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New calamitic mesogens derived from a furan ring: Synthesis, characterization and study of their mesomorphic behavior

Nabih M. Abdulnabi^a, Mazin M. Abdul Razzaq Al-Obaidy^b, Ivan Hameed R. Tomi^{a,*}, Hamed Jasim Jaffer^a

^a Mustansiriyah University, College of Science, Department of Chemistry, Baghdad, Iraq
^b Al-Iraqia University, College of Education, Department of Chemistry, Baghdad, Iraq

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ABSTRACT

A new series of mesogens bearing furan moiety, 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino|phenyl 4alkoxybenzoate (C_{a-k}) was synthesized by different organic methodologies. These mesogens possess an alkoxy chain at one arm and a nitro group at the opposite arm in addition to various linkages (imine and ester). Their chemical structures have been identified by various essential characterization techniques: infrared spectroscopy (FTIR), ¹H and ¹³C nuclear magnetic resonance (NMR), and electron ionization-mass spectrometer (EI-MS). The thermal transition and optical behavior properties of the homologous series have been studied by differential scanning calorimetry (DSC) and a polarizing optical microscope (POM), respectively. The compounds of this series (C_a-C_k) displayed liquid crystalline phases, and all mesogens exhibited an enantiotropic nematic phase (N) in heating and cooling cycles except the compounds (C_d , C_e and C_f), which showed a monotropic nematic phase in the cooling cycle only. Additionally, the last member of this series (C_k) showed a smectic A (SmA) phase in addition to the nematic phase. The obtained results showed that the enantiotropic and monotropic mesogenic properties, in addition to the thermal stability of the mesophase for all mesogens, have been influenced thoroughly by increasing the number of carbon atoms in the terminal alkoxy tail and the nitro group on the other side. In addition to these results, these mesogens could be affected by other factors, such as polarity and polarizability of the linkages and other connected groups in the molecules. The liquid crystalline behaviors of the target compounds have been studied and discussed extensively and compared structurally in related literature.

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1. Introduction

Aromatic moieties, such as phenyl and naphthalene, make up the common core unit in most of the liquid crystal compounds that have been prepared over a long period. The main role of these moieties is to connect the polar π -electron groups with each other to develop the mesogenic character of the synthesized compounds and to make these compounds possess liquid crystalline properties in the ranges used in different applications in this field [1–4]. After extensive work in this field by many researchers, it is found that the compounds containing heterocyclic rings have good mesomorphic properties when they replace the commonly used aromatic groups [5–7]. It is clear that placing such heterocyclic rings as a core part of the mesogen structure creates substantial changes in the mesogenic behaviors in addition to creating new optical and thermal properties. The heteroatoms in these compounds, such as N, O, and S, have the polar character that could expand their applications by improving their mesomorphic properties. The

https://doi.org/10.1016/j.molliq.2020.114562 0167-7322/Published by Elsevier B.V. changes in the mesogenic properties are greatly related to the type and number of heteroatoms in the ring as well as the effects of the polarity and the linearity of the molecules [8–13]. Therefore, many studies in this field were carried out using different five-membered heterocyclic moieties, such as furan, pyrrole, thiophene, 1,2,4- and 1,3,4-oxadiazoles, 1,3,4-thiadiazole and triazol, in the mesogen structure. [14–19]. Moreover, an important research line was developed to study the role of these types of rings in the mesogenic structure and the relationships between the molecule structure and its mesophase property [20]. In addition, the introduction of polar substituents within the chemical structure of the heterocyclic derivatives, such as nitro, cyano, and other polar groups or linkages, might lead to a substantial change in the polarizability structure of the molecules that form to design a new mesogenic system, forming new mesophase textures for the target compounds and having useful thermal and optical applications [21–23].

Based on the above information, furan is a five-member aromatic ring, which contains in its composition four carbon atoms and one oxygen atom. The 2,5-disubstituted derivatives of this ring may appear as liquid crystalline properties, despite containing exocyclic bend angle (C-O-C), a deviation from the linearity (approximately 125°) compared to the benzene derivatives [24]. This might be the reason for the scarcity

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^{*} Corresponding author.

E-mail addresses: ivanhrtomy@yahoo.com, ivanhrtomy@uomustansiriyah.edu.iq (I.H.R. Tomi).

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of reported articles in the literature that relate to the derivatives of this ring and are recorded as mesogens. Therefore, the mesogenic compounds derived from this ring are classified as bent or banana-shaped. Continuing with our interest concerning the design and synthesis of new mesogenic materials derived from five-membered heterocyclic moieties [25–28], we thought it would be valuable to design and synthesize a series of mesogens bearing a furan ring as a core unit that conjugated different linkages (CH=N, O-C=O) and to study their mesomorphic properties.

2. Experimental

2.1. Materials and analysis

No further purification was carried out on the chemicals used in this research. Chemicals were procured by Sigma-Aldrich chemicals Pvt. Ltd. and were utilized as received. Different analyses were used to characterize and confirm the chemical structures of the synthesized final esters and their intermediates. FTIR spectra for all products were recorded on a Shimadzu 8400 (ATR) spectrophotometer, while ¹H and ¹³C NMR analyses were run using a Bruker product model ultrashield at 300 and 75 MHz, respectively. The results were measured in (ppm), tetramethylsilane (TMS) was used as the internal standard and deuterated (CDCl₃ and DMSO- $_{d6}$) as suitable solvents for final compounds and intermediates, respectively. A Shimadzu OP1000EX instrument was used to measure the mass fragments of the synthesized compounds using (EI-MS) mode. Mesomorphic studies of the target compounds were established by polarized optical microscopy (OPM) type (PW-BK 5000 PR), equipped with a hot-stage model (HS- 400). A thin film of small amounts in each compound between two squares of glass as a sandwich was prepared to show the mesogenic textures of the materials using the polarized light in a microscope. Thermal transitions of the mesogens were measured by differential scanning calorimetry (DSC) using the LINSIS instrument (STAPT-1000), indium metal was used as a standard for calibration, and the heating and cooling rates were 5 °C/min in a nitrogen atmosphere.

2.2. Synthesis procedures

2.2.1. 5-(4-nitrophenyl)furan-2-carbaldehyde (A)

The nitro derivative of the furfural aldehyde (A) was prepared using the method described in our previous work [29]. In a mixture solution of 37% HCl (50 mL) and water (33 mL), 4-nitroaniline (28.56 g, 0.207 mol) was dissolved, and a solution of sodium nitrite (14.28 g, 0.207 mol) in water (37.5 mL) was added slowly at a temperature 0–5 °C. The reactants were then left to stir for 20 min at this temperature and then filtered. The resulting filtrate was treated with two solutions simultaneously. The first solution consisted of furan-2-carboxaldehyde (57.05 g, 0.247 mol) in H₂O (75 mL). The second solution consisted of CuCl₂.2H₂O (7.5 g, 0.06 mol) in water (37.5 mL). The mixture solution was carried out at room temperature with continuous stirring for 20 min. The temperature of the reactants was raised to 40 °C and left to stir for an additional 5 h. A dark orange precipitate was formed, filtered by a Buchner funnel and then washed several times with 5% aqueous sodium bicarbonate and distilled water. The crude solid product was dried at room temperature and then purified by recrystallization from absolute ethanol. Yield (65%), mp = (202–204 °C), (202–205 °C, lit. [29], (204–206 °C, lit. [30]; FTIR (ART, cm^{-1}), υ_{max} : 3117 (C-Harom.), 2841 (C-Haldehydic), 1681 (C=Oaldehyde), 1601, 1520 (C=C), 1514, 1342 (NO_{2 *asym.* and *sym.*); ¹H NMR (300 MHz, DMSO-*d*₆, *δ*, ppm):} 7.58 (d, 1H, furan, *J* = 3.75), 7.71 (d, 1H, furan, *J* = 3.75), 8.12 (d, 2H, arom., *J* = 8.80), 8.34 (d, 2H, arom., *J* = 8.80), 9.68 (s, 1H, aldehydic H).

2.2.2. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenol (B)

The titled compound was synthesized using the general Schiff base procedure described in [31,32] with some adjustments. A mixture of

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5-(4-nitrophenyl)furan aldehyde (32 g, 0.262 mol), 4- aminophenol (28.58 g, 0.262 mol), and 7 drops of glacial acetic acid was dissolved in absolute ethanol (300 mL) and placed in a 500 mL round-bottom flask. The reaction mixture was refluxed for one day and then left to cool down to approximately 25 °C. A precipitate of crude product was formed, filtered, washed with cold ethanol (50 mL), and recrystallized from ethanol. Yield (85%), FTIR (ART, cm⁻¹), v_{max}: 2557-3120 (O—H), 3063 (C-H_{aron.}) 2968, 2866, 1620 (C=N), 1595, 1577 (C=C), 1504, 1321 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, DMSO-_{d6}, δ, ppm): 9.58 (s, 1H, phenolic OH), 8.51 (s, 1H, CH=N), 8.34 (d, 2H, Ar-H, Ph attached to $-NO_2$, I = 8.76), 8.08 (d, 2H, Ar—H, Ph attached to $-NO_2$, I =8.74), 7.52 (d, 1H, furan ring, J = 3.64), 7.26 (d, 2H, Ar—H, Ph attached to –OH, *J* = 8.46), 7.25 (d, 1H, furan ring, *J* = 3.97), 6.81 (d, 2H, Ar—H, Ph attached to –OH, J = 8.59); ¹³C NMR (75 MHz, DMSO-_{*d*6}, δ , ppm): 156.70 (aromatic C, C-OH), 153.54 (C furan ring), 152.81 (C furan ring), 146.44 (aromatic C, C-NO₂), 144.57 (CH=N), 142.11 (aromatic C, C-N=CH), 135.16 (aromatic C, C-furan), 125.07 (aromatic C—H), 124.80 (aromatic C—H), 124.52 (aromatic C—H), 122.65 (aromatic C—H), 115.78 (C—H furan ring), 112.47 (C—H furan ring); (EI-MS) (relative intensity %) m/z = 308 (M⁺, 100%, base peak), 291 (25%), 261 (40%).

2.2.3. General procedure for synthesis of 4-[((5-(4-nitrophenyl)furan-2-yl) methylene)amino]phenyl 4-alkoxybenzoate (C_{a-k})

The general procedure for the synthesis of the titled esters was reported in our previous work with slight modifications [33,34]. In a 100 mL round-bottom flask, furanimine phenol (B) (1.00 g, 0.003 mol) and various 4-alkoxycarboxylic acids (X_n) (0.003 mol) were dissolved in dry dichloromethane (DCM) (100 mL). The esterification coupling reagents, N,N-dicyclohexylcarbodiimide (DCC) (0.66 g, 0.003 mol) and 4-(Dimethylamino)pyridine (DMAP) (0.36 g, 0.003 mol), were added to the reactants and then left in the flask at approximately 25 °C to stir for one week. The precipitate formed (1,3-Dicyclohexyl urea DCU) was removed by filtration, and the filtrate was transferred to a separating funnel for the purification process. It was then washed with a dilute solution of acetic acid (5%, 80 mL) and then with distilled water (80 mL). The separated organic layer was dried with anhydrous magnesium sulfate; then the DCM solvent was removed under reduced pressure. The resulted crude products (C_{a-k}) were recrystallized using ethanol.

2.2.4. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-methoxybenzoate (C_a)

Yield (82%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3080 (C-Harom.), 2978, 2895 (C-Haliph.), 1720 (C=O), 1627 (C=N), 1599 (C= C), 1512, 1327 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.30 (d, 2H, Ar-H, Ph attached to $-NO_2$, I =8.89), 8.17 (d, 2H, Ar—H, Ph attached to methoxy, *J* = 8.85), 7.97 (d, 2H, Ar—H, Ph attached to -NO₂, *J* = 8.80), 7.33 (d, 2H, Ar—H, middle phenyl, *J* = 8.83), 7.26 (d, 2H, Ar—H, middle phenyl, *J* = 8.80), 7.14 (d, 1H, furan ring, J = 3.65), 7.04 (d, 1H, furan ring, J = 3.86), 7.00 (d, 2H, Ar—H, Ph attached to methoxy, J = 8.90), 3.90 (3H, s, -OCH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.94 (aromatic C, C-OR), 164. 00 (C=O), 154.27 (C furan ring), 153.27 (C furan ring), 151.43 (aromatic C, C-NO₂), 149.72 (aromatic C, C—O), 148.79 (aromatic C, C-N=CH), 147.38 (CH=N), 135.31 (aromatic C, C-furan), 132.33 (aromatic C, C-C=O), 125.03 (aromatic C-H), 124.36 (aromatic C-H), 122.59 (aromatic C-H), 121.98 (aromatic C-H), 121.71 (aromatic C-H), 118.00 (aromatic, C-H), 113.89 (C-H furan ring), 111.05 (C-H furan ring), 55.54 (OCH₃); (EI-MS) (relative intensity %) m/z = 442 $(M^+, 15\%)$, 135 (CH₃O-Ph-C = O⁺, 100\%, base peak).

2.2.5. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-ethoxybenzoate (C_b)

Yield (79%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3078 (C-H_{arom.}), 2949, 2875 (C-H_{aliph.}), 1714 (C=O), 1626 (C=N), 1602 (C=

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C), 1516, 1327 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.30 (d, 2H, Ar-H, Ph attached to $-NO_2$, I =8.98), 8.15 (d, 2H, Ar—H, Ph attached to ethoxy, *I* = 8.87), 7.97 (d, 2H, Ar—H, Ph attached to -NO₂, *J* = 8.95), 7.33 (d, 2H, Ar—H, middle phenyl, *I* = 8.86), 7.26 (d, 2H, Ar—H, middle phenyl, *I* = 8.82), 7.14 (d, 1H, furan ring, J = 3.66), 7.04 (d, 1H, furan ring, J = 3.64), 6.98 (d, 2H, Ar—H, Ph attached to ethoxy, *J* = 8.90), 4.10–4.17 (q. 2H, -OCH₂), 1.44–1.49 (3H, t, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 166.74 (aromatic C, C-OR), 163. 64 (C=O), 153.28 (C furan ring), 152.78 (C furan ring), 151.07 (aromatic C, C-NO₂), 149.76 (aromatic C, C-O), 148.75 (aromatic C, C-N=CH), 147.37 (CH=N), 135.32 (aromatic C, Cfuran), 132.30 (aromatic C, C-C=O), 125.02 (aromatic C-H), 124.88 (aromatic C—H), 122.60 (aromatic C—H), 121.97 (aromatic C—H), 121.42 (aromatic C-H), 117.99 (aromatic, C-H), 114.35 (C-H furan ring), 111.04 (C-H furan ring), 59.52 (OCH₂), 10.45 (OCH₂CH₃); (EI-MS) (relative intensity %) m/z = 456 (M⁺, 17%), 149 (CH₃CH₂O-Ph-C ≡ O⁺, 100%, base peak), 121 (HO-Ph-C ≡ O⁺, 33%), 94 (Ph-OH⁺, 7%).

2.2.6. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-propoxybenzoate (C_c)

Yield (74%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3075 (C-Harom.), 2968, 2893 (C-Haliph.), 1717 (C=O), 1626 (C=N), 1599 (C=C), 1516, 1329 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH==N), 8.29 (d, 2H, Ar=H, Ph attached to -NO₂, *J* = 8.94), 8.15 (d, 2H, Ar—H, Ph attached to propoxy, *J* = 8.83), 7.96 (d, 2H, Ar—H, Ph attached to $-NO_2$, J = 8.89), 7.33 (d, 2H, Ar—H, middle phenyl, J =8.78), 7.26 (d, 2H, Ar—H, middle phenyl, *J* = 8.75), 7.14 (d, 1H, furan ring, J = 3.60), 7.03 (d, 1H, furan ring, J = 3.59), 6.99 (d, 2H, Ar—H, Ph attached to propoxy, *J* = 8.88), 3.99–4.04 (t, 2H, -OCH₂), 1.80–1.89 (m, 2H, -OCH₂CH₂), 1.04–1.09 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 166.78 (aromatic C, C-OR), 163. 84 (C=O), 153.32 (C furan ring), 152.97 (C furan ring), 151.13 (aromatic C, C-NO₂), 149.88 (aromatic C, C-O), 148.69 (aromatic C, C-N=CH), 147.68 (CH=N), 135.29 (aromatic C, Cfuran), 132.35 (aromatic C, C-C=O), 125.06 (aromatic C-H), 124.91 (aromatic C--H), 122.75 (aromatic C--H), 122.01 (aromatic C--H), 121.65 (aromatic C—H), 118.04 (aromatic, C—H), 114.47 (C—H furan ring), 111.08 (C—H furan ring), 57.52 (OCH₂), 22.45 (OCH₂CH₂CH₃), 10.45 (OCH₂CH₂CH₃); (EI-MS) (relative intensity %) m/z = 470 $(M^+, 16\%)$, 163 $\overline{(CH_3CH_2CH_2O-ph-C = O^+, 100\%)}$, base peak), 121 $(HO-Ph-C \equiv O^+, 50\%), 94 (Ph-OH^+, 4\%).$

2.2.7. 4-[((5-(4-nitrophenyl))furan-2-yl)methylene)amino]phenyl 4-butoxybenzoate (C_d)

Yield (74%) as a vellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3070 (C-H_{arom}), 2935, 2880 (C-H_{aliph}), 1728 (C=O), 1622 (C=N), 1599 (C= C), 1516, 1330 (NO_{2sym, and asym}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.29 (d, 2H, Ar-H, Ph attached to $-NO_2$, J =8.93), 8.15 (d, 2H, Ar—H, Ph attached to butoxy, *J* = 8.83), 7.96 (d, 2H, Ar—H, Ph attached to –NO₂, *J* = 8.96), 7.33 (d, 2H, Ar—H, middle phenyl, *I* = 8.84), 7.25 (d, 2H, Ar—H, middle phenyl, *I* = 8.81), 7.13 (d, 1H, furan ring, *J* = 3.64), 7.03 (d, 1H, furan ring, *J* = 3.63), 6.98 (d, 2H, Ar—H, Ph attached to butoxy, *J* = 8.90), 4.03–4.08 (t, 2H, -OCH₂), 1.77-1.86 (m, 2H, -OCH₂CH₂), 1.46-1.58 (m, 2H, -OCH₂CH₂CH₂), 0.97–1.02 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.99 (aromatic C, C-OR), 163. 64 (C=O), 154.26 (C furan ring), 153.28 (C furan ring), 151.41 (aromatic C, C-NO₂), 149.74 (aromatic C, C-O), 148.76 (aromatic C, C-N=CH), 147.36 (CH=N), 135.31 (aromatic C, Cfuran), 132.30 (aromatic C, C-C=O), 125.58 (aromatic C-H), 124.35 (aromatic C—H), 122.59 (aromatic C—H), 121.97 (aromatic C—H), 121.40 (aromatic C-H), 117.98 (aromatic, C-H), 114.34 (C-H furan ring), 111.06 (C-H furan ring), 68.03 (OCH₂), 31.13, (OCH₂CH₂CH₂CH₃), 19.19 (OCH₂CH₂CH₂CH₃) 13.31 (O(CH₂)₃CH₃); (EI-MS) (relative intensity %) m/z = 484 (M⁺, 18%), 177 (CH₃(CH₂) $_{2}$ CH $_{2}$ O-ph-C = O⁺, 100%, base peak), 121 (HO-Ph-C = O⁺, 62%), 94 (Ph-OH⁺, 6%).

2.2.8. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(pentyloxy)benzoate (C_e)

Yield (70%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3086 (C-H_{arom}), 2945, 2866 (C-H_{aliph}), 1726 (C=O), 1622 (C=N), 1597 (C= C), 1512, 1327 (NO_{2sym, and asym}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.30 (d, 2H, Ar-H, Ph attached to -NO₂, J = 8.38), 8.15 (d, 2H, Ar—H, Ph attached to pentyloxy, *J* = 8.34), 7.97 (d, 2H, Ar—H, Ph attached to –NO₂, *J* = 8.39), 7.33 (d, 2H, Ar—H, middle phenyl, *J* = 8.66), 7.26 (d, 2H, Ar—H, middle phenyl, *J* = 8.35), 7.13 (d, 1H, furan ring, I = 3.41), 7.03 (d, 1H, furan ring, I = 3.48), 6.98 (d, 2H, Ar—H, Ph attached to pentyloxy, J = 8.46), 4.03–4.07 (t, 2H, -OCH₂), 1.79–1.88 (m, 2H, -OCH₂CH₂), 1.37–1.50 (m, 4H, -OCH₂CH₂CH₂CH₂), 0.93–0.97 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 164.99 (aromatic C, C-OR), 163. 63 (C=O), 154.25 (C furan ring), 153.29 (C furan ring), 151.41 (aromatic C, C-NO₂), 149.74 (aromatic C, C-O), 148.78 (aromatic C, C-N=CH), 147.36 (CH=N), 135.32 (aromatic C, C-furan), 132.30 (aromatic C, C-C=O), 125.02 (aromatic C—H), 124.36 (aromatic C—H), 122.60 (aromatic C—H), 121.97 (aromatic C—H), 121.39 (aromatic C—H), 117.96 (aromatic, C-H), 114.34 (C-H furan ring), 111.06 (C-H furan ring), 68.34 (OCH₂), 28.79 (OCH₂CH₂(CH₂)₂CH₃), 28.13, (OCH₂CH₂CH₂CH₂CH₂CH₃), 22.46 (OCH₂(CH₂)₂CH₂CH₃) 14.00 (O(CH₂)₄CH₃); (EI-MS) (relative intensity %) m/z = 498 (M⁺, 16%), 191 (CH₃(CH₂)₃CH₂O-ph- $C \equiv O^+$, 100%, base peak), 121 (HO-Ph-C $\equiv O^+$, 34%), 94 (Ph-OH⁺, 2%).

2.2.9. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(hexyloxy)benzoate (C_f)

Yield (81%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3059 (C-H_{arom}), 2976, 2885 (C-H_{aliph}), 1716 (C=O), 1629 (C=N), 1595 (C= C), 1514, 1323 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.30 (d, 2H, Ar-H, Ph attached to $-NO_2$, J =8.88), 8.15 (d, 2H, Ar—H, Ph attached to hexyloxy, *J* = 8.84), 7.97 (d, 2H, Ar—H, Ph attached to –NO₂, *J* = 8.90), 7.33 (d, 2H, Ar—H, middle phenyl, *J* = 8.74), 7.26 (d, 2H, Ar—H, middle phenyl, *J* = 8.74), 7.14 (d, 1H, furan ring, J = 3.66), 7.04 (d, 1H, furan ring, J = 3.60), 6.98 (d, 2H, Ar—H, Ph attached to hexyloxy, J = 8.88), 4.03–4.07 (t, 2H, -OCH₂), 1.78–1.87 (m, 2H, -OCH₂CH₂), 1.25–1.36 (m, 6H, -OCH₂CH₂) $(CH_2)_3$, 0.85–0.89 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 164.98 (aromatic C, C-OR), 163. 63 (C=O), 154.23 (C furan ring), 151.40 (C furan ring), 149.73 (aromatic C, C-NO₂), 148.77 (aromatic C, C-O), 147.39 (aromatic C, C-N=CH), 147.20 (CH=N), 135.32 (aromatic C, C-furan), 132.31 (aromatic C, C-C=O), 125.03 (aromatic C----H), 124.37 (aromatic C----H), 122.61 (aromatic C-----H), 121.98 (aromatic C—H), 121.37 (aromatic C—H), 118.04 (aromatic, C—H), 114.34 (C—H furan ring), 111.07 (C—H furan ring), 68.36 (OCH₂), 31.55 (OCH₂CH₂(CH₂)₃CH₃), 29.06, (OCH₂CH₂CH₂(CH₂)₂CH₃), 25.66 (OCH₂(CH₂)₂CH₂CH₂CH₃), 22.59 (OCH₂(CH₂)₂CH₂CH₂CH₃), 14.03 (O(CH₂)₅CH₃); (EI-MS) (relative intensity %) m/z = 512 $(M^+, 20\%), 205 (CH_3(CH_2)_4CH_2O-ph-C \equiv O^+, 100\%, base peak), 121$ $(HO-Ph-C \equiv O^+, 6\%).$

2.2.10. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(heptyloxy)benzoate (C_g)

Yield (73%) as a yellowish solid; FTIR (ART, cm⁻¹), v_{max} : 3068 (C-H_{arom.}), 2945, 2848 (C-H_{aliph.}), 1714 (C=O), 1624 (C=N), 1593 (C=C), 1510, 1321 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ , ppm): 8.36 (s, 1H, CH=N), 8.30 (d, 2H, Ar—H, Ph attached to $-NO_2$, J = 8.91), 8.15 (d, 2H, Ar—H, Ph attached to heptyloxy, J = 8.81), 7.97 (d, 2H, Ar—H, Ph attached to $-NO_2$, J = 8.92), 7.33 (d, 2H, Ar—H, middle phenyl, J = 8.74), 7.26 (d, 2H, Ar—H, middle phenyl, J = 8.75), 7.14 (d, 1H, furan ring, J = 3.64), 7.04 (d, 1H, furan ring, J = 3.59), 6.98 (d, 2H, Ar—H, Ph attached to heptyloxy, J = 8.85), 4.02–4.07 (t, 2H, -OCH₂), 1.78–1.85 (m, 2H, -OCH₂CH₂), 1.25–1.48 (m, 8H, O(CH₂)₂) (CH₂)₄), 0.86–0.90 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ , ppm): 165.02 (aromatic C, C-OR), 163. 64 (C=O), 154.26 (C furan ring),

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151.39 (C furan ring), 149.73 (aromatic C, C-NO₂), 148.76 (aromatic C, C–O), 147.38 (aromatic C, C-N=CH), 147.19 (CH=N), 135.31 (aromatic C, C-furan), 132.31 (aromatic C, C-C=O), 125.03 (aromatic C–H), 124.37 (aromatic C–H), 122.61 (aromatic C–H), 121.98 (aromatic C–H), 121.35 (aromatic C–H), 118.03 (aromatic, C–H), 114.34 (C–H furan ring), 111.07 (C–H furan ring), 68.36 (OCH₂), 31.76 (OCH₂CH₂(CH₂)₄CH₃), 29.10, (OCH₂CH₂CH₂CH₂)₃CH₃, 29.03 (OCH₂(CH₂)₃CH₂CH₂CH₂CH₃), 14.09 (O(CH₂)₂CH₂CH₂CH₃), 22.61 (OCH₂(CH₂)₂CH₂CH₂CH₂CH₂CH₃), 14.09 (O(CH₂)₆CH₃); (EI-MS) (relative intensity %) *m/z* = 526 (M⁺, 18%), 219 (CH₃(CH₂)₅CH₂O-ph-C = O⁺, 100%, base peak).

2.2.11. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(octyloxy)benzoate (C_h)

Yield (84%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3070 (C-H_{arom.}), 2939, 2843 (C-H_{aliph.}), 1726 (C=O), 1626 (C=N), 1601 (C= C), 1518, 1332 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.36 (s, 1H, CH=N), 8.29 (d, 2H, Ar-H, Ph attached to $-NO_2$, J =8.94), 8.15 (d, 2H, Ar—H, Ph attached to octyloxy, *J* = 8.83), 7.96 (d, 2H, Ar—H, Ph attached to -NO₂, *J* = 8.93), 7.33 (d, 2H, Ar—H, middle phenyl, J = 8.78), 7.25 (d, 2H, Ar—H, middle phenyl, J = 8.81), 7.13 (d, 1H, furan ring, I = 3.65), 7.04 (d, 1H, furan ring, I = 3.62), 6.98 (d, 2H, Ar—H, Ph attached to octyloxy, I = 8.87), 4.02–4.07 (t, 2H, -OCH₂), 1.78–1.87 (m, 2H, -OCH₂CH₂), 1.30–1.48 (m, 10H, -O(CH₂)₂) $(CH_2)_5$, 0.87–0.92 (t, 3H, -CH₃); ^{13}C NMR (75 MHz, CDCl₃, δ , ppm): 165.01 (aromatic C, C-OR), 163. 64 (C=O), 154.25 (C furan ring), 153.26 (C furan ring), 151.39 (aromatic C, C-NO₂), 149.73 (aromatic C, C-O), 148.76 (aromatic C, C-N=CH), 147.38 (CH=N), 135.31 (aromatic C, C-furan), 132.30 (aromatic C, C-C=O), 125.03 (aromatic C---H), 124.37 (aromatic C---H), 122.61 (aromatic C---H), 121.99 (aromatic C—H), 121.36 (aromatic C—H), 118.05 (aromatic, C—H), 114.34 (C—H furan ring), 111.08 (C—H furan ring), 68.36 (OCH₂), 31.80 (OCH₂CH₂(CH₂)₅CH₃), 29.33, (OCH₂CH₂CH₂(CH₂)₄CH₃), 29.22 $(OCH_2(CH_2)_2CH_2(CH_2)_3CH_3)$, 29.10 $(OCH_2(CH_2)_3CH_2CH_2CH_2CH_3)$, 25.99 (OCH₂(CH₂)₄CH₂CH₂CH₃) 22.66 (OCH₂(CH₂)₅CH₂CH₃) 14.11 (O $(CH_2)_7 CH_3$; (EI-MS) (relative intensity %) m/z = 540 (M⁺, 100%, base peak), 121 (HO-Ph-C ≡ O⁺, 5%).

2.2.12. 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(nonyloxy)benzoate (C_i)

Yield (82%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3038 (C-Harom.), 2945, 2864 (C-Haliph.), 1735 (C=O), 1624 (C=N), 1601 (C= C), 1514, 1327 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.30 (d, 2H, Ar-H, Ph attached to $-NO_2$, I =8.85), 8.15 (d, 2H, Ar—H, Ph attached to nonyloxy, *J* = 8.74), 7.97 (d, 2H, Ar—H, Ph attached to –NO₂, *J* = 8.87), 7.33 (d, 2H, Ar—H, middle phenyl, *J* = 8.76), 7.26 (d, 2H, Ar—H, middle phenyl, *J* = 8.70), 7.14 (d, 1H, furan ring, J = 3.64), 7.04 (d, 1H, furan ring, J = 3.59), 6.98 (d, 2H, Ar—H, Ph attached to nonyloxy, J = 8.80), 4.02–4.07 (t, 2H, -OCH₂), 1.78–1.85 (m, 2H, -OCH₂CH₂), 1.29–1.48 (m, 12H, -O(CH₂)₂ (CH₂)₆), 0.86–0.91 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 165.00 (aromatic C, C-OR), 163. 64 (C=O), 154.27 (C furan ring), 153.26 (C furan ring), 151.40 (aromatic C, C-NO₂), 149.74 (aromatic C, C-O), 148.76 (aromatic C, C-N=CH), 147.38 (CH=N), 135.31 (aromatic C, C-furan), 132.30 (aromatic C, C-C=O), 125.03 (aromatic C-H), 124.37 (aromatic C-H), 122.61 (aromatic C-H), 121.98 (aromatic C--H), 121.36 (aromatic C--H), 118.04 (aromatic, C--H), 114.34 (C—H furan ring), 111.07 (C—H furan ring), 68.36 (OCH₂), 31.87 (OCH₂CH₂(CH₂)₆CH₃), 29.52, (OCH₂CH₂CH₂(CH₂)₅CH₃), 29.37 $(OCH_2(CH_2)_2CH_2(CH_2)_4CH_3)$, 29.25 $(OCH_2(CH_2)_3CH_2(CH_2)_3CH_3)$, 29.10 (OCH₂(CH₂)₄CH₂(CH₂)₂CH₃), 25.98 (OCH₂(CH₂)₅CH₂CH₂CH₃) 22.67 (OCH₂(CH₂)₆CH₂CH₃) 14.12 (O(CH₂)₈CH₃); (EI-MS) (relative intensity %) $m/z = \overline{554}$ (M⁺, 12%), 247 (CH₃(CH₂)₇CH₂O-ph-C = O⁺, 100%, base peak), 43 (CH₃CH₂CH₃⁺, 32%).

2.2.13. $4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(decyloxy)benzoate (C_i)$

Yield (84%) as a vellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3059 (C-H_{arom.}), 2928, 2852 (C-H_{aliph.}), 1732 (C=O), 1622 (C=N), 1599 (C= C), 1514, 1325 (NO_{2sym, and asym}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.39 (s, 1H, CH=N), 8.32 (d, 2H, Ar-H, Ph attached to -NO₂, J = 8.98), 8.17 (d, 2H, Ar—H, Ph attached to decyloxy, *J* = 8.86), 7.99 (d, 2H, Ar—H, Ph attached to –NO₂, *J* = 8.96), 7.35 (d, 2H, Ar—H, middle phenyl, *J* = 8.81), 7.28 (d, 2H, Ar—H, middle phenyl, *J* = 8.80), 7.16 (d, 1H, furan ring, I = 3.66), 7.04 (d, 1H, furan ring, I = 3.62), 7.00 (d, 2H, Ar—H, Ph attached to decyloxy, J = 8.89), 4.04–4.09 (t, 2H, -OCH₂), 1.80–1.87 (m, 2H, -OCH₂CH₂), 1.30–1.49 (m, 14H, -O(CH₂)₂ (CH₂)₇), 0.89–0.93 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 165.02 (aromatic C, C-OR), 163. 63 (C=O), 156.26 (C furan ring), 153.26 (C furan ring), 151.40 (aromatic C, C-NO₂), 149.74 (aromatic C, C-O), 148.77 (aromatic C, C-N=CH), 147.38 (CH= N), 135.32 (aromatic C, C-furan), 132.30 (aromatic C, C-C=O), 125.03 (aromatic C-H), 124.37 (aromatic C-H), 122.61 (aromatic (aromatic, C-H), 114.34 (C-H furan ring), 111.07 (C-H furan ring), 68.36 (OCH₂), 31.90 (OCH₂CH₂(CH₂)₇CH₃), 29.55, $(OCH_2CH_2CH_2(CH_2)_6CH_3), 29.36 (OCH_2(CH_2)_2CH_2(CH_2)_5CH_3),$ 29.32 (OCH₂(CH₂)₃CH₂(CH₂)₄CH₃), 29.10 (OCH₂(CH₂)₄CH₂(CH₂) ₃CH₃), 27.25 (OCH₂(CH₂)₅CH₂(CH₂)₂CH₃), 25.99 (OCH₂(CH₂) ₆CH₂CH₂CH₃) 22.68 (OCH₂(CH₂)₇CH₂CH₃) 14.12 (O(CH₂)₉CH₃); (EI-MS) (relative intensity %) $\overline{m/z} = 568$ (M⁺, 10%), 43 $(CH_3CH_2CH_3^+, 100\%, base peak).$

2.2.14. $4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-(dodecyloxy)benzoate (C_k)$

Yield (85%) as a yellowish solid; FTIR (ART, cm^{-1}), v_{max} : 3074 (C-Harom.), 2970, 2848 (C-Haliph.), 1726 (C=O), 1601 (C=N), 1579 (C= C), 1508, 1334 (NO_{2sym. and asym.}); ¹H NMR (300 MHz, CDCl₃, δ, ppm): 8.37 (s, 1H, CH=N), 8.29 (d, 2H, Ar-H, Ph attached to -NO₂, J = 8.95), 8.15 (d, 2H, Ar—H, Ph attached to dodecyloxy, *J* = 8.84), 7.96 (d, 2H, Ar—H, Ph attached to -NO₂, *J* = 8.94), 7.33 (d, 2H, Ar—H, middle phenyl, J = 8.81), 7.25 (d, 2H, Ar—H, middle phenyl, J = 8.80), 7.14 (d, 1H, furan ring, J = 3.66), 7.04 (d, 1H, furan ring, J = 3.61), 6.98 (d, 2H, Ar—H, Ph attached to dodecyloxy, I = 8.89), 4.02–4.07 (t, 2H, -OCH₂), 1.78-1.87 (m, 2H, OCH₂CH₂), 1.27-1.47 (m, 18H, -O(CH₂)₂(CH₂)₉), 0.86–0.90 (t, 3H, -CH₃); ¹³C NMR (75 MHz, CDCl₃, δ, ppm): 165.02 (aromatic C, C-OR), 163. 63 (C=O), 156.25 (C furan ring), 153.26 (C furan ring), 151.39 (aromatic C, C-NO₂), 149.74 (aromatic C, C-O), 148.76 (aromatic C, C-N=CH), 147.37 (CH=N), 135.31 (aromatic C, Cfuran), 132.30 (aromatic C, C-C=O), 125.03 (aromatic C-H), 124.37 (aromatic C—H), 122.61 (aromatic C—H), 121.98 (aromatic C—H), 121.36 (aromatic C-H), 118.04 (aromatic, C-H), 114.34 (C-H furan ring), 111.07 (C—H furan ring), 68.36 (OCH₂), 31.92 (OCH₂CH₂(CH₂) ₉CH₃), 29.66, (OCH₂CH₂CH₂(CH₂)₈CH₃), 29.64 (OCH₂(CH₂)₂CH₂(CH₂) ₇CH₃), 29.59 (OCH₂(CH_2)₃CH₂(CH₂)₆CH₃), 29.56 (OCH₂($\overline{CH_2}$)₄CH₂ (CH₂)₅CH₃), 29.36 (OCH₂(CH₂)₅CH₂(CH₂)₄CH₃), 29.22 (OCH₂(CH₂) ₆CH₂(CH₂)₃CH₃), 29.10 (OCH₂(CH₂)₇CH₂(CH₂)₂CH₃), 25.99 (OCH₂ (CH₂)₈CH₂CH₂CH₃) 22.70 (OCH₂(CH₂)₉CH₂CH₃) 14.13 (O(CH₂)₁₁CH₃); (EI-MS) (relative intensity %) $m/z = 597 (M^+, 9\%), 61 (CH_3CH_2CH_2CH_3^+, 1000)$ 18%).

3. Results and discussion

3.1. Synthesis

The target of this project includes a synthesis of eleven esters bearing furan ring at the core section conjugated with imine, ester, and phenyl moieties. The synthetic routs, as well as the reaction reagents of the titled compounds (A, B and C_{a-k}) are outlined in Scheme 1.

The synthesis strategy was started with the preparation of 5-(4nitrophenyl)furan-2-carbaldehyde (A) by a previously reported

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Scheme 1. The synthetic route and reagents used in the synthesis of compounds (A, B and C_{a-k}), (i) hydrochloric acid (36.5%), distilled water, sodium nitrite, cupric chloride dihydrate; (ii) glacial acetic acid, absolute ethanol; (iii) N,N-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), dry dichloromethane (DCM), stirring at room temperature around 25 °C for (7 days).

procedure [29]; the spectral analyses (FTIR, ¹H NMR) and the melting point of the aldehyde (A) confirmed its chemical structure. The equimolar quantities of the resulted aldehyde (A) and 4-aminophenol reacted in the presence of glacial acetic acid to produce furan conjugated imine phenol (B) in a good yield. The chemical structure of the phenolic precursor (B) was characterized through spectral methods, such as FTIR, ¹H NMR, ¹³C NMR, and MS techniques. The most important stretching vibration band of the imine was noticed at (1620 cm^{-1}) and a broad phenolic hydroxyl band between 2520 and 3120 cm⁻¹. Moreover, the proton NMR analysis showed the imine proton as a singlet at 8.51 ppm in addition to the proton of hydroxyl in the phenolic group as a singlet signal at 9.58 ppm. Two doublets were assigned to the two protons of furan (H_3 and H_4), which were observed at (7.25-7.26 ppm) and (7.51-7.52 ppm) in the ¹H NMR spectrum of the imine-phenol (B). The ¹³C NMR and MS analysis results were in accordance with the usual values and corroborated the suggested chemical structure of the imine-phenol (B). The overall characterization results obtained concluded the formation and the chemical structure of the imine-phenol intermediate (B).

The target esters in this work were obtained by esterification of eleven 4-alkoxy benzoic acids (X_n) with imine phenol (B) using an efficient coupling reagent (DCC, DMAP) with stirring at room temperature for one week. The 4-alkoxybenzoic acids (X_n) were formerly prepared by a known reported method [35]. Different identification methodologies, such as FTIR, ¹H NMR, ¹³C NMR and EI-MS, were used to characterize the chemical structure of the synthesized esters (C_{a-k}) . A sharp stretching vibration band for carbonyl ester groups of these compounds was observed in the FTIR spectra at 1714 to 1735 cm⁻¹. This observation was associated with the disappearance of the phenolic hydroxyl stretching band in compound (B). In addition, a characteristic aliphatic stretching vibration of the methylene and methyl alkyl groups in alkoxy fragment appeared at the usual position. The ¹H NMR spectra of the synthesized esters demonstrated a clear singlet signal of the imine proton moiety between 8.36-8.39 ppm and two doublet signals for the two protons of the furan ring (H_3 and H_4) at about (7.13–7.14 ppm) and (7.03–7.04 ppm). The electronic spectra of the new esters showed an additional two doublets assigned to four aromatic protons of the new phenyl, which resulted from the reaction of 4-alkoxy benzoic acids and appeared at the usual aromatic area. The mass spectrometry analysis of the esters showed the formation of the important fragment ions and molecular ion peaks (M⁺), which were exactly in accordance with the chemical structures of these compounds (see experimental part). These results provided additional evidence concerning the formation of the target ester compounds. On the other hand, ¹³C NMR spectra of the synthesized esters indicated that the esterification reaction had taken place through clear signals that appeared approximately 165 ppm in spectra assigned to the carbon in the ester linkage. Fig. 1 shows the ¹H NMR spectra of the compounds (B) and (C_h). The representative spectra of mass and ¹³C NMR for C_g and C_e compounds respectively are displayed in Fig. 2.

3.2. Mesomorphic properties

All the synthesized homologue compounds in this series (C_{a-k}) displayed liquid crystalline behaviors. The majority of these compounds (C_{a-c} and C_{g-k}) exhibited the mesomorphic properties during the heating-cooling cycle (enantiotropic mesogens), while some compounds in the middle of the chain (C_{d-f}) were mesogens in the cooling cycle only (monotropic mesogens). The textures of these mesogens have been recorded by a polarizing optical microscope (POM) equipped with a thermal stage. The mesogenic phases were characterized by matching the recorded phases with those previously published in the literature [36,37]. Moreover, the phase transition temperatures and the enthalpy changes were obtained by using a differential scanning calorimetry (DSC) technique. The mesophase transition temperatures and the mesogenic ranges resulted from (POM), and some thermodynamic parameters (enthalpy kJ/mol and entropy J/mol.k changes) resulted from (DSC) measurements and are compiled in Table 1.

3.2.1. POM observations

Most of the eleven mesogens in this series (C_{a-k}) displayed a nematic phase under (POM) in both heating and cooling cycles. The exception is three members (C_{d-f}), which exhibited the nematogenic behavior in the cooling cycle only. The last member in this series (C_k) showed smectogenic behavior (SmA), in addition to the nematic phase, upon heating and cooling tests. The characterization of a liquid crystalline texture type was based on the mesophase type classified by Sackmann [38] and Gray [39]. Heating the sample from room temperature to the isotropic phase and cooling it to the crystal phase with continuous monitoring by POM resulted in different textures of the nematic phase in the homologues in this series: nematic droplets, thread-like associated with nematic phase, marble and Schlieren. These textures are usually

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Fig. 1. ¹H NMR spectra for compounds B (top) and C_h (down).



Fig. 2. Mass spectrum for compound C_g (top) and ¹³C NMR spectrum for compound C_e (down).

observed in the nematic phase. Additionally, the fan-shaped texture of the smectic A in the last member of this series (C_k) was very clear in both heating and cooling scans of this compound. The smectogenic appearance in the last homologue of this series is due to an increase in the number of carbon atoms in the alkyl chain of this compound (n = 12) [40]. Fig. 3 presents selective photomicrographs of different types of the nematic phase in the compounds of this series. On the other hand, Fig. 4 has shown the optical images of the transitions between two mesomorphic phases (nematic and smectic A) by heating from room temperature to the isotropic point and then cooling to the crystal phase for the mesogen (C_k).

3.2.2. DSC results

The transitions that appeared in the DSC curves of all mesogens in this series were measured during heating and cooling cycles between room temperatures and 200 °C, 180 °C, and 160 °C for (C_{a-c}) , (C_{d-f}) and (C_{g-k}) , respectively. The first three members in this series (C_{a-c}) showed two endothermic peaks in the heating process assigned to the crystal (Cr)-to-nematic (N) and (N)-to-isotropic transitions (I), while only one exothermic transition appeared clearly in the cooling curves of the mentioned compounds, which corresponded to the (N)-to-(Cr) transition. Conversely, the DSC thermograms of the second three mesogens (C_{d-f}) showed only one transition in the heating cycle,

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Table 1

Transition temperatures °C, enthalpies ΔH (KJ/mol), entropies ΔS [J/mol.K] and mesomorphic range °C for compounds of the series C_{a-k} in first heating and cooling cycles.

| Entry | $\mathbf{R} = \mathbf{O}\mathbf{C}_{\mathbf{n}}\mathbf{H}_{2\mathbf{n}+1}$ | Phase sequence | | Mesomorphic range [N], (SmA) | |
|----------------|--|---|---|------------------------------|-------------------|
| | (n) | Heating | Cooling | heating | cooling |
| C _a | 1 | Cr-N 140.45 (2.51) [6.07] N-Iso 183.60 (27.44) [60.10] | Iso-N 187.00 ^a NCr 130.15 (-25.77) [-63.91] | [43.15] | [56.85] |
| C _b | 2 | Cr-N 145.75 (5.74) [13.71] N-Iso 183.30 (33.79) [74.05] | Iso-N 197.00ª N—Cr 95.20 (—23.26) [—63.17] | [37.55] | [101.80] |
| C _c | 3 | Cr-N 130.00 (1.66) [4.11] N-Iso 175.75 (43.12) [96.15] | Iso-N 185.00ª N—Cr 89.00 (—28.07) [—77.54] | [45.75] | [96.00] |
| C _d | 4 | Cr-Iso 159.45 (25.84) [59.76] | Iso-N 180.00 ^a N—Cr 100.70 (-21.84) [-58.43] | - | [79.30] |
| C _e | 5 | Cr-Iso 151.00 (26.25) [61.92] | Iso-N 165.00 ^a N—Cr 116.30 (-22.97) [-59.01] | - | [48.70] |
| C _f | 6 | Cr-Iso 147.90 (37.53) [89.18] | Iso-N 156.00 ^a N—Cr 111.95 (-33.65) [-87.42] | - | [44.05] |
| Cg | 7 | Cr-N 123.30 (24.90) [62.82] N-Iso 155.00 ^a | Iso-N 154.00 ^a NCr 74.35 (-23.51) [-67.68] | [31.70] | [79.65] |
| C _h | 8 | Cr-N 116.60 (28.88) [74.14] N-Iso 157.00 ^a | Iso-N 155.00 ^a N–Cr 70.25 (-22.45) [-65.41] | [40.40] | [84.75] |
| C _i | 9 | Cr-Cr ₁ 101.75 (1.18) [3.15] Cr ₁ -Cr ₂ 109.60 (10.67) [27.88] Cr ₂ N 117.30 (20.53) [52.61] N-Iso 150.00 ^a | lso-N 149.00 ^a N—Cr ₁ 81.50 (-27.41) [-77.32] | [32.70] | [67.50] |
| Cj | 10 | Cr-Cr ₁ + Cr ₁ -N 126.45 (36.97) [92.55] N-Iso 150.00 ^a | Iso-N 148.00 ^a N—Cr ₁ 100.95 (-29.22) [-78.13] Cr ₁ —Cr 72.85 (-5.79) [-16.74] | [23.55] | [47.05] |
| C_k | 12 | Cr-SmA 111.90 (35.81) [93.03] SmA-N 135.00 ^a N-Iso 141.00 ^a | Iso-N 139.00 ^a N-SmA 135.00 ^a SmA-Cr 73.35 (<i>—</i> 21.86) [<i>—</i> 63.11] | (23.10) [6.00] | (61.65) [4.00] |

Cr and $Cr_1 = crystal phases; N = nematic phase; SmA = smectic A phase; Iso = isotropic liquid phase; (a) the transition were observed under POM.$

which can be attributed to the direct isotropization transition, (Cr) to (I), where these compounds turned directly to their isotropic points without showing any liquid crystalline properties in the heating scan, as revealed and confirmed by POM results. Upon cooling the melts of these mesogens by decreasing the temperatures at a rate of 5 degrees per min., nematic droplets began to form and then converged to form the Schlieren and thread-like templates, which are clear characteristics of the nematic mesophase. On further cooling, the nematic phase faded and transformed to the Cr phase at 100.70 °C, 116.30 °C and 111.95 °C for the compounds C_d , C_e and C_f , respectively. They appeared as exothermic peaks in the DSC traces of the compounds. The appearance of liquid crystal properties only in the cooling scan characterizes these compounds as monotropic mesogens. The DSC thermographs of the other mesogens in this series (Cg-i) showed a Cr-to-N endothermic transition upon heating at 123.30 °C, 116.60 °C, 117.30 °C, and 126.45 °C for C_g, C_h, C_i, and C_i, respectively. Additionally, the N-to-Cr transitions of these compounds during the cooling process appeared at 74.35 °C, 70.25 °C, 81.50 °C, and 100.95 °C, respectively. Furthermore, the C_i and C_i mesogens showed additional endothermic and exothermic peaks, which can be attributed to the Cr-to-Cr transitions. The last homologue member in this series (C_k) showed one endothermic peak in the heating scan and one exothermic transition in the cooling scan at 111.9 °C and 73.35 °C, respectively. They have been attributed to the transition from the crystal (Cr)-to-Smectic A (SmA) phase in the heating process and to the opposite transition in the cooling process. This compound showed other phase transitions in the (POM) observations, (SmA-N in the heating phase and N-SmA during the cooling phase), but they could not be detected by the DSC thermogram of this mesogen. This phenomenon might be due to the narrow temperature range of these transitions in heating and cooling processes. The DSC thermographs of selected compounds in this series are shown in Fig. 5.

3.2.3. Chemical structure effect on the liquid crystal properties of the synthesized mesogens (C_{a-k})

The Thermo-optical results in Table 1 (exhibiting the mesophase ranges calculated by DSC traces in the cooling cycle) are higher than

those in the heating scan. This behavior may be due to the supercooling phenomenon in the exothermic process, which needs less energy than the endothermic process [41]. The resulting transition temperatures to turn the mesogenic materials to their isotropic points (shown in Table 1) were influenced by the number of carbon atoms in the alkoxy terminal chain on the transition between crystal-liquid crystalline phases. This factor plays a very important role in the nature and thermal stability range of the mesomorphic phase upon heating and cooling cycles. For example, the compound (C_k) , which has the longest alkoxy chain ($R = OC_{12}H_{25}$, n = 12) starts to exhibit a smectic phase from the nematic mesophase; this behavior is attributed to increases in the Van der Waals interaction forces between the methylene groups [42]. From the literature [43], the Van der Waals forces between the molecules are one of the intermolecular interactions that affect the packing of the molecules; these forces increases by increasing the number of methylene groups in the alkyl chain. The gathering of molecules in layered form is one of the important and required conditions that must be contained in the molecules in order to exhibit the smectogenic character. The physical interactions between the molecules, in addition to other factors, such as polarity and polarizability, and the effect of the molecule constitutions contributed to increasing the congregation of these molecules as layers. Conversely, the dipole-dipole interactions in the nitro group are greater than the sum of the van der Waals forces present in the alkyl groups in the molecules. In the case of the compound C_k (n = 12), the van der Waals forces in this compound managed to partially overcome the dipole-dipole interactions in the nitro group in addition to the effects of imine and furan moieties. For these reasons, only the compound C_k has shown a smectic A phase among all the compounds in series C_{a-k}.

Furthermore, it was found that the transformation temperatures from the liquid crystal phase or crystal phase to the isotropic points for the series mesogens began to decrease smoothly, with increases in the length of the alkyl group in the alkoxy chain and a minor exception in some homologues (Table 1). The presented phase diagram in Fig. 6 shows an increase in the curve of the transitions (isotropic-tomesophase and mesophase-to-crystal), and then it goes down and up

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Fig. 3. Selected liquid crystalline images for compounds in series C_{a-k} (a) Schlieren texture of nematic phase for compound (C_d) at 177 °C in first cooling scan, (b) thread-like texture associated with the nematic phase for compound (C_g) at 138 °C in first heating scan, (c) transition from marble texture of nematic phase to crystalline phase for compound (C_a) in second cooling at 131 °C, (d) Schlieren texture of nematic phase for compound (C_j) at 136 °C in second cooling scan, (e) thread-like texture associated with the nematic phase for compound (C_j) at 130 °C in second cooling scan, (e) thread-like texture associated with the nematic phase for compound (C_j) at 110 °C in second cooling scan, (f) thread-like texture associated with the nematic phase for compound (C_i) at 138 °C in first heating scan.

again alternately with increasing carbon atom numbers in the alkoxy chain. The diagram shows that the curve tendency followed the zigzag form that resulted from an odd-even effect, with the overall decline being the tendency of the curve line as the terminal alkoxy chain length increased. It can be seen that both transition curves behaved in a normally established way.

In this work, it is very important to discuss the influence of the presence of a furan ring on the liquid crystalline properties in the compounds of this series (C_{a-K}). To study this effect, the mesogenic properties of a selected compound (C_f) from this series has been compared with a compound that has a similar chemical structure (I_{6c}), as reported by Hagar et al. [44]. The only difference between their chemical compositions is the inserted furan ring between the Schiff base linkage and 4-nitrophenyl group in the compound (C_f).

The results of the comparison showed that the compound (C_f) prepared in this study did not show any mesophase properties upon

heating, but it transformed directly from the solid state to the isotropic point at the temperature of 147.90 °C while it displayed a nematic phase during cooling only with a thermal range equal to 44.05 °C. Conversely, the compound (I_{6c}) showed nematogenic properties both in the heating and cooling cycles, with thermal stability equal to 144.8 °C. The chemical structures of the two compounds (C_f) and (I_{6c}) are shown in Scheme 2.

This fundamental difference in the mesomorphic properties between these two mesogens is due to the difference in their chemical structures, particularly the presence of the furan ring in the compound (C_f), which led to the disappearance of its liquid crystal properties in the heating cycle. This result may be attributed to deviation from the linearity that makes the molecule curved to a degree that loses the linearity required in the calamitic mesogens. The introduction of the 2,5disubstituted furan ring as a core in the structure of the compounds (C_{a-k}) creates a significant difference in their mesogenic behavior

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Fig. 4. The sequence of transition between the liquid crystalline phases both in heating and cooling scans of the compound (C_k) (a) Fan-shaped texture of the smectic A in first heating scan at 124 °C (b) transition from Schlieren texture of nematic phase to isotropic phase in first heating scan at 139 °C, (c and d) transition from nematic droplets to Schlieren texture of nematic phase to Fan-shaped texture of the smectic A phase in second cooling scan at 133 °C, (e) Fan-shaped texture of the smectic A phase in second cooling scan at 133 °C, (e) Fan-shaped texture of the smectic A phase in second cooling scan at 67 °C.

compared to the (I_{6c}) . This may be mainly due to the presence of the bend in the shape of the molecules, which resulted from insertion of furan moiety that curved from the linearity by an angle of approximately 129.5° compared to the 1,4-disubstituted benzene ring [45,46]. Due to the bent nature property related to the furan ring, it can be seen from the literature that the compounds based on furan rings, which were characterized as mesogens, are less than other heterocyclic compounds, as mentioned in the introduction. [47–50]. Another

significant factor that may be contributing to the influence in the mesophase nature and stability is the presence of the polar nitro group substituted to the *para* position in the terminal phenyl ring in the compounds of this series. The high polarity nature possessed by the nitro group, which increases the polarizability of the molecules, may be the reason for an increase in the phase stability in some compounds in this series upon the cooling cycle [42,51]. Additionally, the large size of the NO₂ group contributes to filling the space between

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Fig. 5. Selected DSC thermograms of compounds (a) C_a , (b) C_f and (c) C_k .

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Fig. 6. Diagram of phase transition temperature versus the number of carbon atoms in the terminal alkoxy chain.

the molecules and thus promotes the molecular packing [42,52]. However, in some cases, the increase in polarity is highly regarded as an obstacle to increasing the stability of the liquid crystalline phase [51].

3.2.4. Mesomorphic comparison with related mesogens

The mesomorphic properties of the series prepared in this work (C_{a-k}) were compared with two structurally analogous series reported by Ong et al. [53] (series nBA4MP) and Foo et al. [54] (series nTMAPB), as shown in Scheme 3.

These differences represented in the terminal side group that connected to the Schiff base bond, where it was (4-nitrofuran) in our present series (C_{a-k}), while it was replaced by either pyridine in the Ong series or thiophene in the Foo series. Moreover, in this work, the opposite terminal side-chain contained an alkoxy group with a carbon number atoms of 1–10 and 12, while only even numbers were used in the Ong and Foo series, n = 2-18 and n = 6-18, respectively.

According to the mesomorphic results of the mesogens in the three series (C_{a-k} , nBA4MP, and nTMAPB) shown in Scheme 3, we conclude with the following remarks:

 The homologue series based on a thiophene ring (nTMAPB) displayed nematogenic behavior with the exception of the last member (18TMAPB), which did not show any mesogenic behavior, while the compounds of series nBA4MP with pyridine core exhibited a nematic and/or smectic phase, which was similar to the mesogenic behavior of compounds in the studied series (C_{a-k}).



Scheme 2. Chemical structure and mesomorphic behavior of compounds Cf and IGc.

 $O_{2}N \longrightarrow O_{H} \longrightarrow O_{$

(nTMAPB) n = 6, 8, 10, 12, 14, 16, 18

Scheme 3. Representation of the synthesized compounds (C_{a-k}) and those reported by Ong (nBA4MP) and Foo (nTMAPB).

- A smectic A phase begins from the 8BA4MP member in the compounds nBA4MP (pyridine series), while it has appeared in the last mesogen only from the studied compounds (C_k), but all mesogens of the nTMAPB series did not show any type of smectogenic textures.
- All mesogens of the three series (C_{a-k}, nTMAPB, and nBA4MP) were compatible in terms of the thermal stability of the mesogenic phase, where the temperature range in the cooling cycle was higher than that recorded in the heating scan, regardless of the length of alkoxy chain in most of the members. The thermal stability of the mesogenic phases of the compounds in series C_{a-k}, nTMAPB, and nBA4MP are listed in Tables 1 and 2.
- The overall stability of the mesophases of the synthesized compounds (C_{a-k}) is between 23.55–45.75 °C and 44.05–101.80 °C for

Table 2

Liquid crystalline phases stability [Nematic] and (Smectic) in °C of the compounds in series nBA4MP [49] and nTMAPB [50].



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heating and cooling cycles respectively, while the value of the range in compounds of the compared series was shown between 7.4–17.6 °C (in heating) and 35.7–60.4 °C (in cooling) for the thiophene series and 20.7–77.0 °C (in heating) and 33.5–93.1 °C (in cooling) for pyridine series.

It is obvious that the liquid crystalline materials are flexible molecules that could convert their formations to various shapes, depending on which are more stable. This phenomenon is related to the chemical structure of the mesogens [55]. The variety and differences between the mesomorphic behavior of the synthesized compounds (C_{a-k}) and the reported examples (nTMAPB and nBA4MP) are due to the molecular geometry of the mesogens that usually contribute to the nature and stability of the mesophase. The insertion of a 4-nitrophenyl furan-2-yl segment at the terminal side of the compounds in (C_{a-k}) (instead of pyridine and thiophene rings in the series nBA4MP and nTMAPB, respectively) led to the differences in the length and width of molecules in addition to the polarity, polarizability, and linearity between the synthesized and the reported mesogens, which were reflected in the difference between their mesomorphic behaviors.

4. Conclusion

In summary, the preparation, characterization and the study of liquid crystalline behavior of the newly synthesized series of compounds viz., 4-[((5-(4-nitrophenyl)furan-2-yl)methylene)amino]phenyl 4-alkoxybenzoate (C_{a-k}), has led to the following conclusions:

- All eleven members based on furan moiety in the studied series have been displayed mesomorphic properties.
- Only three homologues (C_d, C_e, and C_f) showed mesogenic behavior in cooling scans only, while other members have exhibited these properties in both heating and cooling cycles.
- The first ten mesogens in this series (C_{a-j}) showed a nematic mesophase only except for the last derivative (C_k) , which displayed both nematic (N) and smectic A (SmA) phases.
- In compounds (C_{a-c} and C_{g-k}), the thermal stability of the nematic phase shown in the cooling cycle was higher than the nematogenic range through the heating scan.
- The increase in the intermolecular forces between the molecules of the last compound due to an increase in its alkoxy chain length led to an appearance of a SmA phase in this compound.
- The inclusion of the furan ring within the structure of the series compounds led to the bending of the molecules, which resulted in a decrease in their thermal stability range when compared to other linear compounds that have the same structure, except for the furan ring (see Scheme 2).
- The length of the terminal alkoxy group and the presence of furan and phenyl rings, as well nitro group and various linkages (Schiff and ester), within the chemical structure of the molecules have great effect on the mesogenic properties, where they showed significant differences in the mesomorphic behavior when compared with other related compounds (see Scheme 3).

Declaration of competing interest

The authors whose names are listed immediately below certify that they have NO affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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Appendix A. Supplementary data

The ¹H, ¹³C NMR and mass spectra as well as DSC thermograms for synthesized compounds in this article (C_{a-k}) can be found in the Supplementary data. Supplementary data to this article can be found online at https://doi.org/10.1016/j.molliq.2020.114562.

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