the series (G_n) show enantiotropic LCs with nematic textures. The mesomorphic results showed that the nature of the mesophase is not largely sensitive to the length of the alkoxy terminal group; only the ΔT_N in cooling scan is wider than in heating scan. These results were very consistent and convincing with other analogues compounds close in their chemical structures; it may provide a better understanding of the type of mesomorphic behaviour and their use in many industrial applications.

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Disclosure statement

No potential conflict of interest was reported by the authors.

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