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Article

Preparation, Characterization and Study of Liquid Crystalline Properties and Biological Activity of Azo-Ethers Series

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Abstract: In this study, a series of ethers (Z5-Z8) were prepared by reacting the prepared azo dyes with sodium carbonate Na_2CO_3 and with alkyl halide, all these materials dissolved in DMF solvent. These prepared compounds were characterized by physical and spectroscopic methods such as melting point and proton nuclear magnetic resonance spectroscopy. The liquid crystalline phases of some prepared compounds were also examined using a polarized light microscope equipped with a POM electric heater. It was noted that the transitions obtained were monotropic during heating only and did not appear during the cooling phase. They also showed liquid crystalline characteristics with varying properties depending on the nature of the mesogenic units of each molecule. The effect of some of the prepared compounds on the growth of two types of bacterial isolates, namely Escherichia coli and Staphylococcus aureus, was also studied. Some of the prepared compounds showed good inhibitory activity against the types of bacteria used.

Keywords: Ethers, Liquid crystalline, Nematic phase, Smectic phase, Biological activity.

Introduction

Liquid crystals have been described as a mesophase [1], as it is considered a fourth state of matter. They were initially called fluid crystals [2]. This state appears between the solid phase and the liquid phase [3]. In the solid phase, the movement of molecules is restricted in the three-dimensional network and has an integrated molecular organization in terms of location and orientation [4]. In the isotropic phase, the molecules move freely they are randomly arranged [5]. The liquid crystals are solid and may be linear, lamellar, or curved in shape [6,7]. Although the liquid crystals exhibit some properties common to the solid and liquid states, they possess special features that do not exist in the two states [8,9]. Studies have proven that there are many organic compounds that show more than one step when moving from the solid state to the liquid state, and that this step is in the range located between the state of highly organized three-dimensionality (crystalline state) and the state of disorder (liquid state) [10, 11]. Through X-ray studies of the compounds that show these intermediate phases, it was found that there is a discrepancy in the geometric shape [12], and this is explained by the unequal intermolecular forces in all directions due to the elongation of the molecules [13], and their parallel

arrangement [14]. From what was stated above, we can realize that the liquid crystalline phases are formed by moving the order of arrangement of molecular bonds to a less regular level than in the crystalline state [15], and this occurs in two cases [16]: The first case: When certain volumes of suitable polar solvents are added to specific quantities of organic compounds [17], these solvents work to rearrange the molecules to a less organized state [18], and give the liquid crystalline phases depending on the change in the concentration of the solvent and the attraction that occurs between the solute and the solvent [19]. The resulting crystals are called This case is called lyotropic liquid crystals [20]. The second state: It is formed due to the gradual increase in temperature, as it includes a rearrangement of the intermolecular forces of the crystalline state [21]. Accordingly, the quality of the intermediate phase formed depends on the amount of thermal energy necessary to change the system of parallel arrangement of molecules within the crystalline network [22], as one of the three dimensions of the crystalline network is destroyed [23]. It leads to the formation of the smectic phase, which is a two-dimensional system [24]. Liquid crystals resulting from a change in temperature are called thermotropic liquid crystals [25].

Materials and Methods

2. Experimental Part

2.1. Preparation of ethers (Z5-Z8)

Dissolve (0.002 mol) of one of the prepared dyes in 15 ml of DMF solvent and add to it (0.003 mol) of sodium carbonate Na_2CO_3. The mixture was heated at a temperature of 130°C in an oil bath for half an hour, then (0.003 mol) of alkyl halide was added to it and continued. Escalation lasts for 12-15 hours until the reaction ends (the course of the reaction was monitored using the TLC technique). After the reaction ended, the mixture was cooled, then poured over ice grits and water, then filtered using Whatman 42 filter paper. The precipitate was washed after filtration with a small amount of petroleum ether (40-60) °C, then dried using a drying oven at a temperature of (40°C), and it was recrystallized from absolute ethanol [26, 27]. Table (1) shows the physical properties and structural formulas of the resulting compounds.

2.2. Diagnosis of liquid crystalline phases of prepared compounds using a polarized optical microscope (POM)

The liquid crystalline phases of the prepared compounds were examined and characterized using a polarized optical microscope (POM), by taking a small amount of the material to be examined, placing it on a glass slide and heating it over an electric heater at a heating rate of (5°C/min) [28, 29].

2.3. The bacterial biological activity

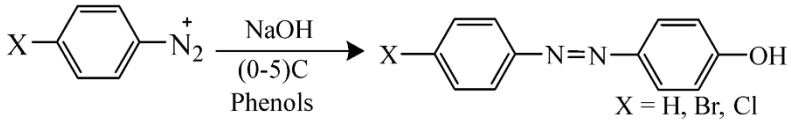
The biological activity of the prepared compounds was studied on two types of bacteria: the gram-positive bacteria ***Staphylococcus aureus*** and the gram-negative bacteria ***Escherichia coli***. The food medium was free of blank bacteria, as was the DMSO solution used for dissolution [30]. The biological activity was measured using the Agar-well diffusion method, whereby the bacterial inoculum was prepared at a concentration of (1.5×10^8) bacterial cells per ml [31]. And spread the bacterial inoculum over the entire culture medium, Mueller Hinton agar [32]. Then drill wells in the middle of the agar using a sterile drill with a diameter of 6 mm for the purpose of loading the chemical solution. The solutions whose effectiveness was to be measured were loaded into the holes with a volume of 100 microliters in each hole on one plate in which one bacterial model was grown. This step was repeated for all bacterial species and the experiment was repeated to ensure the accuracy of the results [33]. After planting and loading the solutions into the pits, the models were incubated at a temperature of 35-37 degrees Celsius in the laboratory incubator for 24 hours, and after the end of the incubation period, the effectiveness was read by observing the diameter of inhibition around the pits loaded with solutions and measuring it in mm using a transparent ruler [34]. As for the solutions that did not appear

Surrounding them was an inhibition halo that made the solutions ineffective against the selected bacteria under study [35]. Please provide concise but complete information about the materials and the analytical and statistical procedures used. This part should be as clear as possible to enable other scientists to repeat the research presented. Brand names and company locations should be supplied for all mentioned equipment, instruments, chemicals etc. All the ethical permission associated in the research work must be specified. Indicate the statistical methods used and identify statistical significance using superscripts (* and **) following the data (*P<0.05, **P<0.01).

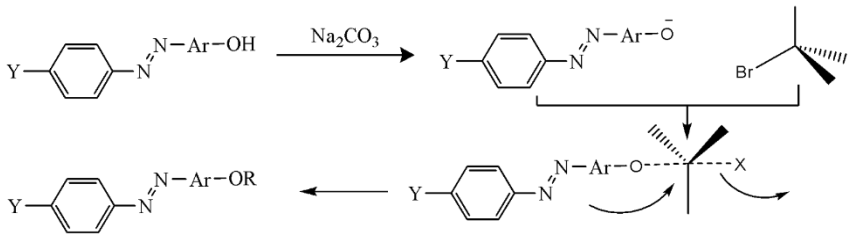
Results

3.1. Mechanism of preparation of ethers (Z5-Z8)

Azo compounds were prepared by pairing the diazonium salt with the phenoxide ion, which was prepared by adding one of the phenol compounds with 10% sodium hydroxide according to the following equations:



The proposed mechanism for this reaction includes preparing the phenoxide ion by reacting one of the phenolic azo dyes with sodium carbonate, followed by attacking the prepared nucleophile on the SN^2 alkyl halide and forming the ether compound [36] as in the scheme (1).



Scheme (1): Mechanism of preparing ethers (Z5-Z8).

3.2. Characterization of ethers (Z5-Z8)

The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the compound (Z5) was studied using a solvent (DMSO-d^6). It was observed that multiple signals appeared at the chemical shift (0.84-2.97) ppm attributed to the protons of the aliphatic groups (CH_3, CH_2). The appearance of a multiple signal in the range (6.93-7.82) ppm is attributed to the protons of the aromatic rings, and the appearance of a signal at the chemical displacement (2.50) ppm is attributed to the protons of the solvent (DMSO-d^6) [37, 38], as in Figure (1).

The proton nuclear magnetic resonance (^{1}H-NMR) spectrum of the compound (Z7) was studied using a solvent (DMSO-d^6). It was observed that multiple signals appeared at the chemical shift (0.86-4.08) ppm attributed to the protons of the aliphatic groups (CH_3, CH_2). The appearance of a multiple signal in the range (6.87-7.91) ppm is attributed to the protons of the aromatic rings, and the appearance of a signal at the chemical displacement (2.50) ppm is attributed to the protons of the solvent (DMSO-d^6) [39, 40], as in Figure (2).

3.3. Diagnose and discuss liquid crystal behavior

In view of the important chemical and physical properties of liquid crystalline systems, the appearance of the liquid crystalline characteristics of the prepared compounds was studied using a polarized light microscope equipped with an electric heater (POM) [41], by taking a small amount of the material to be studied on a glass slide and transferring it to the electric heater [42], and following the thermal transfers of the liquid crystalline phases that occur during the process [43]. The process of heating and cooling, then determining the nature of these transitions and the thermal stability of each phase. To studying

the nature of the transitions occurring and the thermal stability of the identified liquid crystalline phases, some general concepts specific to the liquid crystals of the prepared compounds must be considered [44].

1- New organic compounds have been prepared that have a longitudinal structure that matches the shape of the longitudinal liquid crystalline phases (Rod-like), which is one of the forms of mesogenic units that exhibit liquid crystalline characteristics [45].

2- Mesogenic units were prepared that have a molecular core (core) consisting of more than two aromatic rings, between which there are bonds that increase the electronic sequence along the axis of the molecule, which increases the possibility of the emergence of liquid crystalline characteristics and increases the thermal stability of the identified liquid crystalline phases [46].

The liquid crystal characteristics were studied, the nature of the transitions was diagnosed, and the thermal stability of the identified phases was determined using a polarized light microscope (POM) [47], by taking an amount of the substance to be measured (0.05-0.1) g and following the thermal transitions by heating the sample in a POM device at a heating rate of (5-8) °C/min [48]. Also, a differential scanning calorimeter (DSC) device was used by taking about (10-20) mg of dry matter and heating it in an inert atmosphere of nitrogen gas [49]. It was noted that there was agreement between the degrees of heat transfer measured by the (POM) device and the values. Obtained with a DSC device [51]. It was noted that most of the crystalline compounds that were studied showed liquid crystalline characteristics with varying properties depending on the nature of the mesogenic units of each molecule and in both cases [52, 53].

The structure of the mesogenic unit, which determines the general shape of the molecule, is one of the most important factors that favor the appearance of liquid crystalline phases for rod-like (calamitic) molecules, as the appearance of liquid crystalline phases depends mainly on the ratio of the length of the particle to its average diameter, which is in the order of (L). /d ≥ 4.0-6.4) L=length of particle, d=average diameter of particle [54]. In addition to the presence of peripheral attractive forces, which favor the emergence and stability of the nematic phase, in addition to lateral bonding forces, which favor the emergence and stability of the smectic phases. These forces are represented by the Van der Waals forces, or what is known as the London Dispersion Forces, and hydrogen bonds, in addition to the dipole-dipole forces [55].

The results of the thermal examination of the compounds prepared using a differential scanning calorimeter (DSC) device showed that the thermal transfers are of the endothermic type in the case of heating, while they are exothermic in the case of cooling, meaning that the process of breaking the force between the molecules requires a certain energy, and since the molecules In the crystalline state, it is restricted by a three-dimensional network, so breaking one dimension of that force requires a certain energy that is absorbed from the surroundings [56]. Therefore, the process of breaking bonds is endothermic, and this is what was observed when studying the thermal energy diagram of compounds prepared using the DSC technique [57]. On the contrary, the transition from the random state (the azeotropic phase) to the regular state (crystalline) leads to the release of energy, and this is what was observed in the cooling process [58].

The reason for the appearance of liquid crystalline phases for most of the prepared compounds is attributed to the presence of more than two aromatic rings, which increase the hardness of the molecule [59], in addition to the presence of bonding groups represented by the azo group (N=N), which increases the electronic sequence along the axis of the molecule and thus maintains the tropicality of the molecules [60]. The presence of polarized peripheral groups represented by groups (Cl, Br,) increases the peripheral and lateral forces of attraction, in addition to the presence of aliphatic groups at the second end of the molecule, represented by alkoxy groups [61], which increase the flexibility of the molecule, as the lateral forces favor the appearance and stability of the smectic crystalline phases. Peripheral forces favor the appearance and stability of the nematic phase [62].

When examining the polarized light microscope (POM), the examination results showed smectic phases of the type of SA and SC, the appearance of which depends on the angle of arrangement of the molecule

with the perpendicular on the axis of the molecule and the extent of the arrangement of the molecules with respect to each other, which depends mainly on the order parameter of the molecules [63]. It was observed that the thermal stability of the smectic crystalline phases and the identified nematic phases is greatly affected by the peripheral and lateral attractive forces when comparing the results of the heat transfer values for the liquid crystalline phases of the prepared compounds, as increasing the lateral attractive forces increases the thermal stability of the smectic crystalline phases, while increasing the lateral attractive forces increases the Thermal stability of the nematic phase depends mainly on the polarized end groups and the aliphatic groups [64]. This is what Aaron, Byron, and Gray confirmed that the structural structure of any molecule containing a terminal group X gives a more stable nematic phase than if X = H. When studying the microscopic examination of the prepared compounds [65], it was observed that smectic phases appear with little thermal stability, since the lateral attractive force is weak and that this force is responsible for the appearance and thermal stability of the phase [66]. On the contrary, the thermal stability of the nematic phase is high due to the peripheral bond force [67]. In addition, the thermal stability of the nematic phase decreases with the increase in aliphatic groups and increases with the increase in the peripheral polarization strength [68]. It was also noted that the prepared compounds showed two-phase liquid crystalline phases (Enantiotropic), that is, through the process of heating and cooling [69].

3.4. Evaluation of the bacterial biological activity of some prepared compounds

The biological effectiveness of some of the prepared compounds was evaluated in this thesis on two types of bacteria, namely ***Escherichia coli*** and ***Staphylococcus aureus***. These bacteria were chosen due to their medical importance, as they cause many diseases [70,71]. In addition, they differ in their resistance to antibiotics [72,73]. The biological effectiveness of some of the prepared compounds was evaluated using the etching method and measuring the level of inhibition (Inhibition zone) [74,75]. The results indicate that the compounds preparation could inhibit the growth of bacteria used in both types, positive and negative for the gram stain, in varying proportions [76- 78], as in Table (3) and Figure (10).

Table (1): The physical properties and structural formulas and antibacterial activity of (Z4-Z8)

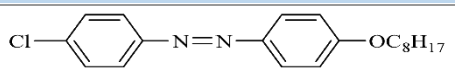
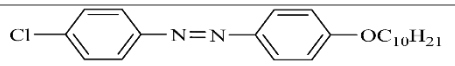
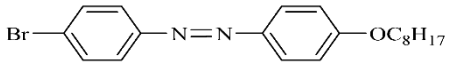
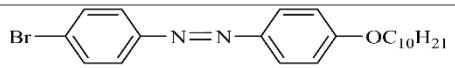
Comp. No.	Comp.	M.wt gm./mole	Color	Yield %	*E. Coil*			*C. Albicans*		
					25	50	100	25	50	100
Z5		344	Light brown	81	0	2	4	0	2	3
Z6		372	Yellow	83	1	2	2	1	2	4
Z7		388	Light yellow	76	0	0	1	1	1	1
Z8		417	Orange	78	1	2	4	2	3	4

Table (2): Degrees of thermal transfers and liquid crystalline phases of the prepared ether series

Comp.			Cr	S_A	S_C	N	ΔS_A	ΔS_C	ΔN
Z5	POM	Heat	87			104			17
		Cool	53		82	100		29	18
	DSC	Heat	85			103			18
		Cool	51		81	98		30	17
Z6	POM	Heat	92			101			9
		Cool	66			92			26
	DSC		90			98			8

			63			89			26
Z7	POM	Heat	90			98			8
		Cool	65			90			25
	DSC		87			93			6
			59			87			28
Z8	POM	Heat	102	119	129	138	17	10	9
		Cool							

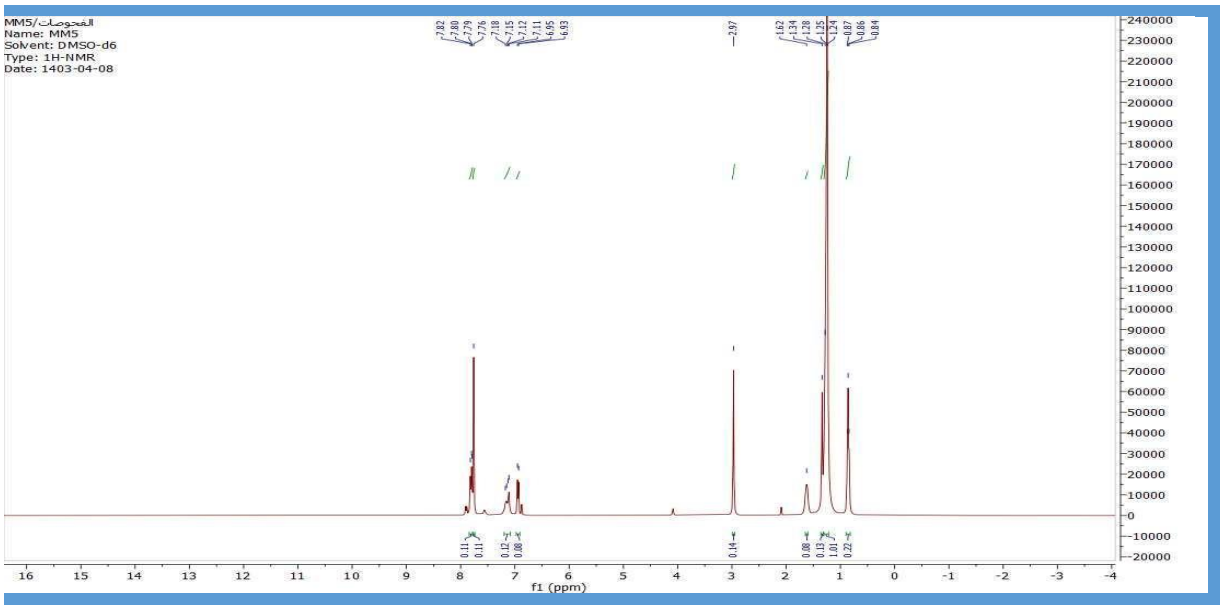


Figure (1): ^{1}H-NMR spectrum of compound (Z5)

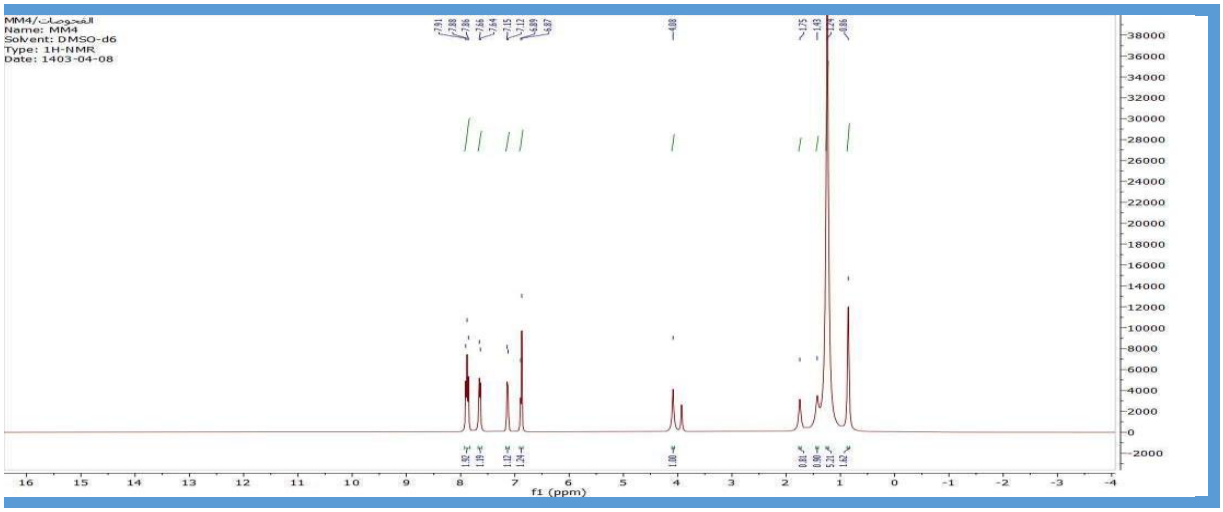


Figure (2): ^{1}H-NMR spectrum of compound (Z7)

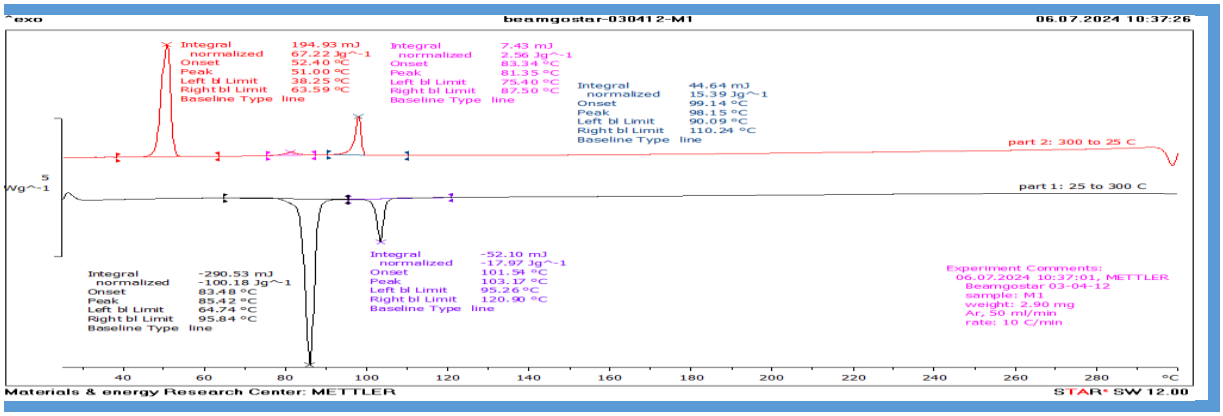


Figure (3): DSC measurement of compound (Z5)

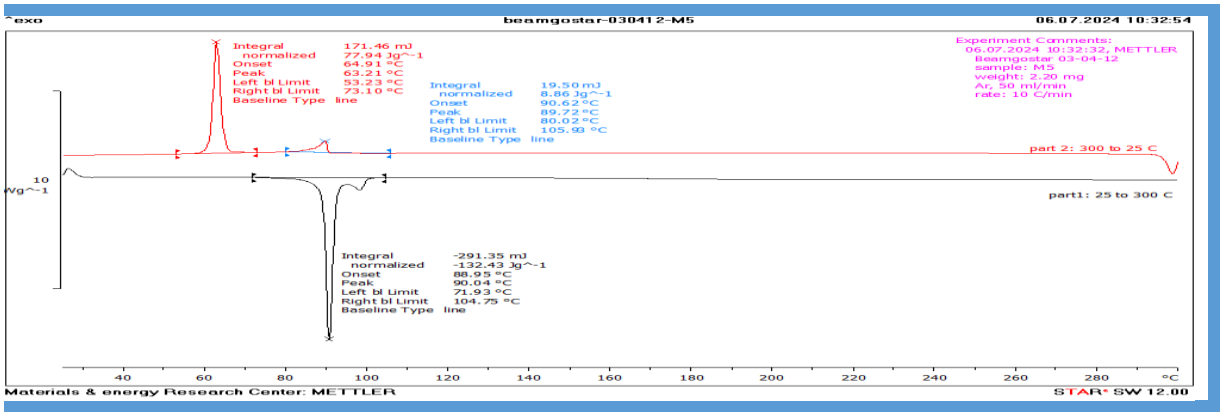


Figure (4): DSC measurement of compound (Z6)

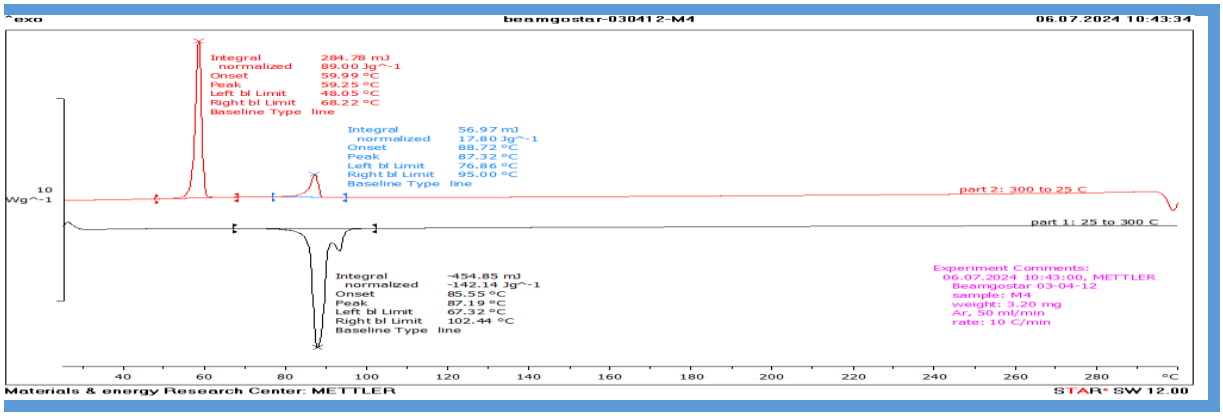


Figure (5): DSC measurement of compound (Z7)

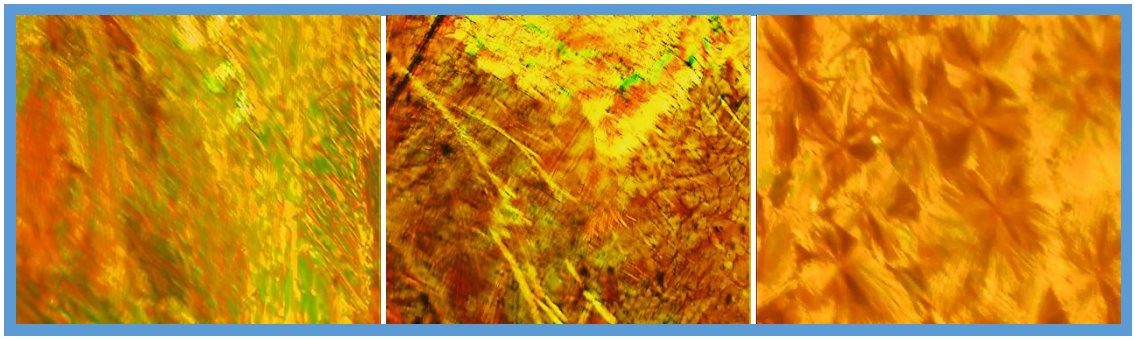


Figure (6): The nematic phase of the compound (Z5), and the smectic phase SC of the compound (Z5)

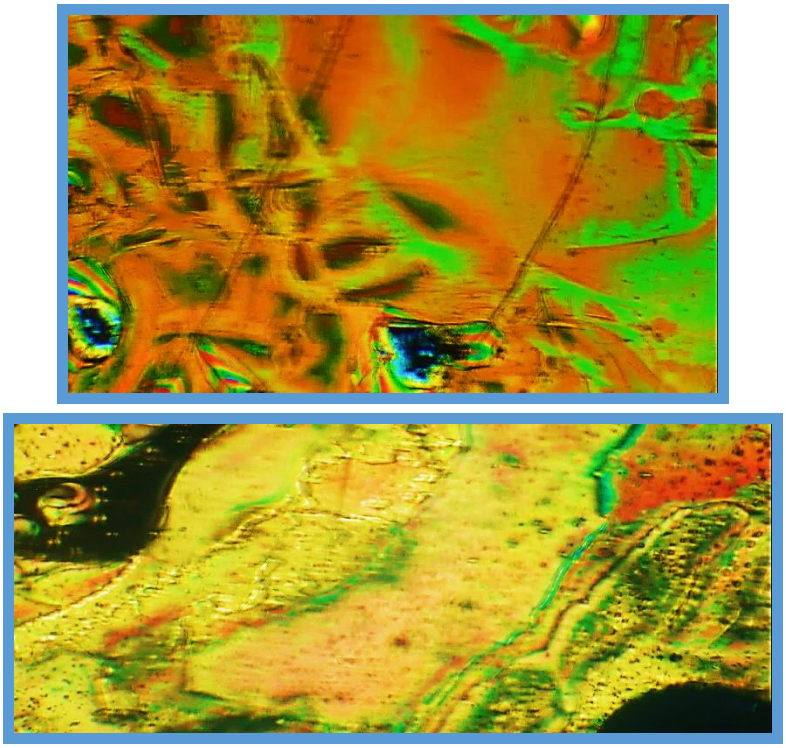


Figure (7): The nematic phase of the compound (Z6), and the nematic phase of the compound (Z6)

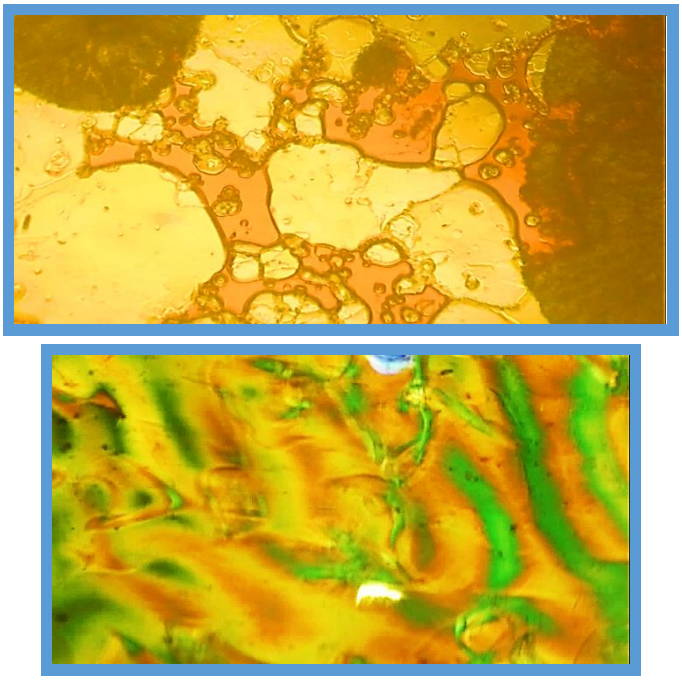


Figure (8): The nematic phase of the compound (Z7), and the nematic phase of the compound (Z7)

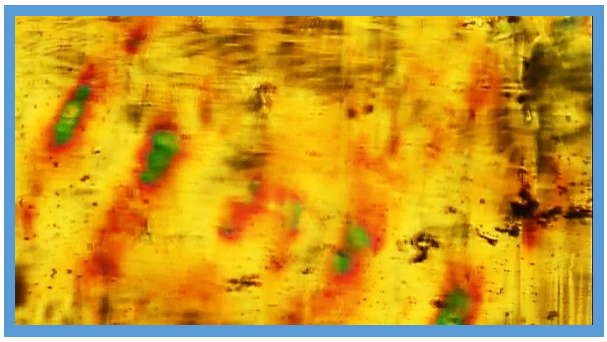
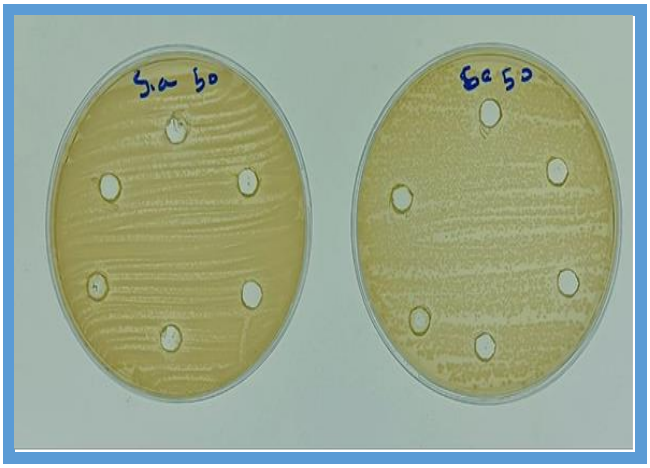


Figure (9): The nematic phase of compound (Z8) (heating)



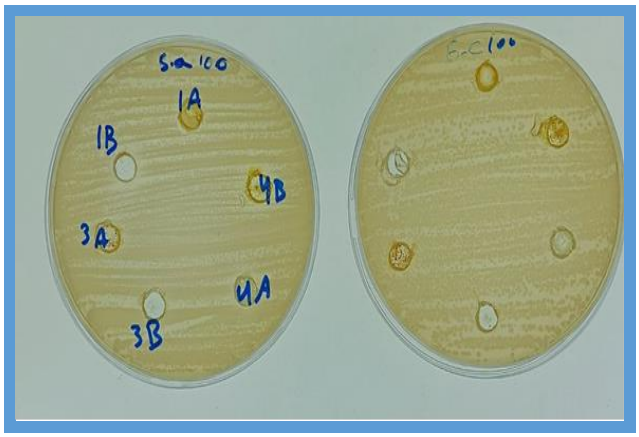


Figure (10): The antibacterial and antifungal activity of the prepared compounds (inhibition zone in mm)

Conclusion

Physical and spectroscopic analyses validated the accuracy of the structural characterization of the synthesized nanocomposites. Among these compounds, certain ones exhibited liquid crystalline properties. The biological evaluation revealed that many of the synthesized compounds possess antibacterial activity, demonstrating the capability to inhibit bacterial growth. Notably, some of these compounds displayed greater biological efficacy than the antibiotics used as reference standards.

Recommendations

The synthesis of novel azo-amide compounds and the investigation of their liquid crystalline properties. The preparation of aliphatic chains of varying lengths featuring an ester linkage in place of an ether, with a focus on evaluating the impact of chain length on the thermal stability of liquid crystalline phases. The development of nanocomposites through the integration of organic nanomaterials with liquid crystalline organic compounds, followed by an examination of their liquid crystalline properties. The exploration of specific applications for the synthesized compounds, such as their use in the adsorption of heavy metals or phenolic compounds from industrial wastewater, or the removal of sulfur compounds from petroleum derivatives. The analysis of the effects of blending different liquid crystalline materials on the properties of the resulting mixtures.

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