Molecular Crystals and Liquid Crystals

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/gmcl20

Synthesis and characterization of symmetrical liquid crystalline compounds based on oxazole and thaizole rings

Tareq K. Ibraheem, Nisreen H. Karam & Ammar H. Al-Dujaili

To cite this article: Tareq K. Ibraheem, Nisreen H. Karam & Ammar H. Al-Dujaili (2020) Synthesis and characterization of symmetrical liquid crystalline compounds based on oxazole and thaizole rings, Molecular Crystals and Liquid Crystals, 710:1, 1-12, DOI: 10.1080/15421406.2020.1824152

To link to this article: https://doi.org/10.1080/15421406.2020.1824152

MOLECULAR CRYSTALS AND LIQUID CRYSTALS
2020, VOL. 710, NO. 1, 1–12
https://doi.org/10.1080/15421406.2020.1824152

Taylor & Francis
Taylor & Francis Group

Synthesis and characterization of symmetrical liquid crystalline compounds based on oxazole and thaizole rings

Tareq K. Ibraheem[a], Nisreen H. Karam[a], and Ammar H. Al-Dujaili[b]

[a]Department of Chemistry, College of Education for Pure Science, Ibn Al-Haitham, University of Baghdad, Baghdad, Iraq; [b]Hamdi Mango Center for Scientific Research, University of Jordan, Amman 11942, Jordan

ABSTRACT

Twelve compounds containing a sulphur- or oxygen-based heterocyclic core, 1,3- oxazole or 1,3-thiazole ring with hydroxy, methoxy and methyl terminal substituent, were synthesized and characterized. The molecular structures of these compounds were performed by elemental analysis and different spectroscopic tequniques. The liquid crystalline behaviors were studied by using hot-stage optical polarizing microscopy and differential scanning calorimetry. All compounds of 1,4- disubstituted benzene core with oxazole ring display liquid crystalline smectic A (SmA) mesophase. The compounds of 1,3- and 1,4-disubstituted benzene core with thiazole ring exhibit exclusively enantiotropic nematic liquid crystal phases.

KEYWORDS
Heterocyclic; liquid crystal; oxazole; thiazole

Introduction

Liquid crystals are unique in their uses due to their excellent optical properties [1–3]. Heterocycles are of great importance as units in thermotropic liquid crystals owing to their ability to impart lateral and/or longitudinal dipoles combined with changes in the molecular shape [4–6]. Generally, the five membered ring heterocyclics are involved and they form part of the core in rod-shaped, bent-shaped or disk-shaped molecules. They have been studied as structural units to liquid crystals contributing to the study of the relation between molecular structure and mesomorphic properties [7,8]. Many compounds containing heterocyclic units with liquid-crystalline properties have been synthesized [9–13].

Furthermore, the incorporation of heteroatoms can result in considerable changes in the corresponding liquid-crystalline phases and in the physical properties of the observed phases [14] because that the presence of a heteroatom can cause profound changes in mesomorphic behavior, due to the electro negativity difference presented in relation to carbon or through changes in molecular geometry [15,16].

The 1,3-oxazole and 1,3-thiazole rings have been incorporated into a variety of mesogenic structures and imparts some favorable characteristics for applications in electro-optical devices, such as low viscosity (anticipated due to the more compact nature of the ring compared with benzene), high birefringence and a significant dipole moments

CONTACT Ammar H. Al-Dujaili ah.aldujaili@gmail.com Hamdi Mango Center for Scientific Research, University of Jordan, Amman, Jordan.

(1.6D for thiazole and 1.3D for oxazole). Besides, they also confer a curvature to the molecule, leading to bent-shaped liquid crystals [17].

The 1,3-oxazole and 1,3-thiazole cores may be either 2,5- or 2,4-disubstituted; the 2,5-disubstituted arrangement is the more linear substitution pattern (the angles defined by extrapolating the C–H bonds are 153 for 2,5-disubstitution and 133 for 2,4-disubstitution when the substituent are hydrogen) which leads to enhanced mesophase thermal stability. There are many examples in literature including the preparation of 2,5-disubstituted oxazole and thiazole mesogenic molecules [13,17–30]. But there are limited number of mesogenic 2,4-disubstituted oxazole and thiazole derivatives have been reported [31–39]. For instance, Murza *et al.*, [31–33] have been synthesized 4-(arylamino)-2-benzylideneamino-4-(p-nitrophenoxy) thiazolees derivatives, which possess monotropic mesomorphism of the nematic type over a wide range of temperature. Also, Murza *et al.*, [34,35] have been synthesized liquid crystalline azomethines 2-benzylideneamino-4-(p-nitrophenoxy) thiazoles derivatives displaying nematic mesomorphism and studied a correlation between the geometric parameters and liquid crystalline properties. Several non-symmetrically 4,4′-diaryl-2,2′-bithiazoles containing alkyl and alkoxy substituents at the 4-positions were synthesized that exhibit wide-range high-temperature smectic C phases [36]. A two series of liquid crystalline Schiff bases containing thiazole moiety with different length of alkoxy spacer were synthesized. Both two-series compounds exhibit liquid crystalline mesophase nematics. The liquid crystalline behavior was analyzed in terms of the relation of structural property [37]. A new series of 2,4-disubstituted thiazole esters was synthesized and introduced and discussed their mesomorphic properties. Some of these compounds demonstrate stable mesophase smectic A [38]. Recently, Seed and Sampson [39] highlighted both recent and well-established synthetic approaches to 2,5- and 2,4-disubstituted 1,3-thiazoles systems using ring closure (Gabriel- and Hantzsch-type approaches) methodology and modifications of an intact 1,3- thiazole ring.

As part of our study of liquid crystal derivatives containing heterocyclic units [37,40–46] the purpose of this research was to synthesize and characterize the recent symmetrical bent and linear-core 2,4-disubstituted 1,3-oxazole and 1,3-thiazole-based liquid crystals and the phase behavior of these compounds.

Experimental

General methods

All chemicals were acquired from Sigma-Aldrich Company in Milwaukee, Wisconsin (USA) and used without further purification. FT-IR spectra were recorded by KBr disk in a Shimadzu (IR Affinity-1). Elemental analyses were performed by Euro EA 3000/Italy. ^{1}HNMR spectra were obtained using a Bruker 300 MHz origin: Switzerl and were reported in ppm (δ), the compounds were dissolved in DMSO-d6 solution with the tetramethyl silane as internal standard. Mass spectrum was determined by scan110 (1.257 min): direct prob-013777.d. The optical behavior observations were made using Olympus BX40 microscope equipped with a Leitz Laborlux 12 Pols hot stage and PR600 controller. The textures of the mesophases shown by the compounds were observed using optical polarized light with crossed polarizer with the sample in a thin film sandwiched between a glass slide and cover slip. Photographs of texture were obtained using a camera Olympus PM-10AD model. Differential scanning calorimetry (DSC) measurements were performed using a STAPT-1000LINSIS Instruments at heating and cooling rates of 10 °C/min with indium as the internal standard (156.6 °C, 28.45 J/g).

Synthesis

The detailed synthesis of derivatives is depicted in Scheme 1.

Synthesis of N,N′-(1,3-Phenylene)bis(2-chloroacetamide) [I]$_a$ and N,N′-(1,4-Phenylene)bis(2-chloroacetamide) [I]$_b$

A mixture of 1,3-phenylenediamine or 1,4-phenylenediamine (1.08 g, 10 mmol), in DMF (15 mL) was mixed with triethylamine (TEA) (18 mL) and chloroacetyl chloride (2.26 g, 20 mmol) was stirred in ice bath for 3 h. The mixture was added to an ice water bath until precipitation occurred; the separated solid was filtered, washed with water, dried and recrystallized from ethanol.

Analytical data

N,N′-(1,3-Phenylene)bis(2-chloroacetamide) [I]$_a$

White powder; yield: 76%; m.p.: 213 °C; FTIR (ν/cm^{-1}): 3259 (NH), 1681 (C = O amide). Anal. Calcd. for $C_{10}H_{10}Cl_2N_2O_2$: C, 45.98; H, 3.83; N, 10.73. Found: C, 46.11; H, 3.73; N, 10.93.

N,N′-(1,4-Phenylene)bis(2-chloroacetamide) [I]$_b$

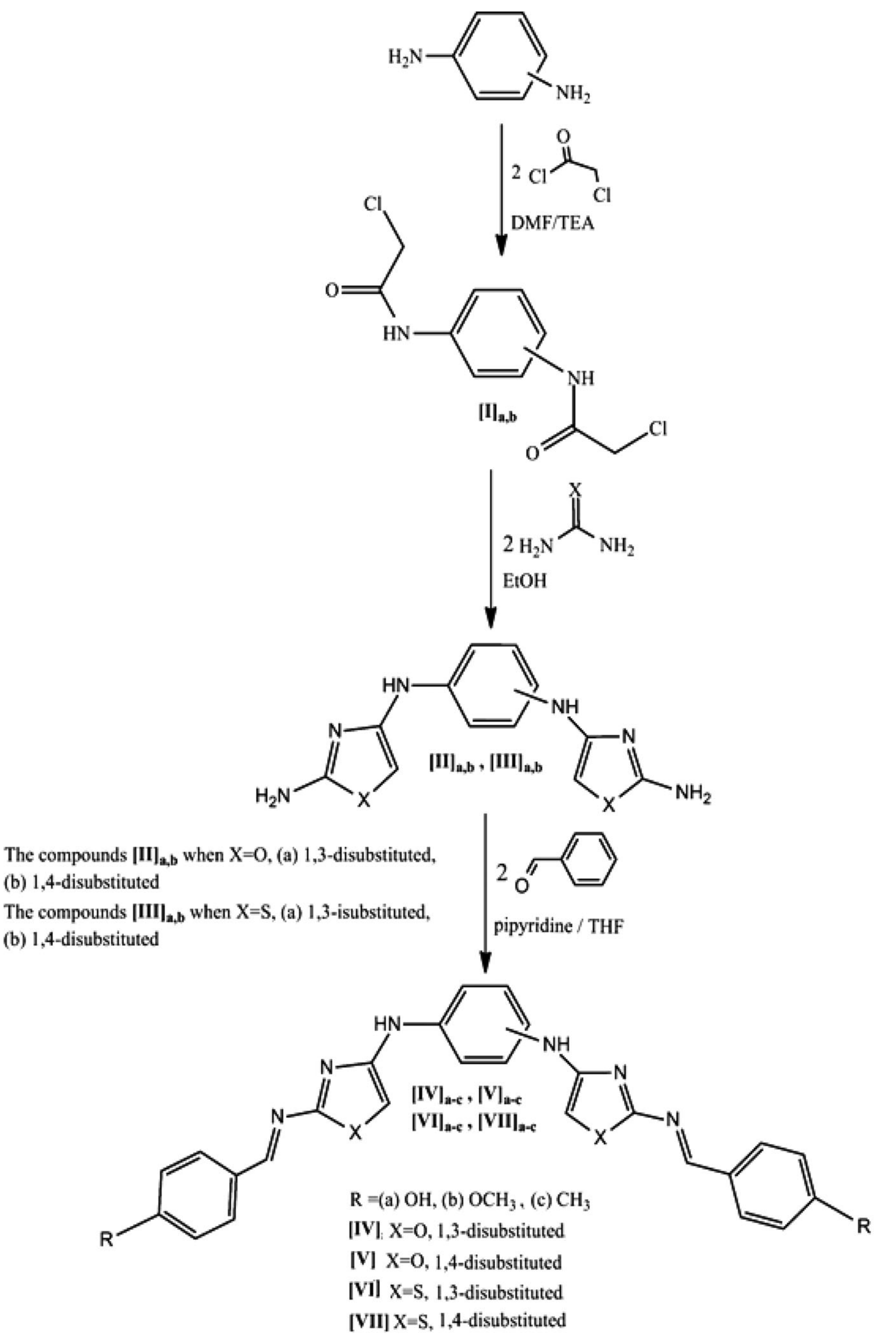
Gray powder; yield: 72%; m.p.: 316 °C; FTIR (ν/cm^{-1}): 3223 (NH), 1673 (C = O amide). Anal. Calcd. for $C_{10}H_{10}Cl_2N_2O_2$: C, 45.98; H, 3.83; N, 10.73. Found: C, 46.23; H, 3.64; N, 10.94.

Synthesis of oxazole compounds [II]$_{a,b}$ and thiazole compounds [III]$_{a,b}$

To a solution of compound [I]$_a$ or [I]$_b$ (2.61 g, 10 mmol) in ethanol 150 mL, urea (1.20 g, 20 mmol) or thiourea (1.52 g, 20 mmol) was added. This reaction mixture was heated under reflux for 12–15 h with occasional stirring. Then, the reaction mixture was concentrated, and the residue obtained was poured over crushed ice, the separated solid was filtered, washed with water, dried and recrystallized from ethanol.

N4,N4′-(1,3-phenylene)bis(oxazole-2,4-diamine) [II]$_a$

White powder; yield: 67%; m.p.: 199 °C. FTIR (ν/cm^{-1}): 3462-3190 (NH_2, NH), 3080 (C-H arom), 1649 (C = N endo cyclic), 1608 (C = C).^{1}HNMR (300 MHz, DMSO-d_6) δ (ppm): 9.89 (s, 2H, 2NH), 7.53 (s, 2H, oxazole ring), 7.48–7.00 (m, 4H –Ar) , 5.39 (s, 4H, $2NH_2$). MS: $m/z + 1 = 273$. Anal. Calcd. for $C_{12}H_{12}N_6O_2$: C, 52.94; H, 4.41; N, 30.88. Found: C, 52.73; H, 4.65; N, 31.04.



The compounds [II]a,b when X=O, (a) 1,3-disubstituted,
(b) 1,4-disubstituted
The compounds [III]a,b when X=S, (a) 1,3-isubstituted,
(b) 1,4-disubstituted

R =(a) OH, (b) OCH_3 , (c) CH_3
[IV]: X=O, 1,3-disubstituted
[V] X=O, 1,4-disubstituted
[VI] X=S, 1,3-disubstituted
[VII] X=S, 1,4-disubstituted

Scheme 1. The synthetic route of compounds **$[IV]_{a,b,c}$, $[V]_{a,b,c}$, $[VI]_{a,b,c}$ and $[VII]_{a,b,c}$.**

N4,N4′-(1,4-phenylene)bis(oxazole-2,4-diamine) $[II]_b$

White powder; yield: 73%; m.p.: 212 °C. FTIR (ν/cm^{-1}): 3244–3174 (NH_2,NH), 3093 (C-H arom.), 1634 (C = N endo cyclic), 1593 (C = C), ^{1}HNMR (300 MHz, DMSO-d_6) δ (ppm): 9.89 (s, 2H, 2NH), 7.53 (s, 2H, oxazole ring), 7.48-7.00 (m, 4H –Ar), 5.39

(s, 4H, $2NH_2$). MS: $m/z+1=273$. Anal. Calcd. for $C_{12}H_{12}N_6O_2$: C, 52.94; H, 4.41; N, 30.88. Found: C, 53.10; H, 4.25; N, 30.64.

N4,N4′-(1,3-phenylene)bis(thiazole-2,4-diamine) [III]$_a$

Dark yellow powder; yield: 69%; m.p.: 254 °C. FTIR (ν/cm^{-1}): 3271–3154 (NH_2, NH), 3099 (C-H arom.), 1656 (C = N endo cyclic), 1596 (C = C). ^{1}HNMR (300 MHz, DMSO-d_6) δ (ppm): 8.97 (s, 2H, 2NH), 8.93–8.71 (m, 4H, –Ar), 8.67(s, 2H), 3.26 (s, 4H, $2NH_2$). Anal. Calcd. for $C_{12}H_{12}N_6S_2$: C, 47.37; H, 3.95; N, 27.63; S, 21.05. Found: C, 47.51; H, 4.15; N, 27.74; S, 20.92.

N4,N4′-(1,4-phenylene)bis(thiazole-2,4-diamine) [III]$_b$

Yellow powder; yield: 76%; m.p.: 237 °C. FTIR (ν/cm^{-1}): 3253–3170 (NH_2, NH), 3089 (C-H arom.), 1662 (C = N endo cyclic), 1587 (C = C). MS: $m/z+1=305$. Anal. Calcd. for $C_{12}H_{12}N_6S_2$: C, 47.36; H, 3.94; N, 27.63; S, 21.05. Found: C, 47.19; H, 3.67; N, 27.44; S, 21.30.

Synthesis of Schiff bases compounds [IV-VII]$_{a\text{-}c}$

To a solution (20 mmol) different aromatic aldehyde and (4 mL) of THF added a few drops of piperidine, then, added (10 mmol) of compound [II]$_{a,\ b}$ or [III]$_{a,\ b}$ and reflux for 4 h. The solvent was evaporated and the residue was extracted by diethyl ether and the obtained solid was filtered, washed with water and recrystallized from an appropriate solvent.

4,4′-((((1,3-Phenylenebis(azanediyl))bis(oxazole-4,2-diyl))bis(azaneylylidene)) bis(methaneylylidene))diphenol [IV]$_a$

White powder; yield: 74%; m.p.: 239 °C. FTIR (ν/cm^{-1}): 3289 (NH), 3253 (O-H), 3048 (C-H arom.), 1648 (C = N), 1591 (C = C). Anal. Calcd. for $C_{26}H_{20}N_6O_4$: C, 65.00; H, 4.17; N, 17.50. Found: C, 65.24; H, 3.96; N, 17.65.

N1,N3′-bis(2-((4-methoxybenzylidene)amino)oxazol-4-yl)benzene-1,3-dia- mine[IV]$_b$

White powder; yield: 81%; m.p.: 161 °C. FTIR (ν/cm^{-1}): 3200 (NH), 3093 (C-H arom.), 2956–2885 (C-H aliph.), 1650 (C = N), 1601 (C = C). MS: $m/z+1=509$. Anal. Calcd. for $C_{28}H_{24}N_6O_4$: C, 66.14; H, 4.72; N, 16.53. Found: C, 66.30; H, 4.83; N, 16.32.

N1,N3′-bis(2-((4-methylbenzylidene)amino)oxazol-4-yl)benzene-1,3-diam- ine [IV]$_c$

Brown powder; yield: 76%; m.p.: 191 °C. FTIR (ν/cm^{-1}): 3184 (NH), 3089 (C-H arom.), 2974–2812 (C-H aliph.), 1622 (C = N), 1598 (C = C). Anal. Calcd. for $C_{28}H_{24}N_6O_2$: C, 70.59; H, 5.04; N, 17.65. Found: C, 70.30; H, 4.84; N, 17.43.

4,4′-((((1,4-Phenylenebis(azanediyl)) bis (oxazole-4,2-diyl)) bis(azaneylylidene))bis(methaneylylidene))diphenol [V]$_a$

White powder; yield: 69%; m.p.: 313 °C. FTIR (ν/cm^{-1}): 3110 (NH), 3253 (O-H), 3021 (C-H arom.), 1616 (C = N), 1600 (C = C). Anal. Calcd. for $C_{26}H_{20}N_6O_4$: C, 65.00; H, 4.16; N, 17.50. Found: C, 64.84; H, 4.30; N, 17.66.

N1,N4′-bis(2-((4-methoxybenzylidene)amino) oxazol-4-yl)benzene-1,4-dia-mine[V]$_b$

Brown powder; yield: 63%; m.p.: 224 °C. FTIR (ν/cm^{-1}): 3172 (NH), 3048 (C-H arom.), 2940-2876 (C-H aliph.), 1656 (C = N), 1610 (C = C). Anal. Calcd. for $C_{28}H_{24}N_6O_4$: C, 66.14; H, 4.72; N, 16.53. Found: C, 66.02; H, 4.59; N, 16.72.

N1,N4′-bis(2-((4-methylbenzylidene)amino) oxazol-4-yl)benzene-1,4-dia- mine[V]$_c$

Brown powder; yield: 82%; m.p.: 245 °C. FTIR (ν/cm^{-1}): 3259 (NH), 3091 (C-H arom.), 2956-2884 (C-H aliph.), 1619 (C = N), 1593 (C = C). ^{1}HNMR (300 MHz, DMSO-d$_6$) δ (ppm): 9.60 (s, 2H, 2NH), 7.77 (s, 2H, two CH = N), 7.58(s, 2H, oxazole ring), (7.53-6.96) (m, 12H-Ar), 2.54(s, 6H, 2CH$_3$). MS: $m/z + 1 = 477$. Anal. Calcd. for $C_{28}H_{24}N_6O_2$: C, 70.58; H, 5.04; N, 17.64. Found: C, 70.73; H, 5.18; N, 17.83.

4,4′-((((1,3-Phenylenebis(azanediyl))bis(thiazole-4,2-diyl))bis(azaneylylidene))bis(methaneylylidene))diphenol [VI]$_a$

White powder; yield: 66%; m.p.: 221 °C. FTIR (ν/cm^{-1}): 3280 (NH), 3283 (O-H), 3048 (C-H arom.), 1651 (C = N), 1599 (C = C). Anal. Calcd. for $C_{26}H_{20}N_6O_2S_2$: C, 60.94; H,3.91; N, 16.41. Found: C, 70.09; H, 3.78; N, 16.69.

N1,N3′-bis(2-((4-methoxybenzylidene)amino)thiazole-4-yl)benzene-1,3-di- amine[VI]$_b$

Yellow powder; yield: 78%; m.p.: 167 °C. FTIR (ν/cm^{-1}): 3323 (NH), 3050 (C-H arom.), 2946–2875 (C-H aliph.), 1660 (C = N), 1600 (C = C). MS: $m/z + 1 = 541$. Anal. Calcd. for $C_{28}H_{24}N_6O_2S_2$: C, 62.22; H, 4.44; N, 15.56. Found: C, 62.43; H, 4.68; N, 15.69.

N1,N3′-bis(2-((4-methylbenzylidene) amino)thiazole-4-yl)benzene-1,3-diam- ine [VI]$_c$

White powder; yield: 63%; m.p.: 221 °C. FTIR (ν/cm^{-1}): 3174 (NH), 3089 (C-H arom.), 2935-2864 (C-H aliph.), 1622 (C = N), 1595 (C = C) .Anal. Calcd. for $C_{28}H_{24}N_6S_2$: C, 66.14; H, 4.72; N, 16.54. Found: C, 65.93; H, 4.68; N, 16.71.

4,4-((((1,4-Phenylenebis(azanediyl)) bis (thiazole-4,2-diyl)) bis(azaneylyli- dene)) bis(methaneylylidene))diphenol[VII]$_a$

Yellow powder; yield: 60%; m.p.: 192 °C. FTIR (ν/cm^{-1}): 3292 (NH), 3311 (O-H), 3041 (C-H arom.), 1658 (C = N), 1595 (C = C). Anal. Calcd. for $C_{26}H_{20}N_6O_2S_2$: C, 60.94; H,3.91; N, 16.41. Found: C, 61.10; H, 3.81; N, 16.26.

N1,N4′-bis(2-((4-methoxybenzylidene)amino) thiazole-4-yl)benzene-1,4-di- amine[VII]$_b$

White powder; yield: 71%; m.p.: 203 °C. FTIR (ν/cm^{-1}): 3232 (NH), 3011 (C-H arom.), 2954-2865 (C-H aliph.), 1653 (C = N), 1597 (C = C). Anal. Calcd. for $C_{28}H_{24}N_6O_2S_2$: C, 62.22; H, 4.44; N, 15.56. Found: C, 62.02; H, 4.53; N, 15.48.

N1,N3′-bis(2-((4-methylbenzylidene)amino) thiazole-4-yl)benzene-1,4-diamine [VII]$_c$

Yellow powder; yield: 81%; m.p.: 204 °C. FTIR (ν/cm^{-1}): 3245 (NH), 3016 (C-H arom.), 2942-2871 (C-H aliph.), 1632 (C = N), 1594 (C = C). MS: $m/z + 1 = 509$. Anal. Calcd. for $C_{28}H_{24}N_6S_2$: C, 66.14; H, 4.72; N, 16.54. Found: C, 66.33; H, 4.69; N, 16.77.

Results and discussion

Synthesis

All of the new synthesized compounds gave satisfactory analysis for the proposed structures, which were confirmed on the basis of their elemental analysis (see analytical data); FTIR, ^{1}HNMR and mass spectroscopy. The compounds **[I]$_a$** and **[I]$_b$** were prepared by reaction of 1,3-phenylenediamine or 1,4-phenylenediamine with two moles from chloroacetyl chloride in dimethylformamide (DMF) and triethylamine (TEA) (as a catalyst). The FTIR spectra for compounds **[I]$_a$** and **[I]$_b$** showed the appearance of absorption stretching bands of N-H at 3259 and 3223 cm^{-1} and C=O groups of (amide moiety) at 1681and 1673 cm^{-1}, respectively, and disappearance of stretching bands of NH_2 groups. The compounds **[II]$_{a,b}$** and **[III]$_{a,b}$** were synthesized by reaction of compound **[I]$_a$** or **[I]$_b$** with two moles from urea or thiourea in absolute ethanol. The FTIR spectra showed disappearance absorption bands of the carbonyl amide for starting material with showed absorption stretching bands for C = N endo cyclic groups at 1649 and 1634 cm^{-1} for compounds **[II]$_{a,b}$** and 1656 and 1662 cm^{-1} for compounds **[III]$_{a,b}$**, respectively. The ^{1}HNMR spectrum for compound **[II]$_a$** showed a singlet signal at δ 9.89 ppm for two protons of NH groups, singlet signal at δ 7.53 ppm for two protons of oxazole rings, many signals at region δ (7.48–7.00) ppm for four benzene protons, a singlet signal at δ 5.39 ppm for two protons of NH_2 groups. The ^{1}HNMR spectrum for compound **[III]$_a$** showed a signal at δ 8.97 ppm for two protons of NH groups, many signals at δ (8.93–8.71) ppm four benzene protons and singlet signal at δ 8.67 ppm for two protons of thiazole rings, a signal at δ 3.26 ppm for two protons of NH_2 groups.

The compounds **[IV–VII]**$_{\mathbf{a,b,c}}$ are formed from the reaction of compound **[II]**$_{\mathbf{a,b}}$ or **[III]**$_{\mathbf{a,b}}$ with two moles from different aromatic aldehydes in THF and few drops of pipyridine. The FTIR spectra for Schiff bases showed disappearance of stretching bands for amine and aldehyde groups for starting material and showed absorption stretching bands of imine groups (-N = CH-) in the region 1656–1619 and 1660–1622 cm^{-1} for the compounds **[IV]**$_{\mathbf{a,b,c}}$, **[V]**$_{\mathbf{a,b,c}}$, **[VI]**$_{\mathbf{a,b,c}}$ and **[VII]**$_{\mathbf{a,b,c}}$, respectively. The ^{1}HNMR spectrum for compound **[V]**$_{\mathbf{c}}$ showed singlet signal at δ 9.90 ppm for two protons of NH groups, singlet signal at δ 7.77 ppm for two protons of CH = N groups, singelat signal at δ 7.58 ppm for two protons of oxazole rings, many signals at δ 7.53–6.96 ppm for twelve aromatic protons, a signal at δ 2.54 ppm for six protons of CH_3 groups.

The mesomorphic properties

The transition temperatures and mesophase type (texture identity) were investigated by using optical polarizing microscopy (OPM) and DSC. Phase transition temperatures observed by OPM were found to be in reasonable agreement with the corresponding DSC thermograms. The mesophases exhibited by the synthesized compounds were identified from their optical textures which were observed by OPM, using the classification systems reported by Richter [47] and Gray and Goodby [48]. The thermotropic liquid crystalline properties and thermodynamic data of **[IV]**$_{\mathbf{a,b,c}}$, **[V]**$_{\mathbf{a,b,c}}$, **[VI]**$_{\mathbf{a,b,c}}$ and **[VII]**$_{\mathbf{a,b,c}}$ are summarized in Table 1.

All the final compounds of 1,3-disubstituted benzene derivatives based on oxazole ring **[IV]**$_{\mathbf{a}}$, **[IV]**$_{\mathbf{b}}$ and **[IV]**$_{\mathbf{c}}$, exhibited liquid crystalline phases characterized by OPM and showed a smectogenic profile in special smectic A (SmA) phase which was found to be present in all three compounds. Representative texture of SmA mesophase by OPM shown by these final compounds are presented in Fig. 1 and shows typical focal conic SmA texture. Contrary to the compounds **[IV]**$_{\mathbf{a,b,c}}$, the compounds of 1,4-disubstituted benzene core with oxazole ring **[V]**$_{\mathbf{a}}$, **[V]**$_{\mathbf{b}}$ and **[V]**$_{\mathbf{c}}$ do not reveal any liquid crystalline behavior, but simply changes from the solid crystalline state to the isotropic liquid at 312, 223 and 244 °C, respectively. The absence of mesomorphic properties of the **[V]**$_{\mathbf{a,b,c}}$ derivatives may be attributed to the presence of the 2,4-disubstituted oxazole ring which causes a significant loss of linearity of 1,4-disubstituted benzene core then disfavoring the mesophases formation [49].

All compounds of 1,3-disubstituted benzene **[VI]**$_{\mathbf{a,b,c}}$ and of 1,4-disubstituted benzene **[VII]**$_{\mathbf{a,b,c}}$ derivatives based on thiazole ring were found to be enantiotropic nematic phase under OPM as shown in Fig. 1. The texture observed by OPM on cooling from the isotropic liquid showed a typical schlieren texture as shown in Fig. 1 which is a characteristic of nematic mesophase. The nematic phase of these compounds could be attributed to the formation of intermolecular hydrogen bonding, *i.e.*, terminal molecular interaction in case of compounds **[VI]**$_{\mathbf{a}}$ and **[VII]**$_{\mathbf{a}}$ and to short methyl and methoxy groups in terminal substituent in compounds **[VI]**$_{\mathbf{b}}$, **[VII]**$_{\mathbf{b}}$, **[VI]**$_{\mathbf{c}}$ and **[VII]**$_{\mathbf{c}}$ (the shorter methyl and methoxy groups led to a higher ratio of terminal to lateral intermolecular attraction forces) which are a favor of nematic mesophase formation [50].

It is interesting to compare compounds **[V]**$_{\mathbf{a,b,c}}$ with compounds **[VII]**$_{\mathbf{a,b,c}}$. Compounds **[V]**$_{\mathbf{a,b,c}}$ and **[VII]**$_{\mathbf{a,b,c}}$ have the same central rigid core and the same

Table 1. Phase transition temperatures (°*C*) and transition enthalpies Δ*H*(kJ/mol) of compounds **[IV]**$_{a,b,c}$, **[V]**$_{a,b,c}$, **[VI]**$_{a,b,c}$ and **[VII]**$_{a,b,c}$ determined by DSC (10 °*C*/min) during first heating.

Compound	Transition temperatures (°C) (ΔH, kJ/mol)
[IV]$_a$	$\mathrm{Cr} \xrightleftharpoons{240\ (11.38)} \mathrm{SmA} \xrightleftharpoons{287\ (3.71)} \mathrm{I}$
[IV]$_b$	$\mathrm{Cr} \xrightleftharpoons{158\ (10.52)} \mathrm{SmA} \xrightleftharpoons{210\ (4.22)} \mathrm{I}$
[IV]$_c$	$\mathrm{Cr} \xrightleftharpoons{188\ (12.32)} \mathrm{SmA} \xrightleftharpoons{234\ (5.08)} \mathrm{I}$
[V]$_a$	$\mathrm{Cr} \xrightarrow{312} \mathrm{I}$
[V]$_b$	$\mathrm{Cr} \xrightarrow{223} \mathrm{I}$
[V]$_c$	$\mathrm{Cr} \xrightarrow{244} \mathrm{I}$
[VI]$_a$	$\mathrm{Cr} \xrightleftharpoons{219\ (19.36)} \mathrm{N} \xrightleftharpoons{290\ (3.31)} \mathrm{I}$
[VI]$_b$	$\mathrm{Cr} \xrightleftharpoons{165\ (17.68)} \mathrm{N} \xrightleftharpoons{215\ (2.97)} \mathrm{I}$
[VI]$_c$	$\mathrm{Cr} \xrightleftharpoons{220\ (18.11)} \mathrm{N} \xrightleftharpoons{280\ (2.35)} \mathrm{I}$
[VII]$_a$	$\mathrm{Cr} \xrightleftharpoons{185\ (18.39)} \mathrm{N} \xrightleftharpoons{256\ (3.28)} \mathrm{I}$
[VII]$_b$	$\mathrm{Cr} \xrightleftharpoons{198\ (19.91)} \mathrm{N} \xrightleftharpoons{241\ (3.27)} \mathrm{I}$
[VII]$_c$	$\mathrm{Cr} \xrightleftharpoons{202\ (21.96)} \mathrm{N} \xrightleftharpoons{266\ (2.93)} \mathrm{I}$

Cr: Crystal; N: Nematic; SmA: smectic A; I: Isotropic transition.

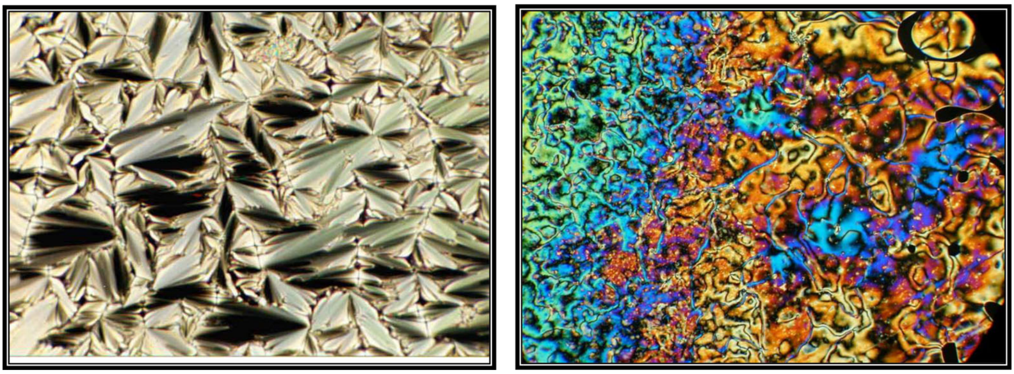


Figure 1. Polarizing microscopy images: The image on the left is focal conic texture of SmA phase at 197 °*C* on cooling of compound **[IV]**$_b$. The image on the right shows the schlieren texture of the nematic phase at 269 °*C* upon cooling of compound **[VI]**$_c$. (200 X magnification).

terminal substituent. The difference between those compounds is the bioxazole rings in **[V]**$_{\mathbf{a,b,c}}$ and the bithiazole rings in **[VII]**$_{\mathbf{a,b,c}}$. All compounds **[VII]**$_{\mathbf{a,b,c}}$ exhibit nematic phase, while, compounds **[V]**$_{\mathbf{a,b,c}}$ do not show mesomorphic behavior, and only crystal to isotropic liquid transition was observed. This results show that the presence of thiazole ring has a profound influence on the mesogenic properties. This could be due to, first, the bend associated with the exocyclic bonds in the 2- and 4- positions of the 1,3-oxazole unit was too extreme to achieve the necessary ordered mesophase packing, and, second, the increased polarizability of the thiazole ring compared to the oxazole ring. The same results were obtained with the analogous 1,3-oxazole and 1,3-thiazole derivatives containing a symmetric rigid core [51–53].

Conclusion

This work describes the synthesis and liquid crystalline properties of 1,3- and 1,4-disubstituted benzene core with oxazole or thiazole rings. The reported 1,3-disubstituted benzene core with oxazole ring were all found to exhibit SmA phases which were in contrast to that compounds of 1,4-disubstituted benzene that do not show any liquid crystalline behavior. All compounds containing symmetrical bithiazole exhibit purely ennatiotropic nematic phases. The influence of the symmetrical bioxazole and bithiazole, the substituted position on central benzene ring and the terminal substituents on the type and temperature range of the mesomorphous properties of these compounds has been discussed.

ORCID

Ammar H. Al-Dujaili http://orcid.org/0000-0002-1759-8585

References

[1] D. Demus *et al.*, *Physical Properties of Liquid Crystals* (Wiley-VCH, New York, NY, 1999).
[2] D. Demus *et al.*, *Handbook of Liquid Crystals, Vol. 2A: Low Molecular Weight Liquid Crystals I* (Wiley-VCH, New York, NY, 1998).
[3] D. Demus *et al.*, *Handbook of Liquid Crystals, Vol. 2B: Low Molecular Weight Liquid Crystals II* (Wiley-VCH, New York, NY, 1998).
[4] L. Da Silva, *Mol. Cryst. Liq. Cryst.* **373**, 181 (2002).
[5] A. S. Matharu and D. Chambers-Asman, *Liq. Cryst.* **34** (11), 1317 (2007). doi:10.1080/02678290701697447
[6] H. Gallardo, R. F. Magnago, and A. J. Bortoluzzi, *Liq. Cryst.* **28** (9), 1343 (2001). doi:10.1080/02678290110066813
[7] A. A. Merlo, H. Gallardo, and T. R. Taylor, *Quím. Nova* **24** (3), 354 (2001). doi:10.1590/S0100-40422001000300012
[8] F. V. Pereira *et al.*, *J. Braz. Chem. Soc.* **17**, 184 (2006).
[9] M. P. Aldred *et al.*, *Liq. Cryst.* **32** (8), 951 (2005). doi:10.1080/02678290500248400
[10] R. Cristiano *et al.*, *Liq. Cryst.* **33** (4), 381 (2006). doi:10.1080/02678290500483304
[11] R. Cristiano, D. M. P. O. Santos, and H. Gallardo, *Liq. Cryst.* **32** (1), 7 (2005). doi:10.1080/026782904123313329288
[12] M. U. Kauhanka and M. M. Kauhanka, *Liq. Cryst.* **33** (1), 121 (2006). doi:10.1080/02678290500429976
[13] A. J. Seed, *Chem. Soc. Rev.* **36** (12), 2046 (2007). doi:10.1039/b612666a

[14] C. K. Lai *et al.*, *Liq. Cryst.* **29** (7), 915 (2002). doi:10.1080/02678290210129957

[15] H. Gallardo and F. C. J. Silva, *Chem. Soc., Perkin Trans.* **3**, 319 (1989).

[16] H. Gallardo and L. Maurmann, *Mol. Cryst. Liq. Cryst.* **378** (1), 23 (2002). doi:10.1080/713738578

[17] A. M. Grubb *et al.*, *Liq. Cryst.* **36** (5), 443 (2009). doi:10.1080/02678290903003121

[18] K. Dolling, H. Zaschke, and H. J. Schubert, *Prakt. Chem.* **321**, 643 (1979).

[19] A. Mori *et al.*, *J. Am. Chem. Soc.* **125** (7), 1700 (2003). doi:10.1021/ja0289189

[20] C. H. Lee and T. Yamamoto, *Mol. Cryst. Liq. Cryst.* **363** (1), 77 (2001). doi:10.1080/10587250108025259

[21] C. H. Lee and T. Yamamoto, *Mol. Cryst. Liq. Cryst.* **369** (1), 95 (2001). doi:10.1080/10587250108030012

[22] M. Mamada *et al.*, *Chem. Mater.* **19** (22), 5404 (2007). doi:10.1021/cm071505s

[23] B. T. Thaker *et al.*, *Mol. Cryst. Liq. Cryst.* **466** (1), 13 (2007). doi:10.1080/15421400601150379

[24] H. Gallardo, D. M. P. O. Santos, and A. J. Bortoluzzi, *Acta Cryst.* **E66** (Supp1 7), o2365 (2010).

[25] A. A. Kiryanov, P. Sampson, and A. J. Seed, *J. Org. Chem.* **66** (23), 7925 (2001). doi:10.1021/jo016063x

[26] A. M. Grubb *et al.*, *Liq. Cryst.* **2012**, 1 (2012).

[27] J. A. Olivares *et al.*, *Phys. Rev. E* **68**, 041704 (2003).

[28] M. Packard, K. Gulliford, and E. Scharrer, *Mol. Cryst. Liq. Cryst.* **647** (1), 186 (2017). doi:10.1080/15421406.2017.1289588

[29] P. Tuzimoto *et al.*, *Liq. Cryst.* **41** (8), 1097 (2014). doi:10.1080/02678292.2014.903003

[30] A. Glebowska *et al.*, *Liq. Cryst.* **42**, 829 (2015).

[31] M. M. Murza, A. S. Golovanov, and M. G. Safarov, *Chem. Heterocycl. Compd.* **32** (4), 477 (1996). doi:10.1007/BF01165916

[32] A. S. Golovanov, M. M. Murza, and M. G. Safarov, *Chem. Heterocycl. Compd.* **33** (11), 1350 (1997). doi:10.1007/BF02320340

[33] M. M. Murza, Z. K. Kuvatov, and M. G. Safarov, *Chem. Heterocycl. Compd.* **35** (9), 1097 (1999). doi:10.1007/BF02251804

[34] M. M. Murza *et al.*, *Chem. Heterocycl. Comp.* **37** (10), 1258 (2001). doi:10.1023/A:1013857829119

[35] Z. K. Kuvatov, M. G. Safarov, and M. M. Murza, *Chem. Heterocycl. Comp.* **40** (4), 500 (2004). doi:10.1023/B:COHC.0000033545.34829.2a

[36] V. V. Mikhailenko *et al.*, *Mol. Cryst. Liq. Cryst.* **542** (1), 115/[637] (2011). doi:10.1080/15421406.2011.570142

[37] N. H. Karam, J. H. Tomma, and A. H. Al-Dujaili, *Chem. Mater. Res.* **3** (9), 162 (2013).

[38] J. M. F. M. Schneider *et al.*, *J. Braz. Chem. Soc.* **25**, 1493 (2014).

[39] A. J. Seed and P. Sampson, *Liq. Cryst.* **44** (12–13), 1894 (2017).

[40] M. K. S. Al-Malki, A. S. Hameed, and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.* **593** (1), 34 (2014). doi:10.1080/15421406.2013.864546

[41] N. H. Karam, A. T. Atto, and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.* **605** (1), 1 (2014). doi:10.1080/15421406.2013.840944

[42] W. M. Hamad, H. J. Azeez, and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.* **652** (1), 67 (2017). doi:10.1080/15421406.2017.1357426

[43] N. H. Karam *et al.*, *J. Mol. Struct.* **1171**, 404 (2018). doi:10.1016/j.molstruc.2018.06.031

[44] J. H. Tomma, T. S. Ghali, and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.* **664** (1), 85 (2018). doi:10.1080/15421406.2018.1468277

[45] N. H. Karam, N. R. Jber, and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.* **675** (1), 39 (2018). doi:10.1080/15421406.2019.1624032

[46] N. R. Jber, N. H. Karam, and A. H. Al-Dujaili, *Mol. Cryst. Liq. Cryst.* **675**, 9 (2018).

[47] D. Richter, *Textures of Liquid Crystals* (VEB Deutscher Verlag, Leipzig, 1980).

[48] G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals: Textures and Structures* (Leonard Hill, London, 1984).

[49] D. R. Santos *et al.*, *Arkivoc* **xvii**, 157 (2008).

[50] G. W. Gray, *Molecular Structure and Properties of Liquid Crystals* (Academic Press, New York, NY, 1962).

[51] M. Parra *et al.*, *Liq. Cryst.* **33** (8), 875 (2006). doi:10.1080/02678290600871614

[52] T. Tasaka *et al.*, *BCSJ.* **76** (3), 569 (2003). doi:10.1246/bcsj.76.569

[53] K. Kishikawa, M. C. Harris, and T. M. Swager, *Chem. Mater.* **11** (4), 867 (1999). doi:10.1021/cm980631g