



Designed New Mesogence Containing
5H-Thiazolo[3,4-B][1,3,4]Thiadiazole : Synthesis
and Investigation of Liquid Crystals Properties

Maha A.Jabar and Nisreen H.Karam

EasyChair preprints are intended for rapid dissemination of research results and are integrated with the rest of EasyChair.

June 23, 2021

Designed New Mesogen Containing 5H-Thiazolo[3,4-b][1,3,4]thiadiazole :Synthesis and Investigation of Liquid Crystals Properties

Maha A. Jabar^{1,a)} and Nisreen H. Karam^{2,b)}

^{1,2} Department of Chemistry, College of Education for Pure Science (Ibn-Al-Haitham), University of Baghdad/Iraq

^{a)} Corresponding Author: maha.adel1996.8@gmail.com

^{b)} E mail : nisreenhkaram@gmail.com

Abstract. This research include synthesized and characterization the compound [I] by reaction terephthaldehyde , mercaptoacetic acid and thiosemicarbazide with concentrated sulfuric acid then this compound reaction with ethyl chloroacetate and sodium acetate to product ester compound [II],the latter compound reaction with hydrazine hydrate to synthesized acid hydrazide [III] after that reaction with 4-alkoxy benzaldehyde[IV]n to synthesized Schiff bases compounds [V]n, the compound[VI] synthesized via reaction compound [I] with chloroacetic acid and sodium acetate then the compound[VI] reaction with 2-phenylenediamine in 4 N hydrochloric acid to product benzimidazole compound[VII]. The compounds characterized by melting points, FTIR and ¹HNMR spectroscopy. The mesomorphic behavior studied by using polarized optical microscopy.

Keywords: Liquid Crystals , Schiff bases , Heterocyclic

INTRODUCTION

Many series of liquid crystalline compounds containing heterocyclic groups have been synthesized due to their potentially wide range of applications, such as in the optical, electrical and biological medical fields [1–5]. Liquid crystal compounds may be composed of molecules containing two mesogenic Groups linked by a flexible spacer. Symmetrical liquid crystalline dimers contain two identical mesogenic units, whereas their non-symmetrical analogues have two different mesogenic groups [6-9]. The importance of using N-heterocycles in the cores of thermotropic liquid crystals (LCs) is associated with their electron deficiency, which may offer good electron-transporting properties and the possibility of developing defect-free layers due to the inherent self-organisation of LC phases [10-15].

The aim of this study is to describe the synthesis of some new derivatives containing 5H-thiazolo[4,3-b]-1,3,4-thiadiazole unite and study their liquid crystalline properties.

EXPERIMENTAL.

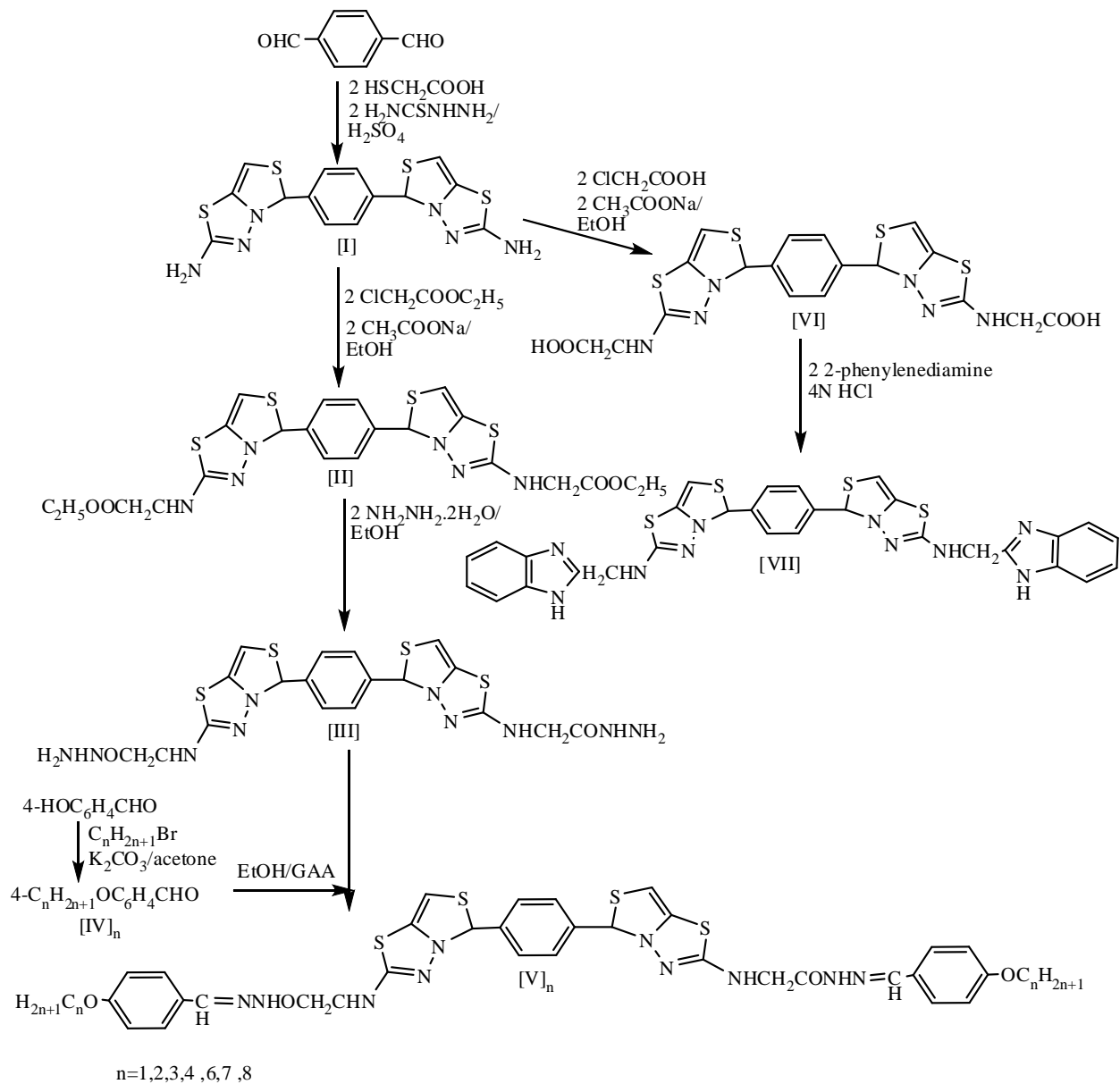
The materials take from Aldrich, Fluka and Merck Co.

TECHNIQUES

FT-IR spectra were recorded by SHIMADZU (IR Affinity-1) FT-IR spectrometer in the wave number range 4000-600 cm⁻¹. ¹H-NMR spectra were measurement by company: Bruker, 400 MHz and were reported in ppm (δ), the compounds were dissolved in DMSO- d₆ solution with the TMS as internal standard .The melting point measurement by, Gallen Kamp apparatus. Liquid crystalline properties were investigated by using a (Meiji MT9000) Polarizing Optical Microscope attached to an INSTEC Hot stage.

SYNTHESIS

The route of synthesized new compounds is represented to Scheme 1.



SCHEME1

Synthesis of 5,5'-(1,4-phenylene)bis(5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-amine)[I]

Terephthalaldehyde (1.34 gm, 0.01 mol) and mercaptoacetic acid (1.84 gm, 0.02 mol) were mixed for 20-25 min. Then thiosemicarbazide (1.5 gm, 0.02 mol) was added, followed by addition of concentrated sulfuric acid (15 mL) portion wise upon cooling. The mixture was kept in the freezer for 24 h. Then treated with crushed ice 40 gm, adding aqueous sodium hydroxide 40% to obtain pH=7-8. The precipitate was filtered [16], dried and recrystallized from ethanol.

Molecular formula: $C_{14}H_{12}N_6S_4$, Yield 60 %, Color yellow, M.P= dec.270 °C. FTIR (cm^{-1}): 3456-3194 (v asym.,sym NH_2), 3005 (v Ar-H), 1643 (v C=N), 1589 (v C=C).

1H NMR (400MHz, DMSO- d_6) δ (ppm): 8.64-6.96 (4H, Ar-H), 5.31 (s,4H,2 NH_2), 3.42(2H (2S-CH-N) in cyclic),3.27 (2H (2S-CH=C) in cyclic).

Synthesis of diethyl 2,2'-(5,5'-(1,4-phenylene)bis(5H-thiazolo[4,3-b][1,3,4]thiadiazole-5,2-diyl))bis(azanediy)diacetate [II]

A mixture of compound [I] (0.39gm, 0.001 mol), ethyl chloroacetate (0.246 gm, 0.002mol) and fused sodium acetate (0.246g,0.003 mol) in ethanol 5 ml was refluxed for 4 hrs. then cooled and poured into cold water. The resulting soiled was filtered and purified by ethanol to give a new ester.

Molecular formula: $C_{22}H_{24}N_6O_4S_4$, Yield 76%, Color dark yellow, M.P= 250°C(dec.). FTIR(cm^{-1}):3271 (v N-H), 3010 (v Ar-H), 2999-2847 (v aliph.-H),1734 (v C=O) , 1635 (C=N), 1580 (C=C), 1267 (C-O).

1H NMR (400MHz, DMSO- d_6) δ (ppm):11.50 (s, 2H, NH),8.46-7.76 (4H, Ar-H),4.04 (s, 2H (2S-CH-N) in cyclic), 3.88 (2S-CH=C) in cyclic),3.47- 3.44(4H, 2(O $\underline{C}H_2$ CH $_3$), 2.09(s,4H, 2(CH $_2$), 1.08-1.05 (t,6H, 2(O $\underline{C}H_2$ CH $_3$)).

Synthesis of 2,2'-(5,5'-(1,4-phenylene)bis(5H-thiazolo[4,3-b][1,3,4]thiadiazole-5,2-diyl))bis(azanediy)diacetohydrazide[III]

To compound [II] (3.38 gm , 0.006mol) added 3mL of hydrazine hydrate 80% then 5mL absolute ethanol the reaction mixture was refluxed for 3hrs [17] then resulting solution was cooled to room temperature, dried and recrystallized from ethanol.

Molecular formula: $C_{18}H_{20}N_{10}O_2S_4$, Yield 82 %, Color pall yellow, M.P gummy°C. FTIR(cm^{-1}):3308-3173 (v asym.,sym. NH_2),3116 (v N-H),3034(v Ar-H), 2958-2829(v Aliph.-H),1716 (v C=O), 1650 (C=N), 1573 (C=C).

Synthesis of 4-n-alkoxybenzaldehyde[IV]n

To a solution of potassium hydroxide (4.87g, 0.087mol) in absolute ethanol 50 ml, 4-hydroxybenzaldehyde (10.61g, 0.087 mol) and n-alkyl bromide (0.13 mol) were added, the mixture was refluxed for 6 hrs., and potassium bromide was precipitated then water 50 ml, diethyl ether 50 ml added. The mixture was extracted, and the organic phase was taken, washed with 25 ml of water and 25 ml of 10% sodium hydroxide solution, then 25 ml of water. The organic phase was dried over magnesium sulphate , then filtered and evaporated to yield oily 4-alkoxybenzaldehyde , yields (75-80%).

Synthesis of new Schiff bases compounds [V]n

A mixture of compound [III] (0.48 gm, 0.001 mol), a different substituted aldehyde[IV]n (0.002mol) in ethanol (10 mL) and some drops of glacial acetic acid (GAA) was refluxed for (5hrs)[18]. The solvent was evaporated under vacuum then the solid recrystallized from ethanol.

2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)-N'-(4-methoxybenzylidene)acetohydrazide compound with 1-(diazomethyl)-4-methoxybenzene[V]₁

Molecular formula: C₃₄H₃₄N₁₀O₄S₄, Yield 86 %, Color pal yellow , M.P=152-154°C. FTIR(cm⁻¹):3296 (ν N-H), 3088 (ν Ar-H), 2972-2839 (ν Aliph.-H), 1680(νC=O), 1647 (C=N),1600 (C=C).

2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)-N'-(4-ethoxybenzylidene)acetohydrazide compound with 1-(diazomethyl)-4-ethoxybenzene[V]₂

Molecular formula: C₃₆H₃₈N₁₀O₄S₄, Yield 85 %, Color yellow, M.P=135-137°C. FTIR(cm⁻¹):3331 (ν N-H), 3080 (ν Ar-H), 2974-2881 (ν Aliph.-H),1716 (νC=O), 1653 (C=N), 1610 (C=C).

2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)-N'-(4-propoxybenzylidene)acetohydrazide compound with 1-(diazomethyl)-4-propoxybenzene [V]₃

Molecular formula: C₃₈H₄₂N₁₀O₄S₄, Yield 80 %, Color yellow, M.P=125-127°C. FTIR(cm⁻¹):3350 (ν N-H),3075 (ν Ar-H), 2974-2881 (ν Aliph.-H),1710 (νC=O), 1674 (C=N),1606 (C=C).

N'-(4-butoxybenzylidene)-2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)acetohydrazide compound with 1-butoxy-4-(diazomethyl)benzene[V]₄

Molecular formula: C₄₀H₄₆N₁₀O₄S₄, Yield 88 %, Color pal yellow, M.P=118-120°C. FTIR(cm⁻¹):3269 (ν N-H), 3060 (ν Ar-H), 2972-2875 (ν Aliph.-H),1703 (νC=O), 1653 (C=N), 1599 (C=C).

N'-(4-(hexyloxy)benzylidene)-2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)acetohydrazide compound with 1-(diazomethyl)-4-(hexyloxy)benzene[V]₆

Molecular formula: C₄₄H₅₄N₁₀O₄S₄, Yield 75 %, Color pal yellow, M.P gummy. FTIR(cm⁻¹):3331 (ν N-H),3078(ν Ar-H), 2997-2856(ν Aliph.-H),1668 (νC=O), 1645 (C=N),1606 (C=C).

N'-(4-(heptyloxy)benzylidene)-2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)acetohydrazide compound with 1-(diazomethyl)-4-(heptyloxy)benzene[V]₇

Molecular formula: C₄₆H₅₈N₁₀O₄S₄, Yield 80 %, Color yellow, M.P=122-124°C. FTIR(cm⁻¹):3331 (ν N-H), 3043 (ν Ar-H), 2953-2856 (ν Aliph.-H),1660 (νC=O), 1622 (C=N), 1602 (C=C).

2-(5-(4-(2-(2-hydroxyethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)-N'-(4-(octyloxy)benzylidene)acetohydrazide compound with 1-(diazomethyl)-4-(octyloxy)benzene[V]₈

Molecular formula: C₄₈H₆₂N₁₀O₄S₄, Yield 85 %, Color yellow, M.P=114-116°C. FTIR(cm⁻¹):3340 (ν N-H), 3050(ν Ar-H), 2974-2818(ν Aliph.-H),1708 (νC=O), 1618 (C=N), 1604 (C=C).

Synthesis of 2-(5-(4-(2-(carboxymethylamino)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-5-yl)phenyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-ylamino)acetic acid[VI]

A mixture of compound [I] (0.39gm,0.001 mol), chloro acetic acid (0.188 gm ,0.002 mol) and sodium acetate(0.16gm, 0.002mol) in ethanol(5mL).The mixture was refluxed for (4 hrs). After cooling the mixture addition to ice water then filtration and acidified by 10%HCl after that, the ethyl acetate was added and separated the organic layer, dried and recrystallized from ethanol. Molecular formula: C₄₀H₄₀N₁₂O₈S₈, Yield 63%, Color yellow, M.P=gummy°C. FTIR(cm⁻¹):3269(ν O-H), 3157 (ν N-H), 3093 (ν Ar-H), 2960-2906 (ν Aliph.-H),1710 (νC=O) ,1633 (C=N), 1600 (C=C).

Synthesis of 5,5'-(1,4-phenylene)bis(N-((1H-benzo[d]imidazol-2-yl)methyl)-5H-thiazolo[4,3-b][1,3,4]thiadiazol-2-amine) [VII]

A mixture of compound [VI] (0.001mol) and 2-phenylenediamine (2.16 g, 0.002mol) in 4 N hydrochloric acid(40 mL) was refluxed for 10 h. Then the solution was neutralized with ammonia to precipitate benzimidazole compound[19].The product was filtered and recrystallized from acetone.

Molecular formula: C₃₀H₂₄N₁₀S₄, Yield 68%, Color black brown , M.P=123-125°C. FTIR(cm⁻¹):3317 (v N-H),3039 (v Ar-H), 2960-2831 (v Aliph.-H), 1626 (C=N), 1583(C=C).

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 analysis(FTIR and ¹HNMR).

Compound [I] was synthesized by treating terephthalaldehyde compound with mercaptoacetic acid and thiosemicarbazide in H₂SO₄ at reflux .FTIR spectroscopy for compound[I] showed absorption bands at (3456-3194) cm⁻¹ which assigned to NH₂ groups and C=N groups were appeared at 1643 cm⁻¹ .Compound [II] was synthesized via reaction compound[I] with two moles from ethyl chloroacetate and fused sodium acetate in ethanol, FTIR spectrum for this compound showed disappearance of absorption stretching bands for NH₂ groups and appearance bands at 1734 cm⁻¹ due to (C=O) ester group.

Subsequently, the reaction of compound [II] with with80% hydrazine hydrate in ethanol gave acid hydrazide compound [III]. FTIR spectrum of compound [III] display stretching vibration asymmetry and symmetry of NH₂ and NH groups in the region (3308-3173 and 3116)cm⁻¹ as well as stretching absorption band at (1716) cm⁻¹ for C=O (amide group) with disappearance of absorption stretching band due to ester group.

The compounds [V]n are formed from the reaction of compound [III] with two moles from different aromatic aldehydes[IV]n in ethanol and few drops of GAA. 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 1674-1618 cm⁻¹

Compound[VI] synthesized by reaction compound [I] with two moles of chloroacetic acid and fused sodium acetate in ethanol, The FTIR spectrum of compound [VI] showed disappearance absorption stretching bands of NH₂ groups for starting material compound[I] and appearance stretching bands of carboxyl and hydroxyl groups for dicarboxylic acid at 1710 and 3269 cm⁻¹,respectively.

Benzimidazole compound [VII] was synthesized by the cyclization of compound [VI] with two moles of 2-phenylenediamine in 4N hydrochloric acid followed by neutralized with ammonia.

The FTIR spectrum of compound [VII] showed absorption stretching bands at 1626 cm⁻¹ of C=N groups for benzimidazole ring and disappearance stretching bands of carboxyl groups for dicarboxylic acid[VI]. The sharp peak at 3317 cm⁻¹ was observed and assigned to the absorption band of NH groups.

THE MESOMORPHIC PROPERTIE

The transition temperatures and mesophase type (texture identity) were investigated by using optical polarizing microscopy (OPM). 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 [20] and Gray and Goodby [21]. The phase transition temperatures for compounds of series [V]n were summarized in Table (1).

TABLE 1. Phase transition temperatures (°C) of compounds [V]_n

Compound	Phase transition
[V] ₁	Cr $\xrightleftharpoons{90}$ N $\xrightleftharpoons{270}$ I
[V] ₂	Cr $\xrightleftharpoons{75}$ N $\xrightleftharpoons{280}$ I
[V] ₃	Cr $\xrightleftharpoons{80}$ N $\xrightleftharpoons{310}$ I
[V] ₄	Cr $\xrightleftharpoons{120}$ N $\xrightleftharpoons{360}$ I
[V] ₆	Cr $\xrightleftharpoons{70}$ S _m A $\xrightleftharpoons{127}$ N $\xrightleftharpoons{260}$ I
[V] ₇	Cr $\xrightleftharpoons{125}$ S _m A $\xrightleftharpoons{180}$ N $\xrightleftharpoons{370}$ I
[V] ₈	Cr $\xrightleftharpoons{45}$ S _m A $\xrightleftharpoons{145}$ N $\xrightleftharpoons{210}$ I

Cr, crystalline phases; SmA, smectic A phase; N, nematic phase and I, isotropic liquid

The compounds [V]₁₋₄ showed enantiotropic nematic phase under POM as shown in Figures (1) and (2) of compounds [V]₂ and [V]₃, respectively.

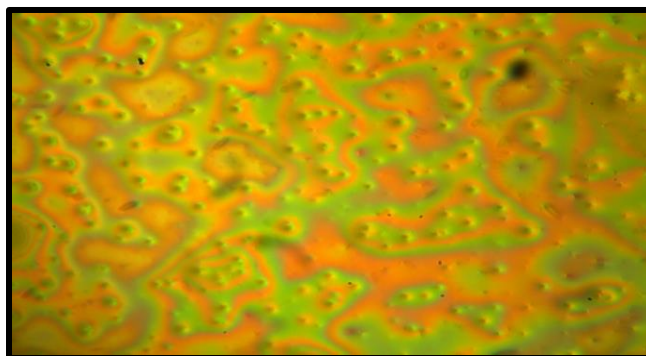


FIGURE.1 Cross-polarizing Optical textures of nematic phase obtained on heating at 270 C° (Magnification 200×) for compound [V]₂

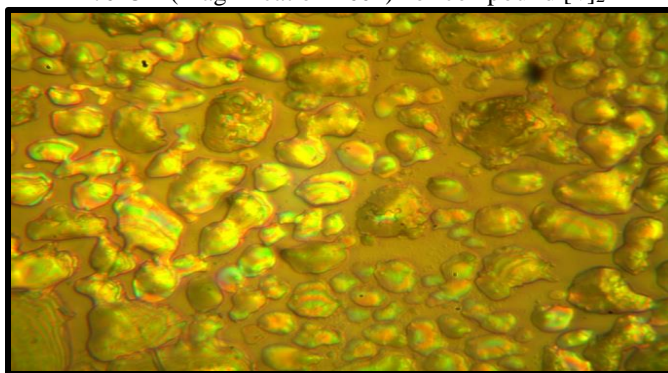


FIGURE.2 Cross-polarizing Optical textures of the droplets nematic mesophase obtained on cooling at 85 C° (Magnification 200×) for compound [V]₃

The compounds [V]₆₋₈ displays dimorphism enantiotropic smectic A (SmA) besides to nematic phases. Figures (3) and (4) of compounds [V]₇ and [V]₈, respectively.

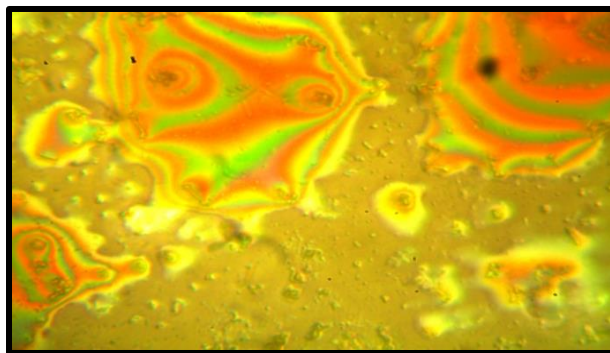


FIGURE.3 Cross-polarizing Optical textures of nematic phase obtained on heating at 340 C° (Magnification 200×) for compound [V]₇

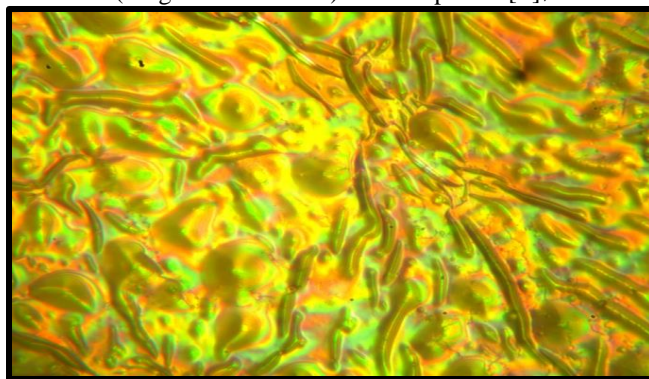


FIGURE.4 Cross-polarizing Optical textures of smectic phase SmA obtained on cooling at 51 C° (Magnification 200×) for compound [V]₈

This behavior can be attributed to the chain length of alkoxy terminal group that interferes with liquid crystalline ordering, this could be explained in term of terminal/lateral (t/l) interaction forces ratio. When this ratio is high, compounds tend to give less ordered mesophases (nematic mesophase), while when this ratio is low, the compounds tend to give high order mesohpases (smectic phase) ⁽²²⁾.

We found the compound [V]_n showed the decrease of the transition temperatures from nematic to isotropic state with the increase of the chain length(n) when n=8 this behavior is parallel to that observed in the literature for this type of mesophases ⁽²³⁾.

CONCLUSION

A new series of liquid crystalline compounds containing 5H-thiazolo[3,4-b][1,3,4]thiadiazole unite with alkoxy groups were designed and synthesized by varying alkoxy terminal chain length (n=1,2,3,4,6,7 and 8). The formation of a mesophase was found to be dependent on the number of methylene unit in alkoxy terminal chains. The compounds with n =1-4, exhibited an enantiotropic nematic phase but compounds with n= 6-8 showed dimorphism enantiotropic smectic A (SmA) besides to nematic phases.

ACKNOWLEDGMENTS

The authors would like to thank the Department of Chemistry, College of Education for Pure Science (Ibn-Al-Haitham), University of Baghdad for their help and cooperation throughout this research

REFERENCES

1. K. Pantalone and A. J. Seed. *Liq. Cryst.* , **29**, 945 (2002).
2. M. Eich and J. Wendorff. *Macromol. Chem. rapid Commun.*, **8**, 467 (1987).
3. L.L. Chapoy. *Advances in Liquid Crystalline Polymers*, Chapoy (Eds), Elsevier, London (1985).
4. E. Meyer, A.C. Joussef, H. Gallardo and A.J. Bortoluzzi, *J.mol. Struct.*, **655**, 361 (2003).
5. S.J. Melo, A.D. Sobral, H. Lopes and R.M. Srivastava, *J. Braz. chem. Soc.*, **9**, 465 (1998).
6. C.T.Imrie and P.A. Henderson, *Curr. Opin. Colloid Interface Sci.*, **7**, 298-311(2002).
7. C.T.Imrie, *Liq.Cryst.*,**33**,1449-1454(2006).
8. C.T. Imrie and P.A. Henderson, *Chem. Soc. Rev.*, **36**,2096-2124(2007).
9. C.T.Imrie and P.A.Henderson , Yeap, G.Y. *Liq. Cryst.*, **36**, 755-777(2009).
10. A.Seed , *Chem Soc Rev.*,**36**:2046–2069(2007).
11. E. Meyer, C. Zucco and H.Gallardo , *J Mater Chem.*,**8**:1351- 1354(1998).
12. J. Bartulin, R. Martinez, H. Gallardo, J. Muller and TR.Taylor, *Mol. Cryst. Liq. Crys. A.* , **225**:175-182(1993).
13. H. Gallardo, C. Zucco and L.Da Silva , *Mol. Cryst. Liq. Cryst.*,**373**:181-190(2002).
14. H. Gallardo, R. Magnago and AJ.Bortoluzzi, *Liq. Cryst.* , **28**:1343-1352(2001).
15. P. Vlachos, B. Mansoor, MP. Aldred, M. O'Neill and SM.Kelly, *Chem Commun.*, 2921-2923(2005).
16. T.K. Ibraheem, N. H. Karam, Z. T. IALKayar, *International Journal of Pharmaceutical Research , Supplementary Issue* **1**,814-817(2020).
17. F. A. Abed, N. H. Karam and J.H Tomma, *Ibn Al-Haitham Jour. for Pure & Appl. Sci.*, **29** (1): 150-165(2016).
18. N. H. Karam and A. K. Shanshal, *Ibn Al-Haitham Jour. for Pure & Appl. Sci.*, **30** (3) : 195-210(2017).
19. T.H. Al-Noor , N. H. Karam , F. H. Ghanim , A. S. Kindeel , A. H. Al-Dujaili, *Inorganica Chimica Acta* **466**, 612–617(2017).
20. D. Richter, *Textures of Liquid Crystals* (VEB Deutscher Verlag, Leipzig, 1980).
21. G. W. Gray and J. W. Goodby, *Smectic Liquid Crystals: Textures and Structures* (Leonard Hill, London, 1984).
22. D. J. Byron , D. Lacey and R.C. Wilson , *Mol. Cryst. Liq. Cryst.*, **62**, 103-114(1980).
23. G. W. Gray ,“ *Molecular Structure and The Properties of Liquid Crystals*”, Academic press, New York (1962).