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Original Article

Synthesis, Characterization, and Investigation of Mesogenic Properties of Bis(2-oxo-2*H*-Chromen-6-yl)Terephthalate and Bis(2-Oxo-2*H*-Chromen-7-yl)Terephthalate

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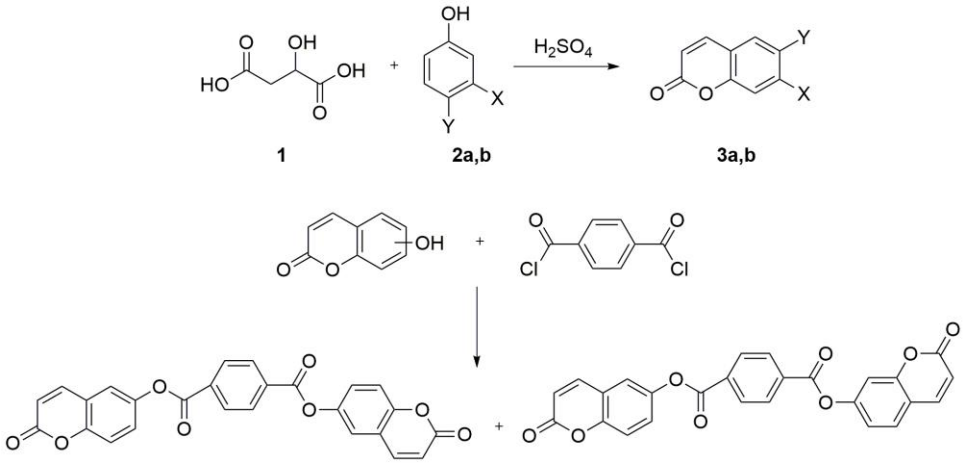
ABSTRACT

The synthesis, characterization, and mesomorphic investigation of new liquid crystals are described. The goal was to synthesize esters starting with 6- and 7-hydroxycoumarin. The structures of the synthesized compounds were actually determined by FT-IR and ^{1}H-NMR. The mesophase behavior of the synthesized compounds was characterized and investigated by using (DSC) differential scanning calorimetry and (POM) polarizing the optical microscopy. The mesophase transitions are enantiotropic, the peaks being sharp and the mesomorphic range wide. The synthesized compounds exhibit a nematic phase.

GRAPHICAL ABSTRACT



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Introduction

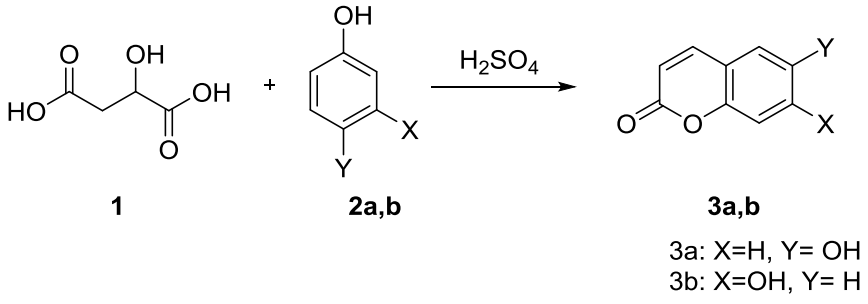
The development of liquid crystals with heterocyclic rings has enabled the creation of a wide range of mesogenic compounds with intriguing properties [1]. Mesogenic properties are affected when a heterocycle is part of a calamitic structure due to the dipole moment of the heteroatomic moiety, loss of molecular symmetry, deviation from linearity, and planarity [2]. The combination of mesomorphic order and the extra physical qualities offers an exciting approach to the functional (intelligent) materials in which molecular organization is critical for a certain attribute to appear or be exaggerated owing to the cooperative effects of the neighboring molecules. The integration of light-generating capabilities with an anisometric molecule structure is one such endeavor [3]. Coumarin dyes have received a lot of interest because of their adaptability as the optical components such as laser dyes, photoactive surfaces, light, and energy harvesting systems, fluorescent tags, or fluoroprobes [4]. As a result, it is unexpected that organized molecular assemblages incorporating the coumarin skeleton are uncommon.

Thermotropic characteristics, photophysical, and photochemical behavior were examined for coumarin-containing side-group polymers [5] and the cyclic oligosiloxanes [6]. It was discovered that thermomesomorphism occurs in low molecular mass systems when aryl substituents are linked to the 6- or 7-position of the benzopyran-2*H*-one core through an ester linkage [7]. Conversely, by modifying the coumarin heterocycle with a carbonyl hydrazide function or fusing with an extra pyrazolone ring [8], hydrogen bonding between the molecules drives mesophase development. The emission behavior of the low molecular mass coumarin mesogens has not been studied. Some of coumarin and its derivatives were synthesized have the anticoagulant activities like 4-hydroxycoumarin and bis hydroxycoumari [9]. Merlo *et al.* [10] synthesized three new coumarin derivatives obtained with different terminal arylalkyne linkages to the 6-position of the coumarin core. The synthesized materials were characterized by NMR, absorption, emission spectroscopy, and the liquid crystal properties were investigated through differential scanning calorimetry and polarized optical microscopy. We report our efforts in the development of calamitic nematic mesophase based on a coumarin chromophore. The idea is to stretch the rod-shaped core, while also expanding the conjugated molecular portion via a direct coupling with an aromatic sub-unit. To tailor the predicted mesomorphic and photoluminescent features, the substitution pattern at terminal and lateral places was methodically varied.

Materials and Methods

The chemicals are used as of the analytical grade i.e. Resorcinol, Hydroquinone, Malic acid, Conc. H_2SO_4, Ethanol, Glacial acetic acid, terephthalic acid, Thionyl chloride, DMF, and Pyridine. The melting points were all tested in open capillaries and are thus incorrect. TLC on silica gel was used to evaluate the chemicals' purity. The FT-IR spectra in the frequency range 4000-400 cm^{-1} were recorded on FT-IR Shimadzu IRAffinity-1 Spectrometer (Shimadzu, Japan). ^{1}H-NMR was performed by using Varian Spectrometer, Model: Inova, 500 MHz.

*Preparation of 6-hydroxycoumarin (**3a**) and 7-hydroxycoumarin (**3b**)*



Scheme 1: Preparation of 6-hydroxyCoumarin (**3a**) and 7-hydroxycoumarin (**3b**)

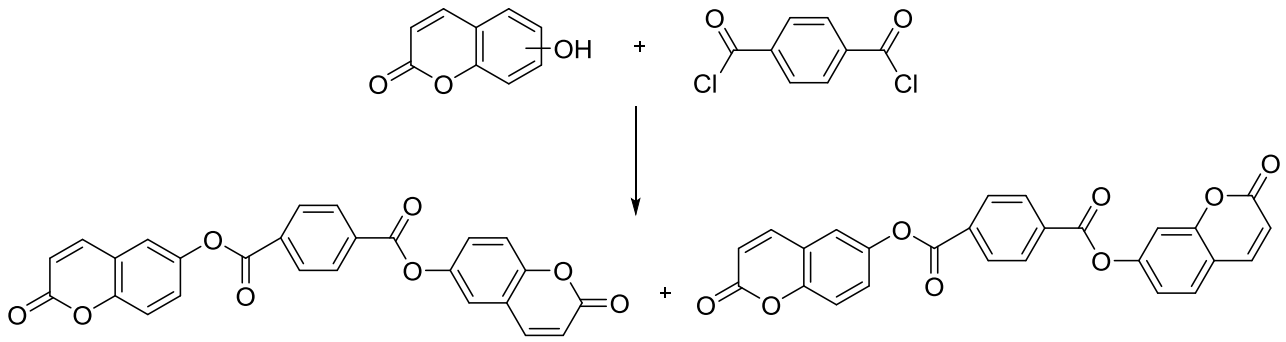
*Coumarin (**3a**) and 7-hydroxycoumarin (**3b**)*

Coumarin was made by reacting substituted phenol (**2a,b**) with malic acid (**1**). The reaction includes the addition of malic acid (0.05 mol, 6.7 g) to the round bottom flask, followed by the addition of 100 mL of absolute ethanol as a solvent, and then the addition of 6 drops of sulfuric acid (H_2SO_4) with simply stirring, and finally the addition of substituted phenol (0.0577 mole). After 10 hours of refluxing, the reactants were cooled at room temperature. The reaction product was filtered out, and a precipitate of 6- and 7-hydroxycoumarin was obtained after drying at room temperature (Scheme 1).

*Synthesis of bis(2-oxo-2H-chromen-6-l)terephthalate (**5a**) and bis(2-oxo-2H-chromen-7-yl)terephthalate (**5b**)*

The synthesis of compounds (**5a** and **5b**) involves two steps: Firstly, terephthaloyl chloride was prepared through the reaction of terephthalic acid (0.01 mol, 1.66 g) with 8 mL of thionyl chloride and two drops of dimethylformamide into the round bottom flask. The reactants were refluxed for one hour, and then cooled at room temperature until it becomes thick so that the excess of the thionyl chloride evaporates (Scheme 2).

Secondly, in the round bottom flask, 6-hydroxycoumarine and 7-hydroxycoumarine (0.02 mol) were mixed with 20 mL of Pyridine and 35 ml of ethanol, and then the terephthaloyl chloride was added that was generated dropwise in the first stage. Because the reaction was exothermic, the flask was placed in a basin of cold water to remove the heat produced. The reaction was simply removed to stir for 8 hours. After that, the chemical resultant was poured into a beaker with cold water and ice and filtered through a separating funnel; the product precipitate was obtained after drying at room temperature [12].



Scheme 2: Synthesis of bis(2-oxo-2H-chromen-7-yl)terephthalate (**5a**) & bis(2-oxo-2H-chromen-6-yl)terephthalate (**5b**)

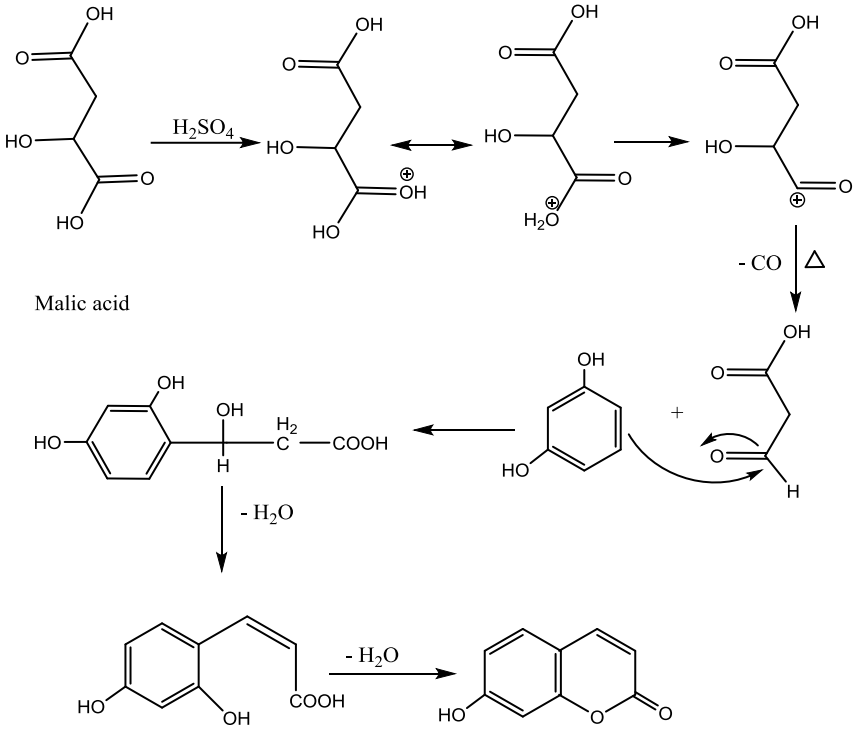
Results and Discussion

To prepare compounds (**3a,b**) dihydroxyphenols (**2a,b**) reacted with malic acid in presence of H_2SO_4 and ethanol as a solvent.

The mechanism of preparation was shown in Scheme 3 involving an acidification followed by dehydration and decarboxylation to form 3-oxopropanoic acid, which was reached with phenol to produce coumarin [13].

As depicted in Figures S1 and S2 (Supporting information), the FT-IR spectra of compounds **3a** and **3b** demonstrated the appearance of absorption bands attributed to the presence of phenolic hydroxyl group ν(O-H) at 3377& 3443 cm^{-1}, ν (C = O) at 1734 and 1732 and ν (C=C) at 1668 and 1653 cm^{-1} which was a good evidence for the formation of compounds **3a** and **3b**.

^{1}H-NMR spectra of compound **3b** showed the following characteristic signals δ 9.5 (s, 1H, OH), (7.99-8.77), (d, 3H, Ar), (7.36-7.61), and (d, 2H coumarin ring) (Figure S3, Supporting information).



Scheme 3: Formation of coumarin

*Synthesis of bis(2-oxo-2H-chromen-6-yl)terephthalate (**5a**) and bis(2-oxo-2H-chromen-7-yl)terephthalate (**5b**)*

The mentioned compounds were created by reacting hydroxycoumarin with terephthaloyl chloride in pyridine as a proton acceptor. The reaction process involved nucleophilic substitution (tetrahydral mechanism) [14], with the first step as the nucleophile addition and the second step including the elimination of the leaving group.

As displayed in Figure S4 (Supporting information), ^{1}H-NMR spectrum of compound **5a** showed the following characteristic signals δ 6.55-6.46 (m, 4H, phenyl ring), 7.48-7.32 (d, 6H, -O-H), 7.13- 6.99 (d, 4H terephthalate ring).

Mesomorphic properties

Because coumarins described in this paper are rod-shaped molecules, their liquid crystal potential was studied by using polarized optical microscopic (POM) research and DSC.

POM investigation attributed mesophase texture to coumarins **5a** and **5b**. Figure 1 illustrates the marble texture of nematic mesophase for the synthesized compounds. The marble texture of the monotropic nematic mesophase was observed when the sample enters into the isotropic state about 10 °C above the clearing temperature, and then quickly removed from the hot stage and analyzed. The nematic phase was identified by its classical Schlieren texture. When heated further, the fan-focal conic texture progressively was converted into black nematic domain patches (Figure 2).

In liquid crystals, the diameter ratio of the molecule is an important consideration in liquid crystals [15]. As a result, adding a flexible ester linkage group to coumarins converted them into the liquid crystals by extending both the length and width of the molecular structure.

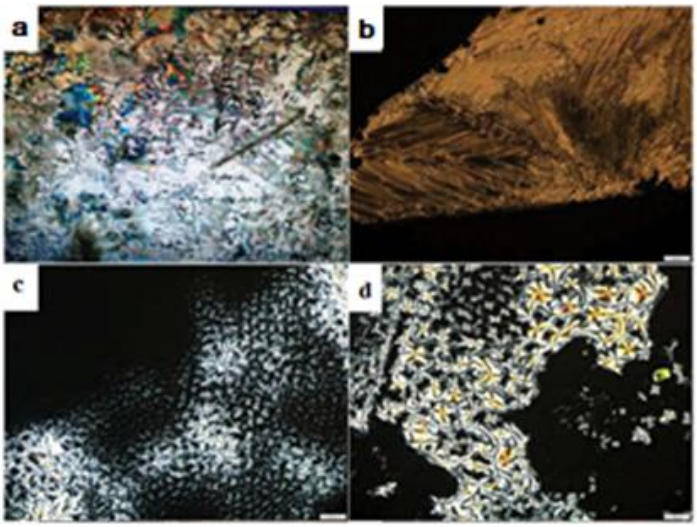


Figure 1: Schlieren texture of the nematic phase upon heating in distinct areas of the sample

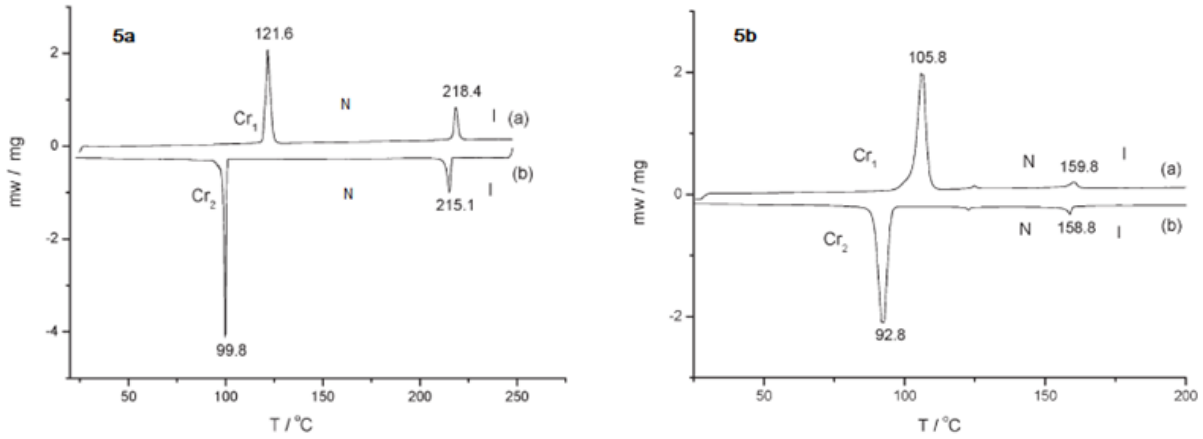


Figure 2: DSC curves **5a** and **5b** on a) heating and b) cooling, show nematic stable transition

Conclusion

Esters of bis(2-oxo-2H-chromen-6-yl)terephthalate and bis(2-oxo-2H-chromen-7-yl) terephthalate were synthesized and characterized by using FT-IR and ^{1}HNMR spectroscopy. The liquid crystalline properties were studied by using POM and DSC thermogram, compounds 5a and 5b depicts the marble texture of the nematic mesophase. The nematic phase was identified by its classical Schlieren texture. Fan-focal conic texture gradually transforms into black areas of the nematic domains upon heating further.

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Authors' contributions

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

Conflict of Interest

The author declared that they have no conflict of interest.

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Detailed spectra of synthesized compounds (PDF)

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