Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis, characterization of new carboxylic acid derivatives bearing 1,3,4-thiadiazole moiety and study their liquid crystalline behaviors

Hamed J. Jaffer, Yasmeen A. Aldhaif & Ivan H. R. Tomi

To cite this article: Hamed J. Jaffer, Yasmeen A. Aldhaif & Ivan H. R. Tomi (2017) Synthesis, characterization of new carboxylic acid derivatives bearing 1,3,4-thiadiazole moiety and study their liquid crystalline behaviors, Molecular Crystals and Liquid Crystals, 643:1, 199-215, DOI: 10.1080/15421406.2016.1266881

To link to this article: http://dx.doi.org/10.1080/15421406.2016.1266881

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2017, VOL. 643, 199–215
http://dx.doi.org/10.1080/15421406.2016.1266881

Taylor & Francis
Taylor & Francis Group

Synthesis, characterization of new carboxylic acid derivatives bearing 1,3,4-thiadiazole moiety and study their liquid crystalline behaviors

Hamed J. Jaffer, Yasmeen A. Aldhaif, and Ivan H. R. Tomi

College of Science, Department of Chemistry, University of Al-Mustansiriyah, Baghdad, Iraq

ABSTRACT

Thirteen carboxylic acid derivatives containing 1,3,4-thiadiazole ring in their core and swinging alkoxy terminal were synthesized. They were characterized by ^{1}H, ^{13}C NMR spectroscopy, FTIR, and mass spectrometry. Their liquid crystalline behaviors have been studied by differential scanning calorimetry (DSC) and polarized optical microscopy (POM). The 1,3,4-thiadiazole compounds in this study were 2,5 di-substituted asymmetrical, alkoxy, and carboxy linkages. The compounds with alkoxy of long carbon chains ($n > 7$) displayed Smectic C phase. The liquid crystal properties were found to be affected by the length of alkoxy chain attached to the phenyl moiety and the two types of the dimeric form were resulted from the hydrogen bonding interaction between carboxylic acid molecules.

KEYWORDS

1,3,4-Thiadiazole mesogens; carboxylic acids; dimers; liquid crystals

Introduction

Mesogenic compounds derived from heterocyclic rings have been prepared by many scientific groups due to their wide range in optical, medicinal, and biological applications [1]. 1,3,4-Thiadiazole core is one of heterocycle materials that has a great importance in designing the molecules that may possess liquid crystals property, especially in expansion the thermotropic calamitic materials [2]. The chemical geometry of 1,3,4-thiadiazole derivatives makes them suitable in different material applications because of their chemical and thermal stabilities [3]. The presence of three heteroatoms (two nitrogen and one sulfur atoms) in 1,3,4-thiadiazole moiety can influence the polarity and polarizibility of the molecules [4], therefore, 1,3,4-Thiadiazole ring is regarded as one of the sulfur–nitrogen heterocycles use as core in variety of mesogenic materials [5–7], this has opened an interesting possibility for designing new mesogens containing thiadiazole ring. Many published results demonstrated on calamitic, hydrogen-bonded, polycatenars, bent and star-shaped mesogens bearing 1,3,4-thiadiazole unit [8–12].

On the other hand, intermolecular interactions are essential factor in the liquid crystal field responsible for arranging the order of mesogenic superstructures. These forces participate in making rigid cores in rode-like molecules [13]. The hydrogen-bonding network is one of the important noncovalent interaction essential to design super-molecules that are constructed

CONTACT Ivan H. R. Tomi ivanhrtomy@uomustansiriyah.edu.iq Department of Chemistry, College of Science, University of Al-Mustansiriyah, Baghdad, Iraq.
Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

in the direction of molecular long axes [14]. The first examples concerning the effect of the hydrogen-bonding interaction on calamitic mesogens were investigated earlier by Jones [15]. Recently, there are many reports for synthesis of various liquid crystals compounds that are depends on noncovalent interactions [16–19].

The dimerization of carboxylic acids through hydrogen bonding creates supermolecular structures which frequently used as mesogenic materials [20]. As we did not found any studies reported on the liquid crystal properties of carboxylic acid compounds incorporating with 1,3,4-thiadiazole derivatives. Therefore and as a part of our interests in the mesomorphic properties of heterocyclic liquid crystals, a series of substituted 1,3,4-thiadiazole compounds with alkoxy and carboxy linkages were synthesized and characterized in this study, their liquid crystalline properties were studied and the relationship between the structure and mesomorphic property, the hydrogen bonding interaction was discussed.

Experimental

General

All starting materials in this study were received from Sigma–Aldrich and used as supplied. Compounds (A, B, E, F_n and G_n) in this study were prepared according to the procedures in our previous reference with a few simple modifications [21]. FTIR spectra of all samples in ATR technique were recorded on Shimadzu 8400S spectrometer. ^{1}H and ^{13}C (NMR) spectra were measured on Bruker ultra-shield at (300 MHz for proton and 100 MHz for carbon) with chemical shifts (ppm scale) relative to tetramethylsilane as an internal standard ($\delta = 0$ ppm) using $CDCl_3$ and DMSO-d_6 as solvents. (SCI-MS) of some compounds were recorded on Shimadzu QP1000EX. Mesophase textures of series (F_n and G_n) were studied using a polarizing optical microscope (POM) (PW-BK 5000 PR) equipped with a hot-stage (HS-400). Transition temperatures, enthalpies, and entropies were determined from differential scanning calorimetry (DSC) (Linseis instrument STA PT-1000), in 5°C/min heating and cooling rates.

Methods

Synthesis of 4-methoxy-N′-(4-methylbenzoyl)benzohydrazide (C)

The titled compound was prepared according to the previously reported method [22] with some modifications. To a round bottomed flask (250 mL) containing (0.12 mol, 18 g) of 4-toluic hydrazide (B) dissolved in (100 mL) of anhydrous pyridine, 4-methoxybenzoyl chloride (0.12 mol, 20.5 g) was added dropwise at −5°C. The reaction mixture was left overnight at room temperature. The product was poured into a cold (250 mL) of 10% HCl to give a light yellow solid. The crude product was boiled in water for 15 min—to dissolve any unreacted materials (compound B and 4-methoxybenzoyl chloride). The residue was purified by recrystallization from ethanol to give the desired product. Yield (91%); mp: 210–212°C; FTIR (ATR, cm^{-1}), ν_{max}: (3207, 3151, 2NH), (2943, 2845, C–H aliph.), (1614, C=O); ^{1}HNMR (DMSO-d_6), δ, ppm: 10.20, 10.17 (2×s, 2H, 2NH), 7.75–7.78 (d, 2H, Ar–H, -ph–CH_3, $J = 8.76$ Hz), 7.60–7.63 (d, 2H, Ar–H, -ph–OCH_3, $J = 8.03$ Hz), 7.15–7.18 (d, 2H, Ar–H, -ph–OCH_3, $J = 8.00$ Hz), 6.88–6.91 (d, 2H, Ar–H, -ph–CH_3, $J = 8.80$ Hz), 3.68 (s, 3H, OCH_3), 2.35 (s, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 166.24, 165.80, 162.47, 142.25, 130.32, 129.81, 129.48, 127.93, 125.22, 114.19, 55.86, 53.16, 21.49, 20.09; MS (SCI) (relative intensity %): $m/z = 284$ (M^+, 100%).

Synthesis of 2-(4-methoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (D=F$_1$)

This compound was prepared by the procedure reported by [23]. Compound C (0.087 mol, 25 g) and phosphorouspenta sulfide (0.087 mol, 24.9) were dissolved in pyridine (150 mL) in a (250 mL) round bottomed flask. The mixture was refluxed for 24 hr and the crude was poured in (500 mL) cold water. The resulted precipitate was filtered and washed with excess of water and recrystallized from ethyl acetate to obtain the product D = F_1. Yield (87%); FTIR (ATR, cm^{-1}), ν_{max}: (3066, C–H arom.), (2964, 2837, C–H aliph.), (1602, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.91–7.94 (d, 2H, Ar–H, -ph–CH_3, $J = 8.71$ Hz), 7.85–7.88 (d, 2H, Ar–H, -ph–OCH_3, $J = 7.97$ Hz), 7.26–7.28 (d, 2H, Ar–H, -ph–OCH_3, $J = 7.88$ Hz), 6.96–6.99 (d, 2H, Ar–H, -ph–CH_3, $J = 8.71$ Hz), 3.86 (s, 3H, OCH_3), 2.40 (s, 3H, CH_3); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.47, 167.45, 163.27, 161.80, 141.33, 129.79, 129.40, 127.73, 127.62, 127.57, 122.94, 114.49, 98.11, 96.77, 63.80, 21.50; MS (SCI) (relative intensity %): $m/z = 282$ (M^+, 97%).

Synthesis of 4-(5-(p-tolyl)-1,3,4-thiadiazol-2-yl)phenol (E)

Compound (D=F_1) (0.0024 mol, 0.68 g) was dissolved in dry benzene (25 mL) and (0.0075 mol, 1.00 g) of anhydrous aluminum chloride was added. The reaction mixture was refluxed for 24 hr. The solvent was evaporated and the residue was poured into water. The resulted solid was filtered then purified by dissolving it in (30 mL) of 10% potassium hydroxide solution. The solution was filtered and the filtrate was neutralized with 10% hydrochloride acid. The formed precipitate was washed with water, dried, and recrystallized from ethanol to give compound (E). Yield (81%); mp: 221–223°C; FTIR (ATR, cm^{-1}), ν_{max}: (3111, broad O–H), (3045, C–H arom.), (2966, 2850, C–H aliph.), (1608, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 10.09 (s, 1H, OH), 7.64–7.66 (d, 4H, Ar–H, -ph–CH_3 and –ph–OH, $J = 8.43$ Hz), 7.13–7.16 (d, 2H, Ar–H, -ph–CH_3, $J = 8.17$ Hz), 6.79–6.77 (d, 2H, Ar–H, –ph–OH, $J = 8.65$ Hz), 2.18 (s, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 167.84, 166.88, 160.85, 141.57, 130.37, 130.11, 129.84, 127.81, 127.46, 121.04, 116.65, 98.22, 96.34, 63.99, 21.44; MS (SCI) (relative intensity %): $m/z = 268$ (M^+, 100%).

Synthesis of 2-(4-alkoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_n, n = 2–10,12,16 and 18)

To a solution of compound (E) (0.01 mol, 2.68 g) in acetone (50 mL), anhydrous potassium carbonate (0.01 mol, 1.38 g) was added. The *n*-alkyl bromide (0.011 mol) was added to the mixture dropwise followed by refluxing the reaction mixture for 12 hr. After cooling, the crude product was added to cold water. The resulted solid was filtered, washed with 5% aqueous potassium hydroxide and with distilled water several times. The solid products were dried and recrystallized from ethyl acetate.

2-(4-Ethoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_2)

Yield (85%); FTIR (ATR, cm^{-1}), ν_{max}: (3080, C–H arom.), (2982, 2866, C–H aliph.), (1605, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.92–7.95 (d, 2H, Ar–H, -ph–CH_3, $J = 8.75$ Hz), 7.88–7.90 (d, 2H, Ar–H, -ph–OR_2, $J = 7.95$ Hz), 7.25–7.27 (d, 2H, Ar–H, -ph–OR_2, $J = 7.91$ Hz), 6.97–7.00 (d, 2H, Ar–H, -ph–CH_3, $J = 8.73$ Hz), 4.06–4.02 (q, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.45–1.41 (t, 3H, -OCH_2-$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.57, 167.41, 163.02, 161.26, 141.34, 129.81, 129.43, 127.77, 127.65, 127.61, 122.80, 114.99, 98.00, 96.69, 63.73, 21.16, 14.73; MS (SCI) (relative intensity %): $m/z = 296$ (M^+, 94%).

2-(4-Propoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_3)

Yield (84%); FTIR (ATR, cm^{-1}), ν_{max}: (3066, C–H arom.), (2964, 2866, C–H aliph.), (1602, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.89–7.91 (d, 2H, Ar–H, -ph-CH_3, $J = 8.75$ Hz),

7.85–7.87 (d, 2H, Ar–H, -ph–OR_3, J = 7.93 Hz), 7.26–7.27 (d, 2H, Ar–H, -ph–OR_3, J = 7.91 Hz), 6.95–6.97 (d, 2H, Ar–H, -ph–CH_3, J = 8.74 Hz), 4.01–3.97 (t, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.90–1.88 (m, 2H, CH_2) 1.09–1.04 (t, 3H, -$O(CH_2)_2$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.59, 167.39, 161.47, 161.27, 141.33, 129.81, 129.42, 127.76, 127.65, 127.60, 122.75, 115.02, 99.99, 88.69, 67.32, 22.50, 21.52, 10.49.

2-(4-Butoxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_4)

Yield (88%); FTIR (ATR, cm^{-1}), ν_{max}: (3068, C–H arom.), (2953, 2868, C–H aliph.), (1600, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.91–7.93 (d, 2H, Ar–H, -ph–CH_3, J = 8.76 Hz), 7.86–7.88 (d, 2H, Ar–H, -ph–OR_4, J = 7.90 Hz), 7.27–7.30 (d, 2H, Ar–H, -ph–OR_4, J = 7.92 Hz), 6.97–6.99 (d, 2H, Ar–H, -ph–CH_3, J = 8.77 Hz), 3.97–4.05 (t, 2H, OCH_2), 2.41 (s, 3H, CH_3), 1.82–1.85 (m, 2H, CH_2), 1.48–1.61 (m, 2H, CH_2), 1.02–0.96 (t, 3H, -$O(CH_2)_3$-$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.56, 167.40, 161.47, 161.31, 141.34, 129.82, 129.77, 129.42, 127.77, 127.64, 122.72, 115.00, 100.00, 87.98, 67.95, 31.20, 21.54, 19.23, 13.86; MS (SCI) (relative intensity %): m/z = 324 (M^+, 100%).

2-(4-Pentyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_5)

Yield (89%); FTIR (ATR, cm^{-1}), ν_{max}: (3067, C–H arom.), (2958, 2870, C–H aliph.), (1602, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.92–7.94 (d, 2H, Ar–H, -ph–CH_3, J = 8.73 Hz), 7.84–7.87 (d, 2H, Ar–H, -ph-OR_5, J = 7.96 Hz), 7.26–7.28 (d, 2H, Ar–H, -ph–OR_5, J = 7.94 Hz), 6.95–6.98 (d, 2H, Ar–H, -ph–CH_3, J = 8.74 Hz), 3.98–4.03 (t, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.81–1.84 (m, 2H, CH_2), 1.42–1.57 (m, 4H, 2×CH_2), 0.88–0.96 (t, 3H, -$O(CH_2)_4$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.61, 167.40, 161.48, 161.33, 141.33, 129.82, 129.42, 129.37, 128.03, 127.77, 122.72, 114.96, 99.98, 87.00, 68.28, 31.58, 29.13, 22.57, 21.53, 14.05; MS (SCI) (relative intensity %): m/z = 338 (M^+, 91%).

2-(4-Hexyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_6)

Yield (80%); FTIR (ATR, cm^{-1}), ν_{max}: (3064, C–H arom.), (2961, 2862, C–H aliph.), (1601, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.95–7.97 (d, 2H, Ar–H, -ph–CH_3, J = 8.76 Hz), 7.84–7.86 (d, 2H, Ar–H, -ph–OR_6, J = 7.92 Hz), 7.23–7.25 (d, 2H, Ar–H, -ph–OR_6, J = 7.96 Hz), 6.95–6.97 (d, 2H, Ar–H, -ph–CH_3, J = 8.79 Hz), 3.98–4.02 (t, 2H, OCH_2), 2.40 (s, 3H, CH_3), 1.78–1.82 (m, 2H, CH_2), 1.40–1.59 (m, 6H, 3×CH_2), 0.95–0.89 (t, 3H, -$O(CH_2)_5$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.62, 167.44, 161.46, 161.30, 141.30, 129.87, 129.46, 129.41, 128.13, 127.81, 122.76, 114.99, 99.96, 87.05, 68.31, 31.62, 29.13, 28.84, 22.62, 21.55, 14.08.

2-(4-Heptyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_7)

Yield (83%); FTIR (ATR, cm^{-1}), ν_{max}: (3060, C–H arom.), (2962, 2852, C–H aliph.), (1603, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.93–7.95 (d, 2H, Ar–H, -ph–CH_3, J = 8.79 Hz), 7.85–7.88 (d, 2H, Ar–H, -ph–OR_7, J = 7.94 Hz), 7.26–7.29 (d, 2H, Ar–H, -ph–OR_7, J = 7.99 Hz), 6.96–6.99 (d, 2H, Ar–H, -ph–CH_3, J = 8.76 Hz), 3.99–4.05 (t, 2H, OCH_2), 2.41 (s, 3H, CH_3), 1.76–1.79 (m, 2H, CH_2), 1.45–1.62 (m, 8H, 4×CH_2), 0.96–0.87 (t, 3H, -$O(CH_2)_6$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.67, 167.56, 161.43, 161.37, 141.35, 129.81, 129.41, 129.38, 128.10, 127.90, 122.83, 114.83, 99.91, 87.09, 68.37, 31.65, 29.17, 29.77, 28.89, 22.57, 21.54, 14.03; MS (SCI) (relative intensity %): m/z = 366 (M^+, 100%).

2-(4-Octyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_8)

Yield (90%); FTIR (ATR, cm^{-1}), ν_{max}: (3072, C–H arom.), (2972, 2853, C–H aliph.), (1604, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.91–7.94 (d, 2H, Ar–H, -ph–CH_3, J = 8.75 Hz), 7.87–7.90 (d, 2H, Ar–H, -ph–OR_8, J = 7.97 Hz), 7.28–7.30 (d, 2H, Ar–H, -ph–OR_8, J = 7.81 Hz),

6.97–6.99 (d, 2H, Ar–H, -ph–CH_3, $J = 8.69$ Hz), 4.00–4.04 (t, 2H, OCH_2), 2.43 (s, 3H, CH_3), 1.78–1.81 (m, 2H, CH_2), 1.37–1.59 (m, 10H, 5×CH_2), 0.87–0.91 (t, 3H, -$O(CH_2)_7$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.73, 167.59, 161.39, 161.55, 149.72, 129.99, 129.55, 129.43, 128.23, 127.95, 122.73, 114.75, 99.96, 87.22, 68.41, 31.44, 29.62, 29.42, 28.69, 26.28, 22.34, 21.66, 14.29; MS (SCI) (relative intensity %): $m/z = 380$ (M^+, 99%).

2-(4-Nonyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_9)

Yield (86%); FTIR (ATR, cm^{-1}), ν_{max}: (3022, C–H arom.), (2955, 2852, C–H aliph.), (1603, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.90–7.92 (d, 2H, Ar–H, -ph–CH_3, $J = 8.77$ Hz), 7.87–7.89 (d, 2H, Ar–H, -ph–OR_9, $J = 7.95$ Hz), 7.29–7.31 (d, 2H, Ar–H, -ph–OR_9, $J = 7.84$ Hz), 6.96–6.98 (d, 2H, Ar–H, -ph–CH_3, $J = 8.73$ Hz), 3.96–4.03 (t, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.79–1.82 (m, 2H, CH_2), 1.34–1.60 (m, 12H, 6×CH_2), 0.85–0.90 (t, 3H, -$O(CH_2)_8$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 168.01, 167.76, 161.65, 161.42, 149.55, 129.89, 129.72, 129.52, 128.53, 127.99, 122.82, 114.55, 99.86, 87.34, 68.54, 31.78, 29.79, 29.62, 28.58, 26.41, 25.89, 22.51, 21.45, 14.67.

2-(4-Decyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_{10})

Yield (91%); FTIR (ATR, cm^{-1}), ν_{max}: (3072, C-H arom.), (2964, 2849, C-H aliph.), (1602, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.91–7.93 (d, 2H, Ar–H, -ph–CH_3, $J = 8.74$ Hz), 7.84–7.87 (d, 2H, Ar–H, -ph–OR_{10}, $J = 7.93$ Hz), 7.27—7.30 (d, 2H, Ar–H, -ph–OR_{10}, $J = 7.83$ Hz), 6.98–7.00 (d, 2H, Ar–H, -ph–CH_3, $J = 8.77$ Hz), 3.97–4.04 (t, 2H, OCH_2), 2.41 (s, 3H, CH_3), 1.80–1.83 (m, 2H, CH_2), 1.36–1.61 (m, 14H, 7×CH_2), 0.83–0.89 (t, 3H, -$O(CH_2)_9$-$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.84, 167.72, 161.66, 161.54, 149.34, 129.91, 129.84, 129.61, 128.66, 128.00, 122.65, 114.67, 99.71, 87.32, 68.66, 31.54, 29.91, 29.81, 28.67, 26.71, 25.76, 25.41, 22.63, 21.54, 14.71; MS (SCI) (relative intensity %): $m/z = 408$ (M^+, 89%).

2-(4-Dodecyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_{12})

Yield (87%); FTIR (ATR, cm^{-1}), ν_{max}: (3057, C–H arom.), (2961, 2848, C–H aliph.), (1604, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.90–7.93 (d, 2H, Ar–H, -ph–CH_3, $J = 8.73$ Hz), 7.86–7.89 (d, 2H, Ar–H, -ph–OR_{12}, $J = 8.14$ Hz), 7.26–7.29 (d, 2H, Ar–H, -ph–OR_{12}, $J = 8.29$ Hz), 6.95–6.98 (d, 2H, Ar–H, -ph–CH_3, $J = 8.76$ Hz), 3.98–4,03 (t, 2H, OCH_2), 2.41 (s, 3H, CH_3), 1.78–1.85 (m, 2H, CH_2), 1.26–1.46 (m, 18H, 9×CH_2), 0.85–0.90 (t, 3H, -$O(CH_2)_{11}$-$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.08, 166.87, 160.97, 160.39, 140.81, 129.31, 128.90, 127.25, 127.15, 122.22, 114.50, 98.90, 67.77, 31.43, 29.67, 29.17, 29.16, 29.11, 29.09, 28.90, 28.87, 28.66, 25.51, 22.21, 21.02, 15.50, 13.40.

2-(4-Hexadecyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_{16})

Yield (88%); FTIR (ATR, cm^{-1}), ν_{max}: (3061, C–H arom.), (2955, 2849, C-H aliph.), (1602, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.90–7.93 (d, 2H, Ar–H, -ph–CH_3, $J = 8.74$ Hz), 7.87–7.90 (d, 2H, Ar–H, -ph–OR_{16}, $J = 7.93$ Hz), 7.27–7.30 (d, 2H, Ar–H, -ph–OR_{16}, $J = 7.83$ Hz), 6.96–6.99 (d, 2H, Ar–H, -ph–CH_3, $J = 8.77$ Hz), 3.99–4.03 (t, 2H, OCH_2), 2.42 (s, 3H, CH_3), 1.79–1.83 (m, 2H, CH_2), 1.25–1.47 (m, 26H, 13×CH_2), 0.84–0.96 (t, 3H, -$O(CH_2)_{15}$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.10, 166.89, 160.97, 140.83, 129.31, 128.91, 128.74, 127.26, 127.15, 122.22, 114.51, 99.11, 67.77, 31.44, 30.95, 29.69, 29.21, 29.19, 29.17, 29.11, 29.08, 28.95, 28.88, 28.66, 28.29, 27.70, 25.51, 22.21, 21.02, 15.50, 13.40; MS (SCI) (relative intensity %): $m/z = 492$ (M^+, 93%).

2-(4-Octadecyloxyphenyl)-5-(p-tolyl)-1,3,4-thiadiazole (F_{18})

Yield (91%); FTIR (ATR, cm^{-1}), ν_{max}: (3059, C–H arom.), (2954, 2848, C–H aliph.), (1603, C=N); ^{1}HNMR ($CDCl_3$), δ, ppm: 7.89–7.92 (d, 2H, Ar–H, -ph–CH_3, $J = 8.73$ Hz), 7.87–7.89 (d, 2H, Ar–H, -ph–OR_{18}, $J = 7.91$ Hz), 7.27–7.29 (d, 2H, Ar–H, -ph–OR_{18}, $J = 7.86$ Hz), 6.95–6.98 (d, 2H, Ar–H, -ph–CH_3, $J = 8.73$ Hz), 3.98–4.03 (t, 2H, OCH_2), 2.41 (s, 3H, CH_3), 1.77–1.84 (m, 2H, CH_2), 1.26–1.48 (m, 30H, 15×CH_2), 0.93–0.98 (t, 2H, -$O(CH_2)_{17}$–$\underline{CH_3}$); ^{13}CNMR ($CDCl_3$), δ, ppm: 167.08, 166.91, 160.90, 140.79, 129.32, 128.88, 128.69, 127.24, 127.15, 122.21, 114.50, 99.22, 67.78, 31.41, 30.97, 29.66, 29.20, 29.17, 29.16, 29.12, 29.05, 28.97, 28.90, 28.63, 28.22, 27.71, 25.52, 22.24, 21.04, 15.54, 13.55.

Synthesis of 4-(5-(4-alkoxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_n, n = 1–10,12,16 and 18)

A solution of potassium permanganate, (0.02 mol, 3.33g) in (10 mL) distilled water was added dropwise to a solution of compound D = F1 (as example of series Fn) (0.0025 mol, 0.77 g) in (20 mL) pyridine at about 70°C with continuous stirring. The resulted violet solution was heated under reflux for 24 h. After cooling, water (25 mL) was added to the crude product which was slightly warmed and filtered. The resulted solution was acidified with (2 M HCl) and the precipitated carboxylic acid (G_n) was filtered, washed with water and dried. Note: use a minimum amount of water in case ($n > 6$).

4-(5-(4-Methoxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_1)

Yield (93%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3112–2546, broad O–H), (2947, 2845, C–H aliph.), (1683, C=O), (1604, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.32–13.43 (s, 1H, br., COOH), 7.91–7.97 (2×d, br., 4H, Ar–H, -ph-COOH), 7.81–7.84, $J = 7.95$ and 6.97–6.99, $J = 7.81$ (2×d, 4H, Ar–H, -ph-OCH_3), 3.94 (s, 3H, CH_3O); ^{13}CNMR (DMSO-d_6), δ, ppm: 196.51, 168.18, 166.81, 165.99, 161.33, 154.44, 133.71, 130.41, 130.26, 130.09, 129.55, 127.99, 127.67, 121.71, 115.42, 69.44; MS (SCI) (relative intensity %): $m/z = 312$ (M^+, 100%).

4-(5-(4-Ethoxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_2)

Yield (83%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3091–2548, broad O–H), (2980, 2841, C–H aliph.), (1685, C=O), (1607, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.25–13.46 (s, 1H, br., COOH), 8.09–8.13 (2×d, br., 4H, Ar–H, -ph–COOH), 7.96–7.99, $J = 7.17$ and 7.11–7.14, $J = 6.96$ (2×d, 4H, Ar–H, -ph-OR_2), 4.12–4.15 (q, 2H, CH_2O), 1.37–1.39 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 196.21, 167.98, 167.31, 165.91, 161.72, 149.94, 133.69, 130.41, 130.29, 130.23, 129.43, 127.81, 127.60, 121.87, 115.34, 63.53, 21.18; MS (SCI) (relative intensity %): $m/z = 315$ (M^+, 89%).

4-(5-(4-Propoxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_3)

Yield (83%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3102–2558, broad O–H), (2964, 2872, C–H aliph.), (1685, C=O), (1606, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.29–13.44 (s, 1H, br., COOH), 8.14–8.12 (2×d, br., 4H, Ar–H, -ph–COOH), 7.97–8.00, $J = 6.91$ and 7.13–7.16, $J = 6.67$ (2×d, 4H, Ar–H, -ph–OR_3), 4.03–4.05 (t, 2H, CH_2O), 1.75–1.79 (m, 2H, CH_2), 0.99–1.03 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 195.87, 168.19, 166.88, 165.91, 161.30, 154.57, 133.65, 130.28, 130.24, 130.13, 129.42, 127.96, 127.61, 121.69, 115.36, 69.32, 21.89, 10.29.

4-(5-(4-Butoxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_4)

Yield (79%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3099–2544, broad O–H), (2956, 2872, C–H aliph.), (1684, C=O), (1605, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.29–13.37 (s, 1H, br., COOH), 8.09–8.12 (2×d, br., 4H, Ar–H, -ph-COOH), 7.96–7.99, $J = 8.63$ and 7.12–7.15, $J = 8.72$ (2×d, 4H, Ar–H, -ph–OR_4), 4.06–4.10 (t, 2H, CH_2O), 1.71–1.81 (m, 2H, CH_2), 1.42–152 (m, 2H, CH_2), 0.93–0.98 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 196.41, 168.23, 166.60, 165.89, 161.33, 154.65, 133.14, 130.28, 130.21, 130.13, 129.66, 129.22, 127.81, 127.54, 121.68, 115.37, 71.74, 30.56, 18.65, 13.64.

4-(5-(4-Pentyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_5)

Yield (81%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3101–2557, broad O–H), (2961, 2857, C–H aliph.), (1683, C=O), (1604, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.32–13.47 (s, 1H, br., COOH), 8.08–8.11 (2×d, br., 4H, Ar–H, -ph-COOH), 7.97–7.99, $J = 6.90$ and 7.13–7.16, $J = 7.14$ (2×d, 4H, Ar–H, -ph–OR_5), 4.05–4.09 (t, 2H, CH_2O), 1.73–1.83 (m, 2H, CH_2), 1.22–143 (m, 4H, 2×CH_2), 0.87–0.93 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 195.77, 168.67, 166.55, 165.71, 161.33, 155.11, 133.21, 130.33, 130.19, 130.02, 129.45, 129.32, 127.69, 127.44, 121.64, 115.37, 67.86, 30.94, 28.47, 22.03, 16.56.

4-(5-(4-Hexyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_6)

Yield (77%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3098–2555, broad O-H), (2953, 2854, C-H aliph.), (1684, C=O), (1604, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.35–13.42 (s, 1H, br., COOH), 8.11–8.14 (2×d, br., 4H, Ar-H, -ph-COOH), 8.01–8.04, $J = 6.97$ and 7.10–7.13, $J = 7.01$ (2×d, 4H, Ar-H, -ph-OR_6), 4.02–4.07 (t, 2H, CH_2O), 1.75–1.84 (m, 2H, CH_2), 1.21–141 (m, 6H, 3×CH_2), 0.89–0.95 (t, 3H, CH_3); ^{13}CNMR (DMSO-*d6*), δ, ppm: 194.61, 168.91, 166.81, 165.77, 161.54, 154.22, 133.26, 130.31, 130.25, 130.11, 129.43, 129.21, 127.69, 127.41, 117.26, 115.36, 67.85, 30.87, 28.65, 28.20, 23.01, 15.87; MS (SCI) (relative intensity %): m/z = 382 (M^+, 71%).

4-(5-(4-Heptyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_7)

Yield (86%); mp: > 350°C; FTIR (ATR, cm^{-1}), ν_{max}: (3101–2556, broad O–H), (2953, 2855, C–H aliph.), (1683, C=O), (1605, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.32–13.39 (s, 1H, br., COOH), 8.10–8.13 (2×d, br., 4H, Ar–H, -ph–COOH), 7.97–7.99, $J = 8.84$ and 7.13–7.15, $J = 8.84$ (2×d, 4H, Ar–H, -ph–OR_7), 4.05–4.10 (t, 2H, CH_2O), 1.73–1.78 (m, 2H, CH_2), 1.24–143 (m, 8H, 4×CH_2), 0.86–0.90 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 193.91, 169.01, 167.11, 165.88, 161.29, 154.19, 133.21, 130.45, 130.31, 130.09, 129.66, 129.34, 127.73, 127.43, 127.19, 115.42, 67.88, 30.78, 28.61, 28.43, 28.26, 23.02, 15.91; MS (SCI) (relative intensity %): $m/z = 396$ (M^+, 94%).

4-(5-(4-Octyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_8)

Yield (81%); FTIR (ATR, cm^{-1}), ν_{max}: (3101–2556, broad O–H), (2953, 2855, C–H aliph.), (1699, 1683, C=O), (1605, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.43–13.55 (s, 1H, br., COOH), 8.10–8.13 (2×d, br., 4H, Ar–H, -ph–COOH), 7.96–7.99, $J = 8.75$ and 7.12–7.15, $J = 8.83$ (2×d, 4H, Ar–H, -ph–OR_8), 3.99–4.05 (t, 2H, CH_2O), 1.74–1.79 (m, 2H, CH_2), 1.25–1.41 (m, 10H, 5×CH_2), 0.84–0.89 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 192.00, 168.76, 166.57, 165.71, 161.45, 154.27, 133.27, 130.42, 130.32, 130.11, 129.45, 129.22, 127.81, 127.65, 127.22, 114.99, 67.43, 30.81, 28.76, 28.59, 28.39, 28.19, 23.12, 15.78.

4-(5-(4-Nonyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_9)

Yield (88%); FTIR (ATR, cm^{-1}), ν_{max}: (3088–2551, broad O–H), (2955, 2852, C–H aliph.), (1701, 1683, C=O), (1605, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.01–13.12 (s, 1H, br., COOH), 8.09–8.12 (2×d, br., 4H, Ar–H, -ph–COOH), 7.96–7.99, J = 7.59 and 7.12–7.15, J = 7.75 (2×d, 4H, Ar–H, -ph–OR_9), 4.01–4.07 (t, 2H, CH_2O), 1.72–1.77 (m, 2H, CH_2), 1.23–1.40 (m, 12H, 6×CH_2), 0.82–0.87 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 194.82, 168.79, 166.66, 165.61, 161.39, 154.02, 133.67, 130.39, 130.31, 130.03, 129.38, 129.21, 127.82, 127.71, 127.32, 115.01, 67.44, 30.74, 28.83, 28.66, 28.53, 28.32, 28.11, 24.11, 14.98.

4-(5-(4-Decyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_{10})

Yield (90%); FTIR (ATR, cm^{-1}), ν_{max}: (3092–2549, broad O–H), (2955, 2853, C–H aliph.), (1701, 1684, C=O), (1605, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.28–13.39 (s, 1H, br., COOH), 8.09–8.12 (2×d, br., 4H, Ar–H, -ph–COOH), 7.97–8.00, J = 7.63 and 7.10–7.13, J = 7.66 (2×d, 4H, Ar–H, -ph–OR_{10}), 4.00–4.06 (t, 2H, CH_2O), 1.74–1.79 (m, 2H, CH_2), 1.26–1.38 (m, 14H, 7×CH_2), 0.83–0.89 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 194.71, 168.88, 166.67, 165.43, 161.43, 154.12, 133.56, 130.41, 130.33, 130.11, 129.41, 129.23, 127.99, 127.86, 127.43, 115.12, 67.34, 30.73, 28.83, 28.65, 28.63, 28.31, 28.22, 27.88, 24.11, 14.98.

4-(5-(4-Dodecyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_{12})

Yield (85%); FTIR (ATR, cm^{-1}), ν_{max}: (3103–2561, broad O–H), (2948, 2851, C–H aliph.), (1698, 1683, C=O), (1604, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.35–13.44 (s, 1H, br., COOH), 8.11–8.14 (2×d, br., 4H, Ar–H, -ph–COOH), 7.98–8.01, J = 7.66 and 7.08–7.11, J = 7.69 (2×d, 4H, Ar–H, -ph–OR_{12}), 3.98–4.03 (t, 2H, CH_2O), 1.77–1.81 (m, 2H, CH_2), 1.25–1.40 (m, 18H, 9×CH_2), 0.80–0.86 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 192.92, 168.75, 166.71, 165.33, 161.56, 154.23, 133.61, 130.55, 130.29, 130.12, 129.40, 129.24, 127.87, 127.72, 127.34, 115.42, 67.66, 30.67, 28.91, 28.88, 28.65, 28.31, 28.22, 28.00, 27.88, 27.83, 24.21, 14.67; MS (SCI) (relative intensity %): m/z = 466 (M^+, 83%).

4-(5-(4-Hexadecyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_{16})

Yield (83%); FTIR (ATR, cm^{-1}), ν_{max}: (3098–2544, broad O–H), (2953, 2848, C–H aliph.), (1699, 1685, C=O), (1605, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.43–13.51 (s, 1H, br., COOH), 8.06–8.08 (2×d, br., 4H, Ar-H, -ph-COOH), 7.99–8.02, J = 7.53 and 7.08–7.10, J = 7.62 (2×d, 4H, Ar-H, -ph-OR_{16}), 3.96–4.00 (t, 2H, CH_2O), 1.76–1.80 (m, 2H, CH_2), 1.23–1.39 (m, 26H, 13×CH_2), 0.83–0.88 (t, 3H, CH_3); ^{13}CNMR (DMSO-*d6*), δ, ppm: 193.12, 168.82, 166.76, 165.53, 161.88, 154.32, 133.60, 130.41, 130.33, 130.23, 129.37, 129.19, 127.65, 127.54, 127.32, 115.32, 67.12, 30.54, 28.95, 28.81, 28.78, 28.63, 28.41, 28.32, 28.20, 27.81, 27.65, 27.43, 26.12, 24.33, 15.71; MS (SCI) (relative intensity %): m/z = 522 (M^+, 76%).

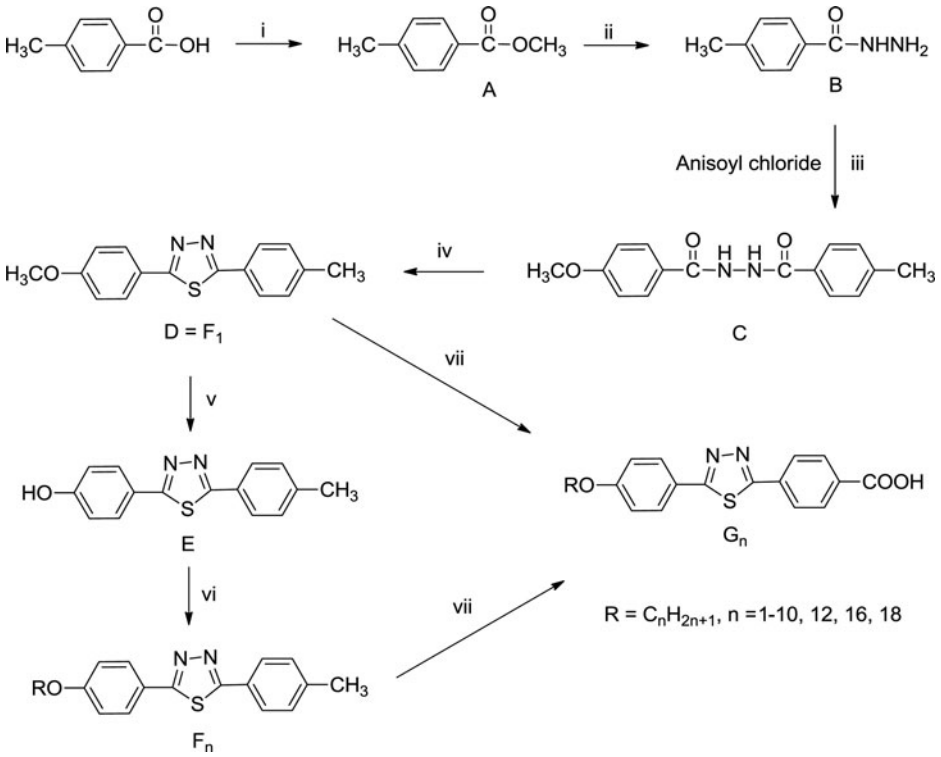
4-(5-(4-Octadecyloxyphenyl)-1,3,4-thiadiazol-2-yl)benzoic acid (G_{18})

Yield (78%); FTIR (ATR, cm^{-1}), ν_{max}: (3112–2557, broad O–H), (2955, 2849, C–H aliph.), (1697, 1687, C=O), (1604, C=N); ^{1}HNMR (DMSO-d_6), δ, ppm: 13.42–13.53 (s, 1H, br., COOH), 8.10–8.13 (2×d, br., 4H, Ar–H, -ph–COOH), 8.00–8.03, J = 7.79 and 7.10–7.13, J = 7.83 (2×d, 4H, Ar–H, -ph–OR_{18}), 3.94–3.99 (t, 2H, CH_2O), 1.72–1.77 (m, 2H, CH_2), 1.26–1.41 (m, 30H, 15×CH_2), 0.85–0.89 (t, 3H, CH_3); ^{13}CNMR (DMSO-d_6), δ, ppm: 194.43, 168.71, 166.69, 165.61, 161.88, 155.12, 133.63, 130.45, 130.23, 130.19, 129.57, 129.37, 127.63, 127.51, 127.41, 114.97, 67.52, 30.42, 28.95, 28.81, 28.71, 28.69, 28.54, 28.40, 28.32, 28.18, 27.79, 27.60, 27.42, 26.32, 25.97, 24.46, 14.99.

Results and discussion

Synthesis

The mesophase compounds, 4-(5-(4-alkoxyphenyl)-1,3,4-thiadiazole-2-yl)benzoic acid (G_n), and their corresponding precursors were prepared by the synthetic route described in Scheme 1.



Scheme 1. Reactions and reagents: (i) methanol, H_2SO_4; (ii) ethanol, $NH_2NH_2.H_2O$; (iii) pyridine, 0°C; (iv) P_2S_5, pyridine; (v) $AlCl_3$, benzene; (vi) RBr, acetone; (vii) $KMnO_4$, pyridine, H_2O.

The chemical structures of the synthesized compounds in this study were confirmed on the basis of their FTIR, ^{1}HNMR, ^{13}CNMR and some of them by mass spectroscopy.

Methyl *p*-toluate (A) was prepared in good yield according to the standard esterification procedure of 4-methylbenzoic acid. The hydrazide compound (B) was prepared by the reaction of compound (A) with hydrazine hydrate in ethanol. This compound was condensed with anisoyl chloride in pyridine to form 4-methoxy-*N*'-(4-methylbenzoyl)benzohydrazide (C). The two singlet signals in ^{1}HNMR spectrum of compound (C) at 10.17 and 10.20 ppm were corresponded for two protons of two NH groups in addition to amidic carbonyl in FTIR are a good indicator for the formation of this compound. The 1,3,4-thiadiazole derivative (D) was prepared by the sulfuration reaction of compound (C) using P_2S_5 in anhydrous pyridine, the disappearance of amidic carbonyl groups in FTIR and two NH signals in ^{1}HNMR spectra of compound C are a good proof on cyclization reaction success. The compound (D) was converted, with anhydrous aluminum chloride in dry benzene, to desired 2-(4-hydroxyphenyl)-5-(4-methylphenyl)-1,3,4-thiadiazole (E). The ^{1}HNMR spectrum of compound (E) showed the appearance phenolic hydroxyl group in FTIR and at 10.09 ppm in ^{1}HNMR is good proof

that demethylation reaction was obtained. The homologous compounds of series (F_n, n = 2–10, 12, 16, and 18) were prepared by alkylation reaction of compound (E) with n-alkyl bromide in acetone with the presence of anhydrous K_2CO_3. The disappearance of hydroxyl peak of compound (E) and the appearance of alkyl signals in ^{1}HNMR and FTIR spectra for compounds (F_n) are clear index of success the alkylation reaction. The acids derivatives (G_n) were prepared by oxidation of compounds (F_n) using pyridine–water mixture, the FTIR spectra of these compounds displayed broad O–H stretching between 3090 and 2550 cm^{-1} and C=O stretching at 1680 cm^{-1} for compounds G_1–G_7, and two peaks at 1680 and 1700 cm^{-1} for compounds G_8–G_{10}, G_{12}, G_{16}, and G_{18}. Also, the ^{1}HNMR spectra of the prepared carboxylic acids showed weak broad peaks between 13.30 and 13.50 ppm which were assigned for protons of COOH groups in compounds G_n, Fig. 1 show ^{1}HNMR spectra of compounds G_3 and G_4 as examples of series G_n.

Mesomorphic properties

The liquid crystals properties of compounds of the two series, (F_n) and (G_n), were investigated by polarizing optical microscopy (POM) and deferential scanning calorimetry (DSC). Thin films of the samples were obtained by sandwiching them between a glass slide and cover slip.

Mesomorphic properties of compounds F_n

We have studied the mesomorphic properties of all compounds in series (F_n) (F_{1-8}, F_{10}, F_{12}, F_{16}, and F_{18}) using (POM) and (DSC) techniques. The results were in agreement with those reported by Han et al. (24–25) (F_{1-8} and F_{10}). The newly synthesized compounds (F_9, F_{12}, F_{16}, and F_{18}) behaved as a thermotropic liquid crystal properties. On heating scan, the (DSC) curves of compounds (F_9) and (F_{12}) displayed three endothermic peaks which were assigned to (Cr–SmC), (SmC–N), and (N–I) transitions, also on cooling, three exothermic peaks were observed which were assigned to (I–N), (N–SmC), and (SmC–Cr). The SmC and N phases of compounds (F_9) and (F_{12}) were Schlieren texture type. In compounds F_{16} and F_{18}, the nematic phase was disappeared due to the increases in number of carbon atoms in the terminal alkyl chains. The increasing in molecule length (F_{16} and F_{18}) led to the formation of SmC only; this was due to the enhanced of Van der Waals forces and dipole–dipole interaction between alkyl chains [26]. The (DSC) thermographs of these compounds showed only two transitions on first heating (Cr–SmC and SmC–I), and two peaks cooling assigned to (I–SmC and SmC–Cr) transitions. The SmC phase of compounds (F_{16} and F_{18}) was Schlieren texture type under optical microscope. The mesophase assignments according to (POM) observations are in good agreement with the corresponding (DSC) curves. Selected (POM) images of some (F_n) mesogens obtained by heating or cooling and (DSC) curve of compound (F_{18}) as an example of these compounds are collectively showed in Fig. 2. The phase transition temperature (T/°C), enthalpies (ΔH/ KJ mol^{-1}) and entropies (ΔS/J mol^{-1} K^{-1}) data of compounds (F_9, F_{12}, F_{16}, and F_{18}) were listed in Table 1.

Mesomorphic properties of compounds G_n

The liquid crystalline behaviors of carboxylic acid derivatives (G_1-G_{10}, G_{12}, G_{16}, and G_{18}) were investigated by (POM) and (DSC) techniques. The first seven compounds of this series (G_1–G_7) exhibited no liquid crystalline phases when heated up to 350°C on (POM). Higher

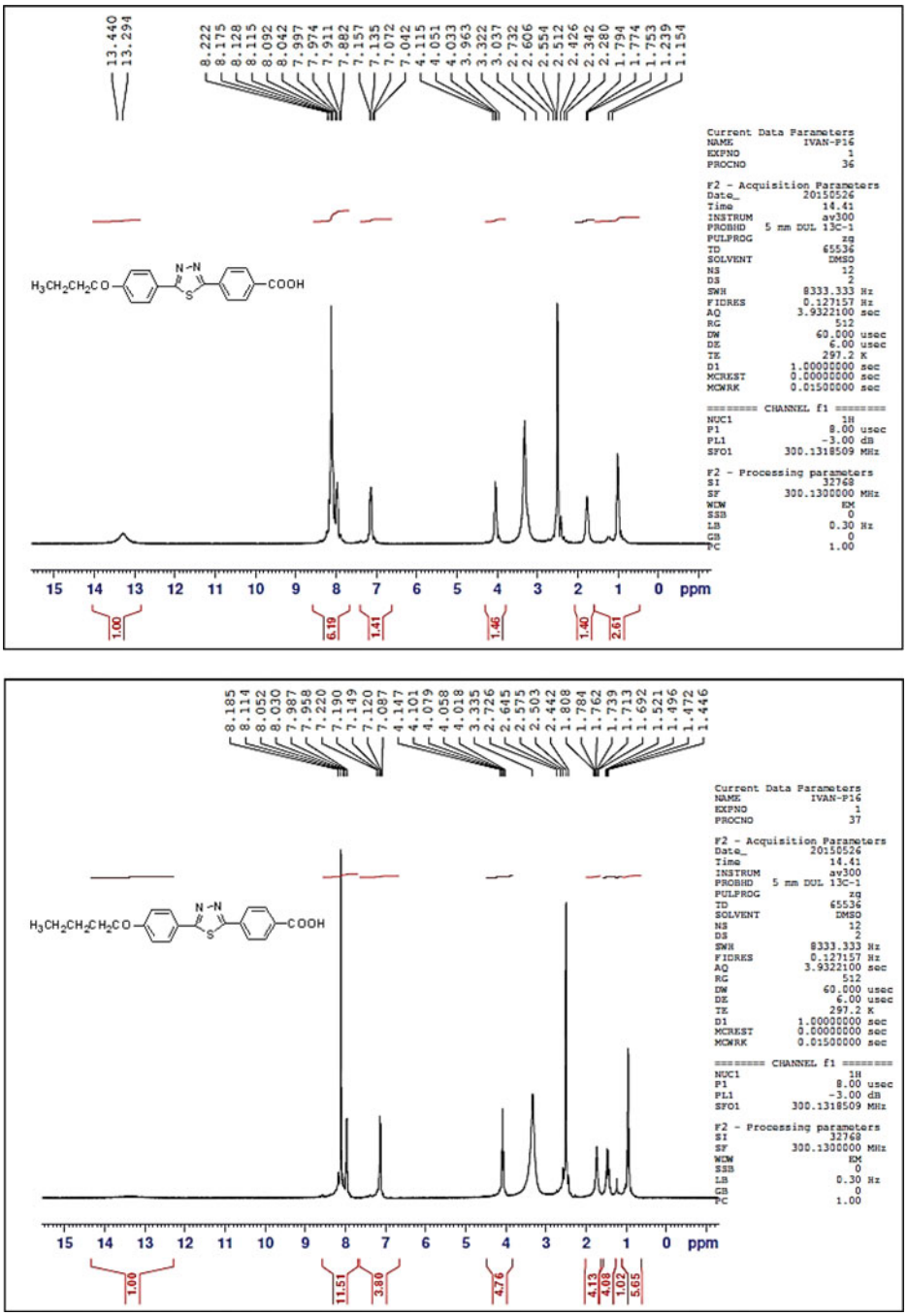


Figure 1. [1]HNMR spectra of compounds G_3 (up) and G_4 (down).

melting points of these compounds (G_1–G_7) caused disappearance the liquid crystal character; this was due to shorten of alkyl terminal softening groups. The rest of the series which possess longer terminal alkoxy tail ($n = 8$–10, 12, 16, and 18) exhibited mesomorphic properties, the increases in the length of alkoxy tails led to increase interaction forces between the molecules resulted as a mesophases behavior, particularly SmC phase typical of calamitic liquid crystals [27]. Although these compounds showed SmC phase, however, they suffer

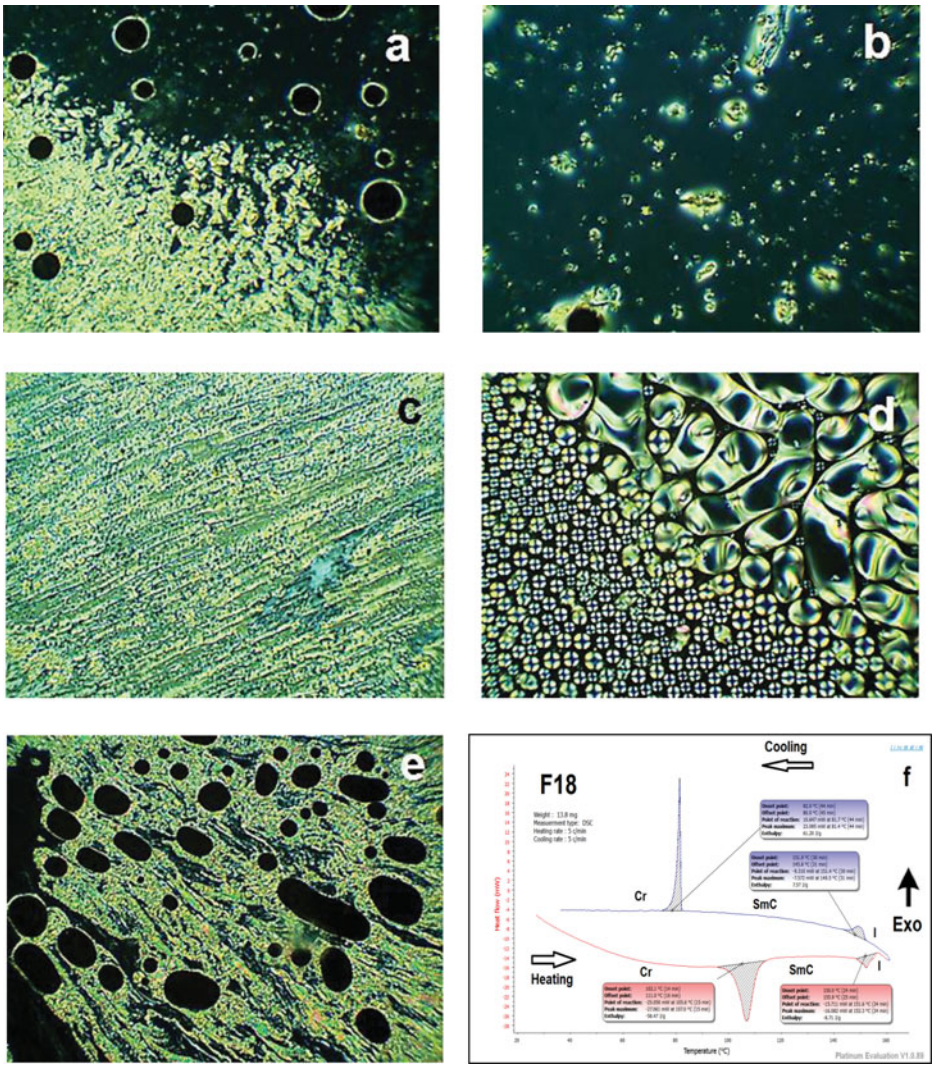


Figure 2. (a) Transition from smectic C to nematic textures of compound F_9 on heating at 121°C; (b) nematic (Schlieren) texture of compound F_9 on heating at 157°C; (c) smectic C texture of compound F_{12} on heating at 118°C; (d) nematic droplets from cooling compound F_{12} at 153°C; (e) smectic C texture of compound F_{18} on heating at 141°C transition; (f) DSC thermogram of compound F_{18}.

thermal decomposition started near 220°C which was very clear in (DSC) thermographs. This phenomenon prevents us from further study of their liquid crystalline properties on cooling from their melts.

The (DSC) thermographs of compounds (G_8–G_{10}, G_{12}, G_{16}, and G_{18}) showed two or three endothermic transitions that are represented to Cr–Cr or Cr–SmC phases, also, the (DSC) curves showed exothermic transitions assigned to SmC–dec. on first heating scan, a further heating above 220°C in (DSC) technique led to decomposition of the materials accompanied by the loss of their liquid crystal properties. This phenomenon was confirmed by (POM) darkening in SmC textures near this temperature. Figure 3 shows the (DSC) thermograms of compounds (G_8) and (G_{10}) as representative examples of the studied series (G_n). Phase details and transition temperatures of all compounds in series (G_n) are summarized in Table 2.

Table 1. Phase transition temperatures (T/°C), phase transition enthalpy changes (ΔH/ KJ mol^{-1}) and entropies (ΔS/ J mole^{-1} K^{-1}) of the compounds F_9, F_{12}, F_{16}, and F_{18} in first heating and cooling cycles.

Compound	n	Phase transitions T°C (ΔH/ kJ mol^{-1}) [ΔS/J mole^{-1} K^{-1}] on first heating	Phase transitions T°C (ΔH/ kJ mol^{-1}) [ΔS/J mole^{-1} K^{-1}] on first cooling
F_9	9	Cr–SmC 100.30 (21.01) [56.28] SmC–N 126.60 (2.42) [6.06] N–I 171.5 (3.27) [7.36]	I–N 168.50 (−2.93) [−6.64] N–SmC 122.60 (−2.34) [−5.92] SmC–Cr 75.55 (−18.33) [−52.59]
F_{12}	12	Cr–SmC 100.95 (24.51) [65.54] SmC–N 141.75 (2.53) [6.10] N–I 163.50 (3.28) [7.51]	I–N 159.40 (−3.01) [−6.96] N–SmC 138.55 (−2.32) [−5.64] SmC–Cr 81.80 (−23.23) [−65.47]
F_{16}	16	Cr–SmC 105.50 (24.53) [64.81] SmC–I 158.30 (3.01) [6.98]	I–SmC 155.80 (−3.49) [−8.14] SmC–Cr 80.35 (−25.92) [−73.36]
F_{18}	18	Cr–SmC 106.55 (30.40) [80.11] SmC–I 152.95 (4.53) [10.64]	I–SmC 148.85 (−3.94) [−9.34] SmC–Cr 81.00 (−31.82) [−89.89]

Abbreviations: Cr = crystal phase; SmC = smectic C phase; N = nematic phase; I = isotropic phase.

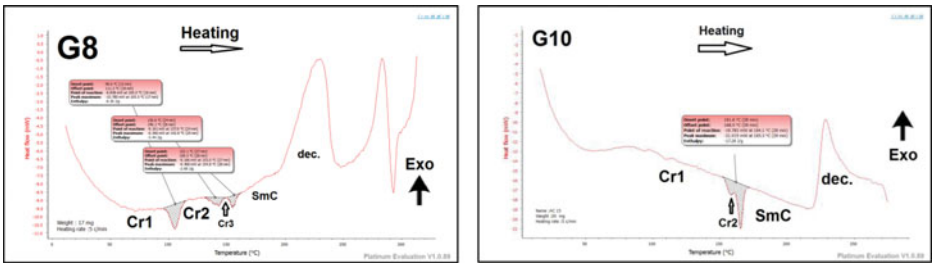


Figure 3. DSC thermograms of compounds G_8 and G_{10}.

Table 2. Phase transition temperatures (T/°C), phase transition enthalpy changes (ΔH/kJ mol^{-1}) and entropies (ΔS/J mole^{-1} K^{-1}) of the compounds G_8–G_{10}, G_{12}, G_{16}, and G_{18} in first heating cycles.

Compound	n	Phase transitions T°C (ΔH/kJ mol^{-1}) [ΔS/J mole^{-1} K^{-1}] on first heating
G_8	8	Cr_1–Cr_2 104.90 (3.81) [10.08] Cr_2–Cr_3 141.35 (1.41) [3.40] Cr_3–SmC 155.30 (1.10) [2.57]
G_9	9	Cr_1–Cr_2 99.93 (4.12) [11.05] Cr_2–SmC 157.24 (1.41) [3.28]
G_{10}	10	Cr_1+Cr_2–SmC 165.05 (7.57) [17.28]
G_{12}	12	Cr_1–Cr_2 112.25 (3.98) [10.33] Cr_2–SmC 166.47 (1.67) [3.80]
G_{16}	16	Cr_1–Cr_2 97.89 (4.04) [10.89] Cr_2–SmC 182.48 (2.05) [4.50]
G_{18}	18	Cr_1–Cr_2 84.45 (3.92) [10.97] Cr_2–SmC 188.65 (2.45) [5.31]

Abbreviations: Cr_1, Cr_2, Cr_3 = crystal phases; SmC = smectic C phase.

The study by polarizing microscope upon heating, a schlieren texture of SmC was observed for the last six compounds of series (G_n) (G_8-G_{10}, G_{12}, G_{16}, and G_{18}). Figure 4 shows examples of polarizing optical photomicrographs of some compounds of this series.

The FTIR spectra for acid derivatives in (G_n) series in the solid state at room temperature revealed that the first seven compounds are present as cyclic hydrogen-bonded dimers

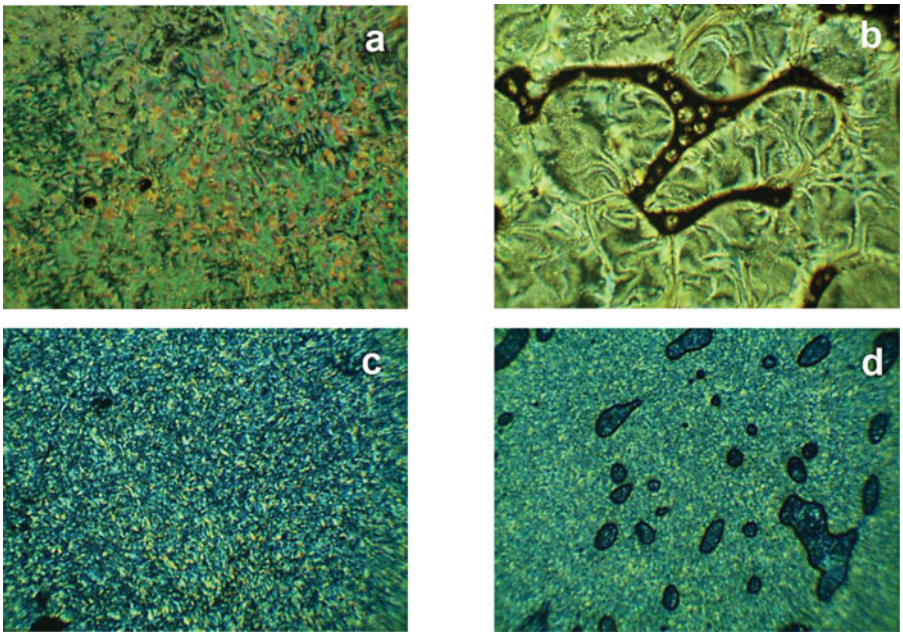
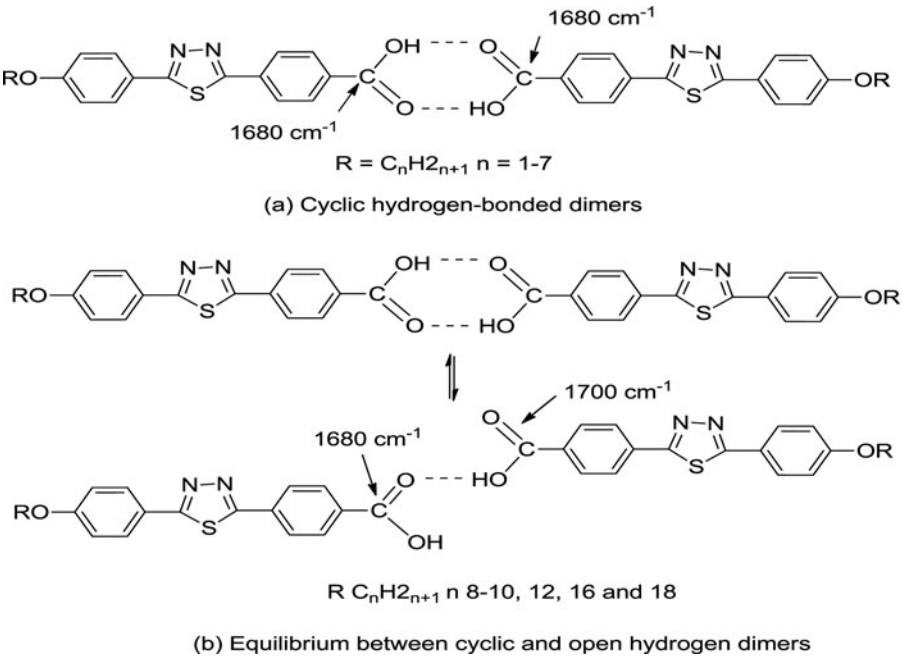


Figure 4. Smectic C textures of (a) compound G_8 on heating at 189°C, (b) compound G_9 on heating at 184°C, (c) compound G_{12} on heating at 172°C, and (d) compound G_{18} on heating at 164°C.

(Scheme 2a). The stretching frequencies data of carbonyl bands of these compounds were appeared near 1680 cm^{-1} which it evidence that these compounds are in this form. The rest compounds of this series have the longer alkoxy terminal swinging groups (G_8–G_{10}, G_{12}, G_{16}, and G_{18}) are exist in two equilibrium dimeric forms (cyclic hydrogen-bonded dimer and open



Scheme 2. The schematic representation of H-bonded dimers in the compounds $(G)_n$.

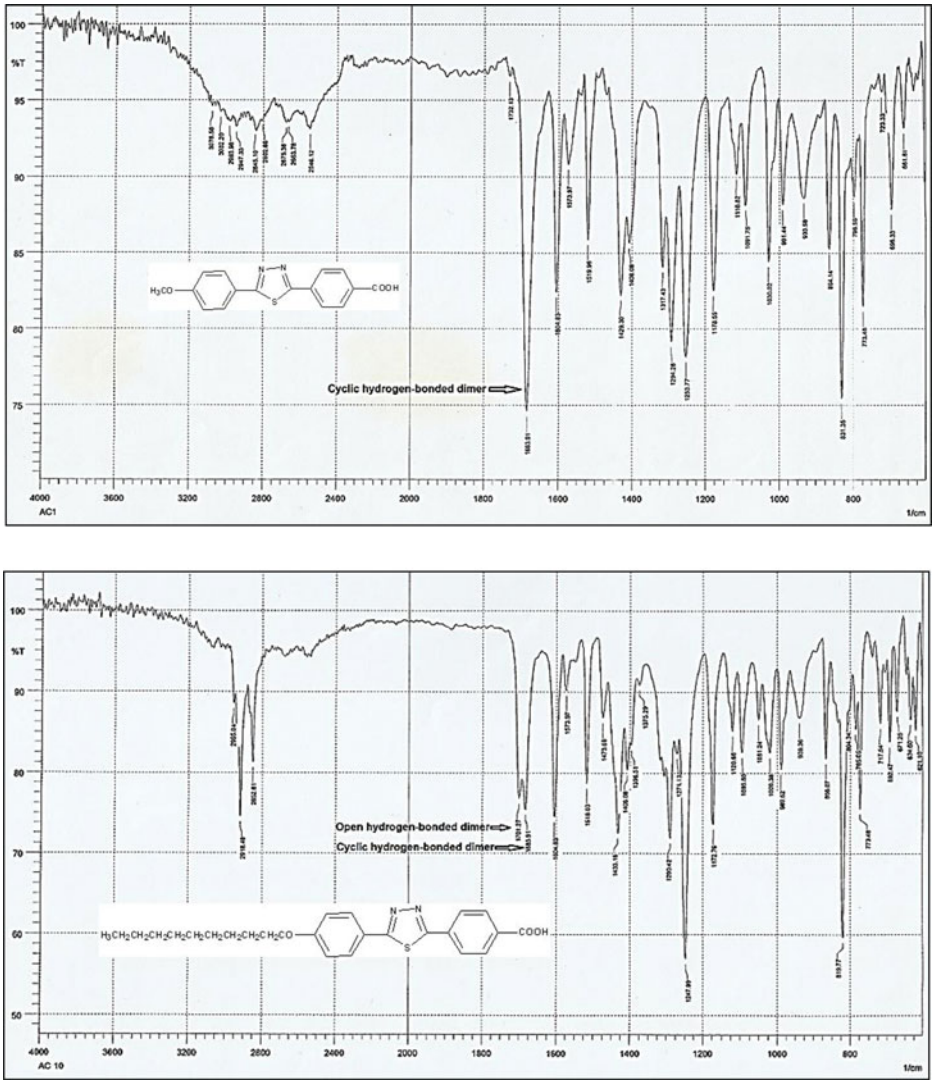


Figure 5. FTIR spectra of compounds G_1 (up) and G_{10} (down).

hydrogen-bonded dimer, Scheme 2b). The FTIR spectra of these compounds showed two frequencies for carbonyl bands near 1680 and 1700 cm^{-1} confirming the suggested two equilibrium dimeric forms. These results are consistent with those reported by Martinez-Felipe et al. [28, 29] and Paterson et al. [30]. Figure 5 shows examples of FTIR spectra of some compounds in (G_n) series. It is clear that increasing the length of alkoxy group in these compounds derive some molecules to prevent formation of cyclic hydrogen bonding dimer via their relatively easy movement or swinging.

The hydrogen bonding represents one of the important factors that affect the liquid crystalline properties of the compound; therefore, new properties could be arising from the influence of such interaction between the molecules [31].

In this study, our results indicated that hydrogen bonding in compounds of series (G_n) is greatly influences the appearance of mesomorphic properties of the last compounds in this series. These properties could be resulted from the overall effect of the types of hydrogen bonding between the molecules. The FTIR of the first seven compounds of this series revealed

that these compounds exist in cyclic hydrogen-bonding dimer form only; therefore, they have high melting points (> 350°C). The (POM) analysis of these compounds proves that no of them is mesogen probably due to their existence in this form of dimerization, which is more stable thermodynamically and higher melting points than the open hydrogen-bonded dimer [32].

The increase in length of alkoxy terminal chains in last six derivatives of series might prevent molecules from constructing cyclic dimer form by intramolecular hydrogen bonding and force them to be in the equilibrium state between cyclic and open forms dimers. The proposed equilibrium is reflected directly on the melting points and appearance the liquid crystalline properties.

The limited difference in chemical structures between compounds of the two series, (F_n and G_n), have a large impact on their liquid crystals properties which we can summarized as follows: (a) all compounds of series F_n are mesogens while only last six compounds of series (G_n) have liquid crystal properties; (b) all the compounds of series (F_n) displayed enantiotropic liquid crystals with nematic and smectic C phases, while only compounds of series (G_n) have alkoxy tail of ($n > 7$) exhibited smectic C phase; (c) the thermal stability of compounds (F_n) is more than those of compounds (G_n) which are decompose around 220°C; (d) the mesomorphic temperature ranges of all compounds in (F_n) series are wider than the last six compounds in (G_n) series.

The main difference in chemical structures between compounds (F_n and G_n) is related to the one terminal group, (terminal-CH_3 substituent in F_n compounds and terminal-COOH substituent in G_n compounds). It is evident the strong relationship between the mesomorphism character and chemical constituents of the organic compounds (mesogens).

The electron-donating methyl group in compounds of (F_n) series tends to form the nematic and smectic C mesophase, while the compounds bearing carboxy electron-withdrawing substituent in series (G_n) will be able to form smectic C phase only ($n > 7$). The free rotation of methyl croup in compounds (F_n) drive them to be mesogens. However, the conjugation of carboxy group with phenyl moiety in addition to the formation of cyclic hydrogen bonding dimer may cause the disappearance of the mesomorphic properties of first seven compounds and appeared in short extents in the rest of series (G_n).

Conclusions

Two series (F_n and G_n) of asymmetrical liquid crystalline compounds with 1,3,4-thiadiazole central core have been synthesized and characterized by different spectral techniques. All the compounds of series (F_n) show good mesomorphic properties, exhibiting calamitic mesophases (nematic and smectic), while only last six compounds of series (G_n) were mesogens with smectic type only. We observed that the type of terminal groups substituted in the two series and the chain length were significantly affected the mesomorphic properties of these compounds and the thermal stability of the produced liquid crystal phases. The results indicated that the dimeric forms resulted from the hydrogen bonding interaction between the carboxylic acid derivatives are responsible for the formation of the liquid crystal property in the last six compounds in series (G_n). Therefore, the replacement of the terminal (CH_3) group in compounds of series (F_n) by (COOH) group in compounds of series (G_n) led to drastic changes in liquid crystalline behaviors of these compounds.

Acknowledgments

The authors are grateful to the staff of chemistry department in Al-Mustansiriyah University (Baghdad, Iraq) for their help and cooperation's with us. Also many thank to Dr. Mohanad H. Masad (Al

al-Bayt University, Jordan) and Dr. Dhafir Al-Heetimi (Baghdad University) for their help us in carrying out ^{1}HNMR and DSC analysis, respectively. We are indebted to ASTF (Arab Science of Technology Foundation), for their generous support by providing us with optical polarizing microscope (OPM) and hot-stage.

References

[1] Selvarasu, C. & Kannan, P. (2015). *J. Chem. Sci.*, *127*, 1831.
[2] Elgueta, E. Y., Parra, M. L., Díaz, E. W., & Barberá, J. (2014). *Liq. Cryst.*, *41*, 861.
[3] Cioanca, E. R., Carlescu, I., Wilson, D., & Scutaru, D. (2010). *Rev. Chem.*, *61*, 1158.
[4] Parra, M. L., Elgueta, E. Y., Ulloa, J. A., Vergara, J. M., & Sanchez, A. I. (2012). *Liq. Cryst.*, *39*, 917.
[5] Tomma, J. H., Rou'il, I. H., & Al-Dujaili, A. H. (2009). *Mol. Cryst. Liq. Cryst.*, *501*, 3.
[6] Han, J., Wang, Q., Wu, J., & Zhu, L.-R. (2015). *Liq. Cryst.*, *42*, 127.
[7] Kuo, H.-M., Li, S.-Y., Sheu, H.-S., & Lai, C. K. (2012). *Tetrahedron*, *68*, 7331.
[8] Han, J., Chang, X.-Y., Wang, Y.-M., Pang, M.-L., & Meng, J.-B. (2009). *J.Mol. Struct.*, *937*, 122.
[9] Lai, L.-L., Yang, Y.-G., Chen, J.-J., Chen, W.-Y., & Wang, E. (2002). *Liq. Cryst.*, *29*, 985.
[10] Elgueta, E. Y., et al. (2016). *Liq. Cryst.*, *0*, 1.
[11] Seltmann, J., et al. (2011). *Chem. Mater.*, *23*, 2630.
[12] Al-Malki, M. K. S., Hameed, A. S., & Al-Dujaili, A. H. (2014). *Mol. Cryst. Liq. Cryst.*, *593*, 34.
[13] Kohmoto, S., Someya, Y., & Kishikawa, K. (2010). *Liq. Cryst.*, *37*, 209.
[14] Paraschiv, I., et al. (2007). *Liq. Cryst.*, *34*, 1029.
[15] Jones, B. (1935). *J. Chem. Soc.*, *1*, 1874.
[16] Setoguchi, Y., et al. (2003). *Thin Solid Films*, *438–439*, 407.
[17] Guo, H., Fang, X., Yang, F., & Wu, Y. (2015). *Tetrahedron Lett.*, *56*, 5465.
[18] Korkmaz, B., et al. (2016). *J. Mol. Liq.*, *219*, 1030.
[19] Vijayakumar, V. N., & Madhu Mohan, M. L. N. (2012). *Optik*, *123*, 1044.
[20] Nessim, R. I. & Nessim, M. I. (2010). *Thermochim. Acta*, *511*, 27.
[21] Tomi, I. H. R., Al-Mahdawi, M. T. S., Latif, I. S., Khlili, F. I., & Al-Dujaili, A. H. (2011). *J. Chem. Chem. Eng.*, *5*, 946.
[22] Prajapati, A. K., & Modi, V. (2010). *Phase Transit.*, *83*, 634.
[23] Kuo, H.-M., Li, S.-Y., Sheu, H.-S., & Lai, C. K. (2012). *Tetrahedron*, *68*, 7331.
[24] Han, J., et al. (2009). *Liq. Cryst.*, *36*, 157.
[25] Han, J., et al. (2008). *Liq. Cryst.*, *35*, 1379.
[26] Tomi, I. H. R., Al-Daraji, A. H. R., Al-Qaisi, Z. H. J., Al-Heetimi, D. T. A., & Al-Qaisi, A. H. J. (2016). *Tetrahedron*, *72*, 4390.
[27] Srividhya, D., Manjunathan, S., Thirumaran, S., Saravanan, C., & Senthil, S. (2009). *J. Mol. Struct.*, *927*, 7.
[28] Martínez-Felipe, A. & Imrie, C. T. (2015). *J. Mol. Struct.*, *1100*, 429.
[29] Martínez-Felipe, A., Cook, A. G., Wallage, M. J., & Imrie, C. T. (2014). *Phase Transit.*, *87*, 1191.
[30] Paterson, D. A., et al. (2015). *Liq. Cryst.*, 1.
[31] Ahmed, H. A., & Naoum, M. M. (2015). *Liq. Cryst.*, *43*, 222.
[32] Sùrensen, H. O. & Larsen, S. (2003). *Acta Cryst.*, *B59*, 132.