



Original Article

Synthesis and Characterization of Heterocyclic Compounds-Based Liquid Crystals

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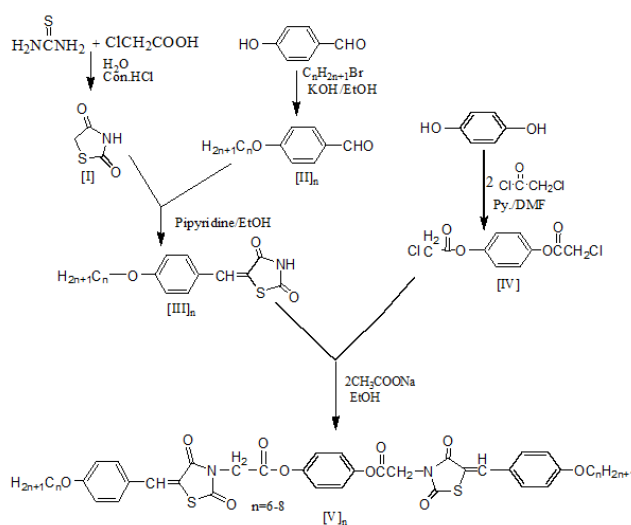
Hydroquinone

Nematic phase

ABSTRACT

This research includes the synthesis, characterization, and investigation of liquid crystalline properties of new rod-shaped liquid crystal compounds 1,4-phenylene bis(2-(5-(four-alkoxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate), prepared thiazolidine-2,4-dione (I) by the thiourea reaction with chloroacetic acid and water in the presence of the concentrated hydrochloric acid. The n-alkoxy benzaldehyde (II)_n synthesized from the reacted 4-hydroxybenzaldehyde and n-alkyl bromide with potassium hydroxide, and then the compound (I) was reacted with (II)_n in the presence of piperidine to produce compounds (III)_n. Also, hydroquinone was converted into a corresponding compound (IV) by refluxing with two moles of chloroacetyl chloride in pyridine and DMF. After that, the compounds (III)_n was interacted with sodium acetate to form compounds (V)_n. FT-IR and ¹H-NMR spectroscopy were really used to determine the structures of the produced substances. By using the polarized optical microscopy, these mesogens' mesomorphic characteristics were studied (POM). The produced compounds displayed enantiotropic liquid crystal phases, while the substances (V)₆₋₈ displayed a smectic enantiotropy in a variation on the nematic phases.

GRAPHICAL ABSTRACT



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Introduction

LCs have multiple intermediate phases that are distinguished by their molecular orientations, including anisotropic networks, photoconductors, semiconductor materials, display technology, organic light emitting diodes, and the other practical applications of LCs in science and technology [1-3].

Numerous mesogens, particularly thermotropic liquid crystals, have been created and studied as a result of the high need for new liquid crystals for applications [4, 5].

Over the years, various thermotropic liquid crystals have been produced by using heterocyclic building blocks since they have a higher proportion of polarisable heteroatoms than carbon, like nitrogen, oxygen, and sulfur atoms. On the other hand, the addition of heterocyclic rings to the electronegative heteroatoms definitely influences the polar induction power of a compound [6]. The heterocyclic moieties can lead to the significant changes in the mesophases and physical features of thermotropic liquid crystal [7, 8]. General structure of calamitic LC molecules can be described as a combination of relatively rigid parts, typically aromatic cores with/without linking groups, with flexible parts, usually represented by terminal alkyl chains [9]. Heterocyclic composites are a significant class of the organic chemicals with numerous scientific uses, and particularly five-membered heterocyclic ring-containing liquid crystalline substances have been effectively tested [10-12]. The hunt for new heterocyclic compounds has recently focused on several significant groups, including thiazolidine-2,4-dione.

In this paper, the synthesis of the novel symmetrical homologous series bearing two arms contain thiazolidine-2,4-dione with alkyloxy chain and describe the mesomorphic properties. No substances resembling these have been described in relation to the creation and characteristics of the liquid crystals. The mesomorphic properties of the homologous molecules are explained by different alkyl chain lengths. This work also explores the relationship

between liquid crystal properties and molecular structure.

Materials and Methods

The materials of this study were provided from Merck Co., Fluka, and Aldrich. With the TMS serving as an internal standard, the compounds were dissolved in DMSO-d₆ solution. For the ¹H-NMR spectra, which were determined at 400 MHz and reported in ppm (δ) by the company Bruker (δ). SHIMADZU recorded FT-IR spectra (IR Affinity-1) 4000-600 cm⁻¹ wave number range FT-IR spectrometer. The method used by Gallen Kamp was applied to test the melting point. An INSTEC Hot stage and a Meiji MT9000 Polarizing Optical Microscope were used to examine the properties of liquid crystals.

Synthesis

The pathway of newly produced chemicals is depicted in [Scheme 1](#).

Synthetic procedures

Preparation of the Thiazolidine-2,4-dione (I)

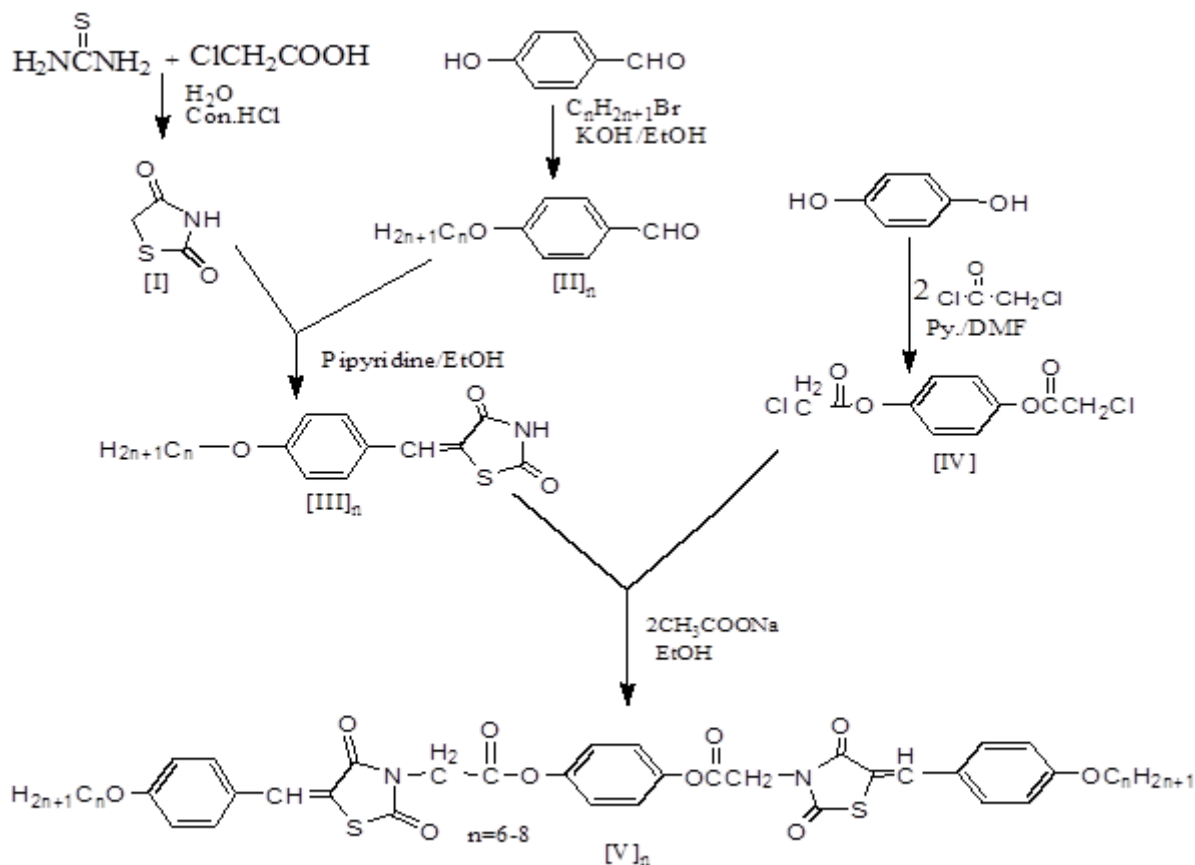
60 mL of water was used to dissolve a mixture of 45.6 g (0.6 M) of thiourea and 56.4 g (0.6 M) of chloroacetic acid, and then it was placed in 250 mL three-necked flask. Until the appearance of white precipitates, the mixture was stirred for 15 minutes. After being refluxed for 10 to 12 hours at 100-110 °C, the reaction mixture was stirred, and 60 mL of strong hydrochloric acid was slowly added from a dropping funnel to dissolve the precipitates. The reaction mixture was solidified into a mass of white needle clusters after cooling. The product was filtered, washed with water, and dried to remove any remaining hydrochloric acid. From ethanol, it was recrystallized, producing 80%, at 123-125°C [13]. FT-IR (cm⁻¹): 3135, 3047, 2947-2823, 1735 to 1654, 617.

General procedure of preparing 4-n-alkoxybenzaldehyde[II]n

Bromide of n-alkyl 4-hydroxybenzaldehyde (10.61 g, 0.087 mol) (0.13 mol), potassium hydroxide (4.87 g, 0.087 mol), absolute ethanol (50 mL), diethyl ether (50 mL), water (50 mL)

and potassium hydroxide (4.87 g, 0.087 mol) were all added to an absolute ethanol solution of potassium hydroxide. The mixture was then refluxed with 25 mL of water. After that, by using 25 mL of a 10% sodium hydroxide solution and 25 mL of water, the organic phase of the mixture

was separated. The oily 4-alkoxybenzaldehyde [14] was produced by drying the organic phase on magnesium sulphate, its filtering, and evaporating to provide yields of 75–80%.



Scheme 1: pathway of newly produced chemicals

Synthesis of 5-arylidene-thiazolidine-2,4-dione[III]*n*: General Procedure

Compound (I) (2.21 g, 0.01 mole), aromatic aldehyde (II)*n* (0.01 mol), and 5 mL of ethanol were refluxed for three hours while piperidine (0.5 mol) was present. Then, the outcome was cooled before being placed in chilly water. After that, the solid was filtered, cleaned, dried, and finally recrystallized by using acetone.

5-(4-hexyloxybenzylidene) thiazolidine-2,4-dione (III)₆

Molecular formula: C₁₆H₁₉NO₃S, light brown, yield 85%, mp 158 °C. FT-IR (cm⁻¹): 3320, 3078, 2935-2877, 1735-1689, 1600, and 1257.

5-(4-heptyloxybenzylidene)thiazolidine-2,4-dione (III)₇

Molecular formula: C₁₇H₂₁NO₃S, light green, yield 95%, mp 106 °C. FT-IR (cm⁻¹): 3414, 3097, 2935-2870, 1739-1689, 1600, and 1261.

5-(4-octyloxybenzylidene)thiazolidine-2,4-dione (III)₈

Molecular formula: C₁₈H₂₃NO₃S, white, yield 95%, mp 120 °C, FT-IR (cm⁻¹): 3414, 305, 2924-2854, 1747-1685, 1597, and 1257.

Preparation of 1,4-phenylene bis(2-chloroacetate) (IV) [15]

A solution of hydroquinone (0.11 g, 0.001 mol), pyridine (1 mL), and DMF (2 mL) was agitated at °C with the addition of chlororo acetylchloride

(0.002 mol) gradually. 10% HCl was added, the precipitate was filtered, washed with water, dried, and the residue was recrystallized from ethanol after the mixture was stirred for three hours at room temperature. Molecular formula: $C_{10}H_8O_4Cl_2$, white, yield 78%, mp 122-123 °C.

Synthesis of 1,4-phenylene bis(2-(5-(4-alkoxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate) (V)_n

Refluxing was done for four hours with a mixture of compounds (III)_n (0.002 mol), compound (IV) (0.001 mol), sodium acetate (0.16 g, 0.002 mol), and ethanol (5 mL). Ice water was then added once the mixture had been chilled. After the mixture was filtered and 10% HCl was used to acidify it. After adding ethyl acetate, the organic layer was separated and dried to obtain compounds (V)_n

1,4-phenylene bis(2-(5-(4-hexyloxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate) (V)₆

Molecular formula: $C_{42}H_{44}N_2O_{10}S_2$, brown, yield 90%, mp 83 °C. FT-IR (cm^{-1}): 3064 (ν (C-H arom.)), 2927-2854, 1732-1689, 1604, 1257, 1180.

1,4-phenylene bis(2-(5-(4-heptyloxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate) (V)₇

Molecular formula: $C_{44}H_{48}N_2O_{10}S_2$, brown, yield 90%, mp 98 °C. FT-IR (cm^{-1}): 3043, 2958-2870, 1739-1689, 1600, 1257, 1164, 1H -NMR (400 MHz, DMSO- d_6): δ 7.95-6.10 (m, 12H, Ar-H), 6.08 (s, 2H, CH=C), 4.49-4.14 (t, 4H, OCH₂), 3.93 (s, 4H, 2CH₂N), 3.66-1.53 (m, 20 H, 2(CH₂)₅), 1.25-1.18 (t, 6H, 2CH₃).

1,4-phenylene bis(2-(5-(4-octyloxybenzylidene)-2,4-dioxothiazolidin-3-yl)acetate) (V)₈

Molecular formula: $C_{46}H_{52}N_2O_{10}S_2$, brown, yield 70%, mp 204 °C. FT-IR (cm^{-1}): 3035, 2924-2854 1739-1685, 1593, 1253, 1145. 1H -NMR (400 MHz, DMSO- d_6): δ 7.74-6.66 (m, 12H, Ar-H), 6.55 (s, 2H, 2CH=C), 4.14 (t, 4H, 2 OCH₂), 3.72 (s, 4H, 2 CH₂N), (3.65-1.22) (m, 24H, 2 (CH₂)₆), 0.86(t, 6H, 2 CH₃).

Results and Discussion

Thiourea and chloroacetic acid were combined in equimolar proportions to create the 2,4-thiazolidinedione (I). In pure ethanol, 4-hydroxybenzaldehyde, alkylbromide, and potassium hydroxide were used to create the molecules (II)_n.

By combining the molecules (III)_n with aromatic aldehydes (II)_n, Knoevenagel condensation was used to create derivatives of the 5-arylidene-thiazolidine-2,4-dione. The infrared spectra of these compounds revealed a prominent functional group absorption band between 1597 and 1600 cm^{-1} , or C=C, and 1747 and 1685 cm^{-1} , or the thiazolidine-2,4-dione ring's carbonyl at positions 2 and 4 [16].

We combined hydroquinone with two moles of chloroacetyl chloride in pyridine and DMF to create the chemical (IV). The spectrum of the compound [IVFTIR] revealed a disappearing band for the OH group presented in the starting material and C=O of the ester group was linked to a novel absorption stretching band at 1764 cm^{-1} . In addition, a CH₂Cl stretching band was seen at 758 cm^{-1} .

Two moles of compounds (III)_n and one mole of compound (IV) were combined with sodium acetate in ethanol to produce the compounds (V)_n. The absorbance bands of N-H and CH₂-Cl for the starting materials were vanished from the FT-IR spectra of these substances, and new bands of C-N groups appeared at 1180-1145 cm^{-1} and bands of C=O ester groups at 1739-1685 cm^{-1} .

Liquid crystalline properties

By using a polarizing optical microscope, the unique liner-shaped compounds' textures and phase-transition temperatures were assessed (POM). The values for the transition temperatures were indicated in Table 1. Microscopy examinations were used to determine the mesophase's texture by using the categorization systems [17, 18].

Table 1: The temperatures at which compounds in series enter the phase transition (V)_n

Compound	A phase change
(V) ₆	Cr $\xrightleftharpoons{120}$ SmA $\xrightleftharpoons{155}$ N $\xrightleftharpoons{285}$ I
(V) ₇	Cr $\xrightleftharpoons{90}$ SmA $\xrightleftharpoons{180}$ N $\xrightleftharpoons{290}$ I
(V) ₈	Cr $\xrightleftharpoons{160}$ SmA $\xrightleftharpoons{205}$ N $\xrightleftharpoons{310}$ I

Cr: Crystalline Phases; N, Nematic phase, I, and SmA, Smectic A Phase, respectively.

The substances (V)₆₋₈ shows smectic A phases in addition to the enantiotropic A phases. The smectic A and nematic textures for compound (V)₈ are displayed in Figures 1a and 1b, respectively.

This behavior can be characterized in terms of the terminal/lateral (t/l) contact forces ratio, which resulting from the size of the alkoxy terminal chain. Chemicals create less structured mesophases (nematic mesophase) when this ratio is high, and more ordered mesophases (smectic phase) when this ratio is low (smectic phase).

Cross-polarizing optical textures is displayed in Figure 1a. A phase for compound (VII) was called smectic. The nematic phase for compound (VII)₆ was obtained by heating at 130 °C and cooling at 170 °C (c). The chemical (VII) was produced in the nematic phase at 7 after heating to 100 °C (d) 7 that was obtained after heating the compound (V) to 190 °C (e) in the smectic A phase (SmA). Compound (V)₈ enters the nematic phase after heating to 200 °C (magnification 200).

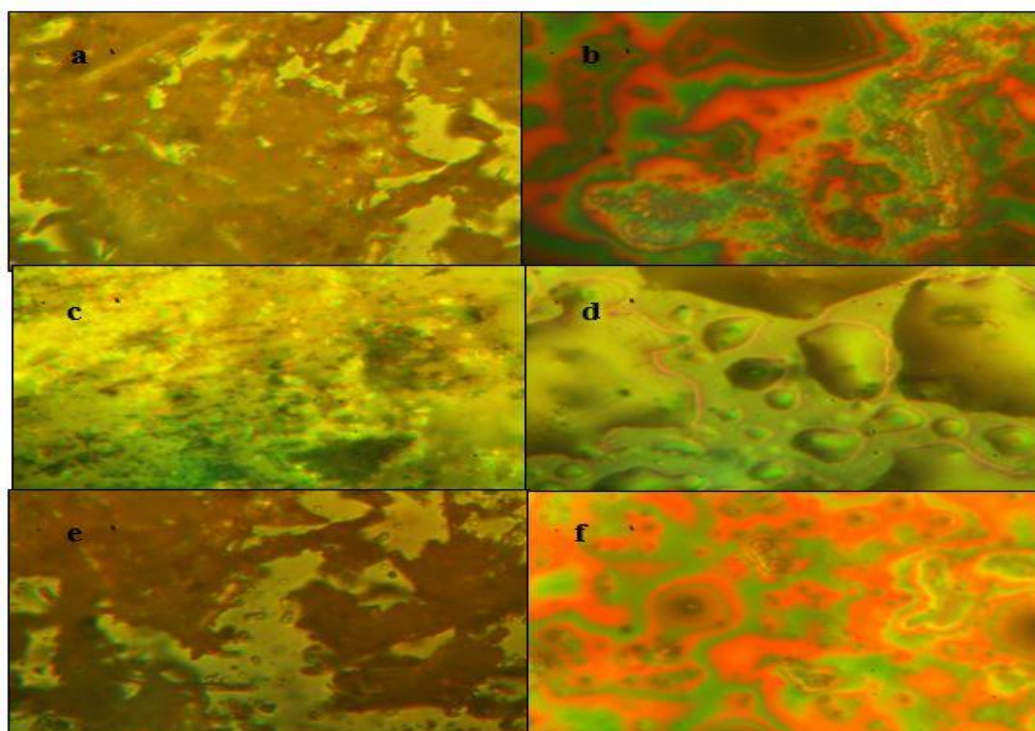


Figure 1: smectic A and nematic textures for compound (V)₈

Conclusion

The successful multi-step synthesis of the novel symmetrical compounds was done with two arms containing thiazolidine-2,4-dione and was connected to the core by 1,4-phenylene. Thus, it can be inferred that to manage the phase-transition properties of LC compounds, it is

crucial to consider both the molecular geometry and the length of the flexible alkoxy unit. The compound [V]₆₋₈ displays the smectic A besides to N phases.

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Authors' contributions

All authors contributed to data analysis, drafting, and revising of the paper and agreed to be responsible for all the aspects of this work.

Conflict of Interest

The author declared that they have no conflict of interest.

References

- [1]. Petti L., Rippa M., Fiore A., Manna L., Mormile P., Optically induced light modulation in an hybrid nanocomposite system of inorganic CdSe/CdS nanorods and nematic liquid crystals, *Optical Materials*, 2010, **32**:1011 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [2]. Shurpo N.A., Vakshtein M.S., Kamanina N.V., Effect of CdSe/ZnS semiconductor quantum dots on the dynamic properties of nematic liquid-crystalline medium, *Technical Physics Letters*, 2010, **36**:319 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [3]. Hoang M.H., Cho M.J., Kim K.H., Lee T.W., Jin J.I., Choi D.H., Semiconducting 2, 3, 6, 7, 10, 11-Hexakis {[4-(5-dodecylthiophen-2-yl) phenyl] ethynyl} triphenylene and its discotic liquid crystalline properties, *Chemistry letters*, 2010, 39:396 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [4]. Luan C., Luan H., Luo D., Application and technique of liquid crystal-based biosensors, *Micromachines*, 2020, **11**:176 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [5]. P. Rajak, L. K. Nath and B. Bhuyan, *Indian J. Pharm Sci.*, 2019, **81**:11 [[Crossref](#)], [[Publisher](#)]
- [6]. Ghosh T., Lehmann M., Recent advances in heterocycle-based metal-free calamitics, *Journal of Materials Chemistry C*, 2017, **5**:12308 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [7]. Karam N.H., Atto A.T., Al-dujaili A.H., Synthesis and mesomorphic behavior of two new homologous series containing azobenzene and 1, 3, 4-oxadiazole units, *Molecular Crystals and Liquid Crystals*, 2014, **605**:1 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [8]. Ibraheem T.K., Karam N.H., Al-Dujaili A.H., Synthesis and characterization of symmetrical liquid crystalline compounds based on oxazole and thiazole rings, *Molecular Crystals and Liquid Crystals*, 2020, **710**:1 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [9]. Andrienko D., Introduction to liquid crystals, *Journal of Molecular Liquids*, 2018, **267**:520 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [10]. Abed F.A., Karam N.H., Tomma J.H., *Ibn Al-Haitham Jour. for Pure and Appl. Sci.*, 2016, **29**:150 [[Google Scholar](#)]
- [11]. Jber N.R., Karam N.H., Al-Dujaili A.H., Supramolecular columnar discotic nematic liquid crystal by hydrogen bonding: Synthesis and characterization, *Molecular Crystals and Liquid Crystals*, 2018, **675**:29 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [12]. Jabar M., Karam N., Synthesis and characterization of azo liquid crystal compounds based on 5H-Thiazolo [3, 4-b][1, 3, 4] thiadiazole unit, *Revis Bionatura 2022*, 2000, **7**:17. [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [13]. Pinheiro D.S., Junior E.N.S., Consolini G., Aguiar M.J., Silva R.R.O., VIEIRA R., PALMA M., Optimized synthesis and characterization of thiazolidine-2, 4-dione for pharmaceutical application, *MOJ Biorg Org Chem*, 2017, **1**:122 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [14]. Karam N.H., Ibraheem T.K., *Journal of Global Pharma Technology*, 2018, **10**:63 [[Publisher](#)]
- [15]. Karam N.H., Shanshal A.K., Synthesis, Characterization and Study of Mesomorphic Behavior of New Bent and Liner Core Compounds Containing Heterocyclic, *Ibn AL-Haitham Journal For Pure and Applied Science*, 2017, **30**:195 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [16]. Jain V.S., Vora D.K., Ramaa C.S., Thiazolidine-2, 4-diones: Progress towards multifarious applications, *Bioorganic & medicinal chemistry*,

- 2013, **21**:1599 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [17]. Dierking I., Textures of Liquid Crystals, Wiley, 2006 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]
- [18]. Goodby J.W., Introduction to Defect Textures in Liquid Crystals, 2012 [[Crossref](#)], [[Google Scholar](#)], [[Publisher](#)]

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