Bulgarian Chemical Communications, Volume 56, Issue 3 (pp. 274-281) 2024 *DOI: 10.34049/bcc.56.3.SM-M*

Synthesis, characterization and effects to cholesteric lyotropic liquid crystal media of -ONNO- type Schiff bases and metal complexes

S. Meral[1*], A. Alaman Ağar[2]

[1] *Boyabat Vocational School, Sinop University, Sinop, Turkey*
[2] *Faculty of Arts and Sciences, Department of Chemistry, Ondokuz Mayıs University, Samsun, Turkey*

Received June 1, 2024; Accepted: August 17. 2024

Lyotropic liquid crystals (LLC) are remarkable candidates in biomimetic applications, and in this respect, their interaction mechanisms with the target molecule are controversial. The study aims to create an ordered host system for biosimilar guest molecules to determine interactions. -ONNO- type tetradentate julolidine derivative, symmetric Schiff bases were synthesized with 1,2-ethandiamine and 1,4-butanediamine, and then copper complexes were obtained from Schiff bases with a cage-like structure. To characterize the synthesized compounds FT-IR, ^{13}C and ^{1}H-NMR and UV-vis spectroscopies were employed. Decylammonium chloride (DACl), NH_4Cl, H_2O and the optically active amphiphilic molecule L-alanine decyl esther (L-ADE) as a chiral dopant were utilized in the host system. The properties of lyotropic cholesteric phases and the effects of the synthesized compounds were examined using a polarized optical microscope (POM) by measuring the helical pitch as a parameter. Synthesized Schiff bases and metal complexes (2.5-20 mM) were added to the cholesteric phase whose helical pitch was measured at 110 μm without destroying anisotropic properties. The synthesized compounds caused a lengthening in helical pitch due to settled micelles on the surface or within the micelle core, leading to a change in micelle-micelle interaction. Specifically, $Cu(ac)_2 \cdot H_2O$ shortened the helical pitch.

Keywords: Cholesteric lyotropic liquid crystal, julolidene derivative Schiff base, Metal complex, Host-guest interaction

INTRODUCTION

Liquid crystal is a smart material that has solid-like molecular order and anisotropic structure, as well as liquid-like mobility, which has been observed *in vivo* or *in vitro* biological environments. LLC, one of its notable types, is a solvent environment in which micelle formation and interaction of micelles are fundamental processes resulting from the interaction of hydrophobic and hydrophilic molecules [1, 2]. Long-range order in one, two, or three dimensions is effective in different LLC phases, thus demonstrating the ability to self-assemble into micelles. The mentioned ordered media are suitable for biological and industrial applications due to controllable ingredient quantities, making them applicable due to different polar domains and huge surface areas for molecule carrier systems. Nowadays, water-soluble peptides, unsoluble drug molecules, and degradable enzymes can be delivered to desired areas. In addition, cream-like ingredients applied to the skin can be used more effectively in different polar regions [3-6]. Positional and orientational order, changing molecular mobility, symmetrical and optical properties are also driving factors that enable the formation of well-defined micellar domains through interaction, thus becoming applicable and adaptable in crystallization or polymerization reactions [7, 8].

As an important N-heterocyclic aromatic compound containing three six-membered-ring systems julolidene is a structural derivative of aniline [9, 10]. The electro-optical properties and fluorescence efficiency attract attention in sensor applications with high sensitivity to many desired biological compounds and in molecular rotors used as viscosity sensors [11-16]. Especially Schiff bases and metal complexes of julolidene derivatives are commonly researched because of diverse biological properties, and remarkable electro-optical properties with extensive conjugation [17-19]. Imine compounds have carbon-nitrogen double bonds that behave as Lewis acids and are preferred molecules for developing new drugs [20-22]. Imine compounds, especially 2-hydroxy derivatives, act as donor molecules. This behavior is frequently encountered in biological processes because they form highly coordinated compounds with metal ions, leading to increased biological and chemical effects [23, 24].

The LLC acts as a well-ordered supramolecular host, with all its controllable and adaptable properties, and is a remarkable field for determining the interactions of compounds and influencing factors. Especially for important issues of today, such as imaging and diagnostic applications, LLC offers a unique controllable, and biocompatible

* To whom all correspondence should be sent:
E-mail: *smeral@sinop.edu.tr*

encapsulation material. This ordered environment containing polar-nonpolar domains provides an evaluation environment for investigating the properties of screening compounds, such as optimal charge and activity [25-27]. In the study, the interactions between the prepared LLC systems and the synthesized compounds were evaluated by measuring the changes in the helical pitch depending on concentration and temperature.

EXPERIMENTAL

Synthesis of Schiff bases and copper complexes

To synthesize a symmetric Schiff base, 8-hydroxy-1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1h,5h-pyrido[3,2,1-ij]quinoline-9-carbaldehyde (1) was refluxed with 1,2-ethandiamine and 1,4-butandiamine separately at a 2:1 stoichiometric ratio in ethanol for about 18 h. The yellow needle crystals that had collapsed in the reaction mixture were separated, washed three times with diethyl ether and ethanol, and recrystallized in a hot ethanol solution. To obtain copper complexes, the synthesized Schiff bases and $Cu(ac)_2 \cdot H_2O$ were reacted at a 1:1 stoichiometric ratio in ethanol for approximately 12 h. Excess $Cu(ac)_2 \cdot H_2O$ was washed with water and the complexes were recrystallized in ethanol. The synthesized compounds are given in Figure 1.

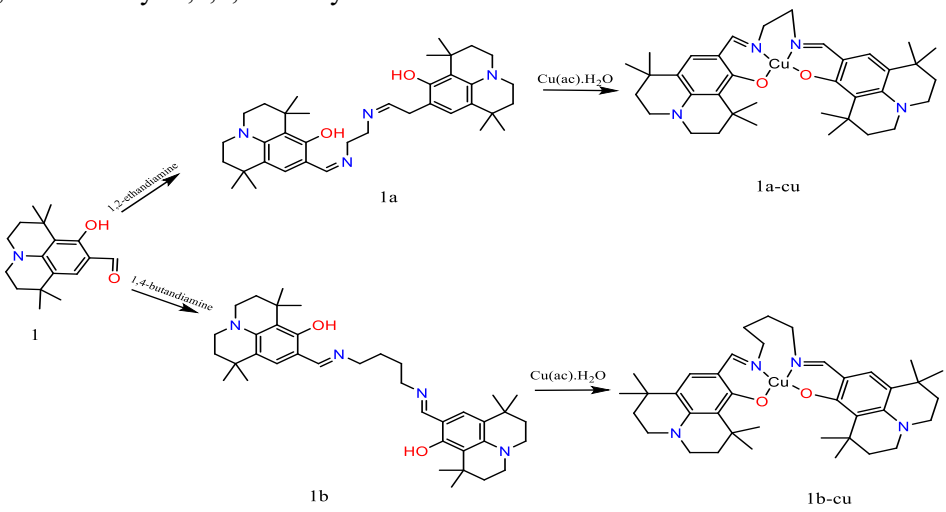

Fig. 1. The synthesized compounds

Preparation of the LLC system

DACl were synthesized according to [28] and L-ADE [29]. To obtain the lyotropic phases, the required amounts of components were weighed for DACl/ NH_4Cl /H_2O; DACl/ *L-ADE/* NH_4Cl/ H_2O and DACl/ DEOH/ L-ADE/ NH_4Cl/ H_2O systems and heated in a water bath at 50°C. After the dissolution process was completed, the mixture was centrifuged and the obtained phase was examined with a polarized optical microscope. For investigation of the effect of the guest molecules on LLC, n-decanol solutions of the synthesized compounds were prepared in different concentrations and then added to the LLC media, heated in a water bath at 50°C to obtain a homogenous mixture, centrifuged, and examined with a polarized optical microscope.

RESULTS AND DISCUSSION

Imine groups are easily functionalized substances that behave like Lewis acids and are inclined to electron transfer to metal ions. The synthesized symmetrical Schiff bases have a hydroxyl group near the imine group and a -ONNO- type tetra-dentate structure. The alkyl chain can also provide flexibility, which facilitates the formation of chelates by surrounding the metal. The Schiff bases and copper complexes were obtained by condensation reaction and investigated using FT-IR, ^{1}H NMR and ^{13}C NMR, UV-vis spectroscopies.

In Figure 2, the FT-IR spectra of the compounds are given. Upon examining the FT-IR spectrum of the synthesized compound in 1a, one distinct hydroxyl peak was replaced by a broad peak in the 2400-2600 cm^{-1} region due to the tautomeric structure and conjugation. Still, in 1b, a distinct hydroxyl peak was observed at 3396 cm^{-1} due to the increased flexibility of the molecule with a butane chain [30, 31]. The C=O bond was transformed to a C=N bond, shifting the carbonyl peak to a lower wavelength at around 1615 cm^{-1} and 1619 cm^{-1} for 1a and 1b respectively, providing a crucial clue for the desired molecules [32, 33]. Amine groups are detected at 3300-3400 cm^{-1} as a double peak [34] and for synthesized symmetric Schiff bases the mentioned peaks testified that both amine groups are transformed into imine bonds.

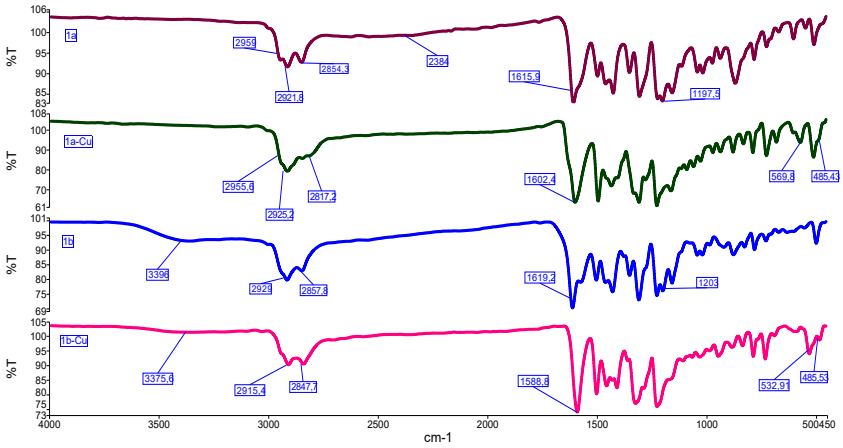

Fig. 2. FT-IR spectra of the synthesized compounds

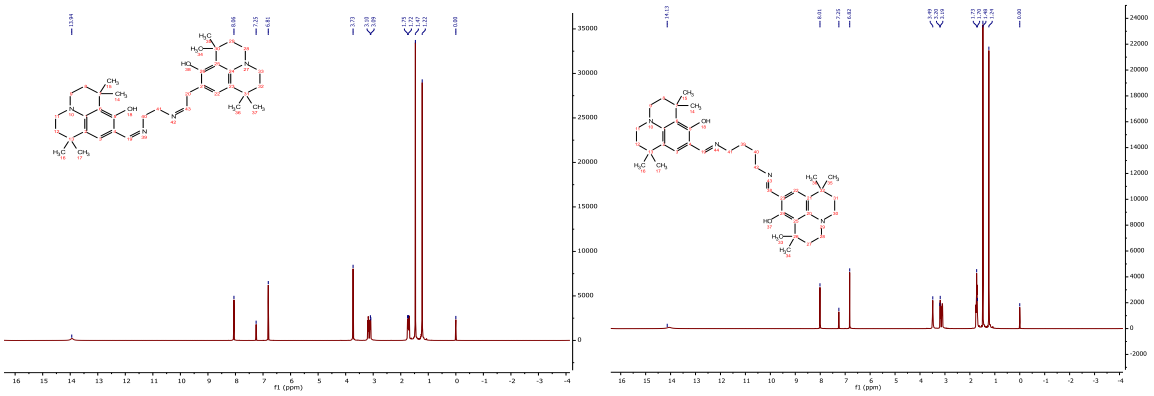

Fig. 3. ^{1}H NMR spectra of 1a and 1b

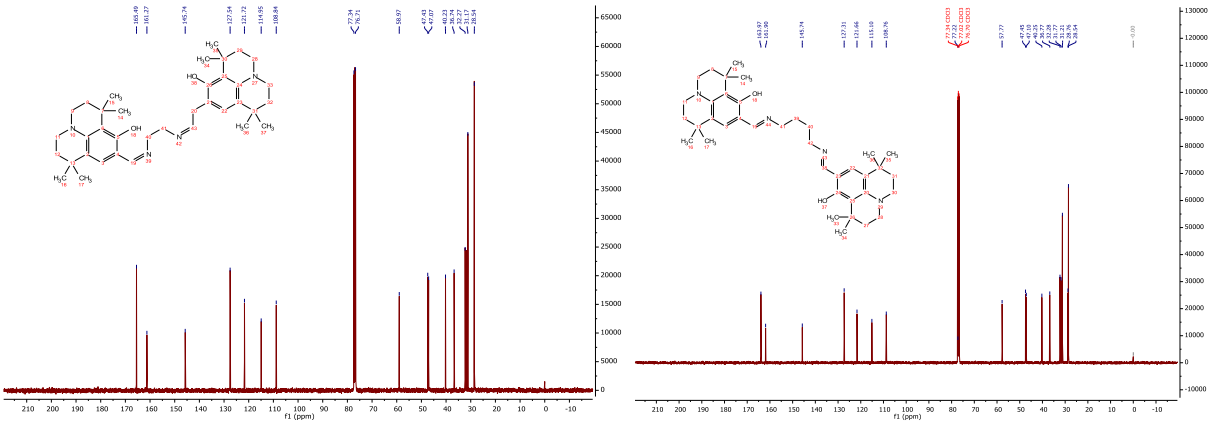

Fig. 4. ^{13}C NMR spectra of 1a and 1b

Copper ions participated in the formation of the complex through oxygen and nitrogen atoms, and in this case, the imine peaks shifted to lower regions at 1602 and 1588 cm^{-1}, and at the same time, the hydroxyl peaks were not observed in 1a-Cu, whereas for 1b-Cu they were determined at a lower wavelength at 3375 cm^{-1} [35, 36]. In copper complexes, new peaks were detected in the FT-IR spectra at 485 and 569-532 cm^{-1}, indicating M-N and M-O bonds [37, 38]. Line with the literature aliphatic C-H, aromatic C-H and C=C vibrations were observed at 2955-2820 and 1420-1497 cm^{-1} for the synthesized compounds [39]. In Figure 3, ^{1}H NMR spectra of the synthesized compounds in chloroform are provided. In harmony with FT-IR spectra, the imine proton was observed in the ^{1}H NMR spectrum replacing the aldehyde proton at 8.06 and 8.01 ppm as a single peak for 1a and 1b, respectively. Looking at the chemical structure, the hydroxyl peak was seen at 13.94 and 14.13 ppm for 1a and 1b upfield with the tautomeric interaction hydroxyl proton [40]. Aromatic protons were detected at 6.82-7.25 ppm as multiplet peaks, CH_2 protons between two conjunctive julolidene moieties

at 3.73 and 3.49 ppm, -N attachment aromatic protons at 3.09-3.10 and 3.19-3.20 ppm and CH_3 protons at1.75 ppm for 1a and 1b [41, 42].

In Figure 4, ^{13}C NMR spectra are given for 1a and 1b in chloroform. The most important peak in the ^{13}C NMR spectra of compounds 1a and 1b is the imine peak, which was replaced by the carbonyl peak downfield at 165 and 163 ppm, respectively [43]. The ^{13}C NMR spectra of both compounds showed a peak at 161 ppm due to their phenolic carbons [40]. At 145 ppm, the aromatic carbon atoms attached to nitrogen were determined and at the same time, aromatic carbons were in the 127-108 ppm range. At 77 ppm, the ethylene carbons attached to the julolidene moiety were observed in 1a, while in 1b, butyl carbons were observed at 77-76 ppm. The compounds have cycloalkane carbons attached to nitrogen atoms and are observed in the 58-31 ppm range for 1a and 1b. The peaks observed around 28 ppm are attributed to aliphatic carbons [44, 45].

In electronic spectra, n-π* and π-π* transitions were detected in a range of 200-400 nm concerning chromophore groups. In Figure 5, UV-vis spectra of synthesized compounds in different polar protic and aprotic solvents such as methanol, ethanol, acetonitrile and chloroform are seen. Observation of a blue shift at 263 nm with increasing polarity corresponds to n-π* transition for 1a, while detected at 279 nm for 1a-Cu indicated electron transfer to the copper ion. The π-π* transition of 1a was recorded at 346 nm with a red shift resulting from the increased polarity. For the copper complex of 1a, π-π* transition was observed at 353 nm. Similarly, it was determined that the n-π* transition at 266 nm showed a red shift with increasing polarity in compound 1b, and this transition was observed at higher wavelengths in the copper complex of 1b [46, 47]. The π -π* transition for 1b was seen at 346 nm in ethanol and higher wavelength due to complex formation. The coordinated metal ion is also seen in complexes' spectra in the range 640-680 nm. d-d transitions are observed with a weak intensity for 1a-Cu and 1b-Cu [48].

To design and control interactions for biosimilar molecules, the lyotropic liquid crystal was preferred in the study because it can provide an environment similar to biological systems, where compounds with different polarities are stable and can be dissolved within applicable limits. It is crucial to investigate the formation and properties of a superstructure from micelles and synthesized compounds with flexible and similar structural regions, particularly how the type or concentration of components can control it. The host system contains two surfactants and a co-surfactant and therefore the micelles have a significant non-polar character and also the optically active LADE ensures that the micelles are arranged in a helical structure and the system has chirality. The guest molecules have a large structure that can easily be accommodated in micelles with apolar aromatic bodies and the polar imine moiety in the polar heads. As a result, this association can be determined by the observed changes in phase type or helical pitch length, leading to growth, division, gap formation and disorientation in micelles. Many host-guest interactions have been interpreted in the literature, especially in the liquid crystal environment, and it has been reported that the system properties are very sensitive to additives, but there is not enough information about Schiff bases and metal complexes as a guest molecule, which contain molecular groups with remarkable interaction types [49]. Firstly, the nematic phase was determined with threaded texture and after adding chiral LADE, the fingerprint texture was formed. The amounts of the components are given in Table 1 and phase textures obtained from POM are given in Figure 6.

Table 1. Amounts of compounds in prepared systems and helical pitch

System	1	2	3	4	5	6	7	8	9
DACl $_{(\%xi)}$	5.45	5.44	5.43	5.42	5.42	5.35	4.045	4.026	4.184
NH_4Cl	1.97	1.97	1.97	1.96	1.96	1.94	1.467	1.460	1.517
H_2O	92.58	92.43	92.27	91.97	92.17	91.08	93.872	93.434	97.117
LADE	-	0.16	0.33	0.65	1.43	1.62	0.235	0.701	0.972
DEOH	-	-	-	-	-	-	0.006	0.006	0.006
P(μm)	N	100	60	40	30	L	150	110	L

D: Droplet phase *I: Isotrope phase*
N: Nematic phase *L: Lamellar phase*

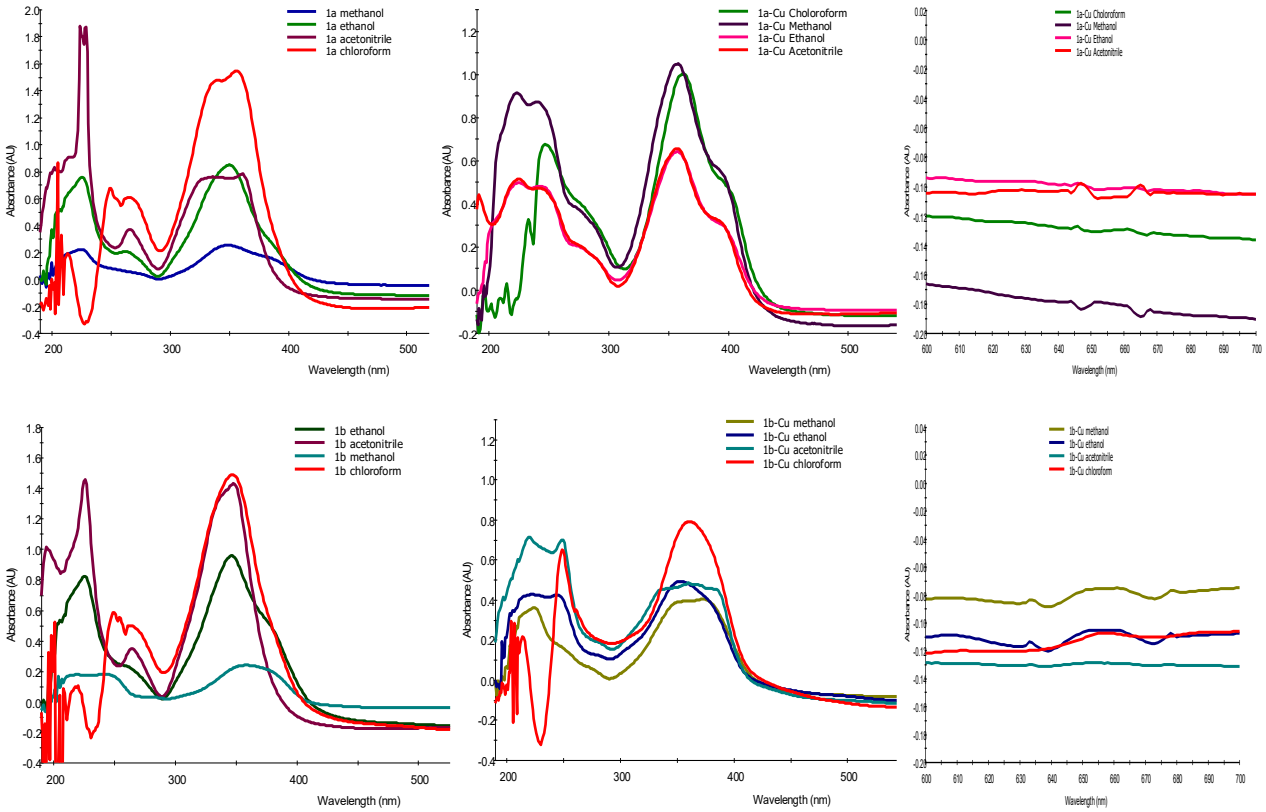

Fig. 5. UV-vis spectra of compounds in different solvents

Fig. 6. Nematic and cholesteric phase textures

Table 2. Helical pitch of DACl/ NH_4Cl/ H_2O/ L-ADE/Aldehyde(1) and DACl/NH_4Cl/H_2O/ L-ADE/ $Cu(ac)_2.H_2O$ systems

DACl/ NH_4Cl/ H_2O/ L-ADE/ 1					*DACl/ NH_4Cl/ H_2O/ L-ADE/ $Cu(ac)_2.H_2O$*				
System	10	11	12	13	System	14	15	16	17
Con/ Tem. (mM/ °C)	2.5	5	10	20	Con/Tem. (mM/ °C)	2.5	5	10	20
25	130	140	200	200	25	110	100	90	90
27	120	130	200	200	27	110	100	90	90
30	120	130	190	190	30	110	100	90	90
35	120	130	190	190	35	110	100	90	90
40	120	130	190	190	40	110	100	90	90
45	I	I	190	190	45	110	I	D	D
50	I	I	I	I	50	I	I	I	I

For the DACl/ NH_4Cl/ H_2O/ L-ADE systems, the helical pitch was shortened as the amount of optically active L-ADE increased. It is mentioned in the literature that the micelle size in the cholesteric phase may be smaller or larger than that in the nematic phase depending on adding chiral dopant [50]. The observed shortening in the helical pitch can be explained by the fact that chiral micelle-micelle

interactions at appropriate distances become more effective with increasing chirality. For system 6, an arrangement in which the hydrophilic tail is aligned along the water surface and the hydrophobic tail parts are surrounded by water layers, in other words, the lamellar phase, was detected. The mentioned system is an important arrangement seen in biological membrane bilayers [51]. The fact that L-ADE is an amphiphilic molecule like DACl and its non-polar parts are compatible and increasing specific packing of the head groups can be seen as the reason for the increase in density [29]. Decanol was added to the prepared system as a co-surfactant to easily incorporate the synthesized compounds and increase the interaction, and it was determined that the helical pitch shortened with the increase in the amount of LADE, similar to the system without decanol. In systems with and without decanol, with the increase in amphiphilic molecules, a lamellar phase was observed. To determine each structural effect, the aldehyde used, $Cu(ac)_2.H_2O$, 1a, 1b, 1a-Cu and 1b-Cu, were added to the system with a helical pitch of 110 µm. The added amounts of aldehyde, $Cu(ac)_2.H_2O$ and helical pitch are given in Table 2 and some selected system phase textures are given in Figure 7.

Fig. 7. Some obtained cholesteric phase textures

The aldehyde used (1) contains various functional groups, including an aromatic ring, a non-bonding electron pair connected to the π system, alkyl and hydroxyl groups. Owing to these different chemical groups, it could be incorporated into the liquid crystal system within a range of 2.5-20 mM without disrupting the anisotropy feature. With the increasing amount of aldehyde added at 25 °C, the helical pitch lengthened. At 20 mM, the helical pitch lengthened by 81 %. With the increase in temperature, the helical pitch was shortened by 5-7 %. After 45 °C, the liquid crystal phase feature began to disappear and an isotrope phase was observed. On the other hand, when $Cu(ac)_2.H_2O$ was added to the system, it was observed that, unlike the aldehyde, the helical pitch was shortened and it was not affected by temperature. These differences imply that micelles may exhibit different types of interactions depending on the nature of the added components. Cu^{2+} ions can be expected to settle around the head group, thus preventing the interaction between the micelles by surrounding the ions with an electrical double layer of ions [26]. Therefore, while the helical pitch was the same at low concentrations, a change was observed with increasing concentrations. The shortening observed in the helical pitch at high concentrations caused an increase in the chirality interaction and an increase in the helical order. The added amounts of 1a, 1b and helical pitch are given in Table 3.

The synthesized Schiff bases have two imine units attached to an alkyl chain, which provides a flexible structure, while the benzene and hydroxyl groups have a rigid structure. This flexible and symmetric structure is expected to be significantly compatible with polar and non-polar groups in lyotropic environments. The results showed that in the added concentration range, both Schiff bases settled into the lyotropic medium without disturbing the anisotropic property. For 1a, at 25 °C a phase transition to nematic phase was determined but at higher temperatures cholesteric phase was obtained with a long helical pitch. The situation demonstrated that 1a compound changed micelle interaction and a less ordered structure occurred. The same situation was detected for compound 1b, but unlike 1a, the increasing alkyl chain caused transformation to the cholesteric phase over a higher temperature range. 1b has a more flexible alkyl chain and can cause situations that can affect the molecular order, such as the disintegration of micelles or aggregation so that the helical order can only be reestablished at higher temperatures [52]. The added amounts of 1a-Cu, 1b-Cu and helical pitch are given in Table 4. Copper complexes, like the other components examined, were found to be suitable for lyotropic media and similarly caused a lengthening of the helical pitch with changing concentration. Compared to copper complexes and Schiff bases, alkyl chains appear to have a significant effect. It can be stated that with complexation, the flexibility of the molecule settled around the metal decreases and it exhibits a harder structure. The molecule with increased rigidity can take part in the existing order by settling into the micelle or on its surface.

Table 3. Helical pitch of DACl/ NH_4Cl/ H_2O/ L-ADE/ 1a and DACl/ NH_4Cl/ H_2O/ L-ADE/1b systems

DACl/ NH_4Cl/ H_2O/ L-ADE/ 1a					*DACl/ NH_4Cl/ H_2O/ L-ADE/ 1b*				
System	18	19	20	21	System	22	23	24	25
Con/Tem. (Mm)/(°C)	0.625	1.25	2.5	5.0	Con/Tem. (Mm)/(°C)	1.25	2.5	5.0	10.0
25	N	N	N	N	25	N	N	N	N
27	120	150	150	150	27	N	N	N	N
30	120	150	150	150	30	200	200	210	210
35	120	120	150	150	35	200	200	210	210
40	120	120	120	120	40	200	200	210	210
45	120	120	120	120	45	200	200	210	210
50	I	I	I	I	50	I	I	I	I

Table 4. Helical pitch of DACl/ NH_4Cl/ H_2O/ L-ADE/ 1a-Cu and DACl/ NH_4Cl/ H_2O/L-ADE/1b- Cu systems

DACl/ NH_4Cl/ H_2O/ L-ADE/ 1a-Cu					*DACl/ NH_4Cl/ H_2O/ L-ADE/ 1b-Cu*				
System	26	27	28	29	System	30	31	32	33
Con/Tem. (Mm)/(°C)	0.625	1.25	2.5	5.0	Con/Tem. (Mm)/(°C)	0.156	0.312	0.526	1.25
25	130	130	N	N	25	150	160	180	200
27	130	130	200	N	27	140	160	180	200
30	120	130	200	N	30	140	160	180	200
35	120	120	150	N	35	140	160	180	200
40	120	120	150	D	40	140	160	180	200
45	I	D	D	D	45	D	D	D	D
50	I	I	I	D	50	I	I	I	I

CONCLUSION

The synthesized molecules were added as guest molecules in the cholesteric phase as a component in a co-surfactant. Interactions were examined on an optically active, an optically inactive amphiphilic molecule and imine compounds. The addition of any substance can greatly affect the size and shape of the micelle, which in turn changes the properties of the host phase. This effect depends on the substance's ability to interact with the hydrophilic surface and the hydrophobic core of the micelle. The helical pitch was used as a parameter of molecular interactions of the host-guest system. $Cu(ac)_2.H_2O$ shortened the helical pitch due to increasing helical order, other compounds extended it. It is possible to establish the necessary distance for chirality transfer due to electrostatic interaction in this case. It seems that the transfer of chirality in Schiff bases does not continue, particularly at low temperatures. This may be due to increased aggregation in micelles with the alkyl chain of Schiff bases or irregular movements caused by increased flexibility. Compared to the synthesized molecules used, copper complexes are more suitable for maintaining cholesteric order with their rigid structures. It is observed that this rigid structure settles within the inner part of the micelles, maintaining their existing order. The molecules or parts of the molecules that are close to the surface have a major effect on the interaction between micelles. Temperature was adjusted to accommodate guest molecules without destroying their anisotropic character. Researched host-guest systems are suitable for controlling interactions, especially within the biological temperature range, to utilize different phenomena in lyotropic systems. It has been determined that the investigated host-guest system, phase type, that is, packing ratio and interfacial mean curvature, can be controlled by the chemical structure and concentration of the synthesized compound. The host-guest system allows the placement of julolidene-containing compounds, which are not water-soluble and can exhibit fluorescence properties, in a biocompatible and water-containing environment.

Acknowledgement: *This work was supported by Sinop University Scientific Research Coordination Unit. (Project Number BMYO-1901-21-001).*

REFERENCES

1. X. Mulet, B. J. Boyd, C. J. Drummond, J. *Colloid Interface Sci*., **393**, 1 (2013).
2. C. V. Kulkarni, O. Glatter, in: Self-Assembled Supramolecular Architectures, John Wiley & Sons, Inc. New York, 2012, p. 157.
3. K. Garbovskiy, J. Larsson, *Phys. Chem*.**,** 93, 7304 (1989).
4. W. Q. Ding, H. Liu, S. Y. Qin, Y. Jiang, X. Lei, A. Q. Zhang, *ACS Appl. Bio. Mat.,* **12**, 8989 (2020).

5. E. Kemiklioglu, B. Gurboga, E. B. Tuncgovde, Optik, 248, 168110 (2021)
6. H. Suhaimi, L. C. Rose, *Orient. J. Chem*., **32**, 2073 (2016).
7. R. C. Pasquali, C. Bregni, R. Serrao, *Acta Farm Bonaer*., **453** (2005).
8. M. A. DePierro, C. A. Guymon, *Macromolecules*, **47**, 5728 (2014).
9. P. A. S. Smith, T. Yu, *J. Org. Chem*., **17**, 1281 (1952).
10. J. J. Holt, B. D. Calitree, J. Vincek, M. K. Gannon, M. R. Detty, *J. Org. Chem*., **72**, 2690 (2007).
11. F. Jbilou, I.N. Georgousopoulou, S. Marinkovic, S. Vouyiouka, C. D. Papaspyrides, B. Estrine, P. Dole, A. Cottaz, C. Joly, *Eur. Polym. J.,* **78**, 61 (2016).
12. E. Ablinger, S. Leitgeb, A. Zimmer, *Int. J. Pharm*., **441**, 255 (2013).
13. D. J. Lichlyter, M. A. Haidekker, *Sens. and Actuators B: Chem.,* **139**, 648 (2009).
14. Y. Yang, F. Liu, H. Wang, M. Zhang, H. Xu, S. Bo, J. Liu, L. Qiu, Z. Zhen, X. Liu, *Phys. Chem. Chem. Phys*.,**16**, 1 (2014).
15. P. Li, R. Li, K. Wang, Q. Liu, B. Ren, Y. Ding, R. Guan, D. Cao, *Spectrochim. Acta A Mol. Biomol. Spectrosc*., **276**, 121213 (2022).
16. V. R. Holland, B. C. Saunders, *Tetrahedron*, **27**, 2851 (1971).
17. O. Halter, H. Pleni, Eur. J. Inorg. Chem., 25, 2935 (2018)
18. D. Maity, A. K. Manna, D. Karthigeyan, T. K. Kundu, S. K. Pati, T. Govindaraju, *Chem. - Eur. J.,* **17**, 11152 (2011).
19. W. Akarasareenon, S. Chanmungkalakul, L. Xiaogang, P. Rashatasakhon, *J. Photochem. Photobiol. A: Chem*., **437**, 114422 (2023).
20. R. S. Joseyphus, C. Shiju, J. Joseph, C. J. Dhanaraj, D. Arish, *Spectrochim. Acta A Mol Biomol. Spectrosc.,* **133**, 149 (2014).
21. A. Datta, N. K. Karan, S. Mitra, G. Rosair, *Naturforsch*., **57**, 999 (2002).
22. S. Kothavale, A. G. Jadhav, N. Sekar, *Dyes and Pigm*., **137**, 329 (2017).
23. R. I. Kureshy, N. H. Khan, S. H. R. Abdi, S. T Patel, P. Iyer, *J. Mol. Catal. A Chem.* **150**, 175 (1999).
24. P. Mayurachayakul, O. Chantarasriwong, N. Yotapan, A. Kamkaew, W. Mingvanish, C. Srisuwannaket, M. Sukwattanasinitt, N. Niamnont, *Spectrochim. Acta A Mol Biomol. Spectrosc*., **279**, 121382 (2022).
25. N. Alcaraz, B. J. Boyd, *Curr. Med. Chem.,* **24**, 470 (2017).
26. B. W. Muir, D. P. Acharya, D.F. Kennedy, X. Mulet, R. A. Evans, S. M. Pereira, *Biomaterials*, **33**, 2723 (2012).
27. S. Sivakumar, K. L. Wark, J. K. Gupta, N. L. Abbott, F. Caruso, Adv. Funct. Mater., 19, 2260 (2009)
28. M. Acımış, L. W. Reeves*, Can. J. Chem*., **58**, 1542 (1980).
29. M. Acımış, E. Akpınar, *Phys. Chem. Chem. Phys*., **5**, 4197 (2003).
30. V. T. Kasumov, A. A. Medjidov, N. Yaylı, Y. Zeren, *Spectrochim. Acta A*, **60**, 3037 (2004).
31. Z. Popovic, G. Pavlovic, D. M. Calogovis, V. Roje, I. J. Leban, *Mol. Struct*., **615**, 23 (2002).
32. K. Z. Ismail, *Transit. Met. Chem*., **25**, 522 (2000).
33. B. Dutta, P. Bag, B. Adhikary, U. Florke, K. *J. Org. Chem*., **69**, 5419 (2004).
34. B. S. Garg, P. K. Singh, J. L. Sharma, *Synth. React. Inorg. Met.-Org. Chem*., **30**, 80 (2000).
35. J. M. Sece, M. Quiros, M. J. G. Garmendia, *Polyhedron*, **19**, 1005 (2000).
36. M. Thomas, M. K. M. Nair, P. K. Radhakrishnan, *Synth. React. Inorg. Met Org. Chem*., **25**, 471 (1995).
37. A. Jain, R. Goyal, D. D. Agarwal, *J. Inorganic Nuclear Chem*., **43**, 2005 (1981).
38. M. I. Khan, A. Khan, I. Hussain, M. A. Khan, S. Gul, M. Iqbal, F. Khuda, *Inorg. Chem. Commun*., **35**, 104 (2013).
39. A. Cınarlı, D. Gürbüz, A. Tavman, A. S. Birteksöz, *Bull. Chem. Soc. Ethiop*., **25**, 407 (2011).
40. E. Tas, M. Aslanoglu, M. Ulusoy, H. Temel, *J. Coord. Chem*., **57**, 677 (2004).
41. H. L. Sıddıquı, A. Iqbal, S., Ahmad, G. W. Weaver, *Molecules*, **11**, 206 (2006).
42. T. F. Anjong, Y. M. Park, H. Y. Jang, J. Kim, *Bull. Korean Chem. Soc*., **37**, 905 (2016).
43. J. Y. Noh, S. Kim, I. H. Hwang, G. Y. Lee, J. Kang, S. Kim, J. Min, S. Park, C. Kim, J. Kim, *Dyes and Pigments*, 99, 1016 (2013).
44. S. Y. Lee, S. Y. Kim, J. A. Kim, C. Kim, *J. Lumin*., **179**, 602 (2016).
45. Y. Kaya, H. Mutlu, G. Irez, *G. U. J. Sci*., **23**, 1318 (2010).
46. A. Gonciarz, M. Zuber, J. Zwoździak, *Chemistry Open*, **30**, 677 (2018).
47. P. R. Reddy, S. Rajeshwar, B. Satyanarayana, *J. Photochem. Photobiol. B*, **160**, 217 (2016).
48. E. Akpinar, G. Frank, M. Acımıs, *Liquid Crystals*, **40**, 1183 (2013).
49. H. D. Dörfler, *Adv. Colloid. Interface Sci.,* **98**, 285 (2002).
50. L. L. M. Van Deenen, The molecular basis of membrane function, Prentice-Hall, New Jersey. 1969, p. 47.
51. V. Luzzati, F. Husson*, Med. J. Cell Biol*., **12**, 207 (1962).
52. Y. Zhao, X. Yue, X. Wang, X. Chen, *J. Colloid Interface Sci.,* **389**, 199 (2013).