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NEW THERMOTROPIC SYMMETRICAL MESOGENS CONTAINING HETERO RINGS: SYNTHESIS AND CHARACTERIZATION

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Abstract:

A variety of liquid crystals comprising heterocyclics 1,3,4-oxadiazol ring [III], aminooxazol [IV]a, and aminothiazol [IV]b were synthesized through a number of steps, beginning of the reaction of 3, 3'- dimethyl - [1, 1'-biphenyl] -4, 4'- diamin, ethyl monochloroacetate and sodium acetate to synthesize diacetate compound[I]. The diester reacted with hydrazine hydrate(N_2H_4-H_2O) to give dihydrazide compound [II], then reacted with Pyruvic acid and phosphorous oxychloride to produce diketone compound [III]. The last compound was reacted with urea and thiourea to give aminooxazol and aminothiazol respectively. The synthesized compounds actually characterized and determined the structures by melting points, FT-IR and 1H-NMR spectroscopies. By using POM and DSC spectroscopies, characterized the properties of liquid crystalline. The produced molecules displayed liquid crystal phases, the compounds [III] and [IV]a showed smectic A phase and nematic phase, whereas compound [IV]b displayed enantiotropic nematic phase only.

Keywords: Heterocyclics, Mesomorphic, liquid crystal, 1,3,4- oxadiazole, aminooxazol ,aminothiazol.

Introduction:

Heterocycles are the main and most diverse family of organic compounds and essential to human life, and their structural subunits are found in a wide variety of products, so Heterocycles have wide applications in medicinal, biological, industrial, optical, and electrical fields. **(1-6)** Five- and six-membered rings are the greatest communal heterocycles. Heterocycles are a specific part of the structure of a large number of natural products and unnatural compounds. It is widely acknowledged that the molecular arrangement in liquid crystal phases is largely determined by the mesogenic core structure, linking units, lateral groups, and terminal groups. As a result, changing these structures is thought to be an effective way to significantly alter mesomorphic properties. **(7, 8)**

Thiazol and oxadiazoles are two of the most widely used five-membered heterocycles in LCs. Due to the ease of synthesis of 1,3,4- and 1,2,4-oxadiazoles, there are numerous accounts on their synthesis and mesomorphic studies.**(9,10)** In accordance with research on phase transition

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behavior, some synthesized oxadiazoles exhibit LCs phases, which have a significant potential for use as liquid crystalline monomers. [11, 12]

High yields were achieved in creating the liquid crystalline molecules that link the thiazol and oxadiazole heterocycles. This rigid core having high thermal stability, and displaying greater flexibility, they can change from one phase to another by changing the number of terminal chains. 1,3,4- oxadiazol, and thiazol heterocycle directly conjugated, and can improve the photo physical performance. Last but not least, this study illustrated how combining both heterocycles results in promising properties for various applications. [13, 14]

The molecular structures of the target molecules contain the rings 1,3,4oxadiazole, oxazole, and thiazol. The combination of dipolar forces and packing considerations resulting from the molecules' shape anisotropy may lead to the expectation that the mesogens with high dipole moments from the heterocyclic rings will exhibit polar phases.

Experimental:

All the materials have gotten from Aldrich, Fluka, and Merck Co.

Techniques:

FTIR spectrum data from the SHIMADZU (IR Affinity-1), 4000-600 cm^{-1} range of wave number. The ^{1}H-NMR spectrum was measure by the broker, 400 MHz, in ppm (δ), using the solvent DMSO-d^{6}, and the internal standard was TMS serving. Gallen Kamp apparatus used to determine melting point. Additionally, the POM model Leica DM2500 M was used to study of the liquid crystal characterization.

Synthesis:

According to a synthetic route shown in Scheme1, the conventional methods in references (15–18), were used in synthesized all novel compounds.

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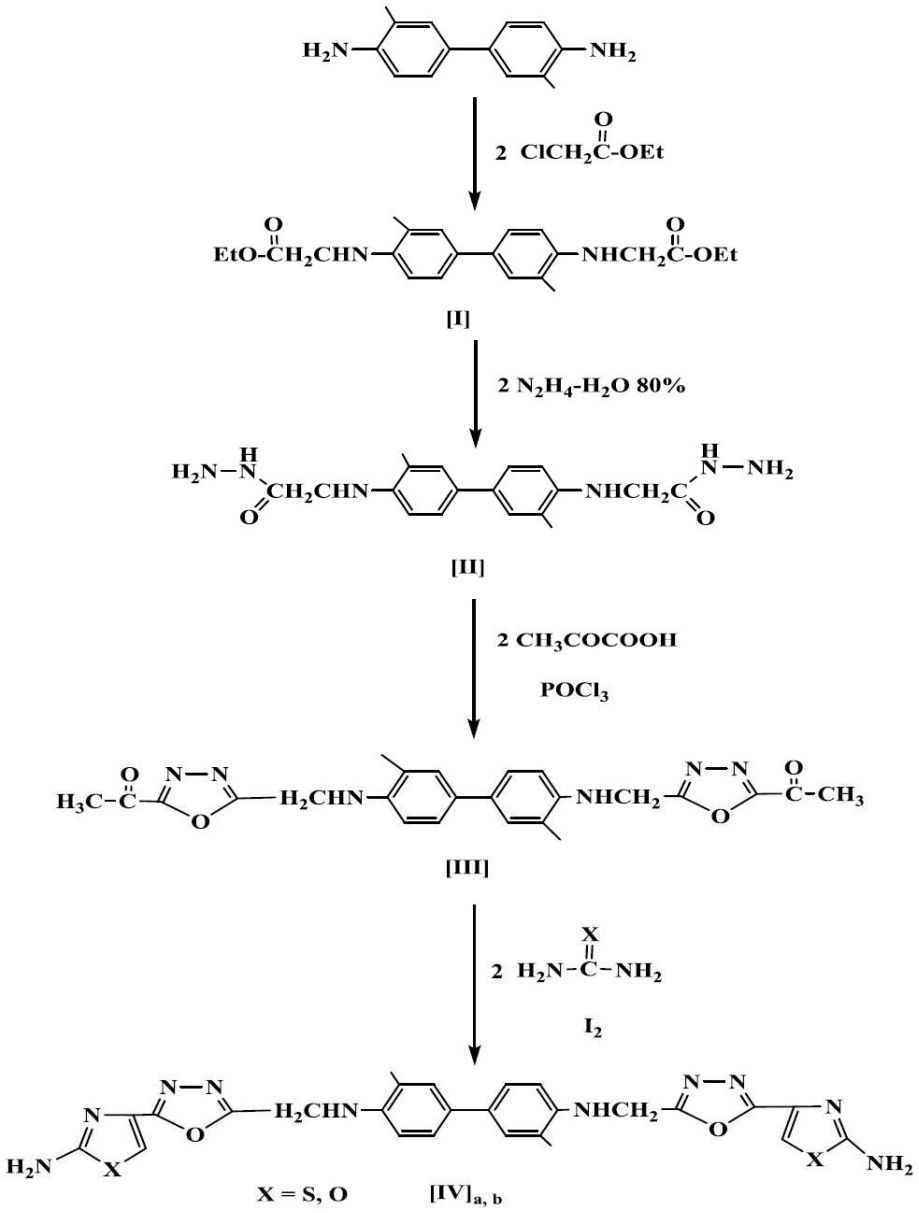

Scheme 1. The synthetic route of compounds [I]-[IV]$_{a,b}$

Synthesis of compound diethyl 2,2'- ((3,3'- dimethyl - [1, 1'- biphenyl]- 4, 4' diyl) bis (azanediyl))diacetate[I]

3,3'-dimethyl-[1,1'-biphenyl]-4,4'-diamine (2.12 gm, 0.01 mol), ethyl αchloroacetate (2.46 gm, 0. 02 mol), and sodium acetate (1.64 gm, 0.02 mol) mixture was refluxed for 4 hours in 10 ml ethanol. The product was cooled and poured into cold water, then filtered and purified by ethanol to give ester.

The compound [I], has a brown colour, gummy, yield 63%. FTIR (ν/cm^{-1}): 3354 (NH), 3020 (Ar-H), 2916, 2820 (aliph. C-H), 1735 (C=O), 1600 (C=C) .The ^{1}HNMR (400 MHz, DMSO-d6) δ (ppm): 7.95 (s, 2H of 2 NH), 7.48-6.59 (m, 6H, Ar- H), 4.36-4.30 (q, 4H, 2OCH$_2$),

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2.22 (s, 4H, 2N$\underline{CH_2}$), 2.18-2.08(t, 6H, 2$CH_2\underline{CH_3}$),1.33 (s, 6H, 2CH_3).

Synthesis of compound 2, 2'- ((3,3'- dimethyl - [1, 1'- biphenyl] - 4, 4'-diyl) bis (azanediyl)) di (acetohydrazide)[II]

Compound [I] (3.84 gm, 0.01mol), (1 gm, 0.02 mol) hydrazine hydrate 80% and 15mL absolute ethanol were mixed, and refluxed for 3hours. The resulting solution was cooling at room temperature, and then the solvent was evaporated, a solid formed was recrystallised from ethanol. The compound [II], has a greenish black colour, gummy, yield 65%.

FTIR (ν/cm^{-1}) : 3309-3209 (NH, NH_2), 3010 (Ar-H), 2970, 2900 (aliph. C-H),

1697 (C=O), 1605 (C=C). ^{1}HNMR (400 MHz, DMSO-d^6) δ (ppm) : 9.20 (s, 2H, 2$\underline{NH}NH_2$), 8.70 (s, 2H, 2$\underline{NH}CH_2$), 7.21-6.35 (m, 6H, Ar-H), 4.74 (s, 4H, 2NH_2), 3.70 (s, 4H, 2 CH_2), 1.22 (s, 6H, 2CH_3).

Synthesis of compound 1,1'- ((((3, 3'- dimethyl - [1, 1'- biphenyl] -4, 4'diyl) bis (azanediyl)) bis (methylene)) bis (1,3,4- oxadiazole-5,2-diyl))bis(ethan-1-one) [III].

Phosphorous oxychloride (5mL) was refluxed with compound [II] (3.56 gm, 0.01 mol) with pyruvic acid (1.76 gm, 0.02 mol) for 24 hours, then the product was treated by carefully with ice water, and made more basic by adding sodium bicarbonate solution. The solid result product was filtered, and purified by ethanol. Compound[III], is dark brown, yield 87%, m.p = 258-260 ^{0}C. FTIR (ν/cm^{-1}): 3379 (NH), 3010 (Ar-H), 2923, 2854 (aliph. C-H), 1681 (C=O), 1650 (C=N), 1600 (C=C).

Synthesis of N4,N4'-bis((5-(2-aminooxazol-4-yl)-1,3,4-oxadiazol-2-yll)methyl)3,3'-dimethyll-[1,1'-biphenyl]-4,4'-diamin[IV]$_a$, and N4,N4'-bis((5-(2-aminothiazol-4yl)-1,3,4-oxadiazol-2-yll)methyl)-3,3'-dimethyll-[1,1'-biphenyl]-4,4'-diamin[IV]$_b$

In to flask 250 ml added iodine (2.53 gm, 0.01 mol), urea (1.2 gm, 0.02 mmol) or thiourea (1.52 gm, 0.02 mol) and (4.60 gm, 0.01 mol) from compound [III], on the water bath, then heated the mixture for 8 hours. After cooled, purified with diethyl ether and a solution of sodium thiosulfate, then the product dissolved by hot water, then filtered and recrystalized from ethanol.

The compound[IV]$_a$ has dark brown, yield 93%, m.p = 225-227 ^{0}C.

FTIR (ν/cm^{-1}) : 3332-3209 (NH_2, NH), 3045 (Ar-H), 2916, 2852 (aliph. C-H), 1650

(C=N), 1589 (C=C). ^{1}HNMR (400 MHz, DMSO-d^6), (ppm) δ : 9.11 (s, 2H , 2NH), 8.36 -6.69 (m, 6H, Ar-H), 6.07 (s, 2H of two oxazol rings), 3.45(s, 4H, 2NH_2), 2.67(s, 4H, 2NH$\underline{CH_2}$), 2.34-1.22 (s, 6H, 2CH_3).

The compound[IV]$_b$ has also dark brown, yield 95%, m.p = 243-245 ^{0}C. FTIR (ν/cm^{-1}) : 3348-3209 (NH_2, NH), 3020 (Ar-H), 2916, 2847 (aliph. C-H), 1668 (C=N), 1570 (C=C). ^{1}HNMR (400 MHz, DMSO-d^6) (ppm) δ : 9.33 (s, 2H , 2NH), 8.89-6.86 (m, 6H, Ar- H), 6.76 (s, 2H of two thiazol rings),3.70(s,4H , 2NH_2), 2.67 (s, 4H, 2NH$\underline{CH_2}$), 2.45-2.08 (s, 6H, 2CH_3).

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Results and Discussions

A reaction of starting material (diamine compound) and ethyl α-chloroacetate with sodium acetate was used to synthesize the compound [I]. The spectrum of FTIR observed disappearance absorbance bands of NH_2 in starting substance. The observed bands in 3354 cm^{-1}, and 1735 cm^{-1} were assigned respectively to ν NH and (C=O) groups. The ^{1}HNMR spectrum showed singlate signal at δ 7.95 ppm of two protons of 2 NH, mutiplate signals at δ 7.48 - 6.59 ppm of six aromatic protons, quartette signal at δ 4.36 - 4.30 ppm of four protons of 2 OCH_2 groups, singlate signal at δ 2.22 ppm of four protons of 2 NCH_2 groups, triplate signal at δ2.18-2.08 ppm of six protons of 2 $CH_2\underline{CH_3}$ and singlate signal at δ 1.33 ppm of six protons of 2 CH_3 groups.

The compound [II] was synthesized through reacting of compound[I] with hydrazine hydrate 80% in solvent ethanol. The spectrum of FTIR observed bands to NH, NH_2 and C=O functional groups at 3309-3209 cm^{-1}, and 1697 cm^{-1}, respectively. ^{1}HNMR spectrum showed singlate signals at δ 9.20 and 8.70 ppm of protons of $\underline{NH}NH_2$ and $\underline{NH}CH_2$ groups, respectivaly, mutiplate signals at δ 7.21-6.35 ppm of six aromatic protons, singlate signalat δ 4.74 ppm of four protons of 2 NH_2 groups, singlate signalat δ 3.70 ppm of four protons of 2 CH_2 groups, and singlate signal at δ 1.22 ppm of six protons of 2 CH_3 groups.

The compound [II] reacted with pyruvic acid and phosphorous oxychloride, to synthesize the compound [III], the spectrum of FTIR to compound[III] showed absorbtion bands at 1681cm^{-1}, and 3379 cm^{-1} assigned to (C=O), and NH groups, respectively.

One mole of compound [III] and two moles of urea or thiourea with iodine, reacted, and produced compounds $[IV]_{a,b}$. The spectrum of FTIR for these compounds observed bands at 3332-3209 cm^{-1} and 3348-3209 cm^{-1} for NH_2 and NH groups, 3045 cm^{-1}, and 3020 cm^{-1} for C-H aromatic, 2916, 2852 cm^{-1}, and 2916,2847 cm^{-1} for aliphatic C-H, 1650 cm^{-1}, and 1620 cm^{-1} for C=N groups, 1589 cm^{-1} and 1570 cm^{-1} for C=C, respectively.

The ^{1}HNMR spectra for these compounds showed : singlate signal at δ 9.11, 9.33ppm of NH groups,many signals at δ (8.36 -6.69), (8.89-6.86)ppm of aromatic protons , singlate signal of protons for oxazol and thiazol rings at δ 6.07, 6.76ppm, singlate signal of NH_2 groups at δ 3.45, 3.70ppm, singlate signal of $NH\underline{CH_2}$ groups at δ2.67, 2.67ppm and singlate signal at δ 2.34-1.22, 2.45-2.08ppm of CH_3 groups, respectively.

The properties of liquid crystalline:

Using a polarizing optical microscope POM, and differential scanning calorimetry DSC, the phase-transition temperature behaviour and textures of the new liner-shaped compounds were assessed. Table (1) shows the values of transition temperature were identified the mesophase texture using the report of classification systems by Richter, and Gray & Goodby. **(19, 20)**

Table 1: The temperatures of phase transition for synthetic compounds.

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Comp. No.	Phase transition
[III]	Cr $\xrightarrow{92}$ SmA $\xrightarrow{275}$ N $\xrightarrow{364}$ I
$[IV]_a$	Cr $\xrightarrow{81}$ SmA $\xrightarrow{225}$ N $\xrightarrow{339}$ I
$[IV]_b$	Cr $\xrightarrow{120}$ N $\xrightarrow{280}$ I

Cr: Crystalline Phases, SmA: Smectic A phase, N: Nematic phase, and I: Isotropic Liquid.

The compounds [III], and $[IV]_a$ showed smectic A phase and nematic phase but the compound $[IV]_b$ observed only enantiotropic nematic phase as Fig.1a-c for nematic phase for compounds [III]-$[IV]_b$, respectively. The DSC thermograms for compounds [III] and $[IV]_a$ as Fig. 2 a,b. respectively.

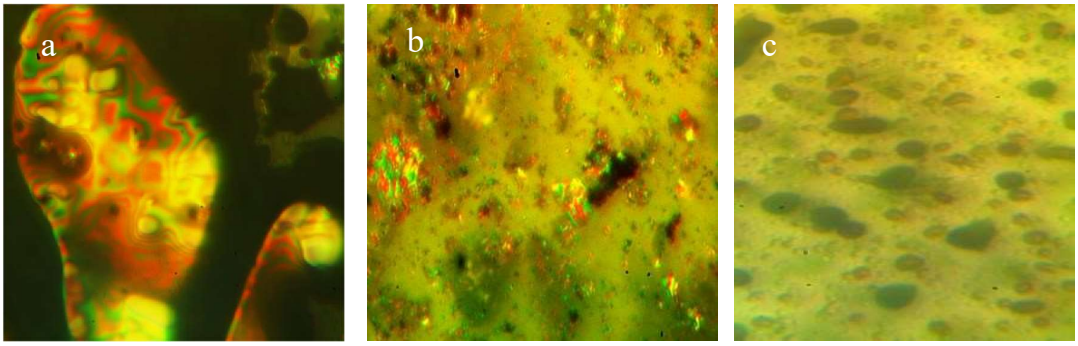

Figure (1): Polarizing optical textures of (a) nematic phase for compound[III] at 290°C, (b) nematic phase for compound$[IV]_a$ at 250°C, (c) droplets nematic phase for compound $[IV]_b$ at 230 °C.

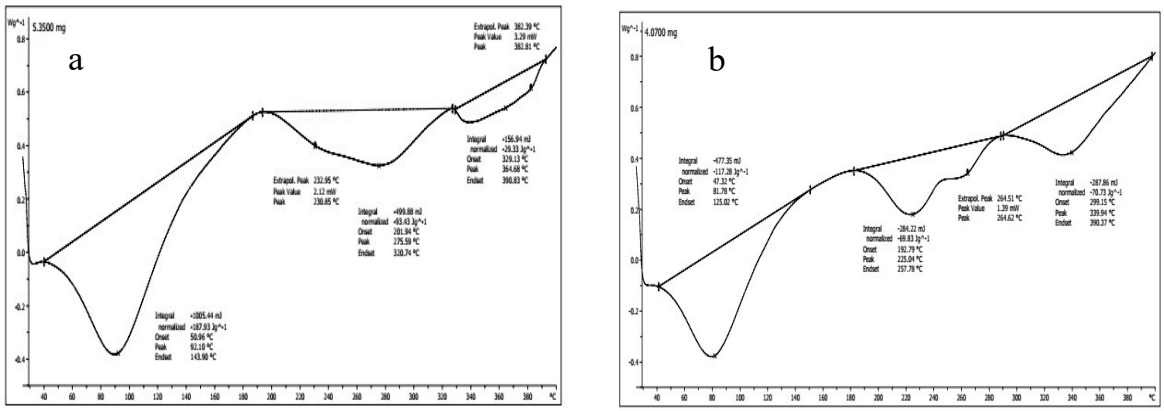

Figure (2):DSC thermogram for (a)compound [III] (b)compound $[IV]_a$

These findings demonstrate that the mesogenic properties are significantly influenced by the existence of the oxadiazole, oxazol, and thiazol rings, that is the same findings producted from

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the analogous derivatives 1,3-thiazole, and 1,3-oxazole have a symmetric rigid core. [21] Along with the terminal amino group found in compounds $[IV]_{a,b}$, which may be used for intermolecular hydrogen bonding. The compounds [III], $[IV]_a$, and $[IV]_b$ exhibit liquid crystal characteristics because H-bonds are critically for the stabilizing of functional properties of liquid crystal. [22]

Conclusion

This study investigated synthesis, and the properties of liquid crystalline of compounds with a 3,3'-dimethyl-biphenyl core that contain oxadiazol, oxazol, and thiazol rings, as well as amino as a terminal group. The reported that the compounds with hetero rings found to display liquid crystalline properties.

References

1- Jampilek, J. (2019). Heterocycles in medicinal chemistry. *Molecules*, *24*(21), 3839.
2- Al-Mulla, A. (2017). A review: biological importance of heterocyclic compounds. *Der Pharma Chemica*, *9*(13), 141-147.
3- Kerru, N., Gummidi, L., Maddila, S., Gangu, K. K., & Jonnalagadda, S. B. (2020). A review on recent advances in nitrogen-containing molecules and their biological applications. *Molecules*, *25*(8), 1909.
4- Dze, K. C., & Samad, F. (2020). Heterocycles, their synthesis and industrial applications: a review. *Int J Appl Sci Eng Technol*, *8*, 36-56.
5- Marinescu, M., Cinteză, L. O., & Zarafu, I. (2020, November). Synthesis of some Heterocyclic Compounds with Nonlinear Optical Properties. In *Proceedings* (Vol. 57, No. 1, p. 3). MDPI.
6- Kang, S., Byeon, S. E., & Yoon, H. J. (2021). N-Heterocyclic Carbene Anchors in Electronics Applications. *Bulletin of the Korean Chemical Society*, *42*(5), 712-723.
7- Shanker, G., Kumar, K. S., & Paul, B. (2022). Perspective on structure-property relationship of room temperature single-component liquid crystals. *Liquid Crystals*, *49*(12), 1545-1603.
8- Foo, K. L., Ha, S. T., & Yeap, G. Y. (2022). Synthesis and phase transition behavior of calamitic liquid crystals containing heterocyclic core and lateral ethoxy substituent. *Phase Transitions*, *95*(2), 178-192.
9- Fouad, F. S., Ness, T., Wang, K., Ruth, C. E., Britton, S., & Twieg, R. J. (2019). Biphenylyl-1, 2, 4-oxadiazole based liquid crystals–synthesis, mesomorphism, effect of lateral monofluorination. *Liquid Crystals*, *46*(15), 2281-2290.
10- Fouad, F. S., Khairuddean, M., & Twieg, R. J. (2022). Diphenyl-1, 3, 4oxadiazoles: synthesis and influence of side chain semifluorination and lateral ring fluorination on liquid crystalline properties. *Molecular Crystals and Liquid Crystals*, *732*(1), 64-75.
11- Ali, G. Q., & Tomi, I. H. R. (2022). Non-symmetrical bent-core homologous series bearing 1, 2, 4-oxadiazole core with a cholesterol terminal arm: Synthesis, characterization and their liquid crystalline properties. *Journal of Molecular Structure*, *1257*, 132610.
12- Baidya, A., Das, B., Majumder, S., Saha, S. K., Nath, R. K., & Paul, M. K. (2022). The unique asymmetric nano-cluster formation by the uneven hockeystick-shaped mesogen based on 1, 3, 4-oxadiazole in Langmuir–Blodgett thin film. *Journal of Dispersion Science and Technology*, *43*(8), 1208-1218.

13- Al-Hamdani, U. J., Abbo, H. S., Al-Jaber, A. A., & Titinchi, S. J. (2020). New azo-benzothiazole based liquid crystals: synthesis and study of the effect of lateral substituents on their liquid crystalline behaviour. *Liquid Crystals*, *47*(1415), 2257-2267.

14- Santos, A. B., Manfredi, A. M., Salla, C. A., Farias, G., Girotto, E., Eccher, J., ... & Gallardo, H. (2021). Highly luminescent liquid crystals by connecting 1, 3, 4oxadiazole with thiazolo [5, 4-d] thiazole units. *Journal of Molecular Liquids*, *321*, 114887.

15- Karam, N. H., Tomma, J. H., & AL-dujaili, A. H. (2017). Synthesis and characterization of heterocyclic compounds derived from 4-hydroxy and 4amino acetophenone. *Ibn AL-Haitham Journal For Pure and Applied Science*, *26*(3), 296-312.

16- Karam, N. H., Kurdi, A. N., & Al-Dujaili, A. H. (2022). Designed new mesogens via Vilsmeier–Haack reagent: synthesis and phase transition study. *Phase Transitions*, *95*(8-9), 634-641.

17- Karam, N. H., & Shanshal, A. K. (2017). 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*, *30*(3), 195-210.

18- Mohan, M., Murugan, V., Mahesh, Kataria, K., Geetha K. (2018). Synthesis of bis-[2-(Chloroethyl) amino] Acetamido-4-substituted Phenyl thiazole derivatives as possible antioxidant and alkylating anticancer agents. International journal of pharmaceutice & drug analysis. 6(3), 352-360.

19- Dupre, D. B., Samulski, E. T., & Ed.: F. Saeva. (1979). Liquid Crystals—The Fourth State of Matter. *Ed. FD Saeva*, 203.

20- Gray, G. W., & Goodby, J. W. (1984). Smectic liquid crystals: Textures and structures. *HEYDEN & SON, 247 SOUTH 41 ST ST., PHILADELPHIA, PA 19104, USA, 1984, 256*.

21- Ibraheem, T. K., Karam, N. H., & Al-Dujaili, A. H. (2020). Synthesis and characterization of symmetrical liquid crystalline compounds based on oxazole and thaizole rings. *Molecular Crystals and Liquid Crystals*, *710*(1), 1-12.

22- Hussain, N. B., & Karam, N. H. (2022). Heterocyclic compounds-based liquid crystals: Synthesis and mesomorphic properties. *International Journal of Health Sciences*, *6*(S10), 609–619.