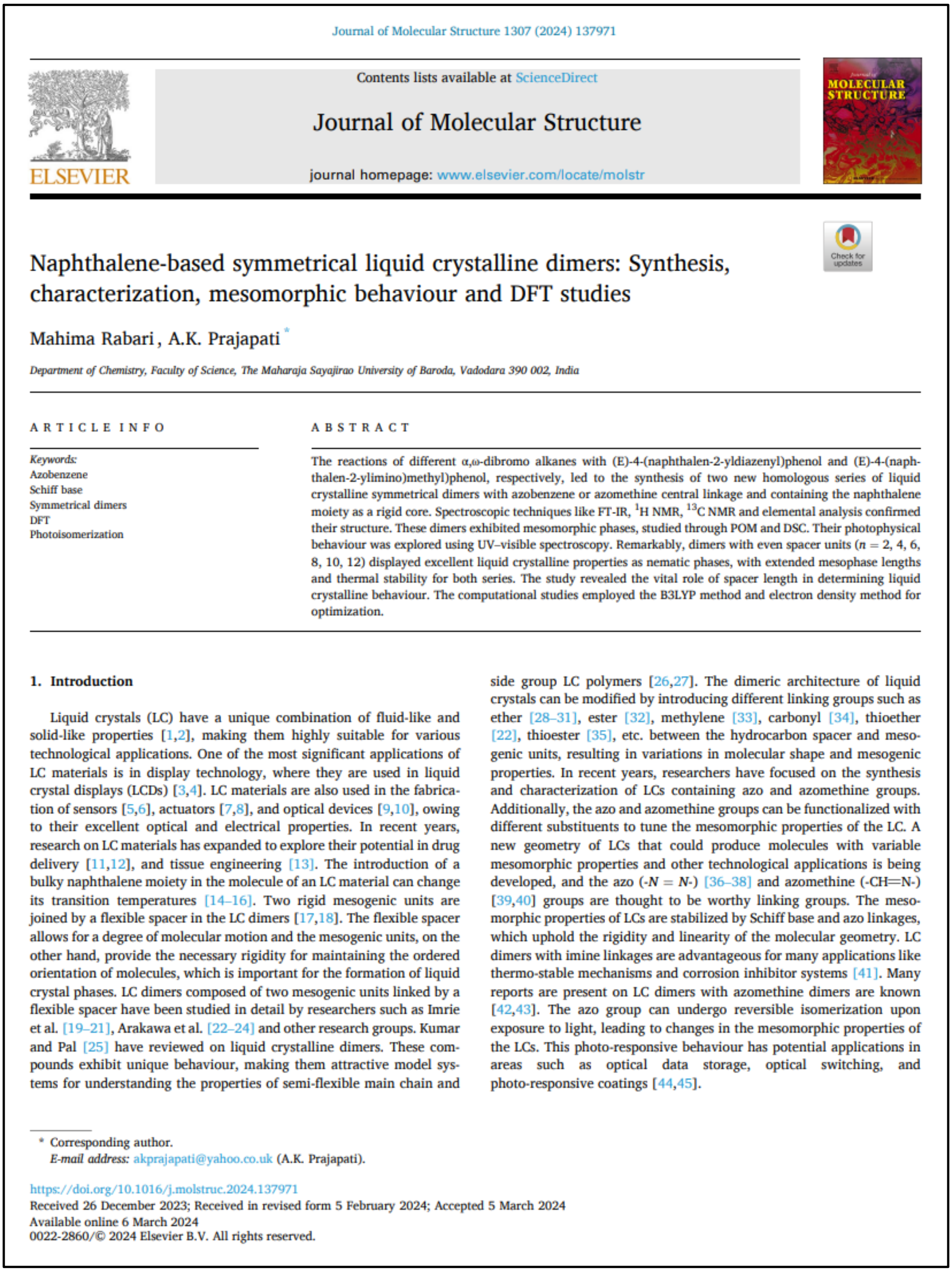

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Naphthalene-based symmetrical liquid crystalline dimers: Synthesis, characterization, mesomorphic behaviour and DFT studies

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A R T I C L E I N F O

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A B S T R A C T

The reactions of different α,ω-dibromo alkanes with (E)-4-(naphthalen-2-yldiazenyl)phenol and (E)-4-(naphthalen-2-ylimino)methyl)phenol, respectively, led to the synthesis of two new homologous series of liquid crystalline symmetrical dimers with azobenzene or azomethine central linkage and containing the naphthalene moiety as a rigid core. Spectroscopic techniques like FT-IR, ^{1}H NMR, ^{13}C NMR and elemental analysis confirmed their structure. These dimers exhibited mesomorphic phases, studied through POM and DSC. Their photophysical behaviour was explored using UV–visible spectroscopy. Remarkably, dimers with even spacer units ($n = 2, 4, 6, 8, 10, 12$) displayed excellent liquid crystalline properties as nematic phases, with extended mesophase lengths and thermal stability for both series. The study revealed the vital role of spacer length in determining liquid crystalline behaviour. The computational studies employed the B3LYP method and electron density method for optimization.

1. Introduction

Liquid crystals (LC) have a unique combination of fluid-like and solid-like properties [1,2], making them highly suitable for various technological applications. One of the most significant applications of LC materials is in display technology, where they are used in liquid crystal displays (LCDs) [3,4]. LC materials are also used in the fabrication of sensors [5,6], actuators [7,8], and optical devices [9,10], owing to their excellent optical and electrical properties. In recent years, research on LC materials has expanded to explore their potential in drug delivery [11,12], and tissue engineering [13]. The introduction of a bulky naphthalene moiety in the molecule of an LC material can change its transition temperatures [14–16]. Two rigid mesogenic units are joined by a flexible spacer in the LC dimers [17,18]. The flexible spacer allows for a degree of molecular motion and the mesogenic units, on the other hand, provide the necessary rigidity for maintaining the ordered orientation of molecules, which is important for the formation of liquid crystal phases. LC dimers composed of two mesogenic units linked by a flexible spacer have been studied in detail by researchers such as Imrie et al. [19–21], Arakawa et al. [22–24] and other research groups. Kumar and Pal [25] have reviewed on liquid crystalline dimers. These compounds exhibit unique behaviour, making them attractive model systems for understanding the properties of semi-flexible main chain and side group LC polymers [26,27]. The dimeric architecture of liquid crystals can be modified by introducing different linking groups such as ether [28–31], ester [32], methylene [33], carbonyl [34], thioether [22], thioester [35], etc. between the hydrocarbon spacer and mesogenic units, resulting in variations in molecular shape and mesogenic properties. In recent years, researchers have focused on the synthesis and characterization of LCs containing azo and azomethine groups. Additionally, the azo and azomethine groups can be functionalized with different substituents to tune the mesomorphic properties of the LC. A new geometry of LCs that could produce molecules with variable mesomorphic properties and other technological applications is being developed, and the azo (-$N = N$-) [36–38] and azomethine (-CH=N-) [39,40] groups are thought to be worthy linking groups. The mesomorphic properties of LCs are stabilized by Schiff base and azo linkages, which uphold the rigidity and linearity of the molecular geometry. LC dimers with imine linkages are advantageous for many applications like thermo-stable mechanisms and corrosion inhibitor systems [41]. Many reports are present on LC dimers with azomethine dimers are known [42,43]. The azo group can undergo reversible isomerization upon exposure to light, leading to changes in the mesomorphic properties of the LCs. This photo-responsive behaviour has potential applications in areas such as optical data storage, optical switching, and photo-responsive coatings [44,45].

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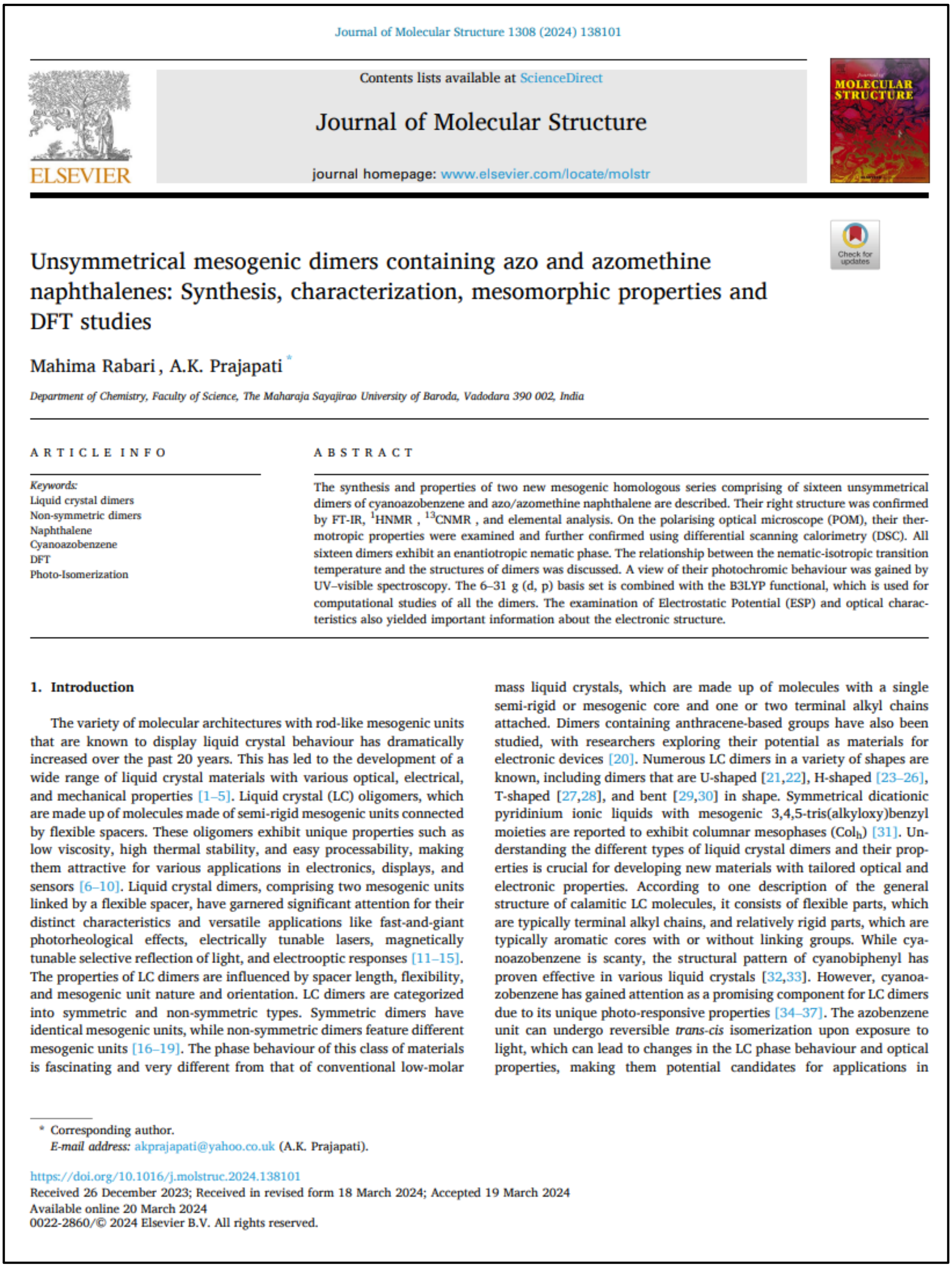

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Unsymmetrical mesogenic dimers containing azo and azomethine naphthalenes: Synthesis, characterization, mesomorphic properties and DFT studies

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ABSTRACT

The synthesis and properties of two new mesogenic homologous series comprising of sixteen unsymmetrical dimers of cyanoazobenzene and azo/azomethine naphthalene are described. Their right structure was confirmed by FT-IR, ^{1}HNMR , ^{13}CNMR , and elemental analysis. On the polarising optical microscope (POM), their thermotropic properties were examined and further confirmed using differential scanning calorimetry (DSC). All sixteen dimers exhibit an enantiotropic nematic phase. The relationship between the nematic-isotropic transition temperature and the structures of dimers was discussed. A view of their photochromic behaviour was gained by UV–visible spectroscopy. The 6–31 g (d, p) basis set is combined with the B3LYP functional, which is used for computational studies of all the dimers. The examination of Electrostatic Potential (ESP) and optical characteristics also yielded important information about the electronic structure.

1. Introduction

The variety of molecular architectures with rod-like mesogenic units that are known to display liquid crystal behaviour has dramatically increased over the past 20 years. This has led to the development of a wide range of liquid crystal materials with various optical, electrical, and mechanical properties [1–5]. Liquid crystal (LC) oligomers, which are made up of molecules made of semi-rigid mesogenic units connected by flexible spacers. These oligomers exhibit unique properties such as low viscosity, high thermal stability, and easy processability, making them attractive for various applications in electronics, displays, and sensors [6–10]. Liquid crystal dimers, comprising two mesogenic units linked by a flexible spacer, have garnered significant attention for their distinct characteristics and versatile applications like fast-and-giant photorheological effects, electrically tunable lasers, magnetically tunable selective reflection of light, and electrooptic responses [11–15]. The properties of LC dimers are influenced by spacer length, flexibility, and mesogenic unit nature and orientation. LC dimers are categorized into symmetric and non-symmetric types. Symmetric dimers have identical mesogenic units, while non-symmetric dimers feature different mesogenic units [16–19]. The phase behaviour of this class of materials is fascinating and very different from that of conventional low-molar mass liquid crystals, which are made up of molecules with a single semi-rigid or mesogenic core and one or two terminal alkyl chains attached. Dimers containing anthracene-based groups have also been studied, with researchers exploring their potential as materials for electronic devices [20]. Numerous LC dimers in a variety of shapes are known, including dimers that are U-shaped [21,22], H-shaped [23–26], T-shaped [27,28], and bent [29,30] in shape. Symmetrical dicationic pyridinium ionic liquids with mesogenic 3,4,5-tris(alkyloxy)benzyl moieties are reported to exhibit columnar mesophases (Col$_h$) [31]. Understanding the different types of liquid crystal dimers and their properties is crucial for developing new materials with tailored optical and electronic properties. According to one description of the general structure of calamitic LC molecules, it consists of flexible parts, which are typically terminal alkyl chains, and relatively rigid parts, which are typically aromatic cores with or without linking groups. While cyanoazobenzene is scanty, the structural pattern of cyanobiphenyl has proven effective in various liquid crystals [32,33]. However, cyanoazobenzene has gained attention as a promising component for LC dimers due to its unique photo-responsive properties [34–37]. The azobenzene unit can undergo reversible *trans-cis* isomerization upon exposure to light, which can lead to changes in the LC phase behaviour and optical properties, making them potential candidates for applications in

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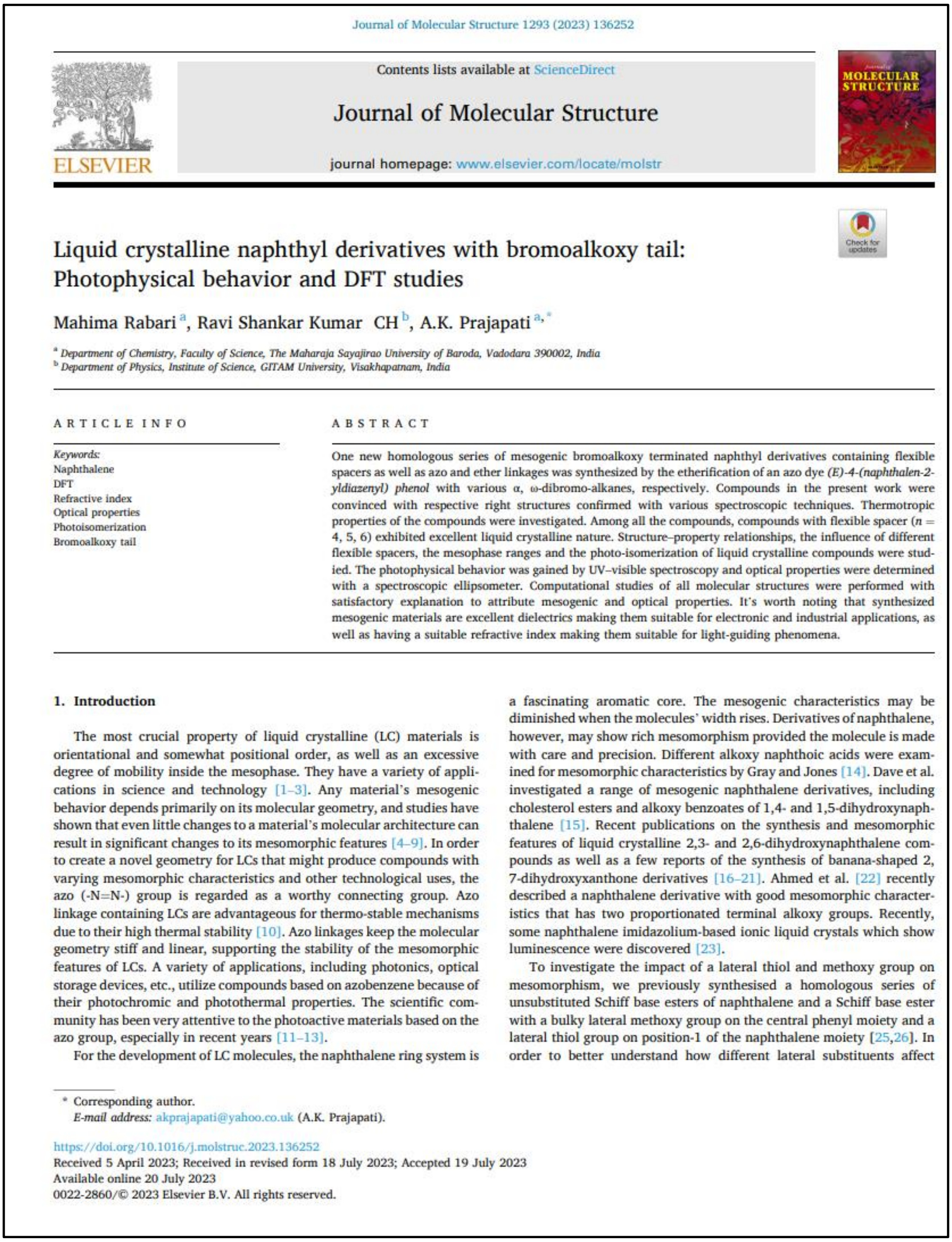

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Liquid crystalline naphthyl derivatives with bromoalkoxy tail: Photophysical behavior and DFT studies

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Optical properties
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ABSTRACT

One new homologous series of mesogenic bromoalkoxy terminated naphthyl derivatives containing flexible spacers as well as azo and ether linkages was synthesized by the etherification of an azo dye *(E)-4-(naphthalen-2-yldiazenyl) phenol* with various α, ω-dibromo-alkanes, respectively. Compounds in the present work were convinced with respective right structures confirmed with various spectroscopic techniques. Thermotropic properties of the compounds were investigated. Among all the compounds, compounds with flexible spacer (n = 4, 5, 6) exhibited excellent liquid crystalline nature. Structure–property relationships, the influence of different flexible spacers, the mesophase ranges and the photo-isomerization of liquid crystalline compounds were studied. The photophysical behavior was gained by UV–visible spectroscopy and optical properties were determined with a spectroscopic ellipsometer. Computational studies of all molecular structures were performed with satisfactory explanation to attribute mesogenic and optical properties. It's worth noting that synthesized mesogenic materials are excellent dielectrics making them suitable for electronic and industrial applications, as well as having a suitable refractive index making them suitable for light-guiding phenomena.

1. Introduction

The most crucial property of liquid crystalline (LC) materials is orientational and somewhat positional order, as well as an excessive degree of mobility inside the mesophase. They have a variety of applications in science and technology [1–3]. Any material's mesogenic behavior depends primarily on its molecular geometry, and studies have shown that even little changes to a material's molecular architecture can result in significant changes to its mesomorphic features [4–9]. In order to create a novel geometry for LCs that might produce compounds with varying mesomorphic characteristics and other technological uses, the azo (-N=N-) group is regarded as a worthy connecting group. Azo linkage containing LCs are advantageous for thermo-stable mechanisms due to their high thermal stability [10]. Azo linkages keep the molecular geometry stiff and linear, supporting the stability of the mesomorphic features of LCs. A variety of applications, including photonics, optical storage devices, etc., utilize compounds based on azobenzene because of their photochromic and photothermal properties. The scientific community has been very attentive to the photoactive materials based on the azo group, especially in recent years [11–13].

For the development of LC molecules, the naphthalene ring system is a fascinating aromatic core. The mesogenic characteristics may be diminished when the molecules' width rises. Derivatives of naphthalene, however, may show rich mesomorphism provided the molecule is made with care and precision. Different alkoxy naphthoic acids were examined for mesomorphic characteristics by Gray and Jones [14]. Dave et al. investigated a range of mesogenic naphthalene derivatives, including cholesterol esters and alkoxy benzoates of 1,4- and 1,5-dihydroxynaphthalene [15]. Recent publications on the synthesis and mesomorphic features of liquid crystalline 2,3- and 2,6-dihydroxynaphthalene compounds as well as a few reports of the synthesis of banana-shaped 2, 7-dihydroxyxanthone derivatives [16–21]. Ahmed et al. [22] recently described a naphthalene derivative with good mesomorphic characteristics that has two proportionated terminal alkoxy groups. Recently, some naphthalene imidazolium-based ionic liquid crystals which show luminescence were discovered [23].

To investigate the impact of a lateral thiol and methoxy group on mesomorphism, we previously synthesised a homologous series of unsubstituted Schiff base esters of naphthalene and a Schiff base ester with a bulky lateral methoxy group on the central phenyl moiety and a lateral thiol group on position-1 of the naphthalene moiety [25,26]. In order to better understand how different lateral substituents affect

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Mesogenic cholesterol-naphthalene dimers: Synthesis, characterization, mesogenic properties, photochromic behaviour and theoretical insights

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ARTICLE INFO

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Unsymmetrical dimers
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ABSTRACT

Synthesis and characterization of two new series of unsymmetrical dimers combining cholesterol with azo (Series *I-n*) or azomethine (Series *II-n*) naphthalene moieties were reported. The chemical structures were confirmed using FT-IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry, and elemental analysis. Their thermotropic properties were investigated using POM, DSC and XRD. The analysis revealed that the first lower members (n = 1, 2) of each series lack mesogenic properties due to short, flexible spacers, while higher members (n = 3–5, 7, 9, 10) exhibit enantiotropic chiral nematic phases. Notably, higher members with odd spacers (n = 5, 7, 9) also display SmC* phases, highlighting the influence of spacer length and odd–even effects on molecular interactions. Dimers from series *I-n* demonstrated slightly higher clearing temperatures ($T_{N\text{-}Iso}$) compared to series *II-n*. UV–Vis spectroscopy showed trans–cis isomerization, with a photoconversion efficiency of 56.7 % for the ***I-7*** dimer. Computational studies using the B3LYP functional with a 6-31g (d, p) basis set provided insights into the electronic structure through electrostatic potential (ESP) and optical property analysis.

1. Introduction

Chiral liquid crystals (LCs) are notable for their unique physical properties. Cholesterol is a significant biologically active organic compound and is a key source of chiral mesophases due to their distinctive structural features. The incorporation of cholesterol allows the induction of chirality in liquid crystals, influencing the formation of various phases [1–3]. Chirality plays a pivotal role in the exploration of liquid crystalline dimers, particularly those incorporating cholesteryl groups, which are not only significant for fundamental research but also hold technological promise. Various chiral non-symmetric liquid crystalline dimers have been synthesized, often featuring a cholesteryl group covalently linked to a mesogenic core via a flexible spacer, leading to the manifestation of multiple mesophases such as chiral smectic phase (Sm*), twist grain boundary phases (TGB*), chiral nematic phase (N*), and blue phases (BPs) [4–7]. Moreover, cholesteric liquid crystals exhibit distinctive properties such as circular dichroism, strong optical rotation, and selective reflection, making them an interesting research topic in the field of liquid crystal materials [8,9] with tailored properties for applications in displays, photonic devices, and optical modulation. Cholesterol-calamitic dimers have gained significant recognition among reported dimer formations. Various liquid crystalline phases have been identified in substances containing a cholesteryl moiety connected via a spacer to one or more variety of aromatic/ aliphatic/ heterocyclic ring systems with suitable linkages including ethers, azo-, azomethine, aromatic ester, biphenyl, or terphenyl units [10].

Azo bond linking unit exhibits a remarkable property wherein it undergoes mutual transformation between cis and trans structures under different light induction, a feature particularly prominent in azobenzene liquid crystals [11–13]. This conformational alteration induced by light radiation confers special photo-responsive characteristics to the materials, rendering them suitable for applications in photochromic phase change and optical storage [14,15]. Fig. 1 depicts a few examples of unsymmetrical dimers with cholesterol moiety. Changcheng Wu introduced a series of dimers featuring cholesteryl ester and 4′-nitroazobenzene groups, with different methylene spacer lengths ($(CH_2)_n$; n = 2, 4, 6, 8) [16]. Meanwhile, Tamaoki et al. described a series of photoresponsive chiral dimesogenic compounds [17]. Kidowaki et al. reported LC dimers with a unique spacer of docosanedioic acid and have studied the effect of varying terminal chain length [18]. Zhang et al. described a range of LC dimers comprising both a cholesteryl group and substituted azobenzene, along with a branched allyl chain [19]. Jin et al. presented findings on two sets of asymmetric dimers composed of cholesterol and azobenzene-based components linked

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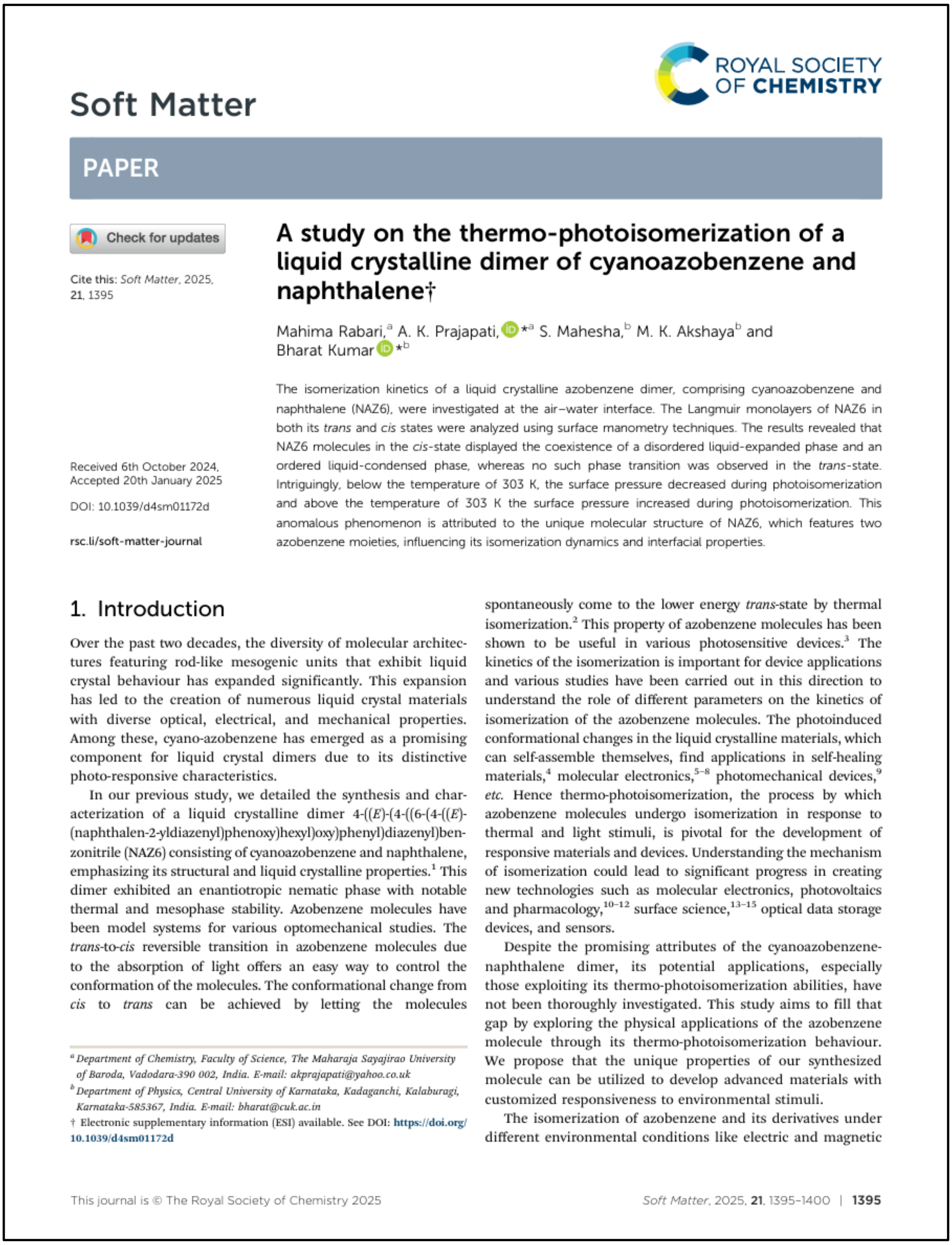

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A study on the thermo-photoisomerization of a liquid crystalline dimer of cyanoazobenzene and naphthalene†

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The isomerization kinetics of a liquid crystalline azobenzene dimer, comprising cyanoazobenzene and naphthalene (NAZ6), were investigated at the air–water interface. The Langmuir monolayers of NAZ6 in both its *trans* and *cis* states were analyzed using surface manometry techniques. The results revealed that NAZ6 molecules in the *cis*-state displayed the coexistence of a disordered liquid-expanded phase and an ordered liquid-condensed phase, whereas no such phase transition was observed in the *trans*-state. Intriguingly, below the temperature of 303 K, the surface pressure decreased during photoisomerization and above the temperature of 303 K the surface pressure increased during photoisomerization. This anomalous phenomenon is attributed to the unique molecular structure of NAZ6, which features two azobenzene moieties, influencing its isomerization dynamics and interfacial properties.

1. Introduction

Over the past two decades, the diversity of molecular architectures featuring rod-like mesogenic units that exhibit liquid crystal behaviour has expanded significantly. This expansion has led to the creation of numerous liquid crystal materials with diverse optical, electrical, and mechanical properties. Among these, cyano-azobenzene has emerged as a promising component for liquid crystal dimers due to its distinctive photo-responsive characteristics.

In our previous study, we detailed the synthesis and characterization of a liquid crystalline dimer 4-((*E*)-(4-((6-(4-((*E*)-(naphthalen-2-yldiazenyl)phenoxy)hexyl)oxy)phenyl)diazenyl)benzonitrile (NAZ6) consisting of cyanoazobenzene and naphthalene, emphasizing its structural and liquid crystalline properties.[1] This dimer exhibited an enantiotropic nematic phase with notable thermal and mesophase stability. Azobenzene molecules have been model systems for various optomechanical studies. The *trans*-to-*cis* reversible transition in azobenzene molecules due to the absorption of light offers an easy way to control the conformation of the molecules. The conformational change from *cis* to *trans* can be achieved by letting the molecules spontaneously come to the lower energy *trans*-state by thermal isomerization.[2] This property of azobenzene molecules has been shown to be useful in various photosensitive devices.[3] The kinetics of the isomerization is important for device applications and various studies have been carried out in this direction to understand the role of different parameters on the kinetics of isomerization of the azobenzene molecules. The photoinduced conformational changes in the liquid crystalline materials, which can self-assemble themselves, find applications in self-healing materials,[4] molecular electronics,[5–8] photomechanical devices,[9] *etc.* Hence thermo-photoisomerization, the process by which azobenzene molecules undergo isomerization in response to thermal and light stimuli, is pivotal for the development of responsive materials and devices. Understanding the mechanism of isomerization could lead to significant progress in creating new technologies such as molecular electronics, photovoltaics and pharmacology,[10–12] surface science,[13–15] optical data storage devices, and sensors.

Despite the promising attributes of the cyanoazobenzene-naphthalene dimer, its potential applications, especially those exploiting its thermo-photoisomerization abilities, have not been thoroughly investigated. This study aims to fill that gap by exploring the physical applications of the azobenzene molecule through its thermo-photoisomerization behaviour. We propose that the unique properties of our synthesized molecule can be utilized to develop advanced materials with customized responsiveness to environmental stimuli.

The isomerization of azobenzene and its derivatives under different environmental conditions like electric and magnetic

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